

ELECTROCHEMISTRY CONFERENCE - 2019

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Electrochem2019

Welcome Message

It is my pleasure to be welcoming you to Istanbul for Electrochem2019 (12th Electrochemistry Meeting of Turkey) on behalf of the organizing committee.

As Electrochemistry is at the forefront of almost every technological forefront from consumer electronics to mobility, from energy efficiency to energy accessibility, this meeting is designed to bring electrochemists of Turkey together with leading electrochemists of the world.

After 11 successful electrochemistry meetings in Turkey, this meeting is intended to restart a lively discussion centered around the broad topic of electrochemistry that has stalled after the 2013 meeting in Konya.

Thanks to efforts from the organizing committee, we have been able to secure commitments from world-leading electrochemists as Plenary speakers. Prof. Abrufia who is a fellow of the ECS, ISE and AAAS , Former ECS president Prof. Scherson, ISE Fellow Prof. Unwin, in addition to Prof. West, Prof. Yildiz and Prof. Yazami are all star electrochemists that we are honored to be hosting. This unique level of quality allowed us to attract over 200 abstract submissions from 23 countries, with roughly 30% international attendance.

There are many people that I would like to thank for the organization. First, ARBER company with all employees, especially, Onur Nail Arda and Feryal Arber for their help throughout the organization process. Further, all the members of the organizing committee for their ideas, help and communication. Last, I would like to thank our sponsors, whose support is invaluable for the meeting.

I would also like to mention the support from International Society of Electrochemistry, whose outreach is way more valuable than any financial contribution. It is due to the help of the ISE that we have confirmed attendees from all over the world including countries as far as Japan, Brazil, Nigeria and Finland.

Finally, I would like to thank each and every one of you for your valuable contributions to our meeting. I wish you a fruitful and productive meeting and a pleasant stay in Istanbul.

Burak Ulgut

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ID: 174

Topic:

Bioelectrochemistry and Biomedical Applications

(Electrochemical and electroanalytical aspects of biological processes)

An Emerging Field at the Boundary between Biology, Chemistry, and Engineering

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Over the last two decades ingenious devices have been developed for converting chemicals present in biofluids in living organisms into electrical energy with potential application in a variety of areas of fundamental and practical relevance. Efforts in our laboratories have focused on the development of such biofuel cells that could be implanted into insects and provide the power required not only for the operation of electronics for sensing, information storage and wireless communication, but also for the stimulation of the nervous system, a strategy that will ultimately allow control of certain aspects of the insect behavior. An attractive feature of this approach is that it provides a continuous and autonomous source of power, thereby avoiding the need for an external battery as implemented recently by other groups who succeeded in controlling wirelessly the path of motion of a cockroach. To this end, we designed, constructed and successfully tested an implantable biofuel cell incorporating a bienzymatic anode capable of dissociating trehalose, a disaccharide found at concentrations of up to tens of mM in the hemolymph of insects, to yield glucose, which is then oxidized to gluconolactone by the enzyme glucose oxidase. As shown recently in our laboratories, this type of biofuel cell can generate up to $15.6 \mu\text{W}/\text{cm}^2$ when implanted in a live insect and power a transmitter attached to its body capable of sending radio signals wirelessly to a distant receiver.

ID: 175

Topic:

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Multiscale Correlative Electrochemical Multi-Microscopy: Building an Understanding of Electrochemical Interfaces From Single Entities Upwards

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Electrodes used electrochemistry, with applications in electrocatalysis, energy storage, sensor technologies and corrosion, show heterogeneity and complexity on a range of lengthscales. The activity of these electrodes is often determined by old classical macroscopic electrochemical techniques that provide an average response of an electrode and are unable to detect and analyze spatially heterogeneous fluxes that govern the electrode response. We propose new approaches to study electrochemical and electrocatalytic phenomena, whereby the activity of an electrode is visualized by electrochemical microscopy in the form of “activity maps” and “activity movies”, and these quantitative data are then related to co-located electrode structure from complementary high-resolution microscopy and spectroscopy techniques applied in the same area of the electrode. This new age of correlative electrochemical multi-microscopy seeks to relate electrode structure to activity clearly and unambiguously. This contribution will discuss the use of nanoscale scanning electrochemical cell microscopy (SECCM) and scanning ion conductance microscopy (SICM) for the acquisition of electrochemical activity-electrode topography maps, coupled with a wide range of microscopy techniques, spanning electron microscopy and electron backscatter diffraction, micro-Raman spectroscopy and atomic force microscopy to pinpoint particular active sites in the same area. This is a general platform for investigating electrochemical interfaces, and illustrative examples of this approach will include: layered materials (2D and 3D), structurally and/or compositionally heterogeneous surfaces such as polycrystalline metals and conducting polymers, and ensemble electrodes comprising of nanoparticles on an electrode support surface, with applications in electrocatalysis and energy storage (batteries).

A key thesis of our work is that electrochemistry of complex electrode surfaces can be broken down and studied as set of simpler “single entities” (e.g., individual steps, terraces, defects, crystal facets, grain boundaries, single particles). The resulting nanoscale understanding of reactivity can then be used to create scalable models for electrochemical interfaces that will ultimately facilitate the rational design of functional (electro)materials. Countless talented people at Warwick and elsewhere have contributed to our work in this area and will be acknowledged in the presentation.

ID: 176

Topic:

Electrochemical Energy Storage and Conversion

(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Studies of Transport Processes in Li-Ion Cathodes

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Batteries are complex, with important phenomena arising from multiple length scales. Advances thus require multiscale experimental inquiries, and mathematical models, including multiscale models, may be employed to design, analyze and integrate studies. In early-stage research efforts, close collaboration with experimental efforts may result both in dramatically improved model fidelity and in more optimal utilization of experimental resources. We present approaches to augment physics-based models of Li-ion cathodes with statistical methodologies. Several examples are illustrated.

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Rutin Determination at Pd Nanoparticles Modified Polymer Film Electrode

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Rutin (3,4,5,7-tetrahydroxy-flavone-3-rutinoside) also known as vitamin P, is a member of flavonoid family. It is naturally found in more than 70 plants, majorly in *Fagopyrum esculentum*, *Ruta graveolens*, and *Sophora japonica* (Gullón et al., 2017). Rutin and its derivatives were used as an additive in food products, especially meat due to its antimicrobial and antioxidant ability. Moreover, it has protective activity against diabetic complications, anti-tumor and anti-inflammatory property (Niu et al., 2018).

Neutral red (3-Amino-7-dimethylamino-2-methylphenazine hydrochloride) is an organic phenazine dye. Besides its common use in optical field, it is also used as electrode modifier which is simply electropolymerized on the electrode surface due to the primary amino groups in its structure (Naik and Swamy, 2017). Wide range of applications employed with PNR due to its high stability, easy modification and fast electron transfer ability (Pauliukaite and Brett, 2008). Metal nanoparticles (MNPs) are one of the most widely used modifiers which facilitate electron transfer rate and increase the active surface area of electrode (Zhang et al., 2019). Pd has an important place in MNPs due to its ability to promote electrode reaction and high stability.

In this study, Pd nanoparticles were electrochemically deposited on polymerized neutral red film electrode on glassy carbon electrode. The resulting electrode was employed for sensitive and selective rutin determination in pH 3 Britton Robinson buffer solution. Under the optimized conditions, rutin signal was linear with its concentration between 0.04 μM – 1 μM and 2 μM – 60 μM and detection limit was found as 0.02 μM with differential pulse voltammetry.

DRAFT

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**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Electrodeposition of Copper (II) Sulfide and Zinc Sulfide onto Polycrystalline Gold Electrode

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Underpotential deposition (UPD) of metals enables specially controlled modifications on the catalyst surface, so it has been extensively studied. Electrochemical atomic layer epitaxy (ECALE) is one of the UPD-based electrochemical deposition methods and it works with the sequential and separate UPD of different elements. In another UPD-based electrochemical technique, co-deposition has focused on the electrodeposition of a compound from the same solution at a common UPD potential. The mainly used technique for photovoltaic applications is electrodeposition of polycrystalline semiconductor thin films, but a little effort has been made for sulfides of copper and zinc (Pauporte & Lincot, 2000). Also, a little attention has been given for the nucleation kinetics and characterization of zinc deposition on polycrystalline electrodes (Dogel & Freyland, 2003). Therefore, additional electrochemical characterization is necessary to understand the semiconducting properties of coated surfaces. For that, a new, simple and economical electrodeposition-based process was developed in this work. There are a lot of applications in the literature using one of the UPD methods. However, ECALE and co-deposition methodologies on a comparable basis were employed to grow CuS and ZnS thin films as photovoltaic semiconductors on polycrystalline gold electrode for the first time. The deposition potentials of copper, zinc and sulfur were defined separately by cyclic voltammetry. Thin films were created from an electrolyte solution containing CuSO₄, Na₂S and ZnSO₄. The influence of bath temperature at the deposition potential was also studied to determine the crystallinity of deposits. From the chronoamperometry results including the transients obtained within the under potential region, the overall shape of the experimental depositions were proposed and the growth process was considered. Thus, this work was fundamentally targeted at polycrystalline surfaces instead of single crystal surfaces which were prepared using complex systems to accumulate metals. At the same time, binary systems and thin films were created by proposed practical new approach.

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Copper; Zinc; Under potential deposition; Co-deposition; ECALE.

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Platinum Black -modified Microelectrode for Real-Time Detection of Antipsychotics

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Today, clozapine (CLZ) is considered the most effective antipsychotic medication for schizophrenia, and it is the only one whose treatment efficacy can be predicted by a simple blood test. However, CLZ is still one of the most underutilized medication due to burdensome treatment monitoring schemes, and of adverse side effects.[1] Here, we present the development of a miniaturized electrochemical sensor that allows a minimally invasive, real-time and in situ monitoring of CLZ levels in microliter volume of undiluted serum samples. Current methods for measuring CLZ blood levels, requires laborious sample preparation steps (e.g., liquid chromatography–mass spectrometry; LC-MS [2]), destroys the sample, and changes the levels of CLZ in the process, thus impeding their utilization for in situ, real-time analysis. By utilizing the redox-active nature of CLZ, an electrochemical sensor can overcome these limitations. However, the analytical performance of an electrochemical sensor dramatically decreases for undiluted serum due the presence of overlapping signals from other redox-active molecule. As part of this work, we focused on the main challenge of state-of-the-art methods for in situ analysis of unlabeled redox molecules in biofluids—redox molecules other than the analyte generating overlapping and interfering electrochemical signals (e.g., uric acid).[3] We modified a microfabricated sensing microelectrode with a platinum black (PB). The modification increased the electrocatalytic activity of the microelectrode towards CLZ oxidation and improved the overall selectivity of the sensor. Differential pulse voltammetry technique was used to measure the CLZ (0-5 μM) oxidation currents with the PB -modified microelectrode in undiluted and microliter volume of whole blood. We observed a characteristic dose response effect that resulted in a limit-of-detection of $0.60 \pm 0.04 \mu\text{M}$ and a sensitivity of $1.7 \pm 0.4 \text{ A/M}$ whereas the bare microelectrode was unable to differentiate between the different doses of CLZ. Importantly, the PB –modified microelectrode demonstrated a limit of detection, which is below the clinical threshold (1-3 μM).[4] Our preliminary work anticipates production of miniaturized and wearable testing devices, designed for schizophrenia treatment management.

The authors thank the Ilse Katz Institute for Nanoscale Science & Technology for the help in Microfabrication and material characterization. The authors also thank the Brain and Behavior Research Foundation for funding the Project.

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electrochemical sensor, schizophrenia, blood test, and biofluid

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Comparison of Polycarbazole Films Bearing Carboxylic Acid and Cyanoethyl for Optoelectronic Applications

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Organic materials (both low molecular weight compounds and polymers) have recently gained attention as an important component of light-emitting diodes, field effect transistors, charge storage devices, photodiodes, sensors, etc. [1]. These organic electroactive and photoactive materials are usually based on polycarbazole, polypyrrole, polyaniline, and polythiophene [2]. Carbazole based polymers also have been of greater interest because of their interesting thermal, electrical, and photophysical properties [3,4]. Polycarbazole and its derivatives can be built onto desired electrodes by electrochemically deposition technique to yield conductive thin films.

In this study, the compounds based on carbazole derivatives (N-positions were occupied by carboxylic acid and cyanoethyl) were synthesized by well-known chemistry from readily available reagents. Their polymers were prepared on ITO/glass substrate by repetitive cyclic voltammetry (CV) scanning of the monomer solutions containing NaClO₄-LiClO₄ electrolyte dissolved in acetonitrile. The electrochemical and spectroelectrochemical characterization of the polymers were investigated and compared with those of different N-substituted with groups attaching on the active sites of the carbazole units. The structures of the monomers and polymers were characterized by ¹H-NMR, ¹³C-NMR, and FTIR. In-situ spectroelectrochemical studies revealed that N- positions occupied by carboxylic acid (PCz-COOH) and cyanoethyl (PCz-CN) films exhibited a multichromic behaviour under various applied potentials. The π - π^* transitions for the neutral form of polymer films show the absorption maximum of 305 nm for PCz-COOH and 303 nm for PCz-CN. The optic band gaps of the polymers, defined as the onset of the π - π^* transitions in other words from their onset absorption edge of the neutral state spectrum, were determined as 3.6 eV and 3.5 eV for PCz-COOH and PCz-CN, respectively. Also, the effect of N-substituted groups on the properties of solubility, molecular weight and conductivity have been discussed further.

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Keywords: Polycarbazoles, Electropolymerization, Electrochromic material

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

**Fabrication of Prostate Cancer Immunosensor Platform Based on Aminated-Gold Nanoparticle
Modified Screen-printed Electrode**

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Label-free immunosensor based on cysteamine-gold nanoparticle (Cys-AuNp) modified screen-printed gold electrode (SPGE) were developed using a drop-casting method for the detection of prostate specific membrane antigen (PSMA) in different mediums consisting PSMA protein/cells. ATR-FTIR and UV-Vis spectroscopy analysis proved that the amine formation was efficiently achieved on AuNps' surface. TEM images showed that, synthesized colloidal Cys-AuNp particles were uniformly distributed with 37.9 ± 6.7 nm in average diameter, whereas hydrodynamic radius was calculated as 43.3 ± 7.2 by dynamic light scattering measurements. After drop-casting Cys-AuNps onto SPGEs' working electrodes' surface, SEM analysis were performed. The SEM images demonstrated that, Cys-AuNp nanoparticles were homogeneously anchored on the surface of the SPGEs. Finally, electrochemical measurements were carried out, and the results showed that the electron transfer kinetics between the analyte and electrode was enhanced after modifying SPGEs with Cys-AuNp, resulted by an enhanced effective surface area thus created higher immobilization capacity of PSMA antibodies on the surface. Performance studies revealed that herein proposed immunosensor having a linear detection limit of 20-100 pg, LOQ was found to be 16.3 pg that makes the proposed sensor a potential analytical tool for the prostate cancer detection, even in early stages of the cancer.

This study was partially supported by Tubitak 2214-A research grant.

Keywords: prostate cancer, electrochemical immunosensor, PSMA, gold nanoparticle

Analytical Electrochemistry

(Experimental and theoretical aspects of electroanalytical processes.

Electrochemical sensor devices and the methods used therein)

Immobilization of Hemoglobin on TiO₂-graphite Paste Film Electrodes for the Electrochemical Sensing of H₂O₂

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The present work describes the preparation of a hybrid material of Graphite and low temperature synthesized TiO₂ nanoparticles (TiG) functionalized with Hemoglobin (Hb) for the development of a low cost, sensitive and selective electrochemical hydrogen peroxide (H₂O₂) biosensor. TiO₂ film electrodes have been used successfully in the past for the immobilization of proteins, for studying protein/electrode interactions and developing electrochemical biosensors. This is due to their fascinating properties combining high surface area, physical rigidity, open pore structure, biocompatibility, chemical and thermal stability. However, their preparation could be a lengthy and complicated process involving sol-gel synthesis and sintering. [1] In addition, these films exhibit limited conductivity at low negative potentials, act as insulators at positive potentials, exhibit relatively slow electron transport and a rapid recombination rate of the electrogenerated electrons and holes, limits their use as catalysts and the quality of the electrochemical signals obtained. [2] Graphite on the other hand, offers various exciting features such as wide potential window, good electrical conductivity, low noise, inexpensive, biocompatibility, non-toxicity, simple preparation method in commercial grade, good physical and chemical stability and easy availability. [3]

Therefore in this work graphite was incorporated into the active layer of mesoporous TiO₂ films resulting in TiG hybrids with improved electrical conductivity. The hybrid material was deposited on indium tin oxide (ITO) glass substrates and was investigated in terms of morphology and structural analysis. Modification of the electrodes with an aminosilane prior to protein immobilization is found to enhance protein binding attributed to more favorable protein/electrode electrostatic interactions. The direct interfacial electron transfer without the use of electron mediators and catalytic redox chemistry of the immobilized Hb is demonstrated by the use of cyclic voltammetry (CV). Quasi-reversible redox peaks were obtained for the Hb/TiG electrodes with a midpoint potential of -0.19 V (vs. Ag/AgCl) and an interfacial electron transfer rate constant of $1.16 \pm 0.01 \text{ s}^{-1}$. Differential pulse voltammetry (DPV) was used for displaying the high electrocatalytic activity of the proposed biosensor for H₂O₂ detection exhibiting a linear range from 5 to 100 μM with a correlation coefficient $R^2 = 0.9975$ and a limit of detection (LOD) of $3.27 \times 10^{-6} \text{ M}$. Our biosensor demonstrated good repeatability, stability and selectivity and was found to be applicable for use in determining H₂O₂ concentration in commercial honey samples.

This research was partially supported by Grant 80669 from the Research Committee of the University of Patras via "C. CARATHEODORI" program.

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Keywords: Hemoglobin, Graphite, TiO₂, CV, DPV, H₂O₂, Biosensor

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

**Electrodes Modified by Double Metal Nanoparticles Containing Nickel
(and a second metal) for Electroanalytical Applications**

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Nanoparticle catalysts containing two different metals play a very important role in many fields such as the petrochemical reforming, in hydrogenation rates and in many other industrial processes. Scientists have long known that the combination of metals can lead to enhanced catalytic activity in comparison with the monometallic catalysts. Nickel based materials such as nickel, its oxides, hydroxides and oxy-hydroxides exhibit excellent electrocatalytic performance toward many molecules. Nickel is widely used for fuel cells, energy storage, organic synthesis, wastewater treatment and electrochemical sensors for pharmaceutical, medical, food or environmental analysis. Among the electrochemical sensors, the nickel-based ones have been extensively explored in recent years due to their excellent characteristics, such as long life cycling, well-defined electrochemical redox activity and good stability in alkaline electrolytes. It is also noteworthy the characteristics of Ni compounds to build batteries and supercapacitors. In the last years, we have developed sensors constituted by hydroxides of two metals, which were precipitated simultaneously. Electrodes modified with these materials presented differentiated performance for the detection of different compounds, such as pharmaceuticals compounds like isoniazid ($\text{Ni}_{1-x}\text{Co}_x(\text{OH})_2$), prednisone ($\text{Ni}_{1-x}\text{Ce}_x(\text{OH})_2$), n-acetylcysteine ($\text{Ni}_{1-x}\text{Pb}_x(\text{OH})_2$), hydralazine ($\text{Ni}_{1-x}\text{Pt}_x(\text{OH})_2$), uric acid ($\text{Ni}_{1-x}\text{Pb}_x(\text{OH})_2$). In our presentation, we will give an overview about this field and the perspectives of the applications of these materials.

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[1] Supporting agencies: CNPq (proc. 311847-2018-8), FAPESP (proc. 2018/16896-7) and CAPES.
Modified electrodes with $\text{NiMe}(\text{OH})_2$ nanoparticles, sensors, pharmaceutical analysis. batch

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

**Fabrication of Shape-controlled Gold Nanostructures on 1T-MoS₂ Nanosheets and
their Electrochemical Drug Sensing Application**

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Since the discovery of graphene, two-dimensional (2D) layered transition metal dichalcogenides (TMDs) have attracted great attention due to their interesting properties in various application fields, such as electronic and sensor devices, energy-storage, catalysis and composite materials.¹⁻⁴ Molybdenum disulfide (MoS₂), one of the most interesting 2D materials, features properties such as a direct band gap (1.9 eV), high carrier mobility (200–500 cm² V⁻¹ s⁻¹) and promising electrocatalytic activity. MoS₂ is commonly found as a polytype involving the 2H phase (2H-MoS₂) with semiconducting properties and the 1T phase (1T-MoS₂) with metallic properties.⁵ 1T-MoS₂ features a conductivity up to 107 times higher than 2H-MoS₂, as well as superior charge transfer ability. Therefore, 1T-MoS₂ could be considered as a novel promising electrode material for sensing purpose. In addition, MoS₂, which allows its surface modification with metal nanoparticles (Au, Pt or Ag etc.), is a suitable 2D material for electrochemical sensing applications.⁶ It is known that the decoration of Au nanostructures on MoS₂ surface has been improved the electrochemical performance and electrocatalytic activity towards the important biological molecules.⁶⁻⁷ In this study, we report a highly efficient route to fabricate the electrochemical sensor based on 1T-MoS₂ prepared by metal intercalation process with NaK alloys, and its combination with different shaped Au nanostructures. Then, the electrochemical activity of the fabricated MoS₂-based composite materials has been performed towards the doxorubicin (DOX) as an anticancer agent. A pair of well-defined redox peaks was obtained at developed MoS₂-based sensors in pH 6 PBS buffer solution. The developed MoS₂-based sensor demonstrated a good electrochemical performance with a low detection limit at nano-molar levels for DOX detection. As a conclusion, the proposed MoS₂-based electrochemical sensor could be alternative portable analytical tool for the detection of anticancer agents such as DOX in clinical samples.

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Keywords: Molybdenum disulfide; chemical exfoliation; Au nanostructures; electrochemical sensor; doxorubicin

**Bioelectrochemistry and Biomedical Applications
(Electrochemical and electroanalytical aspects of biological processes)**

Electrochemical Behavior and Surface Characterization of Screen-Printed Electrode for Biosensor Development

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Today, electrochemical techniques have an increasing importance. The electrochemical methods used in the development of sensors attract more attention than other methods due to their advantages such as high sensitivity, short response time and low cost. Screen Printed Electrodes (SPE) can be used in sensor formation by electrochemical impedance spectroscopy (EIS) for studying the trace amount of harmful chemical and biological hazards in food, cosmetics or dietary supplements. Having knowledge about surface properties and electrochemical activity of SPE is of great importance in the biosensor formation stage. In this study, electroanalytical performance of the SPE electrode was investigated by electrochemical activity of different solutions in different concentrations by EIS and cyclic voltammetry (CV) methods. Surface morphology and microstructural properties of the SPE electrodes were examined by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) analysis, and Atomic Force Microscopy (AFM) in addition to electrochemical characterization by using $K_3[Fe(CN)_6]$ and KCl redox probes. Cyclic voltammograms and impedance plots have been investigated for each process conditions.

In the present study, the redox probes in the frequency range of 10 kHz to 0.1 Hz showed that when the concentration of $K_3[Fe(CN)_6]$ increased at different concentrations (2mM-5mM-50mM), the electrolyte resistance (R_e) and charge transfer resistance (R_{ct}) decreased. In addition, $K_3[Fe(CN)_6]$ with the equi-volume solution of 0.1M KCl showed that KCl had an effect of decreasing these resistances, as well. After all the results obtained, a detailed examination of the surface characterization and electroanalytical performance of the SPE electrode was investigated for optimization biosensor development stages has been demonstrated.

The authors would like to thank Scientific Research Projects Funds (BAP 2018-2065) of Eskisehir Osmangazi University for the support of this study.

Keywords: Biosensor, Screen Printed Electrode, Electrochemical, Electrochemical Impedance Spectroscopy

**Bioelectrochemistry and Biomedical Applications
(Electrochemical and electroanalytical aspects of biological processes)**

Nanosecond Laser Treatment of Thin Gold Films on ITO Electrodes for Bioelectrocatalysis

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Redox enzymes such as bilirubin oxidase (BOD) have been widely used in biotechnological devices for O₂ reduction into water[1]. By modulation of the pH of adsorption of BOD on SAM-functionalized gold electrodes, we previously demonstrated that electrostatic interactions were the main processes controlling the orientation of the enzyme for fast interfacial electron transfer[2]. It was concluded that adsorbed amount of enzyme does not directly translate to enzyme activity. In fact, bioelectrodes prepared with least amount of adsorbed enzymes show maximum specific catalytic activity indicating that enzyme-enzyme interaction in a densely populated enzyme adlayer could degrade the catalytic performance. To investigate further this relationship between activity and enzyme density on electrodes, we moved toward gold nanoparticles prepared by laser ablation (LA-AuNps). Laser can provide the ability to accurately deliver a large amount of energy to a material, which can be used to rapidly introduce significant amount of heat into a solid. The unique interactions of laser radiation with metal surfaces lead to permanent changes on the material properties in a specific region such as local chemistry, crystal structure and morphology of the material. In this work, by laser ablation of a thin gold film, a stable monolayer of AuNps was prepared with controlled size and density on the electrode surface. Hence, the specific adsorption of enzyme on these AuNps can nullify local enzyme interactions. We initiated our work using different thicknesses of gold films deposited on Indium-Tin Oxide (ITO). BOD was immobilized on as-produced nanoparticles. The effect of AuNps size and density on the orientation of BOD and on the induced catalytic currents for O₂ reduction will be discussed.[4] Furthermore, possibility to develop other nanostructured electrodes by laser ablation will be exploited as a clean and robust platform for enzyme adsorption.

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Keywords: Biocatalysis, Laser, Gold Nanoparticles, SAMs, redox enzyme

**Bioelectrochemistry and Biomedical Applications
(Electrochemical and electroanalytical aspects of biological processes)**

Binderless Graphene / Three-dimensional Microfibrous Carbon Paper Composites Electrode for Electrochemical Applications

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Recent advances in nanoscale science and technology provides new opportunities in achieving highly efficient electrodes for electrochemical applications such as: energy storage devices, sensors, catalysts. Synergizing with material chemistry, various nanostructures have great potential in stabilizing and activating the electroactive materials with performances well beyond the scope of traditional fabrication technologies. One of the most promising materials is graphene.

Graphene, a 2D planar sheet of hexagonally configured sp² hybridized carbon atoms, has attracted immense interest since its discovery in 2004. This new material shows excellent tensile strength, ballistic electrical conductivity (in the range of 200,000 cm² v⁻¹ s⁻¹), high thermal stability (around 5000 Wm⁻¹ K⁻¹), very highly theoretical surface area estimated to 2630 m² g⁻¹ and outstanding Young's modulus (1100 GPa). These exceptional physical and chemical characteristics make graphene an excellent candidate as a compound in nanocomposites materials for many applications.

For electrochemical applications, the use of graphene needs an electrode preparation process. Conventional methods of preparation of these electrodes comprise three steps: (i) the dispersion of graphene in solution (ii) the formation of composite film with an appropriate binder, and (iii) the assembly of the composite film on a current collector. This conventional process is complicated, inefficient, and expensive.

In this work, we report on the development of highly attractive nanostructured samples derived from three-dimensional microfibrous carbon paper uniformly covered with graphene without binder. The synthesized materials were characterized by using scanning electronic microscopy, X-ray diffraction, Raman spectroscopy, cyclic voltammetry, galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy techniques.

Results of structural characterization confirm the effectiveness of the graphene deposition on the three-dimensional microfibrous carbon paper method. Results of electrochemical tests showed high-resolution responses in different chemical media, which indicate good electrical contact between the graphene and the three-dimensional microfibrous carbon paper substrate. These architectures hold great promise for incorporation into energy storage devices, sensors, catalysts. As first application, the developed process was used to fabricate an efficient electrode for electrochemical capacitor.

**Bioelectrochemistry and Biomedical Applications
(Electrochemical and electroanalytical aspects of biological processes)**

An Emerging Field at the Boundary between Biology, Chemistry, and Engineering

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Over the last two decades ingenious devices have been developed for converting chemicals present in biofluids in living organisms into electrical energy with potential application in a variety of areas of fundamental and practical relevance. Efforts in our laboratories have focused on the development of such biofuel cells that could be implanted into insects and provide the power required not only for the operation of electronics for sensing, information storage and wireless communication, but also for the stimulation of the nervous system, a strategy that will ultimately allow control of certain aspects of the insect behavior. An attractive feature of this approach is that it provides a continuous and autonomous source of power, thereby avoiding the need for an external battery as implemented recently by other groups who succeeded in controlling wirelessly the path of motion of a cockroach. To this end, we designed, constructed and successfully tested an implantable biofuel cell incorporating a bienzymatic anode capable of dissociating trehalose, a disaccharide found at concentrations of up to tens of mM in the hemolymph of insects, to yield glucose, which is then oxidized to gluconolactone by the enzyme glucose oxidase. As shown recently in our laboratories, this type of biofuel cell can generate up to $15.6 \mu\text{W}/\text{cm}^2$ when implanted in a live insect and power a transmitter attached to its body capable of sending radio signals wirelessly to a distant receiver.

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**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Fibrous Carbon Structures as Interlayers for Li-S Batteries

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Lithium sulfur (Li-S) batteries have received enormous interest owing to high theoretical specific capacity, 1675 mAh/g, and low cost of sulfur. Lithium sulfur batteries have been considered in applications including electric vehicles, unmanned aerial vehicles, satellites, and other energy-storage areas. However, poor cycling and C-rate performance limit commercializing lithium sulfur batteries. There are three major problems which prevent commercialization of Li-S batteries; low conductivity of sulfur and lithium sulfide, shuttling of the polysulfides and huge volume fluctuation during cycling. The 3D continuous conductance is influenced by low conductivity of sulfur. The shuttling effect results in a low

Coulombic efficiency and the rapid degradation of Li-S. Large volume changes leads to failure of the cells. Modifying separator and using conductive interlayer with high porosity could be efficient ways to improve electrochemical properties of lithium sulfur batteries. Conductive and porous coatings have been commonly studied to improve active material utilization and prevent shuttle effect. In addition, interlayer that could chemically attract polysulfides and trap large amount of polysulfides could be an alternative way to improve the lifespan and performance of Li-S batteries. In this study, different fibrous structures were investigated and improvement on the electrochemical performance was presented.

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Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Linear and Nonlinear Electrochemical Impedance Spectroscopy Studies of Li/SOCl₂ Primary Batteries

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Primary (i.e. non-rechargeable) batteries are the main electrochemical energy storage devices for diverse important applications such as military, aerospace and specialty emergency services. Lithium Thionyl Chloride (Li/SOCl₂) batteries are the most commonly used due to their high energy density, high operating cell voltage, voltage stability over 95% of the discharge, large operating temperature range (-55 to 70 °C) and long storage life [1]. For primary batteries, linear and stable Electrochemical Impedance Spectroscopy (EIS) is challenging due to the lack of a well-defined charging reaction. The difficulty for Li/SOCl₂ specifically rises the inconsistent anode passivation of the cell in addition to the irreversible operation chemistry.

The very scarce literature examples lack proper measurement protocol and accurate EIS data [2]. In this work [3], we demonstrate how accurate, linear and stable EIS data can be obtained by performing Galvanostatic-EIS in discharge mode. We will present the details of how experimental parameters influence not only the measurement, but also the cell itself. We will present linear and stable data that is compatible with the Kramers-Kronig relations in frequency ranges as wide as 10 kHz to 1 mHz for fully charged to fully discharged cells. Moreover, we will present the nonlinear responses obtained from the EIS measurement utilizing Harmonic Analysis which shows that the passivation phenomena in the anode is a major cause for the nonlinearities.

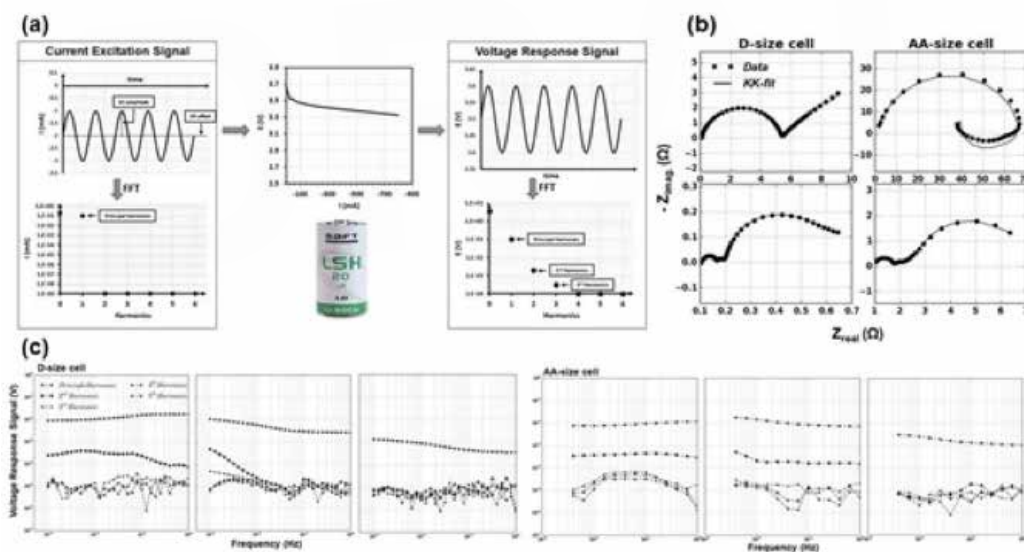


Figure 1. a) The G-EIS with discharge plus harmonic analysis measurement protocol, b) EIS of Li/SOCl₂ battery and c) Harmonic spectra for nonlinear responses

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Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Zero Free Parameter, EIS Based Performance Prediction for Hybrid Energy Storage Systems

Mohammed ZABARA, Can Berk UZUNDAL, Zülal Beyza DEMIRKAYA, Burak ÜLGÜT

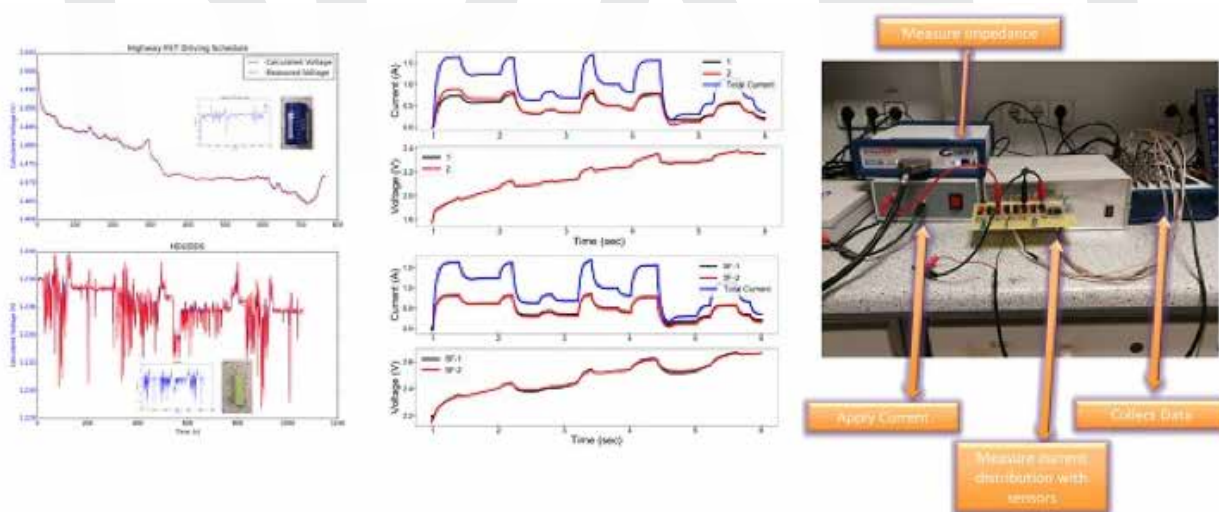
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The energy storage system dictates most properties of electrified devices. In transportation it controls the range, in consumer electronics it controls the lifetime and in all cases, it controls the size and the geometry of the device. With the plethora of choices in chemistry, construction and geometry, testing each combination is time-prohibitive. Therefore predicting the performance of the potential energy storage systems under real life conditions is one of the most important tasks in the design. Though the standardized capacity under constant current explains some of the properties, a complete analysis involving the slow and fast responses are required for an accurate prediction.

Electrochemical Impedance Spectroscopy (EIS) is at the center of any such modelling effort, either by providing an equivalent circuit model to be used as the framework for prediction [1] or by providing the tool to obtain information about the fundamental kinetics and transport parameters for a first principles model [2]. The equivalent circuit model based efforts tend to suffer from inaccuracies due to incomplete model and the first principles methods suffer from complicated algebra and insufficient accuracy in the fundamental constants.

In this contribution, we will first present our initial work on our EIS-based, zero-free-parameter modelling methodology for single cells [3](Figure on the left). This method employs the impedance data as-is in the frequency domain, through a complex multiplication by the Fourier transform of the discharge profile. The obtained frequency domain voltage is then back transformed to the time domain for an accurate description of the voltage response of the system.

Further, we will present the extension of our method to parallel combination of similar and dissimilar systems. This extension involves an accurate calculation of the current distribution in addition to the rest of the performance parameters accurately. We will be presenting modeling (middle figure) and experimental efforts (right figure)



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Keywords: Impedance Based Modeling, EIS, Batteries

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Characterization of the Effect of Electrolyte-to-Sulfur Ratio on the Performance of a Lithium-Sulfur Cell

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Bogazici University, Turkey

Lithium-Sulfur (Li-S) batteries have received significant attention in the last decade due to their high theoretical specific energy [1-3]. In Li-S batteries, electrochemical performance is a strong function of the cell design mainly because of the complexity of the cathode kinetics [1-3]. Electrolyte-to-sulfur (E/S) ratio in the cell is a key design factor affecting the Li-S cell performance via the reaction and polysulfide shuttle mechanisms in the cathode [1-3]. A low E/S ratio in the cell is critical for achieving high energy density at the cell and system level [2]. However, sulfur utilization and thus the discharge capacity of the Li-S cell are limited at low electrolyte amounts due to the finite solubility of LiPS in the electrolyte [4]. In this study, we demonstrate a characterization of the electrochemical performance of a Li-S cell as a function of the E/S ratio by means of the initial discharge capacity, capacity retention and cycle life. In addition, by developing a cell-level performance model we project the cell-level energy density and specific energy of the Li-S battery for different E/S ratios. As a result, the impact of E/S ratio not only on the electrochemical performance but also on the energy density and specific energy of a Li-S cell is identified and discussed.

This work was supported by the Bogazici University Research Fund, Grant No: BAP 18A05SUP4.

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Keywords: Lithium-Sulfur Batteries, Electrochemical Characterization, Cell Design

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

A Study on Low Pt Loaded Metal Ceria Based Catalysts for Stable PEM Electrolyzers

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Gazi University, Turkey

For the elimination of high material costs in PEM electrolyzers due to Pt content in cathode and anode electrodes, we focused on hydrogen evolution reaction (HER) on low pt loaded metal ceria based catalysts. Since lanthanides are well known for their corrosion inhibition characteristics on metal surfaces, the stability and activity of HER was decided to be controlled and monitored by different ceria composites treated at different reduction temperatures, pH environment and purging environment. During the search for optimum catalysts at certain pH and reduction temperature, our electrochemical studies indicated that reduction temperature can have a dominant effect on charge transfer resistance compared to pH as seen in Fig. 1. In addition, HER characteristics of ceria based catalysts were improved after hydrogen purging as indicated by cyclic voltammetric studies in Fig. 2. which could be due to in situ reduction in the electrolyte environment.

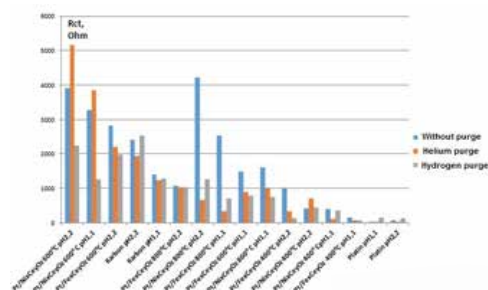


Fig. 1 :Effect of purging environment, pH and reduction temperature on the charge transfer resistance of Pt loaded metal ceria based catalysts at -0.2V vs. SHE.

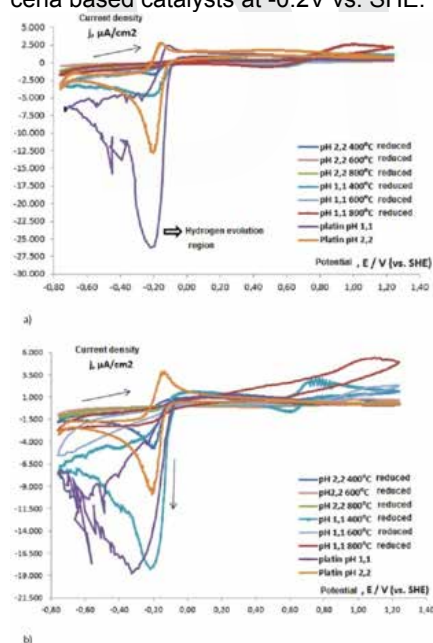


Fig 2. Effect of hydrogen purging on the HER for platinum loaded FexCeyOz electrocatalyst at different pH and reduction temperatures. a) before hydrogen purging b) after hydrogen purging.

This study was financially supported by Gazi University Scientific Research Project, BAP 06-2016-03 and TÜBİTAK 111M474 Project.

Keywords: Electrolyzer, HER, ceria.

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Prussian Blue Analogues as Water Oxidation and Reduction Electrocatalysts

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Cobalt hexacyanometalates, so called Prussian blue analogues (PBAs), have recently been investigated as water oxidation and water reduction electrocatalysts, which are two of the critical steps in water splitting.¹⁻⁴ Cobalt sites, particularly the ones on the surface, have been found to be the active catalytic site in these systems. Although the hexacyanometal site is not the active catalytic site, different cobalt hexacyanometalates (M = Co, Fe, and Cr) exhibit different electrocatalytic activities indicating that these sites either have a morphological or electronic effect, or a combination of both. Herein, our studies on different cobalt hexacyanometalates will be presented to interrogate the effect of hexacyanometal site on the electrocatalytic activity of cobalt sites. Moreover, a possible mechanism has been proposed based on Infrared studies, electrochemical experiments including chronoamperometry and cyclic voltammetry, and computational studies.

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Keywords: Prussian blue, water oxidation, electrocatalysis

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Tailored Activated Carbons Derived from Chemically Activated Waste Tea for Supercapacitors in Both Aqueous and Organic Electrolytes

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Ankara University, Turkey

In this work, waste tea-based activated carbons were prepared and examined as supercapacitor electrodes in both aqueous and organic electrolytes. The activated carbons were produced according to the conventional chemical activation method using K_2CO_3 as activation agent. The surface properties of the activated carbons were altered by changing the amount of K_2CO_3 . Three different activated carbon samples were prepared by mixing the waste tea and K_2CO_3 at the impregnation ratios (IR) of 1:1, 1:1.5 and 1:2 (the ratio of waste tea: K_2CO_3 , wt:wt). Physical and chemical properties of the carbon samples were characterised in terms of the BET surface area, the pore size distribution, laser particle size, FTIR spectroscopy, Raman spectroscopy, XPS and SEM analyses. Coin cell types supercapacitors were prepared in the presence of each carbon samples and the performance of the cells was tested in aqueous (6 M KOH) and organic (1 M Et₄NBF₄:ACN) electrolytes.

The surface and morphological characterisation of the carbon samples showed that the IR substantially affected the porous structure of the samples. The total pore volume, and hence the specific surface area of the samples increased with increase in IR. However, the micropore volume fraction dramatically increased at the IR of 1:1.5, and then decreased again at the IR of 1:2. The highest mesopore volume fraction was obtained at the IR of 1:1. The SEM images of the samples revealed that when the IR increased from 1:1 to 1:1.5, the pore morphology became more uniform with smoother pore shapes and boundaries. With the increasing IR from 1:1.5 to 1:2, the surface of the sample seemed much rougher. The chemical characterisation results showed that the amount of oxygenated groups of the sample produced by IR 1:1 is considerably higher than the other samples. These changes are attributed to the interaction between the raw material and the amount of K_2CO_3 during the activation process.

The electrochemical characterisation of the cells showed that the sample produced by IR: 1:1.5, which had the highest percentage of micropores, exhibited the highest specific capacitance (180 F/g) in 6 M KOH. It also showed good capacitance retention at high current densities (75 %), and excellent long term stability over the 10000 cycles. On the other hand, the sample produced by IR: 1:1 having the lowest surface area and the highest percentage of mesopores showed the best performance (90 F/g and excellent cyclic stability over the 10000 cycles) in 1 M Et₄NBF₄:ACN. The sample produced by IR 1:2, which had highest surface area showed the poorest electrochemical performance in both aqueous and organic electrolytes. This may be due to the high amount of K_2CO_3 that adversely affected interconnected pore network required for the effective charge storage mechanism.

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Keywords: supercapacitors, activated carbon, chemical activation, surface properties, pore structure

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Analysis of Photoelectrochemical Water Splitting Using Machine Learning Techniques

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Bogazici University, Turkey

Machine learning can be an effective tool to analyze large databases for various chemical and electrochemical processes. We recently analyzed the photocatalytic water splitting over perovskite semiconductors successfully [1]. In this work the photoelectrochemical (PEC) water splitting were investigated using machine learning tools. For this purpose a comprehensive database from about 100 articles was constructed using publications in various databases including Elsevier, Wiley Online Library, RSC Advances, Nature, and ACS Publications. The articles on PEC water splitting were studied from 2007 to 2019. According to web of science, it was observed that annual number of publications on PEC water splitting has increased more than 20 times in 2019 [2]. The input variables in the dataset includes the specifications of working, reference and counter electrodes (such as materials, dimensions, particle size, surface area and band gap of WE), electrode preparation procedure, calcination temperature and time, specifications for light sources and ingredients and pH of reaction solution. Our initial analysis indicates that more than 100 different combinations of photo sensitive materials were used as working electrode while the bare and Nb, Mo, Sn, and W doped ZnO, TiO₂, WO₃, BiVO₄, Fe₂O₃, CdS, CuO (over FTO or ITO glass, or Ti sheet) are used the most commonly. However the counter electrode is usually Pt in various forms. More than 70 % of the reference electrodes are Ag/AgCl. In most articles, the electrodes are prepared and coated in-situ while some works involves the coating of pre-synthesized particulate materials using spin-coating, electrodeposition and dip-coating. Generally Xe lamp with the power range of 100-1000 W were used. Various electrolytes like hydroxide, phosphate, sulfate, sulfide, nitrate and nitrite salts of Na and K elements were used at various pH ranges. About 50% of data points were generated in basic (mostly strong) while 35% were in acidic (mostly mild) medium; the rest were carried out in neutral conditions. The band gap of semiconductors varied between 1.3 and 4.2 eV while around 2.4 eV were generally preferred. The photo-current density, hydrogen/oxygen production and photo-conversion efficiencies were treated as the output variables.

The database were analyzed by using explanatory data analysis techniques (trends, average behaviors and distribution of data) and three learning algorithms: association rule mining for factor effects, decision tree for selection rules and heuristics for high PEC performance, neural network for predictive models.

This work is supported financially by Bogazici University through project BAP-18A05D2 and Bogazici University Foundation (BUVAK).

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Keywords: photoelectrochemical water splitting, data mining, machine learning, association rules, decision tree

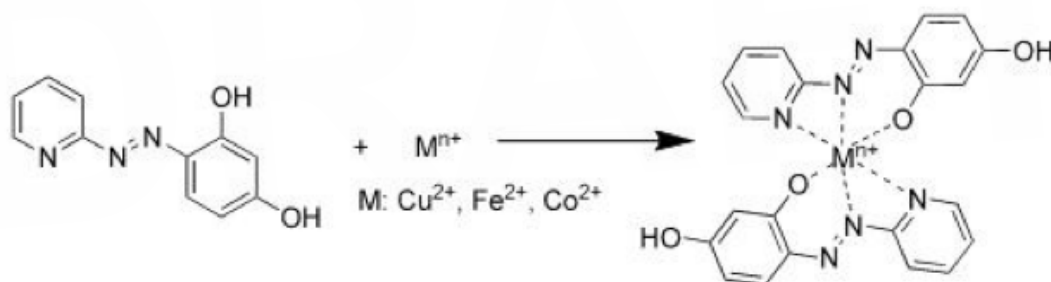
Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

The Synthesis and Solar Cell Assembly of 4-(2-pyridylazo) Resorcinol Metal Complexes for Dye Sensitized Solar Cells

Soner ÇAKAR

Zonguldak Bülent Ecevit University, Turkey

Solar cell has attracted much attention, because it directly converts solar energy into electrical power leaving no environment affect. Established and commercialized solar energy conversion technologies include silicon based (first generations) and thin film devices (second generations), which have reached outstanding performance. Recently, organic photovoltaics, quantum dot, dye sensitized and perovskite solar cells (third generations) are very promising alternatives to the standard silicon solar cells [1]. Dye sensitized solar cells (DSSCs) were firstly devised by Michael Grätzel in 1991 and since then development studies increased substantially [2]. DSSCs, which are composed mesoporous nanocrystalline TiO₂ layer modified with photosensitizing dyes as working electrodes, counter electrodes and redox couples electrolyte, have been actively investigated as photovoltaic system in the next generations of alternatives to silicon solar cells [3]. DSSCs have mainly advantages for the conventional silicon solar cells as following; i) low production cost, ii) shorten electron transportation, iii) low toxicity of the constituent elements, iv) relatively high conversion efficiency of light to electrical energy, etc. However, DSSCs usually show low conversion efficiency values (13%) than silicon based solar cells. In recent years, many dyes have been developed as sensitizer and used in DSSCs. The sensitizers of DSSCs can be subdivided three main groups as following; metal complexes, organic and natural dyes [4]. The maximum solar conversion efficiency of the dye sensitized solar cells was achieved 13% for ruthenium bi-pyridine complex (N719) [5]. Researchers of DSSCs mainly aimed the improved both solar energy conversation and the stability of this type solar cells. Because of the ruthenium is a rare precious metal, researchers are focused on the use of the environmentally friendly, abundant and inexpensive earth alkali metal complexes (especially, transition metals) in DSSCs applications. Transition metal complex dyes are limited use in DSSCs, due to their lower cell efficiency and stability. However, the transition metal complexes have unique properties such as obtainability, complex formation with several organic molecules, processability, low cost and easy synthesis etc.



Herein, 4-(2-pyridylazo) resorcinol (PAR) based metal complex were selected as dye for DSSCs. I have selected Cu, Fe and Co metals in order to metal complexation of PAR. The PAR is known as redox indicators for the analysis of transition metals. The PAR metal complexes were characterized by UV-Vis, CV, and FTIR spectroscopy. In this work, spectroscopic, electrochemical and photovoltaic parameters of different metal based PAR complexes were reported. The energy levels of prepared metal complexes were investigated by CV and DPV. The solar cell performances of these sensitizers were investigated by J-V curve and impedance spectroscopy.

This work was supported by the Scientific Research Projects Commission of Zonguldak Bulent Ecevit University (Project number: 2018-12528785-01).

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Keywords: dye-sensitized solar cells, 4-(2-pyridylazo) resorcinol, metal complexes, third generation solar cel
Electrochemical Energy Storage and Conversion

(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Photoelectrochemical Water Splitting Over Strontium Titanate and Titanium Dioxide Semiconductors

Burcu ORAL, Ramazan YILDIRIM

Boğaziçi University, Turkey

In this work, photoelectrochemical hydrogen production from water on SrTiO₃ and TiO₂ photoelectrodes was studied. Catalysts were prepared using solid state reaction and sol-gel method with various precursors and chelating agents. Dip-coating method was used to coat ITO glass with the catalyst prepared by sol-gel reaction while doctor blade method was used for coating the catalyst prepared by solid state reaction (a paste prepared with ethanol, powder catalyst and PEG-2000). The electrodes are calcined at various temperatures for 3 hours. The photoelectrochemical characterizations are conducted in 3-electrode setup where Au and Pt are used as counter electrodes and Ag/AgCl electrode is used as reference electrode. 300W Xe lamp with AM 1.5G filter is used as light source. The pH of electrolyte is varied between 3 and 10. XRD, UV-Vis and SEM characterizations are done to have a further understanding of the properties of the semiconductors. Pt as counter electrode yielded higher performance than gold while TiO₂ photoelectrodes exhibited higher photocurrent responses compared to SrTiO₃.

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DRAFT

Keywords: Photoelectrochemical, Strontium Titanate, Titanium Dioxide
Electrochemical Energy Storage and Conversion

(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Symmetric Cell Analysis of Solid Oxide Fuel Cell Cathode Materials by Using Electrochemical Impedance Spectroscopy

Oktay DEMIRCAN, Ayşenur Eslem KISA

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The symmetric cell configuration was chosen to study the cathode processes as the data interpretation is simpler compared to a full SOFC analysis. The electrochemical characterization of the cathode material synthesized was performed by means of impedance spectroscopy using a half-cell configuration, being necessary for construction of symmetrical cells with electrode/electrolyte/electrode.

The symmetrical cells based on YSZ (Fuel cell materials) and GDC (Sigma Aldrich) were fabricated as follows. The electrolyte pellets were prepared by pressing commercial powders in a cylindrical stainless-steel mold (5mm in diameter) with a uniaxial dry press at a pressure of 400Mpa for 10mins. After that, the prepared electrolyte disks were initially baked at 400 °C for 2h and followed by sintering at 1300 °C for 2h. For symmetrical cells, cathode samples were mixed thoroughly with organic binder to make the cathode slurry, the paste obtained was painted with a paintbrush on both positions of the pellets (having a diameter of 5 mm and a thickness of about 0.5 mm) which were then dried at 150 °C for 1 h and calcined at 1300 °C for 1h in air to form porous electrodes well adhered to the electrolytes. The final active area of each cathode was about 0.04 cm². Finally, the surface of the pellets was coated with gold paint as collector load. The symmetrical cells were assembled into a lab-designed device that allows performing the experiments in different atmospheres. To determine the resistance of the various cathode processes, the manufactured symmetric cells were characterized by Electrochemical Impedance Spectroscopy (EIS) measurements in ambient air from 400 to 800 °C with an increment of 50 °C. The oxygen partial pressure (PO₂) around the cell during the measurements was maintained using electronic mass flow controllers and Nitrogen was used as the carrier gas. Impedance spectra were measured in the frequency range of 0.1 Hz to 1 MHz with 10 mV amplitude of the AC signal. The spectra were analyzed using GAMRY Interface 1000 Potentiostat/ Galvanostat, which was interfaced with a computer-controlled program for data acquisition.

The high frequency part of the two clearly resolved impedance contributions has an apparent shape in the Nyquist plots below the 500 oC. With increasing operating temperature, the high-frequency arc size decreased noticeably, and the arc was totally disappeared at 500 oC and higher. An additional arc at the low frequency range appeared when the operating temperature was elevated to 700 oC. The impedances of a symmetric cell may arise from both the electrodes and electrolyte. The electrolyte typically performs as an ideal resistor and displays only a dot in the Nyquist plots at high temperatures in the investigated frequency range of 10⁶-10⁻¹ Hz. However, a semi-circle associated with the oxide ion diffusion around the grain boundary of the electrolyte also appeared in the high frequency range with the decrease in operation temperature.

Authors gratefully acknowledged the financial grants supplied by the Technological and Scientific Research Council of Turkey (TUBITAK) (Project No: 112M279 and 214Z094) and Bogazici University, Scientific Research Projects (BAP) (Project No: 5341-10B05S11).

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Keywords: SOFC, EIS, Oxygen reduction reaction (ORR), Perovskite

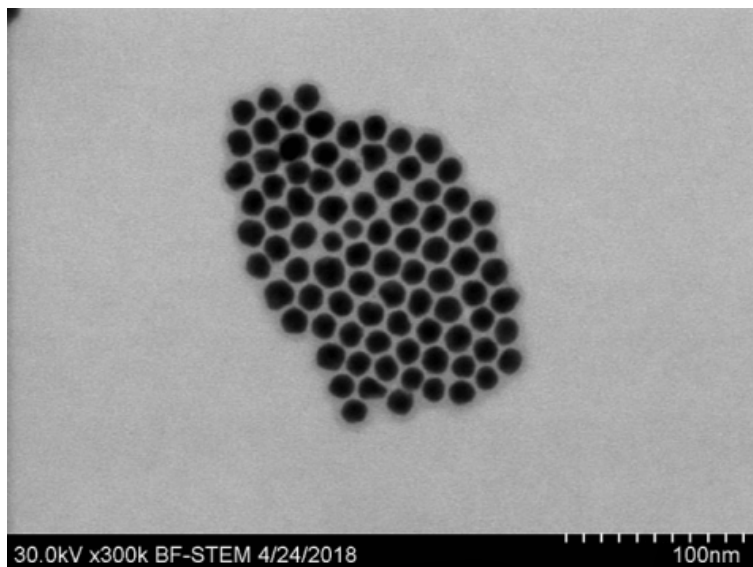
Electrochemical Energy Storage and Conversion

(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Oxygen Evolution on Nanostructured Ni

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Norwegian University of Science and Technology, Norway



Water electrolysis (WE) is the only feasible way of producing hydrogen on a large scale from water. Electrolysis of water comprises two half reactions, which take place at the two electrodes, the cathode and the anode. Molecular oxygen is produced on the anode and molecular hydrogen is produced on the cathode [1]. WE is currently bottlenecked by the sluggish kinetics of oxygen evolution reaction (OER). Numerous of electrocatalysts have been developed in the past decades to accelerate the OER process. Up to now, the first-row transition metal based compounds are in pole position under alkaline conditions, which have become subjects of extensive studies [1].

In this study, Ni nanoparticles as an efficient oxygen evolution reaction (OER) electrocatalyst for electrochemical water splitting application have been synthesized by the thermal reduction procedure consists, the reaction of $[\text{Ni}(\text{acac})_2]$ with oleylamine (OA) and trioctylphosphine (TOP) reactants. OA is the reductant and thus controls the nucleation rate, meanwhile TOP provides a tunable surface stabilization through coordination on the $\text{Ni}(0)$ surface. This synthesis results in monodispersed nanoparticles around 12nm (Fig. 1) [2].

As a basis for establishing appropriate experimental conditions we investigated the effects of adventitious Fe in the electrolyte on the electrochemical results. This is because Fe plays a critical, in enhancing the activity of the Ni-based oxygen evolution reaction (OER) electrocatalysts. Ni nanoparticles showed different electroactivity in rigorously purified (Fe-free) KOH electrolytes from that in KOH electrolytes that were not purified prior to the experiments. In purified electrolyte Ni nanoparticles showed no significant OER current until > 400 mV overpotential, in contrast to an overpotential of approximately $[300 \text{ mV}]$ in non-purified electrolytes. In the latter electrolytes rotation of the electrode (convection) drastically increases the activity of the catalyst, whereas no such effects were seen in the purified electrolyte.

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Keywords: Alkaline water electrolysis, Oxygen evolution reaction, Nickel nanoparticles, Nickel oxide

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

A New Low-cost Semitransparent Electrochromic Device Based on Ni(OH)₂/FTO and AgXOY/Cu Electrodes

Valerii KOTOK, Vadym KOVALENKO

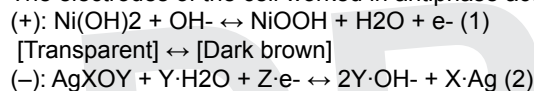
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Electrochromic devices can be used in various applications such as “Smart” windows and mirrors, fenestration, interior design, for conversation rooms, etc. The main problem of these types of devices is their high price, which can be up to 400 USD/m² [1].

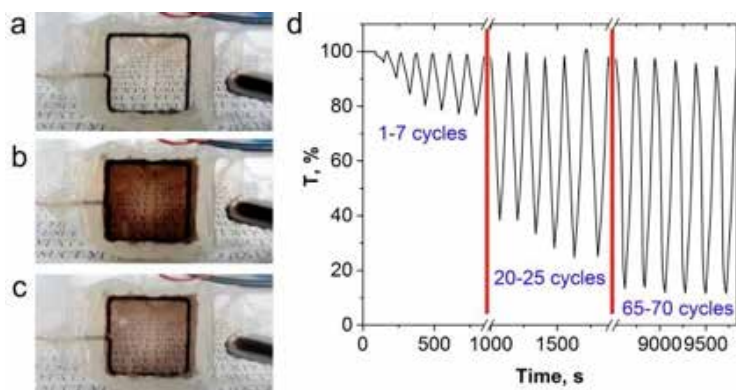
Here we report on the development of low-cost semitransparent electrochromic device based on Ni(OH)₂/FTO and AgXOY/Cu electrodes. Fluorine-doped tin oxide (FTO) was used as a transparent conductive substrate. A thin film of Ni(OH)₂ was deposited on a conductive substrate by the electrochemical method according to the source [2]. The surface resistivity of FTO glass was 10 Ohm/sq. The working area of the electrochromic electrode was 4 cm² (Ni(OH)₂/FTO, 2 x 2 cm). A copper wire was used as a counter electrode plated by silver with a thickness of 30 μm (further in the text (Cu)Ag wire). The diameter of the wire was 1.0 mm. 0.1 M KOH solution was used as an electrolyte.

Before using the counter electrode for the electrochromic cell, it was cycled in 0.1 M KOH in the range of potentials [–600; +1000 mV] with sweep rate 10 mV/s during 5 cycles. Immediately, before assembling of the cell, (Cu)Ag wire was previously charged by potentiodynamic technique: from +200 to +1000 mV with sweep rate 10 mV/s. The last was done for the formation of a silver oxides layer.

The electrodes of the cell worked in antiphase according to the following reactions (1) and (2):



The electrochemical cycling of the device in galvanostatic mode with the constant current (+ and – 1 mA) allowed to conduct colorizing and bleaching processes during about 1.5 min. The colorization process was almost uniform, but the color changes started from Cu(Ag) wireframe – see fig. 1 a, b, c. Colorized, bleached and semicolorized states of the device are shown in fig.1 a, b, c. Transparency changed from the initial T= 95% to the minimum value in colored state T= 15% – fig. 1d. The cycling of the electrochromic device was performed during 70 cycles. No gas evolution during cycling was observed.



Due to the absence of the second FTO glass with the other electrochromic film and propylene carbonate-based electrolyte in the construction, the proposed electrochromic device is cheaper than conventional. The recycling of electrochromic device components could be performed with less harm to the environment. The electrochromic device can be used for the decoration of placement, doors and skylights.

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Keywords: electrochromism, electrochromic device, Ni(OH)₂, silver, silver oxide, transparency

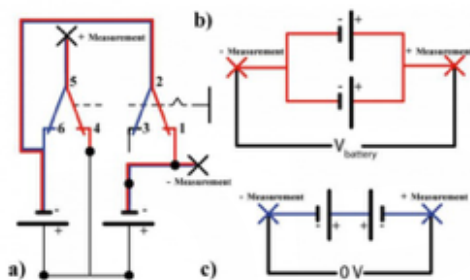
Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Electrochemical Noise Measurements and Their Chemical Origins in Primary Li Batteries

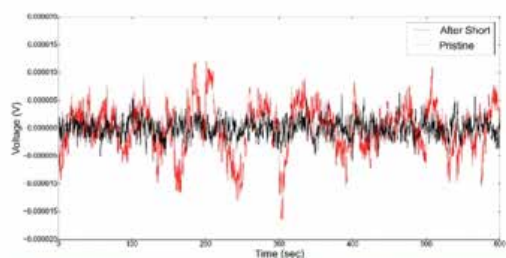
Gözde KARAOĞLU, Can Berk UZUNDAL, Burak ULGUT

Bilkent University, Turkey

Electrochemical noise measurements are well known in the corrosion literature where the noise that is to be measured is appreciable in amplitude. [1] From the measured noise of corroding systems it is possible to identify the mode of corrosion and distinguish between localized corrosion types from the uniform ones. Extensions of these noise measurements into batteries, especially to new generation Li batteries are limited in the literature since [2], batteries are used as low noise voltage sources in electronics. In fact, they are thought as no noise voltage sources. In reality, there is some noise even if they are at low amplitudes, and the main aim of the current work is to see if that noise has relevant and significant information regarding the state of charge, state of health of the batteries [3]. Compared to corrosion measurements, the electrochemical noise measurements on Li batteries are particularly challenging due to the large surface area electrodes employed in the construction of these cells and because of the high DC offset of the battery itself. Recently we have overcome the issues with measurement of electrochemical noise by employing a new offset correction scheme that removes the otherwise overpowering instrumental artifacts that come with resolving small voltage amplitudes over a large DC offset [1,2].



Using this method, we demonstrated the possibility of using electrochemical noise as an indicator of whether a battery is shorted or not. This is particularly attractive for primary chemistries since any conventional method of health determination such as EIS and slow discharge deplete the cell in question during the process. In this presentation, we will first explain the details regarding electrochemical noise measurements and continue on to demonstrate chemical origins of the observed electrochemical noise using ex-situ chemical analysis done on components of primary Li coin cells.



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Keywords: Primary Batteries, Li Battery, Noise,

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Characterization of the Effect of Carbon to Sulfur Ratio on the Lithium Sulfur Cell Resistance Using Electrochemical Impedance Spectroscopy Method

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Bogazici University, Turkey

Lithium sulfur batteries have received great attention due to the high specific capacity but low price of sulfur. However, there are three main problems to be solved before the mass commercialization of these batteries; limited rate capability, fast capacity fading and uncontrolled lithium/electrolyte interface. These problems arise from the insulating nature of the sulfur and solid discharge products, the polysulfide shuttle mechanism and the high reactivity of the lithium metal [1]. Sulfur cathode design is very critical in solving these issues due to the high complexity of cathode kinetics. Carbon to sulfur (C/S) ratio is one of the critical cathode design parameters that affects both the electrochemical performance and the energy density of the entire cell. High C/S ratios increase the surface area for electron transfer, thus increase the sulfur utilization. However, C/S ratio should be optimized to the point where the electrochemical reactions in the cathode are not kinetically limited and the system-level energy density is maximized [2, 3].

In this study, the effect of C/S ratio on the charge transfer and transport resistances in a Li-S cell is investigated as a function of depth of discharge for the initial discharge cycle. Since electrochemical impedance spectroscopy (EIS) is a widely accepted method to determine the mechanisms in a cell, EIS is used to reveal each resistance contribution to the total cell resistance [4]. Measured resistances are linked to the physical and electrochemical processing taking place in the cathode during discharge after an equivalent circuit is proposed by fitting the experimental impedance data. Subsequently, the kinetic and transport mechanisms during the first discharge is determined and discussed as a function of C/S ratio.

C/S ratios of 0.3, 0.5, 1, 2 and 3.5 are investigated in this study. Results show that C/S ratio affects both charge transfer and transport resistances in a cell significantly and there is an optimum C/S ratio at which a minimum cell resistance is attained. Increasing C/S ratio from 0.3 to 1 decreases the resistances during discharge. However, after that point, any further increase of C/S ratio significantly increases the cell resistance. It can be concluded that, Li-S cells with a C/S ratio of 1 have the lowest resistances.

This study is funded by the Scientific and Technological Research Council of Turkey (TUBITAK), Grant No: 116M574.

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Keywords: Li-Sulfur, Carbon-to-Sulfur Ratio, EIS, Cell Resistance

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

A Comparison of Semiconducting Properties of Tin Sulfide Obtained by Chemical and Electrochemical Methods

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Electrochemical measurement techniques, Capacitance measurements and Electrochemical impedance spectroscopy have been employed to study the electronic properties of tin sulfide obtained by chemical and electrochemical methods. The SnS crystallize in an orthorhombic symmetry (SG: Pnma) and a crystallite size were 42 and 52nm obtained. Through the capacitive measurements they are shown that first one is an n-type semiconductor and the second is p- type semiconductor. It was seen the differences concerning thickness of the space charge region, and flat-band potential. The thicker space-charge layer and lower flat-band potential for the thin film while the optical measurements give a direct band gap of 1.33eV and 1.61eV for SnS/Sn. The electrochemical impedance spectroscopy (EIS) measured in the range (10⁻² - 5×10⁻⁴ Hz) shows, that the SnS prepared by chemical route is more homogenous and higher is the value of polarization resistance than that obtained by electrochemical method.

DRAFT

Keywords: Tin sulfide, Mott- Schottky plots, semiconductor properties, EIS

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

The Effect of Aluminum Alloys and Subcritical Water Condition on Hydrogen Production by Electrolysis

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With the development of technology, the demand for energy is increasing day by day. Today, energy is provided from many sources but the important issues are to obtain this energy from renewable and environmentally friendly sources. For this reason, in this study, non-toxic aluminium which is abundant in nature is used in electrolysis of water for production of hydrogen gases. Many studies have been used as an aluminium cathode in the electrolysis system but when used as an aluminium cathode, this material leads too much over-potential[1]. However, when we use aluminium as an anode at the oxygen free atmosphere, it will prevent the formation and reduction of oxygen and it will increase the purity of hydrogen gases and efficiency of hydrogen gas formation with the help of 3 electrons according to anodic half reaction . In addition, in this study; it has been shown that heating the water under sufficient pressure to maintain the boiling point (so-called "subcritical" water) is useful in reducing the energy requirement because of causing physicochemical changes in water [2].

Anodic half reaction: $\text{Al(s)} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 + 3\text{e}^-$

Cathodic half reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

In this study, the effect of pure (Al), Al-6013 and Al-7075 aluminium on the electrolysis of water as anode was investigated and compared with Pt anode. For all electrodes, Pt was used as cathode and Ag / AgCl electrode was used as reference electrode. To determine the most efficient aluminium anode; Electrochemical impedance (EIS) measurements, current-potential measurements were made at open circuit potential and at 2 V , electrolysis current at 2V constant potential during 1800 s was followed and gas volume produced was measured . Energy consumption and hydrogen gases efficiency were also calculated for 25 oC room temperature. After determining the most efficient aluminium anode, the tests were repeated in the sub-critical water environment. In the tests carried out in the sub-critical area, high temperature and pressure resistant reactors were used and the electrodes are designed to withstand high temperature and pressure. An inert atmosphere was provided by passing N₂ (g) from the reactor. The temperature is 130 oC and the pressure is 20 Bar. As a result, the use of aluminium alloys as an anode reduced energy consumption, increased efficiency, and eliminated the gas separation processes by providing pure hydrogen gas production. In addition, by providing subcritical conditions, production efficiency of energy and hydrogen gas increased.

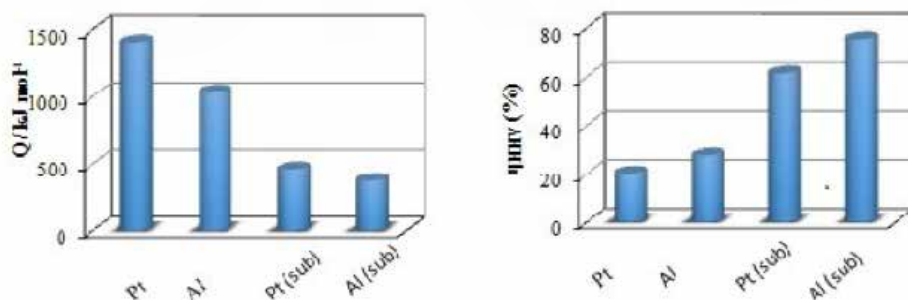


Figure: Energy consumption and hydrogen gases efficiency of Pt and Al electrodes at 25 C and subcritical water condition
The authors are thankful to the Mersin University research fund (2019-1-AP4-3460) and TUBITAK for their financial support.

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Keywords: hydrogen gases, subcritical water, electrolysis, aluminium alloy

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**A salt-assisted Metallothermic Reduction of Silicon Oxides to Silicon for
High-capacity Lithium-ion Batteries**

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The use of silicon nanoparticles as the negative electrodes of lithium-ion batteries have found great interest because of the high theoretical capacity of silicon (3579 mAh g⁻¹). However, relatively high cost and complicated reaction conditions of nanosized silicon production limits the scalability and should be addressed. Silicon oxides, as the abundant raw materials, can be utilized to prepare the nanosized silicon materials via high-temperature thermal processes such as carbothermal reduction at 1700 – 2000°C. The reduction temperatures can be lowered by using metallothermic reactions, such as magnesiothermic and aluminothermic, to 650 – 700°C; however further reduction of the required temperature remains a major challenge. In this study, we investigated the production of nanosized silicon through reduction of a locally-mined silica (SiO₂) via magnesiothermic/aluminothermic reactions utilizing various salts as a solvating agent and/or a heat scavenger. The preliminary results showed that the reduction temperature can be lowered down to 250°C with the help of a salt or a salt mixture with a relatively high reaction efficiency. The obtained silicon material has a highly porous structure and a high first cycle specific capacity.

DRAFT

Keywords: silicon, lithium-ion battery, metallothermic reduction

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Parametric Investigation of Hydrogen Production by Methanol Electrochemical Reforming

Özgü YÖRÜK, Merve GÖRDESEL, Duygu UYSAL ZIRAMAN , Özkan Murat DOĞAN, Bekir Zühtü UYSAL

Gazi University, Turkey

Hydrogen is not a natural source of energy and a primary source of energy is required for its production. On the other hand, hydrogen is accepted as the energy carrier of the future. It can be produced conventionally with 100% purity by electrolysis of water. This is a simple but the most expensive method amongst hydrogen production systems. Therefore, it is an important issue to search and develop innovative technologies for reducing the cost by using different sources in the electrolysis method. Among the sources whereby hydrogen can be obtained, methanol is an attractive option due to its low cost, requirement of low working potential and easy accessibility. Therefore, methanol electrolysis was chosen as the subject of this work.

The effects of various parameters such as concentration of methanol in aqueous solution, materials of electrodes and electrolyte media on hydrogen production were specifically investigated. Experiments were performed using an electrolysis cell with copper and zinc electrodes. The electrolytic solution was acidified with 1 M H₂SO₄ and 1 M HCl. The experiments were carried out at atmospheric pressure. At first, the minimum potential value for the system was investigated at room temperature and was found to be 1 V. In order to investigate the effect of temperature on the current density, measurements were carried out at different temperatures ranging from room temperature to 80°C. Results showed that the current density increased with increasing temperature. Also, hydrogen production using different methanol concentrations (1 M, 2 M, 4 M, 6 M, 8 M and 10 M) was investigated and the best current density was obtained using 4 M methanol. Use of Zn as both cathode and anode material, and H₂SO₄ in the electrolyte gave the best results amongst all experiments.

We would like to thank the Gazi University Projects of Scientific Investigation for financial support (Project No: 06/2019-03). Thanks, are also Clean Energy Research and Application Center (TEMENAR) for laboratory support.

Keywords: hydrogen, electrolysis, methanol

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

From Monometallic to Bimetallic Electrocatalysts: A Comparative Study On Supported Platinum Nanoparticles For Oxygen Reduction Reactions

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Gebze Technical University, Turkey

Proton exchange membrane fuel cells (PEMFCs) are highly efficient and environmentally friendly electrochemical conversion devices which have the potential to play a significant role in hydrogen economy development [1]. However, low cost and low resistance to catalyst poisoning (e.g. CO, S, etc.) of current electrocatalysts are main challenges in the widespread commercialization of PEMFCs. To overcome these challenges, there is intensive research on the decrease of the electrocatalyst cost without decreasing its performance by lowering the platinum loading and partially substituting Pt with a secondary metal such as Co, Fe, Ni, Cu, Mn, etc [2,3]. It is well demonstrated that Pt substitution can effectively enhance the ORR activity and durability of Pt based electrocatalysts owing to the synergetic effect between the Pt and the second metal [4]. Herein, we present a comparative study of ORR activity and fuel cell performance with Pt electrocatalysts both monometallic and bimetallic in nature. We also studied how the carbon based supports affect the electrochemical activity of such electrocatalysts through hybridization. The electrocatalysts were developed using a mild synthetic method relative to literature and characterized by BET, XRD, XPS, TEM and CV techniques. Recent results showed that bimetallic electrocatalysts presented higher electrochemical activities compared to their corresponding monometallic ones. For instance, CuPt based electrocatalysts presented higher mass activity compared to monometallic and even bimetallic NiPt based electrocatalysts. Concerning the Fuel cell performance, we achieved encouraging results with especially on electrocatalysts where Ni was used as a secondary metal. We believe that prevention of carbon corrosion together with the use of hybrid supports enhanced the fuel cell performances. Therefore, our full efforts are towards the development of highly active but low cost and stable electrocatalysts for oxygen reduction reactions (ORR) in PEMFCs.

We would like to thank to TUBITAK-2232 (grant no.114C065) and GTU (grant no.BAP GTU-SU-004).

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Keywords: Electrocatalyst, platinum, copper, nickel, palladium, nanoparticle, PEM fuel cell, carbon, graphene

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

An Alternative HCMS Carbon Catalyst in Bromine Reduction Reaction for H₂/Br₂ Redox Flow Batteries

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Ondokuz Mayıs University, Turkey

As renewable energy resources, such as solar and wind, become more common, need for grid-scale electrical energy storage is increasing to regulate the output of these intermittent energy sources. Among the electrical energy storage systems, redox flow batteries are considered to be highly promising storage units. However, redox flow batteries are not widely used for reasons that are not easy to overcome such as expensive cell components, high electrolyte cost, low cell performance, and durability.

In the present work, a low-temperature redox flow battery powered by bromine and hydrogen was developed due to its high energy efficiency. Although the Pt/C catalyst is quite active in the bromine reduction reaction on the cathode side of the flow battery, this reaction can also be catalyzed by low-cost carbon structures alone. To increase cathode kinetics, high electroactive area bromine electrodes must be used. In this study, hollow core mesoporous shell (HCMS) carbon structures were synthesized as a promising alternative to Pt/C or Vulcan XC72 carbon catalysts and used as cathode electrocatalyst in H₂/Br₂ flow batteries for the first time. TEOS amounts used during HCMS carbon synthesis were changed and carbons were produced with different core/shell structures. Subsequently, the effect of these high surface area carbon catalysts on the flow battery performance was investigated. In this presentation, first, porous transport layer (PTL) consisting of HCMS carbon and gas diffusion layer will be introduced, then the effect of different HCMS carbon structures on flow battery performance will be examined and the effect of electrolyte concentration, flow rate, temperature on battery performance will also be discussed.

DRAFT

Keywords: H₂/Br Flow battery, Porous electrode, HCMS carbon, Energy storage

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Graphene Oxide decorated with Metal/Metal Oxide Nanostructures for
Electrochemical Energy storage and conversion**

Uğur ÜNAL

Koc University, Turkey

One of the most important challenges in today's world is developing alternative energy sources due to steadily rising energy demand. Thus, development of high performance energy systems is crucial for efficient energy storage and conversion. Researchers around the world studies electrochemical water splitting, fuels cells, batteries and supercapacitors. In electrocatalytic reactions for water splitting and fuel cells, the challenge is utilization of cheap transition metals for low cost and efficient systems or trying to decrease the amount of noble metals like Pt and Ru for this kind of applications. For charge storage devices like supercapacitors, researchers trying to improve the energy density and cycle life. Carbon materials have attracted interest in electrochemical charge storage and conversion applications due to high surface area, processability, and electrical characteristics. Graphene is one of the most widely studied carbon material. Graphene promotes fast electron transport with its excellent electrical conductivity, and metal oxides enhances energy density of the system by utilization of redox reactions between multivalent ions present in the structure. Electrodes produced from graphene and metal oxide composites have achieved extraordinary electrochemical performance due to combination of individual properties of these two material classes. Herein, I will demonstrate properties of thin or self standing films of metal/metal oxide loaded graphene systems for supercapacitor, oxygen reduction and hydrogen evolution reactions. Graphene can be utilized as support either in self-standing film form or as 3D highly porous structure in aerogel form. I will show that nanosized metal/metal oxides can be uniformly distributed on graphene films or in graphene aerogel structures for efficient electrochemical reactions. Amount of metal/metal oxide dispersed on graphene films or aerogels can be easily controlled to tune the electrochemical performance of these composite systems.

Koc University Surface Science and Technology Center (KUYTAM)

Keywords: graphene, self-standing film, aerogel, oxygen reduction, hydrogen evolution.

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Graphene Aerogel Supported Nickel Nanoparticles as Water Oxidation Electrocatalysts

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Koç University , Turkey

Molecular hydrogen and oxygen, which are the reactants of a simple H₂-O₂ fuel cell, can be produced by a water electrolysis cell. The anodic reaction of the electrolysis cell, oxygen evolution reaction (OER), is a multistep one with slow kinetics and thus, requires a catalysts to occur at low overpotentials. [1] The choice of catalyst is generally noble metals (Ru, Ir, Pd, Rh, and Pt), but the scarcity and high-cost limit their commercial utilization. [2] For this reason, transition metal (oxides) are attractive candidates as OER electrocatalysts with their high intrinsic activity and much lower cost. In this study, nickel nanoparticles dispersed on mesoporous graphene aerogels (GAs) were utilized as OER electrocatalysts. The synthesis route included a facile one-pot hydrothermal reaction followed by thermal annealing. During the hydrothermal reaction, nickel loading was controlled by changing the initial Ni²⁺ to graphene oxide ratio. Produced Ni nanoparticle loaded GA samples were characterized with X-ray photoelectron and valence band spectroscopy to investigate the electronic structure, as well as nitrogen physisorption to analyze the pore structure. Electrochemical characteristics of the Ni loaded GA samples were analyzed with cyclic voltammetry coupled with a rotating disk electrode. The overpotential required to obtain 10 mA cm⁻² gradually decreased with the increase in metal loading and a remarkable low overpotential (320 mV) was obtained with 40 wt% Ni loaded GA, outperforming commercial noble catalysts like Ru/C and Ir/C. [3] Moreover, this sample exhibited a low Tafel slope of 61 mV dec⁻¹, which is a smaller value compared to its literature counterparts.

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Keywords: oxygen evolution reaction, nickel nanoparticles, graphene aerogel

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Development of Selenium Doped Lithium Titanium Sulfides ($\text{Li}_2\text{TiS}_3\text{-xSex}$)

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Overlithiated rock salts are promising materials for Li ion high energy applications. Despite the earlier results, they can offer much higher capacities ($>250 \text{ mAh.g}^{-1}$) than the stoichiometric compositions. This high capacity is associated to Li rich content, which forms a percolating network along the Li diffusion channels¹.

Lithium titanium sulfide (Li_2TiS_3), which was reported by A. Sakuda², delivered excellent capacity (425 mAh.g^{-1}) due to the multielectron redox reactions. Despite its high capacity, poor cycling stability were also reported. Partial substitution mechanisms are promising solutions in this issue. Here, we propose new Se substituted Li_2TiS_3 materials ($\text{Li}_2\text{TiSexS}_{3-x}$), which have recently been patented. By applying our patented synthesis process, Se substituted materials showed better cycling stability. For comparison, we will provide a comprehensive study of pure and substituted materials through fine characterization tools (XRD, SEM, EDX, ex situ and in situ XRD) in order to examine electrochemical and structural properties. Finally, we will elucidate possible redox mechanisms of pure and substituted materials through XPS analysis.

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Keywords: Li ion batteries, rock salt materials, Li_2TiS_3 as positive material

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Experimental and Statistical Analyses of the Impedance Response of
Commercial 2032-type Li-ion Battery: Taguchi Design of Experiment Method**

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Eskisehir Osmangazi University, Turkey

This study provides the results of impedance measurements on commercially available 2032 Li-ion coin cells. The influences of the cell potential and the temperature on the properties of the Li-ion battery were both experimentally and statistically investigated. Taguchi design of experiment method enabled to identify the effects of the studied factors in the response of the equivalent-circuit parameters of the battery such as ohmic resistance, capacitance, and charge transfer resistances. The L9 orthogonal array was applied to analyze the entire parameter space. The S/N ratios in the response table were used to determine the rank of the factors. A significance level of 0.05 was used as the alpha value. The temperature as the most effective factor on the battery parameters was determined based on the response table and analysis of variance. The significance level of 0.05 indicated that there is a statistically significant association between the temperature and the electrolyte resistance.

DRAFT

Keywords: Li-ion battery, impedance spectroscopy, Taguchi design

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**The Investigation of Electrochemical Phenomena of Na_{0.44}MnO₂
Cathode in Na-based Aqueous Electrolyte**

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Investigation and elucidating of the interphase redox reaction between electrode and electrolyte play a critical role in the commercialization of water-based Na-ion batteries. Na_{0.44}MnO₂ (NMO) could be considered as one of the promising positive electrode materials not only for its good cycle life but also its electrochemical activity in both aqueous and non-aqueous environments. In this study, sodium (de)-intercalation process in Na_{0.44}MnO₂ was electrochemically evaluated with cycling voltammetry (CV), constant current charge/discharge, and electrochemical impedance spectroscopy (EIS) measurements. Na_{0.44}MnO₂ was successfully cycled at different scan rates (from 1mV/s to 15 mV/s) in the range of -0.1 V and 0.95 V (vs. Ag/AgCl) in a three-electrode beaker type cell. Sodium ion diffusion coefficients in 1M Na₂SO₄ electrolyte at 25 oC were calculated by Randles-Sevcik equation over the CV data and found to be 10⁻⁷ cm²/s. Diffusion coefficient of Na-ion that was founded from the CV data was confirmed by EIS characterization techniques. The Na-insertion and -extraction stage into/from NMO under constant current conditions were also investigated by an in-situ Electrochemical Quartz Crystal Microbalance analysis. Specifically, the charge storage behaviour in 1 M Na₂SO₄ were studied by CV and the frequency changes of the Na_{0.44}MnO₂-modified gold patterned quartz resonators were simultaneously monitored which will be discussed during the presentation. After individual electrochemical performances of Na_{0.44}MnO₂ and porous carbon electrodes, NMO-C full cell assembling was also fabricated. This study promises a great prospect for the development and implementation of the rechargeable water-based Na batteries for the large-scale energy systems.

DRAFT

Keywords: Aqueous battery, sodium-ion battery, Na_{0.44}MnO₂, carbon, EQCM

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Electrochemically Dealloyed Carbon Aerogel Supported Bimetallic PtCu
Nanoparticles by Supercritical Deposition as Electrocatalysts for PEMFCs**

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Electrochemically dealloyed carbon supported Pt bimetallic nanoalloys are used as PEMFC electrocatalysts due to their unrepresented electrochemical activity towards kinetically sluggish oxygen reduction reaction (ORR). The electrocatalytic behavior of such binary metal systems depends critically on the structure, composition and size of the alloy nanoparticles, which are in turn governed by the preparation method and the process conditions; these factors can lead to the development of different alloy nanoparticle structures such as core-shell, segregated, disordered or ordered. Supercritical deposition (SCD) emerges as a versatile preparation technique that allows high controllability of the synthesis parameters resulting in highly active electrocatalysts. We studied the scCO₂ assisted preparation coupled with electrochemical dealloying of Carbon Aerogel (CA) supported PtCu bimetallic nanoparticles. We investigated the effect of precursor reduction conditions (ex-situ vs. in-situ), deposition approach (simultaneous vs. sequential) on the morphology, particle size and electrocatalytic performance of PtCu/CA electrocatalysts. Electrocatalysts were annealed at high temperatures under an inert atmosphere to promote alloying. We confirmed the presence of PtCu bimetallic nanoparticles via XRD, TEM/EDXS and XPS. TEM images showed that SCD results in highly dispersed PtCu nanoparticles on CA support with very narrow particle size distributions. Furthermore, we demonstrated that the average particle size of the PtCu bimetallic nanoparticles can be precisely controlled from 1 to 6 nm during conversion and annealing steps regardless of the metal composition and pore size of the support. We have demonstrated that the deposition approach (i.e simultaneous or sequential) have a profound effect on the morphology of the resulting PtCu alloy nanoparticles which in turn results in different electrochemical performances upon dealloying. We have found that simultaneous approach results in higher mass activity and ESA due to a more uniform Pt and Cu composition throughout the PtCu nanoparticle. Whereas the sequential approach results enhanced specific activity due to PtCu core/Cu-rich shell prior to dealloying which upon dealloying results in thin Pt-rich shell/PtCu core showing that the d-band of Pt lowered below the Fermi level so that enhanced specific activities are obtained.[1]

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Keywords: Nanoalloys, Supercritical Deposition, ORR, PtCu, Electrochemical Dealloying, Electrocatalysts, PEMFC

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Supercritical Fluid Assisted Preparation of Co Promoted N-Doped Carbon Aerogel
Electrocatalysts for Oxygen Reduction Reaction**

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Oxygen Reduction Reaction (ORR) electrocatalysts plays an important role in the development of fuel cells due slow kinetics of the reaction. Although carbon supported Pt and its alloys are considered as the best ORR catalysts up to now, high cost and limited supply of noble metals severely hinders the widespread commercialization of these devices. Thus, research efforts are directed to the development of Pt-free carbon-based nanomaterials for ORR. Among others, Co containing N-doped carbon materials are the most promising candidates due to their high electrochemical activities in alkaline media. Various N-doped carbon materials such as carbon nanotubes, graphene and, graphene aerogels have been investigated and displayed promising ORR activities. Among these materials, nanostructured carbon aerogels (CAs) are promising candidates due to their unique properties such as; high surface area, low mass density, high porosity, and high electrical conductivity. CAs are obtained by pyrolysis of organic aerogels that are generally produced by supercritical drying of organic gels. CAs have the advantage of a three-dimensional hierarchical morphology that can be tuned by changing the process parameters during the polymerization, gelation, curing, and pyrolysis steps. Supercritical CO₂ deposition is very suitable to prepare Co containing N-doped CAs because near zero surface tension of supercritical CO₂ prevents collapsing the pores of CA and enables better wettability. Also CO₂ is gaseous under ambient conditions which eliminates solvent removal steps upon deposition. We prepared N-doped Co-promoted CA electrocatalysts via supercritical CO₂ deposition coupled with high temperature N-doping. We investigated the effect of pyrolysis temperature, cobalt presence and loading on the ORR activity via cyclic voltammetry in alkaline media. We compared the electrocatalytic performance of the N-Co-CA catalysts with those of the commercial Pt/C. The electrocatalyst exhibited a cobalt core-carbon shell structure which promoted the formation of electrocatalytically active graphitic-N sites. This catalyst showed high ORR activity through a four-electron reduction process with the onset potential similar to that of commercial Pt/C. Moreover, we obtained good stability and enhanced methanol tolerance compared to the commercial Pt/C catalyst in alkaline medium.

Keywords: Cobalt, N-doped, carbon aerogel, supercritical deposition, oxygen reduction reaction, fuel cell

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Redox Flow Batteries with Bio-Inspired Electrolytes for Grid-Scale Energy Storage

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Redox flow batteries (RFBs) are a promising large-scale energy storage technology for integration of intermittent renewable sources, such as wind and solar, into the electrical grid. Among several types of RFBs under development, non-aqueous redox flow batteries (NRFBs) have recently gained significant interest due to their wide electrochemical potential windows and improved range of operating temperature, offering high performance operation compared to their aqueous counterparts [1]. Despite the attractive features and potential of NRFB technology, active material instability, resulting in poor cyclability, poses a fundamental obstacle to widespread implementation [2].

To address the instability issue of these systems, we demonstrate a fundamentally new design strategy for NRFB active materials. This approach leverages millions of generations of biological evolution as a toolkit to elucidate molecules that provide a stable scaffold for further development. The compounds investigated in this study are based on chelators that have evolved as part of biological metal-transport systems [3]. As a result of natural-selection they exhibit extremely strong metal-binding properties, shutting down decomposition pathways.

In this presentation, we will demonstrate the performance characteristics of the proposed NRFB system using charge/discharge cycling, capacity fade and efficiency analyses. An operando spectroscopic analysis, to demonstrate chemical stability during cycling and tight coupling between current and electrochemical formation of the oxidized and reduced form of the active material will be discussed. Additionally, recent progress to reduce area specific resistance and active material crossover for improved performance will be presented.

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Keywords: Flow battery; grid energy storage; redox active material; spectroelectrochemistry

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Microwave-assisted Synthesis of Carbon Nanofiber Supported Platinum
Nanoparticles for Electrochemical Catalysis**

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Platinum (Pt), having an exclusive catalytic activity for the oxidation and reduction reactions, has been extensively investigated for various applications including polymer electrolyte fuel cells (PEMFC). Since the specific surface area of Pt has a key role in its performance, a proper control on the catalyst particle size and distribution during the synthesis is required. In addition, the catalyst support materials play an important role in Pt utilization and consequently in fuel cell performance. Carbon black, the current catalyst support material, is associated with poor Pt utilization, non-uniform microstructure, mass transport losses and durability issues. In this study, a one-pot microwave-assisted synthesis method was developed to produce carbon nanofiber (CNF) supported Pt catalyst nanoparticles as potential electrode materials for PEMFCs. The effect of the microwave irradiation time, carbonization temperature and presence of SWCNTs in the nanofibers were investigated in terms of Pt nanoparticle size, distribution and final electrocatalytic activity.

This study was supported by the Scientific and Technological Research Council of Turkey (TUBITAK) (Project no: 213M023)

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Keywords: Platinum, electrospinning, carbon nanofibers, PEMFC

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Unusual A-Behavior of High Crystalline β -Ni(OH)₂, Obtained by Two-Stage High-Temperature Synthesis, for Application as an Active Substance of Supercapacitors

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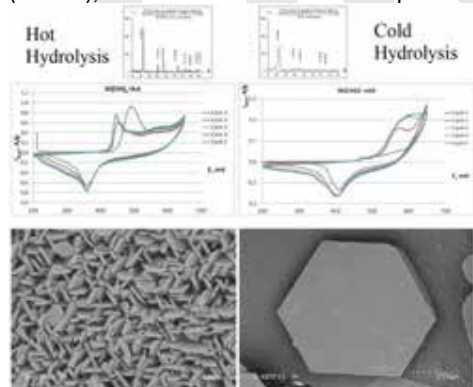
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Hybrid supercapacitors (SC) with nickel hydroxide electrode are widely used as primary or backup power sources for electro vehicles and vehicles with a hybrid engine, for starting of the different types of the electric motor, as a UPS for computer systems, medicine and other equipment, residences, and offices, etc. SC is charged and discharged with high currents, therefor electrochemical processes are situated on the surface and in the thin surface layer of particles. Therefore requirements for Ni(OH)₂ include high specific surface and optimal crystallinity.

For nickel hydroxide, there are two mutually exclusive requirements in Nickel hydroxide type and kroistallichnost. α -Ni (OH) 2 has a higher electrochemical activity than β -Ni(OH)₂, but is much less stable. When a hybrid supercapacitor is used in the Faraday electrode during charge-discharge at a high current density, the active alpha form will be transformed into a beta modification. β -Ni(OH)₂, especially at high crystallinity, is much more stable, but the electrochemical activity of this form is much lower.

The main aim of this investigation is to try to synthesize the Ni(OH)₂ with high specific capacities and high stability. To achieve this aim Two-stage high-temperature synthesis of nickel hydroxide with high specific capacity has been proposed by us with following scheme: «Ni(ClO₄)₂» – «SYNTHESIS» (24 hour, 140°C) - «Na₂NiO₂» - «HYDROLYSIS» (24 hour, 170°C – hot, 20°C - cold) - Ni(OH)₂. Obtained samples have been characterized by XRD, SEM, DSC, DTA, voltammogram and galvanostatic charge-discharge cycling. Specific capacities have been calculated from discharge curves for two modes: full discharge to stable potential and discharge to potential 0 V. Industrial sample of Ni(OH)₂, produced by “Bochemie” (Czech), has used as a referent sample.



By XRD results it was detected that sample obtained with hot hydrolysis is β -Ni(OH)₂ with extra high crystallinity and high texture, but obtained with hot hydrolysis is more defect β -Ni(OH)₂ with medium crystallinity. These conclusions have been confirmed by DSC and DTA analysis. Voltammogram of Ni(OH)₂ sample, obtained with cold hydrolysis, have the anodic and cathodic peak, characterizing for β -Ni(OH)₂. But Ni(OH)₂ sample, with extra high crystallinity, has two types of the anodic peak, characterizing for β -Ni(OH)₂, and α -Ni(OH)₂. First anodic peak shows the α -Ni(OH)₂ electrochemical behavior of high crystallinity β -Ni(OH)₂.

According to SEM images, Ni(OH)₂ sample, obtained with cold hydrolysis, consists of hexagonal plate-type particle. But Ni(OH)₂ sample, obtained with hot hydrolysis, has bigger particles, consists of a smaller hexagonal plate with nano-thickness 36 nm. It was concluded, that unusual α -Ni(OH)₂ electrochemical behavior of high crystallinity β -Ni(OH)₂ has been explained by nano-size of particles

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Keywords: Nickel hydroxide, supercapacitor, electrochemical behavior, voltammogram

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**One-step Electrosynthesis of Polypyrrole/PbOx Composite in Acetonitrile as
Supercapacitor Electrode Material**

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Emerging demand for the energy storage devices stimulates the research for electrochemical supercapacitors, particularly due to their promising characteristics showing resemblances with both capacitors and batteries (1, 2). The electrochemical supercapacitors show a higher specific energy than regular capacitors and higher specific power than batteries, which enables faster charging for advanced technology applications. The main feature that distinguishes batteries and supercapacitors from each other is their charge storage mechanisms. While batteries can store the charge at the bulk of the active material through the redox reaction, the supercapacitors operate on the principle of charge storage on the electrode.

This study explores the single step electrochemical synthesis of polypyrrole/PbOx composite on the Pb-intercalated (intc.) graphite electrode in acetonitrile medium, including Py, TBABF₄, HBF₄, H₂O, Pb(BF₄)₂, TX100 and carboxymethyl cellulose. The coatings on Pb-intc. graphite surface are analyzed by SEM-EDX, BET, TEM, XPS, and XRD techniques. The effects of the additives on the capacitive properties are investigated electrochemically in an H₂SO₄/water medium. PbOx and carboxymethyl cellulose enhance the specific capacitance and the cyclic stability. Although the amount of PbOx in the composite is low (1.2% atomic percentage of Pb), it contributes significantly to the specific capacitance due to the homogenous distribution of PbOx in nanostructures. The amount of specific capacitance of the composite film (4.0 mg cm⁻² loading) on the Pb-intc. pencil graphite is calculated as 377 F.g⁻¹ at 2.0 A.g⁻¹ in 100 mM H₂SO₄ by subtracting that of bare graphite. The two electrode cells (asymmetric and symmetric) are constructed using Teflon Swagelok in polyvinyl alcohol/H₂SO₄ gel electrolyte. In the symmetric supercapacitor configuration, the composite coating (10 mg cm⁻² loading) on Pb-intc. graphite paper electrode has 0.29 kW kg⁻¹ and 22 Wh.kg⁻¹ at 0.5 A g⁻¹. The results also indicate a good cycle performance (94% after 5000 cycles) in the potential range of 0.8 V.

This work is supported by a grant from TÜBİTAK, the Turkish Scientific and Technical Research Council (Grant No. TÜBİTAK/ 117Z340).

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Keywords: Supercapacitor, Electrosynthesis, Composite Coating, PbOx, Polypyrrole

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Application of Through-holed Anodes and Cathodes Prepared with Picosecond Pulsed Laser to Lithium Ion Battery

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Recently, we have reported that the porous current collector could be produced with a pico-second pulse laser system and that graphite electrodes prepared with porous Cu current collectors improved the rate of Li⁺-pre-doping reaction in the laminated graphite electrodes [1-3]. In this study, in order to speed up the rate of the pre-doping reaction more, the porous graphite electrodes were prepared by directly opening the holes on the surface of graphite electrodes with a picosecond laser (Fig. 1). In the cell composed of laminated graphite electrodes and a lithium metal, the Li⁺-doping reaction proceeded much faster than in the cells of the graphite electrodes prepared with porous current collectors and a Li metal. In addition, the results of electrochemical impedance spectroscopy suggested that the transfer of Li⁺ ions through the holes on the graphite electrodes was a rate determining step of the doping reaction of Li⁺ to laminated graphite electrodes and that the decrease in the hole diameter at the constant of opening rate of holes on the graphite electrodes caused the reduction of resistance for Li⁺ ions, resulting in shortening the time for completing the doping reaction of Li⁺ ions.

Fig. 1 SEM images (1: low magnification, 2: high magnification) of prepared porous graphite electrodes in a view from the plane of the incident laser. The opening rate of hole on the electrode: 1%. The average hole sizes were (A) 50, (B) 20 and (C) 10 nm.

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Keywords: Lithium ion battery, pico-second pulsed laser, high rate performance

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Electrocatalytic Properties of M/PRGO (M=Pt or Pt-Au) Composite Synthesized by
UV-Based Photocatalytic Deposition Method**

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Electronic band gap structure of the graphene oxide can be modified by various reducing agent, in order to use as a substrate in photocatalytic deposition of metal ions. The resulted composite may be used as a catalyst layer in polymer electrolyte membrane (PEM) fuel cell. In this regard, following the authors previous studies, two noble metals of Gold and Platinum were successfully deposited on partially reduced graphene oxide, PRGO. The process was conducted by using a handmade reactor for continuous or pulsed irradiation of UV light on an aqueous suspension containing PRGO, metal precursors and Methanol. The difference between the reduction potential of the gold and platinum, demands a specific attention about choosing the parameters in the photocatalytic deposition process. In this study, the electrocatalytic activity of Pt/PRGO and Pt-Au/PRGO composites revealed that, not only the structure and distribution of catalyst particles on the graphene based substrate play a critical role in the composite catalytic activity, but also it is the level of oxygen functional group that determines the interface conductivity of PRGO-Metal through which electrons go/come and take part in reduction/oxidation of an electrolyte containing Oxygen/Hydrogen. By using ascorbic acid as a reducing agent to remove the remaining functional group from the surface of the Metal/PRGO composite, the conductivity of the reduced graphene oxide increases, yet the concentration of the ascorbic acid and the reaction time determines whether the composite can show electrocatalytic activity or not. Moreover, the pulsed UV irradiation increases the metal nucleation zones on the PRGO, however continuous irradiation of UV causes less nucleation zones but more growth of the metal crystallites.

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Keywords: Photocatalytic deposition; Partially Reduced Graphene Oxide (PRGO); hole scavenger; electrocatalytic

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Theoretical Performance Modeling of Primary and Reserve Batteries

Ozge ABANOZ¹, Bilgehan ÇETİNÖZ¹, Burak ÜLGÜT²

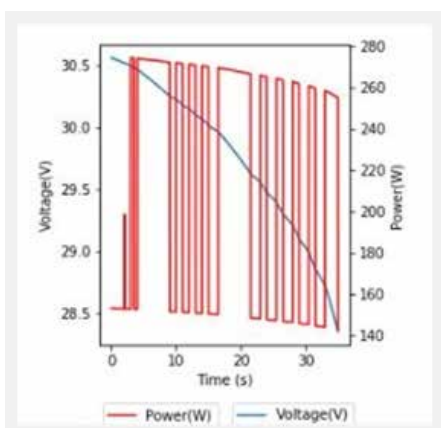
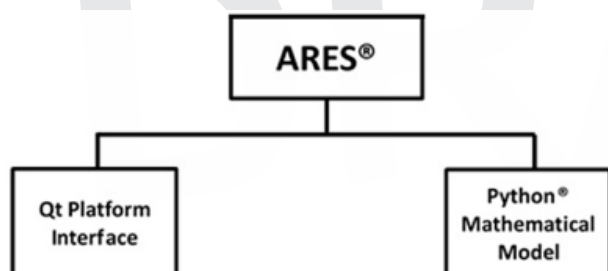
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Energy storage systems (ESS) could provide mobile and active energy to any kind of electricity required system from consumer electronics to military applications. ESSs vary according to their reliability, reproducibility, stability, energy capacity and reusability and they are classified as electrochemical, mechanical, chemical and electrical ESSs [1, 2]. Primary and reserve batteries as two of major electrochemical ESSs are commonly used in space, military, and environmental improvement programs. Among all primary and reserve batteries, the ones including alkali metals become prominent due to their outstanding performance and characteristics. Consequently, these are preferably used in military applications because of their ruggedness, reliability, no maintenance, long shelf life, wide operating temperature range, comparatively high energy/power densities [3].

In dynamic nature of developing systems, it is challenging, time-consuming, and costly to predict the performance and compatibility of batteries in stock by testing under system required environmental conditions. The more the numbers of systems relying on batteries increase, the more the mathematical modeling and defining them mathematically become important. Therefore, development of a mathematical model helping designer to predict and provide insight of capabilities, performances, life time of batteries is crucial, rapid, and productive.

Accordingly, present modeling techniques has been reviewed and based on those examples and specific requirements of military-grade applications a theoretical performance model has been developed for primary and reserve batteries. In this contribution, we will present our driving forces, performance model components (Python® for modeling language, Qt Platform for user interface) (left figure) and user interface/interaction inputs and outputs (right figure).



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Keywords: Batteries, Primary Batteries, Performance Modeling,

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Recent Development in the Nanostructured-based Battery Electrode Materials for
Electric Vehicles (EV) Technology and TÜBİTAK Efficiency Challenge Electric Vehicle:
Overview from 2005 to 2019**

Muslum DEMİR

Osmaniye Korkut Ata University, Turkey

The application of the modern electric power systems are increasing because of growing demand of energy storage worldwide, public awareness of global warming and developing political pressure, integrating large scale renewable power systems, and communication technologies with power system operation. Recently, the development of the energy storage technology for electrical vehicles (EV) is fore electric vehicles (EV) technologymost important. Regarding with this issues, a significant amount of energy storage research and development is underway, both in academia and industry, in order to meet the demand for automotive industries. In regard with designing and fabricating electrode materials, nanostructured approaches have verified numerous benefits for induced energy and power density, cyclability retention and packing safety. In this talk, I offer a recent overview of nanotechnology-based materials, which are either already commercialized (such as Li-ion battery) or near to commercialization for EV applications, Moreover, I also will give presentation on EV materials under development (such as Li-S battery) with the potential to meet the requirements for long-range electric vehicles.

Within the last decade, TÜBİTAK has been organized Efficiency Challenge Electric Vehicle event, which is an annual competition for international universities. The main purpose of this organization is to create awareness on renewable energy sources for automotive technology, to find optimum effective car design, battery and motor performance as well as educate future's engineers to put their knowledge into practice and to work across disciplinary boundaries. The rules provided by TÜBİTAK are aimed to provide teams to exhibit their electric cars' efficiency and assessment the reliability of their mechanics and electrical performance. The event welcomes more than a thousand students each year mostly from engineering and science schools. This event not only provides understanding of alternative energy technologies for EV, but also allows students to improve their marketing and management skills. The competition was first took place in 2005 under the name of Solar Electric Vehicle Challenge (Formula-G). Later on, Fuel cell Vehicle (Hydromobile) category was included in the competition. Taking into account the research and practices all over the world concerning electrical vehicles, we see that battery-fed vehicles are at the forefront and in the near future battery-fed vehicles will become common in our daily lives. For that reason, Battery Electric Vehicle (Electromobile) category has been added to within the scope of the competition since 2014. In this talk, I will give speech about what aims achieved in last decades, prospects for future events for EV and how this prestigious organization helps to design new Turkish EV car.

Finally, as a mentor of OKÜ International Advance Research Engineering Society (IARES), I will describe activities within the IARES organization and our EV car named as HUNTER which was received both TÜBİTAK Jury and Communication awards in 2018 at Kocaeli, Turkey.

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Keywords: Electric Vehicles EV, Efficiency Challenge, nanomaterials, energy storage, Li ion battery

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Cobalt Based Oxygen Evolution Catalyst for Photoelectrochemical Water Oxidation on BiVO₄

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Photoelectrochemical water splitting is an ultimate strategy to convert the energy of the Sun to the energy stored in the chemical bonds of molecular hydrogen and oxygen. Photoelectrodes made of earth abundant elements have poor surface catalytic activity thus catalysts are commonly incorporated onto their surfaces to boost the activities. There are several catalysts shown to be rather effective in water oxidation reaction, however, there is an ongoing debate about the origin of the enhancement in the activity. It has been argued that catalysts decrease the recombination rate of the charge carriers at the photoanode surfaces without being truly involved in the oxidation reaction. Their involvement in charge transport and utilization depends on the catalyst amount and active phase.

We show that single layer Co(OH)₂ can significantly enhance the water oxidation activity of BiVO₄ photoanodes. We used a combination of XPS, XANES (X-ray absorption near edge structure), NEXAFS (Near edge X-ray absorption fine structure) spectroscopy techniques to better understand its local structure on BiVO₄. We have found that the role of Co(OH)₂ covalently anchored onto nano-porous BiVO₄ in the enhancement of the photoelectrochemical performance is a pure catalytic effect, a single catalysts layer both reduces the kinetic overpotential and decreases the charge transfer resistance in electrode/electrolyte interface. Such a high catalytic activity, which is strongly dependent on the local configuration of cobalt oxides, competes with the recombination rate of the charge carriers in BiVO₄ surface and increases the overall photocurrent density.

DRAFT

Keywords: PEC, BiVO₄, photoanode, water oxidation

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Electrochemical Investigation of a Micro-scale Microbial Fuel Cell (μ MFC)

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μ MFCs are small bioreactors converting the energy in the chemical bonds of organic matter into electrical energy through catalytic activity of microorganisms under anaerobic conditions. To obtain higher performance μ MFCs, the internal resistance of μ MFC can be decreased, the start-up time can be decreased or the biofilm formation quality can be increased. To reach this aim, optimization of chamber and/or cell geometries, chamber or electrode materials, and electrode surface characteristics is crucial. In this scope, this paper reports the design, fabrication, and electrochemical investigation of a microliter scale Microbial Fuel Cell (μ MFC) based on silicon MEMS fabrication technology.

MEMS based μ MFC electrodes were designed and fabricated. Since gold is biocompatible, conductive, and compatible with conventional microfabrication techniques, it was preferred as the electrode (both anode and cathode) material. Fabrication steps of μ MFC involved photolithography, wet silicon etching, metal sputtering and deep reactive ion etching. At the end, 330 nm gold layer (1.08 cm² area) having three dimensional serpentine channels (50 μ m height) on silicon substrate was obtained (Figure 1). A two-chamber fuel cell was created by assembling two microfabricated electrodes with gaskets (700 μ m height) and Nafion 117 proton exchange membrane as shown in Figure 2. Each chamber had volume of 100 μ L.

μ MFC system was operated under different loads or open circuit conditions to acclimatize the bacteria faster. *Shewanella oneidensis* MR-1 was preferred to be the biocatalyst in the anode chamber. 30 mM lactate solution was fed as anolyte (1 μ L/min) and 100 mM K₃[Fe(CN)₆] in phosphate buffer (3.5 μ L/min) was fed as catholyte with syringe pump continuously. The internal resistance was calculated as 29.2 k Ω under these conditions using polarization plot. The areal power and current densities were calculated as 0.4 μ W/cm² and 5 μ A/cm² respectively. The same μ MFC system was also characterized by Electrochemical Impedance Spectroscopy using Autolab PGSTAT204 potentiostat. The frequency range was between 0.1 Hz and 1 MHz. When the Nyquist plot from the experimental data was modeled as a simplified Randle's circuit (Figure 3), the internal resistance was calculated as 25.2 k Ω . The difference was 14% between the internal resistance values obtained from different methods. This can be due to the adopting of a simple equivalent circuit model during impedance spectroscopy analysis. Adoption of more complex circuits to model the electrical double layer of the biofilm may result in a smaller difference in the results.

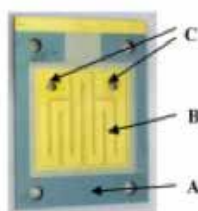


Figure 1. Microfabricated μ MFC electrode (A: Silicon substrate, B: Gold electrode, C: Liquid inlet/outlet).

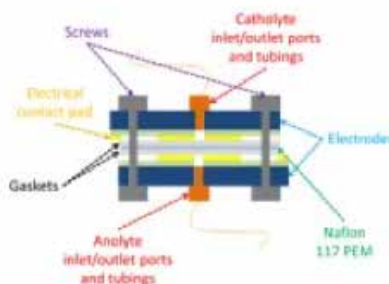


Figure 2. Schematic of μ MFC

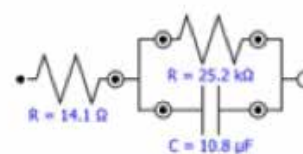


Figure 3. Equivalent R(RC) Circuit

This work was partly funded by Tübitak in the scope of 113E195 Project.

Keywords: Microbial fuel cell, bioelectrochemical system, internal resistance, impedance spectroscopy

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Poly(ϵ -Caprolactone) Based Polymer Blend Lithium Salts Mixtures For Lithium Ion Batteries

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Since world-wide energy shortage is one of the biggest problems in the 21st century, solar, wind and hydroelectric energy, etc. are replaced by non-renewable fossil fuels. efforts have been made to use other green energy sources. Unlike conventional fossil fuels, many of these green energy sources have an uncontrollable and discontinuous nature, so the difficulty in energy storage and regulation results in greater costs.

Lithium polymer batteries have a growing interest in being lightweight, safe and portable. For this reason, intensive studies are carried out on the lithium polymer battery, especially in the field of solid polymer electrolyte. The common goal of the studies is to develop and produce solid polymer electrolytes that do not damage the high thermal stability, mechanical strength, high energy and most importantly environment, and to create battery systems compatible with these electrolytes.

The objective of this study is to prepare polymer electrolytes by synthesizing new environmentally sensitive polymers and mixing them with lithium salts and to determine whether the electrolytes prepared by examining the physical, chemical and electrochemical properties of these electrolytes are suitable for use in lithium polymer batteries. In order to achieve this objective we synthesized poly(ϵ -caprolactone-g-vinyl acetate-co-vinyl pyrrolidone) copolymer by combining ring opening polymerization (ROP) and atom transfer radical polymerization (ATRP) methods. After synthesis resulting polymer was precipitated in hexane for removing and unreacted products and unwanted oligomers. After purification process resulting polymer was characterized by FT-IR, ¹H-NMR, GPC, DSC, SEM and TGA. Then different amounts lithium salts doped in the polymer and resulting product used as electrolyte in Li-Ion battery.

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Keywords: polymer electrolyte, lithium ion batteries ,Biodegradable polymer

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Effect of Electrode Processing and Cell Assembly on the Performance of
Supercapacitor in Prototype Pouch Cell Format**

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Supercapacitors are a key technology for future renewable energy storage due to their high-power density, long cycle life, low maintenance cost and better safety compared to rechargeable batteries.[1] Although the commercial manufacturers mostly prefer the cylindrical cell design for fabrication of large supercapacitors, the alternative pouch cell design are extensively being adopted for a range of applications due to many advantages such as smaller dead volumes both in the cell and on the module level, lower component requirement, lightweight and higher degrees of design freedom.[2] On the other hand, the laboratory scale testing and validation of the different supercapacitor components are mostly carried out using very small quantity of materials assembled in Swagelok cell or coin cell set up. At this level, many parameters related to electrode processing and cell assembly such as electrode thickness, calendaring conditions, current collector surface, electrode composition and mass loading are given less emphasis. However, these parameters significantly affect the overall electrochemical performance in terms of capacity, durability, power and energy density in a commercially viable cylindrical or pouch cell. That is why the performance obtained in laboratory testing does not always replicate when scaled up to larger pouch cells. This report summarizes different problems faced during a prototyping effort of supercapacitor from 1.12 cm² Swagelok cell to a 20.25 cm² pouch cell prototype using state of the art electrodes in standard organic electrolyte. Various electrode processing and cell assembly parameters were evaluated and compared with an industrially manufactured electrode. Finally, multi-layer pouch cell with 25 F capacitance is demonstrated using the best-optimized parameters, which deliver higher specific energy compared to commercially available 25 F cylindrical cell.

Spanish Ministry of Economy and Competitiveness (MINECO/FEDER) (MAT2015-64617-C2-2-R) and the Basque Government (CICe Elkartek 2018) are acknowledged for the financial support of this work.

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Keywords: supercapacitor; pouch cell prototype; current collector; electrode density; internal cell resistance

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Bismuth Oxide Nanoparticles Embedded Carbon Nanofibers as Self Standing
Anode Materials for Na-ion Batteries**

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²Sabanci University, Turkey

Last decades have witnessed the broad usage of Lithium-ion batteries (LIBs) from portable electronics to the electrical vehicles due to their high energy density. Since the limited reserves of lithium on earth, they cannot meet the increasing energy demand, thus, it is necessary to focus on new energy storage technologies. Recently, Sodium-ion batteries (SIBs) have attracted significant attention due to the large abundance of sodium on earth as well as similar chemical properties of sodium with lithium. However, graphite anode which is the most common anode material for LIBs cannot be used for NIBs due to the larger size of sodium than lithium that prevents the intercalation of sodium ions into the graphite efficiently. Therefore, there has been an enormous effort to develop new anode materials.

So far, carbon-based materials as well as metal oxides have been studied as anode materials for SIBs. As a carbon anode materials, hard carbons derived from biomass, carbon nanotubes (CNTs), graphene and carbon nanofibers (CNFs) have been investigated as anode materials for SIBs due to their high electrical conductivity and larger interlayer distance than graphite enables the efficient intercalation of sodium ions. However, due to the limited intercalation of sodium ions to host carbon structure and considering theoretical capacity of carbon anodes (372 mAh/g, based on NaC₆), their specific capacity values do not usually exceed 250-300 mAh/g. In order to meet the need of enhanced capacity values, metal oxides are used as alternative anode materials to carbon-based anode materials. Recently, bismuth oxide (Bi₂O₃) as an anode material for SIBs has been reported and there is only a few scientific work regarding the usage of Bi₂O₃ for SIBs. Bi₂O₃ is considered as promising anode materials due to its large abundance, stable chemical properties and high theoretical capacity (699 mAh/g). Bi₂O₃ is a semiconductor with low electrical conductivity and suffers from huge volume expansion during the electrochemical conversion leads to unsatisfactory capacity performances. To improve the electrical conductivity and to prevent the huge volume expansion of Bi₂O₃, preparation of its composites with carbon materials are usually proposed.

Herein, preparation of CNF-Bi₂O₃ nanocomposite as an anode materials via electrospinning method for SIBs has been introduced. Electrospinning is a practical method to prepare one dimensional (1D) carbon nanofiber (CNF) structures. CNF-Bi₂O₃ anode material exhibited excellent rate performances with a discharge capacity of 490 mAh/g at 130 mA/g current density.

This work was supported through the partial financial supports from the bilateral project between Gebze Technical University and Sabanci University (project contract no: 2016-GTU-SU-05 and I.A.SN-16-01589).

Keywords: sodium-ion batteries, carbon nanofibers, bismuth oxide, electrospinning

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Modeling the Stability of 2D/3D Perovskite Solar Cells

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Perovskite is one of the most popular materials as an absorber medium for solar cells due to its proper band gap, significant light absorption, successful electron movement and long carrier diffusion length [1]. Previous studies were focused on obtaining highest power conversion efficiency of solar cells via usage of three-dimensional perovskites as an absorber layer. However, 3D-perovskites are instable against moisture, heat and light. Therefore, 2D-perovskites were considered as a stable alternative to 3D-perovskites while they cause decrease in performance of solar cells due to their wider band gap [2]. Hence, 2D/3D multidimensional perovskites were introduced to achieve both stable and efficient solar cells [3]. The aim of this work is to extract features of 2D/3D multidimensional perovskites from the literature and to predict the best design for stable and perovskite solar cells. In this study, large number of articles on hybrid 2D/3D perovskite solar cells in the literature were studied and a database were constructed. The database includes various parameters such as band gap, spacer cation of 2D/3D perovskite, crystal structure of perovskite, front contact, electron transport material, hole transport material, back contact, photovoltaic performance, testing method and stability. Then, the models were developed applying various machine learning tools to understand the stability in 2/3D structures.

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Keywords: perovskite solar cells, 2D/3D, stability

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Highly Active Mesoporous NiS₂ for Hydrogen Evolution Reaction in Alkaline Media

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Transition metal sulfides are known to be active for hydrogen evolution reaction (HER). Their activities, stabilities and robustness demonstrate strong dependence on the structural phase, surface composition and termination, active electrochemical surface area, and electrolyte type; new strategies must be developed to have a better control on the parameters that affect the overall performances. We report a facile one-step synthesis protocol to prepare mesoporous NiS₂ thin films via a novel soft templating method without sulfidization process. The mesoporous NiS₂ thin films with high surface area and narrow pore size distribution were prepared by simply annealing the lyotropic liquid crystal in which nickel nitrate hexahydrate, two surfactants (cetyltrimethylammonium bromide and 10-lauryl ether) and thiourea assemble. XRD, XPS, SEM and TEM/EDX investigations indicate that as-prepared films go through a structural transformation and compositional change during HER in alkaline conditions. In-depth analysis on freshly prepared and tested samples reveals that the disulfide species are electrochemically reduced, while remaining Ni species are oxidized and converted to hydroxide. The formation of amorphous NiS_x(OH)_y shows the synergetic effect and enhances the HER activity.

This work is supported by the Turkish Petroleum Refineries Corporation (TÜPRAŞ).

Keywords: NiS₂, HER, mesoporous

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Determination of Optimum Barium Amount in Pb-Ca-based Alloys to Increase the Corrosion Resistance Via Electrochemical Measurements

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The rate of positive grid corrosion, which is one of the factors limiting the life of the battery during oxidation-reduction reactions, is influenced by the following parameters:

- Chemical composition and microstructure of grid material (Alloy)
- Plate potential
- Electrolyte composition
- Temperature

Calcium (Ca) - which is used in the positive grid alloy - prevents the breakdown of H₂O molecules and thus water loss, but because the Pb-Ca alloys have a small particle size, the area to be corroded is large and therefore cracks occur in the active material. To solve this problem, sufficient tin (Sn) was added to the positive grid alloy. Sn contribution to the Pb-Ca based alloys modifies the grain structure of the grid, changes the precipitation mechanism of the alloy and reduces the amount of PbSO₄ or α -PbO₂ formed at the interface.

Lately, it has been established that the mechanical strength and the corrosion resistance of Pb-Ca-Sn alloys increase with the addition of Barium. The high hardness of the Ba-doped alloy is attributed to the BaPb₃ intermetallic compound formed in the alloy [1]. To investigate the effect of Barium on corrosion resistance of Pb-Ca-Sn based alloys, a Barium containing rolled sample was used as a base-alloy. By adding missing Ca and Sn amounts to Pb-Sn-Ca-Ba base alloy under Argon atmosphere three different alloys were prepared. Polarization resistance and cyclic voltammetry measurements are performed to determine the corrosion rate and the redox capacities, respectively. We found that the corrosion rate decreased with the addition of Barium.

This work was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK) 1501 Programme, Grant No: 3160833

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Keywords: Lead acid battery, Grid alloys, Corrosion resistance

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Development and Optimization of Electrochemical Flow Capacitor Technology

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Electrochemical flow capacitor is a rechargeable electrochemical energy storage system that utilizes flow battery architecture and is based on the fundamental working principles of super-capacitors [1–3]. Rapid charging, increased self-discharge rate, cell geometry, membrane architecture and optimized flow process are some of ways to enhance the efficiency of the Flow Capacitor (FC) [4–6]. The finite element method (FEM) based simulations, combining the charge and mass transport, coupled to the charging of electrical double layer of carbon particles in liquid electrode slurry are used to conduct initial simulations of the FC cell. Such simulations assume that the convective movement of liquid electrolyte is negligible and will allow to characterize the basic properties of the system, such as the effect of cell geometry, material properties. Application of mass and charge transport equations, coupled with convective flow simulations makes it possible to find suitable geometries and conduct optimization with maximum mixing of liquid electrolyte as final goal [7–9]. By applying such approach, optimal utilization of the material is reached, leading to maximum charging/discharging rates optimal flow process of the electrode slurry.

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**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Performance Investigation of a 2 kWe PEM Fuel Cell for Microcogeneration Application

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The application of fuel cells for distributed generation applications like microcogeneration has been the subject of significant interest and recent research. A fuel cell is an efficient conversion technology that produces electricity and heat through a very simple chemical reaction between oxygen and a fuel. This electrochemical reaction, which differs from combustion, causes electrons to transfer between molecules through a defined circuit, which generates an electric current as well as heat. This provides electricity to power electrical engines and devices. If the heat is also exploited, this is known as combined heat and power generation (CHP). The technology is very flexible as fuel cells can be fed with different fuels. This allows it to be adapted easily to existing infrastructure. Fuel cells offer many advantages including low to zero emissions, high efficiency (even in small units), fuel flexibility, and are quiet. In some cases, fuel cells have become wellknown for their environmental benefits, including low NO_x and SO_x emissions and a reduction in global warming. Fuel cells, specifically the polymer electrolyte membrane (PEM) fuel cell and the solid oxide fuel cell (SOFC), are considered as an alternative to combustion based technologies utilized to meet heating requirements. This is because they exhibit high efficiencies, low emissions and noise levels, modularity, and a low heat-to-power ratio.

This study outlines the preparation of a PEM fuel cell for microcogeneration application. The modeling and design of the fuel cell is done for stationary application. Polymer composite bipolar plates are produced, the flow channels are processed. Electrodes are produced by ultrasonic spray coating on gas diffusion layers. Membrane electrode assembly is produced by hot pressing of the electrodes with Nafion membrane. The single cell tests are performed for evaluation of the performance. The fuel cell stack is produced by integrating 34 cells together. The performance of the 2 kWe PEM fuel cell system is investigated under different temperatures.

This study is supported by Republic of Turkey Ministry of Energy and Natural Resources General Directorate of Renewable Energy. Technical assistance of Mrs. Ebru Özen and Mr. Aydın Canbaşı are gratefully acknowledged.

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Keywords: fuel cell, polymer electrolyte membrane fuel cell, microcogeneration, reformat gas

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Improving the Charge Acceptance of New Generation Start & Stop Batteries with Carbon Additives

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In this study, effect of different carbons with different amounts on charge acceptance performance lead acid battery negative plates is investigated. Carbon samples were used as negative additives since they have been experimentally observed to suppress hard sulfation on the negative plate surface. Carbon particles take part on the conductivity, increase the active material surface area and limit the sulphate crystal size. By doing that these particles make sure current flow evenly but also increases the hydrogen evolution hence water loss.

Within the scope of this study, negative plates are produced by using three different carbons; carbon black, graphene and carbon nanotubes with different weight percentages. 2 V cells were built by using 2 PAM and 1 NAM. Electrochemical analyses such as, cyclic voltammetry and linear sweep voltammetry tests were performed on 2V cells. Optimum carbon – active material combination is determined in light of these tests.

This work was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK), 1501 Programme, Grant No: 3160727

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Keywords: Lead-acid battery, negative plate, sulphation, carbon, charge acceptance

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Thienopyrroledione Bearing Polymers for Polymer Solar Cell Applications

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In this study, photovoltaic properties of thienopyrroledione (TPD) bearing two random polymers, P1 and P2 were investigated with the device architecture of ITO/ PEDOT:PSS/ polymer:PC71BM/ LiF/ Al. Device fabrications and characterizations were performed in nitrogen filled glove box system. J-V characterizations were carried out under illumination of AM 1.5G solar simulator.

With P1 based polymer solar cells (PSCs) 3.32 % power conversion efficiency (PCE) value was achieved with a VOC value of 0.66V, a JSC value of 8.79 mA/cm² and a fill factor of 57.2%. With the addition of 1,8-diiodooctane (DIO), PCE value was improved to 4.30%.

With P2 based PSCs 3.19% PCE value was achieved with a VOC value of 0.69V, a JSC value of 8.06mA/cm² and a fill factor of 57.3%. With the addition of diphenyl ether (DPE) PCE value was improved to 5.15%. Effect of solvent additives (DIO and DPE), on active layer morphologies were investigated with transmission electron microscopy (TEM). With the addition of solvent processing additives, an improved active layer morphology was obtained where more interconnected polymer PCBM domains were formed, which improves the charge transport and collection efficiency. The PSCs based on P1 and P2 revealed high incident light response with the maximum EQE approaching 70% from 300nm to 720nm.

DRAFT

Keywords: polymer solar cells, conjugated polymers, thienopyrroledione

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Raw and Calcined Graphenes with Different Surface Areas as PEM Fuel Cell Catalyst Support

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PEM fuel cell is mostly known as environmentally friendly energy conversion device for supplying energy demand in the future. The commercial prevalence of the PEM fuel cell systems in the energy area will be possible with some improvements about the electrochemical fuel cell performance. In recent years, different catalyst and catalyst support materials have been tried in the PEM fuel cell systems in order to obtain advancing fuel cell performance.

Graphene has some advantageous properties such as electrical and thermal conductivities, mechanical flexibility, extensive specific surface area. The common idea about the graphene is that it is proper material for being a good catalyst support with these properties all in one package because having electrical conductivity and providing high surface area for uniform distribution of catalyst particles are requested features for candidates of any catalyst support material. In literature, there are some examples about the utilization of graphene and their derivatives as PEM fuel cell catalyst or catalyst support materials [1], [2], [3].

In this study, commercial graphenes (Nanografi) with three different surface areas such as 320, 530 and 800 m²/g were evaluated as PEM fuel cell catalyst support. These graphene samples were used as purchased and also they were calcined with and without melamine under the condition of nitrogen atmosphere and these cases of graphenes were also examined as PEM fuel cell catalyst support material. Graphene samples were physically mixed with melamine at the 1:1 mass ratio and calcined at 900°C under the condition of nitrogen gas flow. They were also calcined under the same conditions except using melamine. These all cases of graphenes were used in the content of PEM fuel cell catalyst and performance evaluations of the cells that contain platinum catalyst supported with these materials were conducted through the experimental process.

Some physical characterizations such as XRD, FTIR, Raman spectroscopy, Elemental analysis, BET, SEM for the graphene samples will be presented. Platinum loading amounts on the graphene samples will be detected by TGA. Commercial platinum catalyst (Tanaka, 67 wt. %) will be loaded over the graphenes by microwave irradiation technique. The catalyst layers (CL) will be prepared via spraying of the catalyst solution that contains platinum catalyst supported with the graphene samples over the gas diffusion layer (GDL). The water contact angles on the prepared catalyst layers were measured by optical tensiometer. Electrochemical characterization of the support materials will also conducted with in-situ PEM fuel cell test station.

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Keywords: graphene, calcination, catalyst support, surface area, PEM fuel cell

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Supercapacitor Device Performences of Ternary Nanocomposites and Real Circuit Evaluations

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Supercapacitors are the most important energy storage devices between conventional capacitors and batteries through the last decade [1-3].

rGO/RuO₂/PVCz, rGO/TiO₂/PEDOT ve rGO/MnO₂/PTTh nanocomposites were synthesized for supercapacitor device fabrications. These ternary nanocomposites have high conductivity, large electroactive surface area, bio-compatibility and electrocatalytic activity so they can be used as potential for supercapacitors. In our study, we designed 3 different conducting polymer including in nanocomposite structure.

Conducting polymers will be supplied strong π - π bonds on rGO/metal oxide nanocomposites and decrease the surface resistance. These three materials will be shown high capacitance, charge/discharge stability, high energy and power density. In this study, we will prevent agglomeration of graphene nanosheets due to metal oxides and therefore capacitance and conductivity values will be increased.

A real electrical circuits will set up for our supercapacitor devices. LED lamps will be performed with high and low resistance of electrical circuits. Our aim is to present higher storage devices of electrical charges.

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Keywords: Reduced graphene oxide, symmetric supercapacitor, real circuit analysis

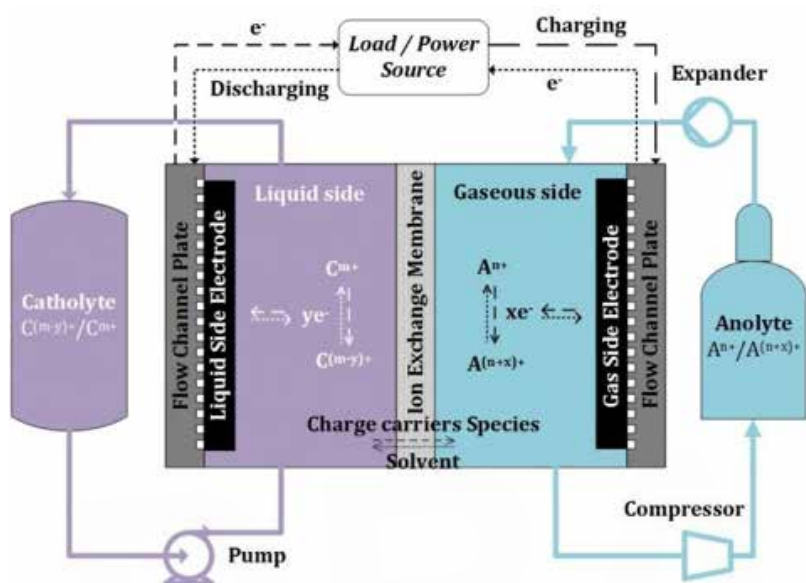
Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Electrode Catalytic Effects of Nanomaterials on Regenerative Hydrogen Vanadium Fuel Cell Systems

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Amongst a myriad of different storage technologies, electrochemical energy storage (EES) can show tremendous potential for both grid-scale and vehicular applications. EES is classified as batteries, electrochemical capacitors, regenerative fuel cells and their hybrids. Flow batteries are a form of EES in which electrical energy is stored via the generation of a physically separated reductant and oxidant, and electrical energy is generated when required by the re-combination of this redox couple. Unlike other forms of EES, flow batteries are characterized by the ability to decouple power and energy, allowing significant cost savings as energy requirements increase, and offer the potential for MW/MWh scale storage. Considerable progress has been made on this technology in recent years, especially within the US, China and the UK (where Imperial College has played a significant role), but challenges remain to understand and improve lifetime and performance in the commercial all-vanadium system and to explore novel approaches which offer significantly reduced cost. In this work, we report the progress with novel chalcogenide-based composite electrodes for testing in a hybrid regenerative hydrogen/vanadium flow battery (RHVFB). The RHVFB has been tested with reduced graphene oxide, nitrogen doped graphene and nano-fiber based electrodes successfully, reporting power densities in excess of 500 mW/cm² and high energy efficiencies for 150 charge/discharge cycles. Successful results have led to scaling-up and potential commercial opportunities that are being explored with RFC Power (Imperial College based spin-out) as well as Potential Reactions Limited. Engineering & Physical Sciences Research Council UK

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Keywords: Redox flow battery; graphene; nanofibres; electrode catalysts

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Guar-gum Based Porous Carbon Electrode Materials for Electrochemical Energy Storage Systems

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Porous carbon materials and composites have attracted intense attention as promising electrode materials for various electrochemical energy storage systems, including supercapacitor, Li-S battery etc. The electrochemical performance of carbon-based materials greatly depends on their chemical composition, ordered microstructure, and specific surface area. Till now, it remains an unmet challenge to prepare porous carbon materials with simple processing techniques, high yield and scalable characters. However, the rapid gelling process because of high affinity between guar gum and metal hydroxide offers a potential solution strategy for the aforementioned problems. Herein, we summarized our recent progress in guar gum-based porous carbon materials applied to supercapacitor and Li-S battery. Furthermore, the challenges as well as the prospects are also discussed to further optimize the guar gum-based electrode material, and meet the requirements of the next-generation electrochemical energy storage systems.

This research was supported by National Natural Science Foundation of China (51702139) and Youth Science Foundation (20151BAB216007, GJJ150637, 20161BAB216122)

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Keywords: porous carbon; guar gum; Gel; electrochemical energy storage

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Next Generation Redox Flow Batteries Based on Solid Boosters for Large-scale Energy Storage

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Large-scale energy storage systems are urgently needed to manage intermittent energy production and improve the flexibility and security of grid systems. Redox flow batteries (RFBs) are an already established technology ideal for large-scale energy storage due to their high safety, long lifetimes, low environmental impact and decoupled power/capacity. However, the low energy density and high raw material cost of the state-of-the-art all-vanadium technology has proven to limit commercialization. During this presentation, ways to realize next generation flow battery systems for large-scale energy storage based on solid boosters and inexpensive redox active materials (such as inorganic metal complexes and organic species) will be discussed. Especially the concept of solid boosters [1,2], where “molecular wiring” to charge and discharge the redox active solid materials present as beads in a packed bed reactor will be discussed, and recent results from our labs will be presented. For example, we have shown that Fe(III/II) electrolyte can be used to reversibly store charge in solid polyaniline/carbon composite [1], and organic N,N,N',N',N'',N'',N'''-heptamethylpiperidinyloxy-4-ammonium chloride redox couple can be used to reversibly charge and discharge solid copper hexacyanoferrate, in both cases leading to significant enhancement of the energy storage density of the system.

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Keywords: redox flow batteries, energy storage, charge transfer

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

A High Molar Extinction Coefficient Bisterpyridyl Homoleptic Ru(II) Complex with Unsaturated Carboxylic Functionality: Potential Material Dye for Dye-Sensitized Solar Cells

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In our continued efforts in the preparation of new ruthenium(II) polypyridine material complexes for industrial applications especially those focusing on the dye-sensitized solar cells (DSSCs), we here describe the facile synthesis, photophysical and electrochemical properties of a Ru(II) terpyridyl complex having trans-2-methyl-2-butenic acid as anchoring ligand for adsorption on TiO₂ semiconductor. In particular, the photophysical and redox properties displayed by the complex as [Ru(L1)₂(PF)₆] are significantly better compared to those of [Ru(tpy)₂]²⁺ and compared very well with those of the best emitters of Ru(II) polypyridine family containing tridentate ligands. Reasons for the improved photophysical and electrochemical properties of the complex may be attributed partly to the presence of a substituted α,β-unsaturated carboxylic acid moiety leading to increase in the length of π-conjugation bond thereby enhancing the MLCT-MC (metal-to-ligand-charge transfer-metal centered) energy gap, and to the reduced difference between the minima of the excited and ground states potential energy surfaces.

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Keywords: homoleptic Ru(II) complex; terpyridine; extended-π-bond conjugation; electrochemistry

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Facile Synthesis of a Core/shell Nanostructured TiO₂@MnO₂ for Free-carbon
Air Breathing Cathode to Enhance Cyclability of Li-O₂ Battery**

Sara PAKSERESHT, Tugrul CETINKAYA, Hatem AKBULUT

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In recent years, instability of carbon material in Li-air batteries has been reported, repeatedly [1]. Formation of undesired Li₂CO₃ during charging prevents the reversible Li-O₂ reaction and leads to limit cycling performance of the battery [2]. Therefore, it is required to develop a new alternative carbon-free cathode material for Li-air batteries.

In this work, we have developed a core-shell structure of TiO₂@MnO₂ nanocomposite to fabricate carbon-free cathode material for lithium air batteries. Recently, nanostructured titanium dioxide (TiO₂) and manganese dioxide (MnO₂) are the most investigated among the nanomaterials due to their unique properties. Researchers have been attempted to fabricate these two materials into TiO₂@MnO₂ nanocomposites, aiming to emerge their intrinsic properties and design a novel complex in various applications such as batteries and supercapacitors. Here, TiO₂ nanoparticles were synthesized by a facile and ecofriendly process using flower extract of *Matricaria chamomilla* (Chamomile) containing phytochemicals that include various functional groups was used as a stabilizing and reducing agent in this process, which was used to form TiO₂ nanoparticles from Titanium Isopropoxide precursor without using any other toxic chemicals. Interestingly, MnO₂ nanocrystals can be grown on TiO₂ nanoparticles, which could provide high surface area to enhance electrochemical activity of electrocatalyst with a higher discharge/charge capacity and longer cycling lifetime compare to bare TiO₂ and MnO₂. The formation mechanism of such architecture is studied. Both properties of TiO₂ with excellent cycle stability and MnO₂ with high capacity were combined.

The morphology, elemental composition, crystallinity, and surface area of the obtained Bio-TiO₂ nanoparticles and TiO₂@MnO₂ nanocomposites were characterized by field emission electron microscopy (FESEM), X-ray diffraction (XRD), Raman spectroscopy and Brunauer–Emmett–Teller (BET). The electrochemical performances of the core-shell structured TiO₂@MnO₂ cathode material have been comprehensively enhanced. The electrochemical performances of active materials were evaluated using ECC-Air test cell. In this cell Bio-TiO₂ and TiO₂@MnO₂ was used as cathode material, lithium foil was used as anode materials and 1M LiClO₄ was the electrolyte. The cell was tested in the voltage range from 2V up to 4.3V at the constant current density of 0.05 mA/cm². Moreover, the internal resistance of the cell was measured using EIS technique and reactions of the cathode active materials with Li⁺ were investigated by cyclic voltammetry.

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Keywords: core/shell structure, biosynthesis, lithium air battery

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

High Cyclability rGO@Pd@ α -MnO₂ Nanocomposite for Lithium-Air Battery Utilized as Air Breathing Cathode

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Lithium–oxygen (Li–O₂) batteries have been developed as the next generation in energy storage due to their high theoretical energy densities (11,140 Wh/kg). Although, in the Li–O₂ battery, short cycle life, low energy efficiency, low charging/discharging rate are critical challenges [1]. Cathode catalysts play a significant role to overcome these limitations and promote oxygen reduction reaction and oxidation for Li–O₂ batteries [2]. Therefore, designing a cathode with porous structure, highly conductive, good chemically stable and high catalytic activity is required.

In this study, we focus on designing enhanced cathode air electrode to improve electrochemical performance of current lithium–oxygen batteries by utilizing high-efficiency nanocatalysts assembled by reduced graphene oxide (rGO)@Pd@ α -MnO₂ nanocomposite. Among the carbon materials, graphene has a great potential to be used for energy storage due to its superior electronic conductivity, large theoretical surface area (2630 m²g⁻¹), excellent structural flexibility and high surface to volume ratio. rGO with noble metals such as palladium have been explored as oxygen evolution reduction (OER) electrocatalysts in Li–air cells to lower the charge overpotentials and exhibited stable cycling performance. Additionally, MnO₂ is an attractive functional metal oxide as catalysis for lithium air batteries due to its structural flexibility, low cost, high catalytic ability, high average voltage, and it is eco-friendly. rGO@Pd@ α -MnO₂ nanocomposite cathode combines unique properties to enhance cyclability with elevated capacity at a high rate to obtain highly practical performance of Li–O₂ cells.

Graphene oxide (GO) was prepared by modified hummers method, followed by deposition of Pd on the surface of GO to assure the strong interactions between cationic Pd²⁺ and the oxygen functional groups (hydroxyl, epoxy and carboxyl groups) on the surface and the edge of the GO sheets, which increase the surface area, avoid aggregation of rGO and lead to enhance electrochemical performance. Afterward, α -MnO₂ nanowires, which synthesized through hydrothermal method, was anchored between as-prepared rGO@Pd sheets by mechanical milling. The prepared samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, field emission scanning microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS). Moreover, we indicate electrochemical performances of rGO@Pd@ α -MnO₂ nanocomposites using ECC-Air test cell. Electrochemical cycling tests of the rGO@Pd@ α -MnO₂ nanocomposite cathodes were carried out in the voltage range of 1.5 V–4.5 V at a constant current density of 0.1 mA/cm². For further electrochemical characterization, EIS spectroscopy measurements were performed in the frequency range of 100 kHz to 0.1 Hz. Moreover, in order to study lithium oxide formation and decomposition reactions, cyclic voltammetry test was performed at a scan rate of 0.5 mV/s.

The authors thank the TUBITAK for supporting this work under the contract number 315M461.

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Keywords: lithium air battery, nanocomposite, graphene

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Electrochemical Behavior of Dual Electrolyte Lithium Air Flow Battery

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In this work, we have targetted to design a lithium air flow battery test cell to overcome tradinational lithium air battery issues such as anode corrosion, clogging of porous cathodes and rapid capacity fade. We designed an own home-made lithium air flow battery which consists of the cell part where there is anode, cathode, electrolytes and membranes, contained part which includes aqueous electrolyte and the last part is the peristaltic pump which assure flowing of the electrolyte from container to cell. The cell part was assembled using lithium as anode, lithium ionic conducting glass ceramic (LATP) as membrane which separate aqueous and organic electrolytes and GDL (sigracet, 24BC) was the cathode. The aqueous electrolyte was stored in a container and provides an electrolyte circulation from container into the cell by a pump. At the same time, oxygen was pumped into the aqueous electrolyte and oxygen was reached to the cell through the aqueous electrolyte. In this cell, we have studied electrochemical behaviour of lithium air flow battery using LiOH and LiCl aqueous electrolytes in order to observe effect of different aqueous electrolytes on the reversible reaction and cycle life of the cell. Electrochemical characterization of the cell was performed using cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge-discharge tests at different currents.

The authors thank the TUBITAK for supporting this work under the contract number 315M461.

DRAFT

Keywords: Lithium air, flow, battery, cyclic voltammetry, impedance, cycle life

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Design of Sulfur-Containing Composites for High-Performance Lithium–Sulfur Batteries

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Sulfur has received considerable attention as a cathode material for lithium-sulfur (Li-S) batteries due to its high theoretical specific capacity (1675 mA h⁻¹), high earth abundance, and environmental benignity. However, because of the dissolution of polysulfides in electrolyte, the shuttle effect that stems from the diffusion of polysulfides from cathode side to anode side severely deteriorates the cycling stability of Li-S batteries. To overcome this issue, our research is aimed to design sulfur-containing composites that utilize strong interactions of sulfur and/or polysulfides with carbon framework to enhance the cycling stability of Li-S batteries. In our recent research,[1] we proposed a facile in situ method for preparing three-dimensional porous graphitic carbon composites containing sulphur nanoparticles (3D S@PGC) with sulphur content up to 90 wt%. Because of the high sulphur content, the nanoscale distribution of the sulphur particles, and the covalent bonding between the sulphur nanoparticles and the PGC, the 3D S@PGC cathodes exhibit high specific capacity (1382, 1242, 1115 mA h g⁻¹ at 0.5, 1, 2 C, respectively), long cycling life (a small capacity decay of 0.039% per cycle over 1000 cycles at 2 C), excellent rate capability at a high charge/discharge current. In addition, cathode materials showing good cycling stabilities of Li-S batteries were also prepared using graphene and carbon nanotubes as conducting frameworks for hosting sulfur.[2-5]

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Keywords: Li-S batteries, porous graphitic carbon, graphene, carbon nanotubes

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Effect of Boron Oxide on the Carbon Nanofibers as Electrode for Supercapacitor Applications

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Carbon nanofibers (CNFs) have been recognized as one of the promising electrodes which greatly affect the capacity, power density and energy density of supercapacitors but challenges still remain because of the low capacitance of CNFs. [1-3]. Chemical doping is one of the most effective methods to tune the electronic properties of carbon nanofibers. In this paper, we report different amounts of B₂O₃ nanoparticles embedded in CNFs synthesized by a simple electrospinning approach and annealing treatment in N₂ atmosphere. A symmetric supercapacitor (SC) based on B₂O₃ doped CNF (B₂O₃@CNF) binder-free and freestanding electrodes were designed. The supercapacitors were tested with a coin cell within 0-1V. Benefiting from the synergistic effect of B₂O₃ nanoparticles and graphitized carbon layers, the electrode performance of obtained B₂O₃@CNF based supercapacitors were found as almost ~150 Fg⁻¹at 1Ag⁻¹. The enhanced performance is attributed to easy electrolyte accessibility as well as porous fibrous carbon morphology. After 10000 cycle test, the capacitance retention can still maintain about more than 80% with an excellent cycling stability. The fabricated symmetric supercapacitor based on B₂O₃@CNF electrodes can deliver energy density of 5.2 Whkg⁻¹ power density of ~ 250Wkg⁻¹. The results show that B₂O₃@CNF electrodes are promising materials for the future generation of high performance supercapacitors.

Acknowledgements We would like to thank ERANET-INCOMERA programme supported by Scientific and Technological Research Council of Turkey (TUBITAK) 1509-International Industrial R&D Projects Grant Programme with Project Number 9160035

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Keywords: Electrospinning, B₂O₃, carbon nanofibers (CNFs), supercapacitors

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Effect of Heating Time on Cobalt Oxides for Electrochemical Energy Storage

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Over the past decade, demand for energy is increasing due to the rapid technological development. Among the energy storage systems, electrochemical capacitor or better known as supercapacitor has been receiving much attention as the anticipated candidates for the next-generation energy storage devices. Metal-organic framework (MOF), a kind of porous and crystalline material, is the excellent choice for an electrode active material in supercapacitors due to their unique morphology, controllable pore size, high surface area and elaborates pore structure. In this work, Co-based MOF was synthesized via solvothermal method by using terephthalic acid as the organic linker. The Co-MOF was then heated at 300 oC for two different heating time, 0.5 and 3.0 h, to obtain the cobalt oxides. X-ray diffraction (XRD), energy dispersive x-ray analysis (EDX), field emission scanning electron microscope (FESEM) will be carried out to analyze the structure and morphology of the Co-based MOF. Electrochemical analysis was done using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) in a three-electrode system in 3M of KOH electrolyte. Specific capacitance for Co₃O₄ obtained at 3 h is higher compared to 0.5 h with the value of 100.21 F/g at 0.5 A/g current density. However, a good cycling stability was observed for both system with the capacitance retention rate of 95-98 % after 1500 cycles.

DRAFT

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Structural and Electrochemistry Study of ZnSnO₃/Porous Carbon Composite for Supercapacitor

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ZnSnO₃/mesoporous carbon composite (PP-ZTO) and porous carbon (PP-C) were synthesized via simple combustion method at 500 °C for supercapacitor application. High porous composite material of 896.39 m²g⁻¹ was achieved in PP-ZTO. Three well-resolved peaks at 27°, 34° and 52° were observed in the XRD pattern can be indexed to ZnSnO₃. FESEM image of PP-ZTO clearly shown the high porous structure along with ZnSnO₃ attached on the carbon surface. The composite material exhibited specific capacitance of 94 Fg⁻¹ at the current density of 0.3 Ag⁻¹. In symmetrical cell, cyclic voltammetry (CV) in PP-ZTO still maintained a nearly rectangular shape as compared to the leaf-shape of PP-C explained the contribution of ZnSnO₃ in enhancing the electrochemical performance. PP-ZTO also performed excellent capacitance retention of ~80% after 3000 charge-discharge cycles with different current densities implying the high durability of the cell. The results indicating that ZTO/carbon as a promising candidate to be applied in supercapacitor.

DRAFT

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Design of Materials for Recycling CO₂ to Produce Renewable Fuels

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Energy storage is one of the major challenges regarding renewable energy systems due to their intermittent nature. One of the practical solutions is to store renewable energy in chemical bonds (high energy density fuels) as nature does in photosynthesis process. Nature recycles CO₂ in presence of sunlight and water to renewable fuels. Renewable fuels have two extraordinary advantages; 1) Renewable fuels provide efficient energy storage option for “surplus renewable energy” into chemical bonds of high energy density fuels and 2) Renewable fuels utilize existing energy supply infrastructure without any further requirements. However, electrochemical production of renewable fuels from waste CO₂ and H₂O to energy dense chemicals is one of the major challenges due to absence of suitable electrocatalysts. A suitable electrocatalyst should exhibit high catalytic activity (i.e. high current density) at low overpotential (energy efficiency) towards a single energy rich product (selectivity), be inactive for competitor reactions such as hydrogen evolution (HER) and have good stability under reaction conditions. Herein we report, we report a novel strategy based on improved material design (Cu, Sn, In, Sb, Pb)[1-3] and enhanced mass transfer for eCO₂R to affordable and scalable CO production. Our results suggest that our designed electrocatalysts suppress the reduction of H⁺ and simultaneously promote the conversion of CO₂, which is highly desired in the electrochemical reduction of CO₂ in aqueous medium.

DRAFT

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Electrochemical Engineering and Process Technology

Atomistic Understanding of Pb-Cu Surface Alloy Mechanism Using Electrochemical Scanning *Tunneling* Microscopy

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Understanding the surface activities and kinetics of solid/liquid interfaces is of great interest in electrochemical process engineering. Electrochemical Scanning Tunneling Microscopy (EC-STM) is a primary characterization tool for investigating the impacts of ongoing reactions on the substrate. The key point of the EC-STM is that the microscopic measurements can be conducted simultaneously with the surface reactions. The mechanism of Pb-Cu surface alloying represents a stimulating system due to the immiscible nature of Pb and Cu atoms. Our research focused on the underpotential deposition (UPD) of Pb on Cu(100) to observe the structural changes on the surface using EC-STM. UPD studies were performed in 0.1 mol/L HClO₄ + 1 mmol/L HCl + 1mmol/L PbClO₄. Finding wide terraces on Cu(100) is critical for clear observations on the surface. Therefore the crystal was mechanically and chemically polished before the STM and UPD studies. Prior to the surface alloying, the relative coverage and surface structure that arise from the competition between Pb and Cl⁻ was explored. Sequential STM images recorded during the potential cycling from a more positive potential to a more negative potential point that Pb deposition on Cu forms c(4x3) phase on the surface. After a while c(4x3) structure decomposes into nanoribbons. EC-STM images demonstrate the formation of surface alloying when this process was repeated several cycles. This study brings up a detailed understanding of low-dimensional surface alloying of Pb and Cu.

DRAFT

Keywords: Scanning Tunneling Microscopy, Underpotential Deposition

Electrochemical Engineering and Process Technology

Direct Electrochemical Production of High Entropy Alloy Compositions

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High entropy alloys are a relatively new class of metallic materials which contain five or more metals whose composition fall in the range of 5-35 atomic percent. A large space for compositional adjustment makes these alloys attractive for upcoming applications and researches. AlCrFeNiV high entropy alloy is a promising matrix for tungsten heavy alloys which are used as kinetic energy penetrators due to their refractory characteristics and good mechanical behaviors at high strain rates. AlCrFeNiV high entropy alloy matrix composition and tungsten were produced at one step by electrochemical reduction technique in molten CaCl₂-NaCl eutectic mixture at 873 K by mixing respective oxide powders and CaWO₄ in this study. Produced powders were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. The produced powders were aimed to be used directly in the liquid phase sintering of the desired tungsten heavy alloy composition.

DRAFT

Keywords: high entropy alloys, tungsten heavy alloys, electrochemical reduction, molten salt processing

Electrochemical Engineering and Process Technology

Composite Lay-up Tool Manufacturing via Nickel Electroforming Process

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Composite lay-up tools are manufactured from different materials such as; Invar, carbon reinforced composites, aluminium, steel and nickel. The parameters that should be considered when selecting the tool material include surface hardness, coefficient of thermal expansion, machinability, service temperature, autoclave processing performance and surface finish quality. Electroform nickel tools are very good candidates for complex shapes and tight tolerances due to their superior properties. An electroform nickel tool was designed and produced using a nickel sulphamate electrolyte in this study. A carbon fiber reinforced composite of exactly negative geometry was used as the mandrel material in the manufacturing of electroform nickel composite lay-up tool. Its surface was prepared for the electroplating process using a graphite based conductive ink. The static/dynamic test results; autoclave performance, welding behaviour and surface finish quality of the tool were analyzed.

DRAFT

Electrochemical Engineering and Process Technology

A New Electrode for Powders Analysis

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A new electrode was fabricated by our team, which can revolutionize the electrochemical analysis domain. This electrode is used as a working electrode, where the powder is pressed on electrode surface. The electrode can be polished and rinsed with distilled water easily. This new electrode is used for qualitative and quantitative electrochemical analysis of conductor or semiconductors powders or composite materials, by all electrochemical technics, as cyclic voltammetry, chronoamperometry, chronopotentiometry, impedance spectroscopy.....etc. This electrode is destined to the electrochemical instruments market, which represent a big market in the worldwide.

The powder or the composite material is pressed on an inert electrode surface, which is inserted inside a teflon tube, this working electrode is better than that used in the literature because this new electrode possesses many advantages, among them: easy for using, good solidity, low fabrication cost, environmentally friendly, it can be used for a long term and resist high temperature, resist to harsh chemicals and can be used for a long term.

In electrochemistry, generally to analysis a powder, it must be mixed thoroughly with graphite with a weight ratio, using high speed electric grinder for a period of time, the obtained mixer was then added into the black mix as binder, which was pressed at a big pressure to form the electrode. The electrode was then mounted in the electrochemical cell. Before the electrochemical measurements were performed, all electrodes were vacuum-wetted to ensure the electrolyte penetration into the pores [1]. Another recent technic that exists to analyze electrochemically the powders or composite materials by using the microelectrodes, also called ultra-microelectrodes, which have some very special diffusion properties. This working electrode can be prepared by melting an ultra-thin metal wire into a glass rod in which the powder or composite material is inserted [2]. The small radius of the wire with only a few micrometers leads to a situation in which the radial resistance of the electrolyte in front of the electrode substitutes the diffusion limitation by the diffusion layer [3].



Fig. 1: Powder electrode

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Keywords: Working Electrode, powder analysis, metallic oxides
Electrochemical Engineering and Process Technology

Transparent Ceramic Preparation in The Use of Thermal Energy

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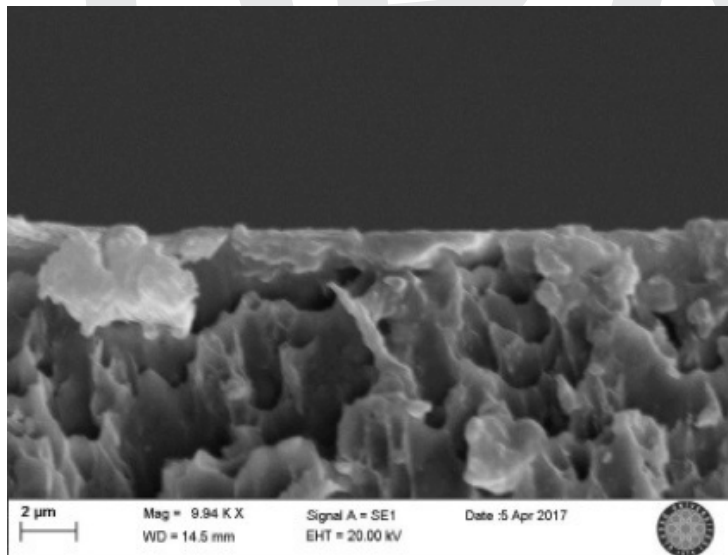
Optical transparency in polycrystalline materials is limited by the amount of light which is scattered by their microstructural features. Light scattering depends on the wavelength of the light. Limits to spatial scales of visibility (using white light) therefore arise, depending on the frequency of the light wave and the physical dimension of the scattering center. Primary scattering centers in polycrystalline materials include microstructural defects such as pores and grain boundaries.

In the formation of polycrystalline ceramics the size of the crystalline grains is determined largely by the size of the crystalline particles present in the raw material during formation (or pressing) of the object. Moreover, the size of the grain boundaries scales directly with particle size.

Computer modeling of light transmission through translucent ceramic alumina has shown that microscopic pores trapped near grain boundaries act as primary scattering centers.

When a light wave of a given frequency strikes a material with particles having the same or (resonant) vibrational frequencies, then those particles will absorb the energy of the light wave and transform it into thermal energy of vibrational motion. Since different atoms and molecules have different natural frequencies of vibration, they will selectively absorb different frequencies (or portions of the spectrum) of infrared light. Reflection and transmission of light waves occur because the frequencies of the light waves do not match the natural resonant frequencies of vibration of the objects. When infrared light of these frequencies strikes an object, the energy is reflected or transmitted.

In this presentation, beside the theoretic approach of storing mechanical energy of motion in condensed matter through thermal energy, fabrication of nano ceramics (such as aluminum oxide or other oxides) by electrochemical processing method will be given. These materials may be used in selective optical applications.



Microstructure of IR reflective ceramic

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Electrochemical Engineering and Process Technology

Fabrication and Evaluation of a Micro-sensor Array Chip for Personalized Medicine of Sickle Cell Disease

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Sickle cell disease is a common inherited blood disorder that leads to major morbidity and early mortality. In order to increase sickle cell treatment efficiency, it is necessary to directly measure the concentration levels of the administered drugs in serum or blood and to establish pharmacokinetics profiles to generate individualized dosing plans. (a) We are developing a low-cost and simple test for rapid quantification of the FDA approved drug hydroxyl urea in biological samples, in order to improve the way the dosing is established and the treatment is monitored.

The main challenge of in-situ analysis of unlabeled redox-active molecules in biofluids is the interference from other redox molecules generating overlapping electrochemical signals (e.g., uric acid, ascorbic acid). We modified the sensing microelectrode with 5 different materials (chitosan hydrogel, alginate hydrogel, molybdenum sulfide, tungsten sulfide, and carbon nano-dots) that allows tuning the partial selectivity of each of the electrode in the array towards hydroxyl urea while decreasing the influence of the interfering molecules.

The selective modification of 32 microelectrodes generates electrochemical interfaces with different properties allowing generating multiple electrochemical signatures corresponding to the drug hydroxyl urea. The physical properties of each electrodeposited material differ, thus generating variable specificity toward the analytes and the interfering redox molecules. The complex variability of the electrochemical signal in the presence of interfering redox active molecules is analyzed via principal component analysis. The determination of hydroxyl urea is possible in finger pricked volumes of a synthetic serum (10-20 micro-L) via the characteristic oxidation peak of hydroxyl urea observed with differential pulse voltammetry at 0.65 V vs Ag/AgCl. The selective functionalization of the 32 microelectrodes also enables the quantification of hydroxyl urea levels in biological samples of sick children with sickle cell disease.

The authors thank the Ilse Katz Institute for Nanoscale Science & Technology for the help in Microfabrication and material characterization. We thank the Cincinnati children hospital and Ben Gurion University BG3C Pediatric Medical Device Initiative for funding. The authors also thank the Marcus family donation which support Dr. Cazelles via the Water Science Fund of the Ben-Gurion University of the Negev.

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Keywords: Multielectrode array (MEA), personalized medicine, finger pricked blood analysis

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Investigation of Electrochemical Synthesis of UiO-66 Thin Films on Zr Foils

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Metal-organic frameworks (MOFs) are propitious materials in the field of chemical sensing. The applicability of MOFs in sensing applications generally suffers from the structural instability of MOFs upon exposure to humidity, and the powder form of most MOFs hinders the direct integration with device electronics. A humidity-resistant MOF synthesized in the form of a thin film on a conductive substrate could address these issues. UiO-66 is the most humidity-resistant MOF synthesized so far in the literature [1]. In this study, we pursue the electrochemical synthesis of UiO-66 thin films on Zr foils. The synthesis is achieved using a 2-electrode setup [2]. The effect of synthesis parameters, such as the chemical formulation of the electrolyte, synthesis modulation by addition of acetic acid and water, etc. are studied. The synthesized metal-organic frameworks are characterized using XRD, FTIR, AFM and SEM. A proper window for synthesis parameters is achieved. Electrochemically synthesized UiO-66 thin films might be promising candidates for use in sensing applications due to the inherent water/humidity stability and capability of direct integration with device electronics.

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Keywords: electrochemistry, MOF, synthesis, sensing

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Investigation on The Protective Power of Graphene Oxide on The Copper Corrosion in Aqueous Chloride Solution, Synergy Effect with Caffeine

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An enormous development in carbon-based nanomaterials has occurred since the experimental realization of graphene in 2004 [1]. It has attracted extreme interest in the scientific and industrial community, due to its high properties in different fields. The chemical inertness and impermeability towards most gasses in combination with its strength and single atomic layer thickness make it a fascinating candidate for coating purposes, particularly for anti-corrosion coatings, a new and better protecting material. One of the roles of the graphene-based composite films is on the corrosion, electrochemical and photo-electrochemical performance of the underlying substrates. Graphene coatings are proved to be a corrosion inhibitor in aqueous media. Recently, there is an increasing interest in exploring the corrosion resistance properties of graphene and its derivatives [2].

In this work, we tend to study the synergic effect of graphene oxide and caffeine on the protection of copper corrosion in aqueous chloride solution. Firstly, graphene oxide dispersions have been prepared and drop cast into films on wellpolished copper sheets and their corrosion inhibition properties in 3.5 wt. % sodium chloride (NaCl) solution at ambient conditions have been investigated and confirmed by electrochemical methods together with surface analysis, demonstrating the strong protection offered by graphene oxide films. Secondly, caffeine has been investigated and proven to be a good corrosion inhibitor for copper corrosion [3], the similar experiment done but the only difference is in the addition of caffeine to 3.5 wt. % NaCl solution.

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Keywords: Corrosion, Copper, Graphene oxide, Caffeine

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Metallization of High Density Polyurethane Surfaces

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Electroplating onto polymeric materials is required for different purposes in various applications. Polyurethane (PU) is an electrically insulator material and it is durable at high temperatures. Furthermore, it has a high thermal conductivity, a low thermal expansion coefficient and a high density foam. In this study, surface metallization of the polyurethane foam, involving activation and sensitization processes, was studied to prepare the surface for subsequent electroplating processes. The surface metallization was carried out by multi-step processes which included degreasing, etching, sensitization, activation and electroless nickel plating. Metallized surfaces were tested for electrochemical nickel plating at different current densities and surface morphology, roughness and physical properties of the coatings were characterized. The results showed that increasing current density adversely affects the surface morphology and surface sensitization and activation processes increased the surface conductivity of foam.

DRAFT

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Bark Resin of Schinus Molle as Green Corrosion Inhibitor for Carbon Steel in HCl Solution

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Carbon steel is the most widely used engineering material. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in petroleum production, refining and pipelines [1]. In the petroleum industry, carbon steel pipelines are susceptible to corrosion by acidic solutions. As acidic media, hydrochloric acid [2] and sulfuric acid are often used as industrial acid cleaners and pickling acids.

During the past decades, inorganic inhibitors have been widely used for corrosion prevention of steel [3], however, they are considered as pollutants for nature and carcinogens. The application of organic inhibitors, as opposed to the inorganic, has the advantages of non-toxicity. Natural compounds such as herb plants are again employed as inhibitors in order to develop new cleaning chemicals for green environment [4]. The aim of the present work is to find a naturally occurring, cheap and environmentally safe substance that could be used for inhibition of corrosion of pipeline steel. The use of such substances will establish, simultaneously, the economic and environmental goals.

The inhibition effect of bark resin of Schinus molle (BRSM) on the corrosion of API 5L X70 pipeline steel in hydrochloric acid solution has been studied for the first time by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements; also, surface morphology has been analyzed by SEM-EDX. The inhibitor (BRSM) has been characterized by Fourier transform infrared spectroscopy (FTIR). The results show that BRSM is a good inhibitor in hydrochloric acid solution. The maximum percentage inhibition efficiency is equal to 94% at 2 gL⁻¹. The adsorption of BRSM on API 5L X70 pipeline steel surface obeys Langmuir adsorption isotherm, and involves physical adsorption. Polarization curves reveal that BRSM acts as a mixed-type inhibitor in hydrochloride acid.

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Keywords: EIS; API5L X70 pipeline steel; Hydrochloric acid; Bark resin of Schinus molle; Acid inhibition

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Electrochemical Properties of Hybrid Air Electrode for High Performance Lithium-oxygen Batteries

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Lithium oxygen batteries have been recognized as one of the next-generation power sources, capable of supplying power for a long time even in an independent extreme environment. For advancing the commercialization of lithium oxygen batteries, it is essential to search the stable and high performance cathode materials. Among the numerous cathode materials, carbon materials have been intensively considered as the candidates of oxygen electrode due to the engineering pore size and morphologies. However, during discharge, the carbon-based electrodes become degraded due to the blocking of the reaction sites with the byproduct, i.e., Li_2O_2 . And the kinetics characteristics of the electrode can be also reduce the properties of the cell due to the sluggish reaction of the oxygen reduction reaction(ORR) and oxygen evolution reaction(OER). So in this study, hybrid air electrode with the carbon-based material (carbon black) and the bifunctional perovskite-structured catalyst for ORR/OER are fabricated and investigated. The kinetics coefficients of the catalytic material for the ORR and the OER reaction have been studied, and the electrochemical properties in real lithium air cell are investigated.

DRAFT

Keywords: lithium-oxygen cell, perovskite catalyst, oxygen reduction reaction, oxygen evolution reaction

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Synergistic Effect of Iodide Ions and Gum Arabic for the Corrosion Inhibition of Carbon Steel in H₂SO₄

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Naturally occurring substances as inhibitors of acid cleaning process has continued to receive attention as replacement for synthesized organic inhibitors which are considered to be very toxic, expensive and environmentally unfriendly. The use of polymers as corrosion inhibitors have drawn considerable attention recently due to their inherent stability and cost effectiveness. In a previous work [1,2] we found that the Gum Arabic is a good inhibitor in 1M HCl. Interestingly, addition of halide salts to acid solutions containing any organic compound had been reported to result in synergistic effect thereby inhibiting iron corrosion. To the best of our knowledge, the only report (using weight loss and hydrogen evolution methods) on synergistic effect of halide ions and Gum Arabic for the corrosion inhibition of mild steel in sulfuric acid was reported by [3], but the maximum inhibition efficiency was 39.3 % (increase from 21.9 % to 39.3%) in 0.1 M H₂SO₄ at 30°C.

The inhibition efficiency of gum arabic (GA) for the corrosion of API5L X70 pipeline steel in sulfuric acid through the addition of iodide ions has been studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements; also, surface morphology has been analyzed by SEM-EDX. The results show that substantial corrosion inhibition (99%) using 2 g L⁻¹ GA and 0.5mM KI can be obtained in synergistic manner. The adsorption of GA in combination with iodide ions follows Langmuir adsorption isotherm. GA combined with KI acts as a mixed type inhibitor in sulfuric acid.

DRAFT

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Keywords: API5L X70 pipeline steel, EIS, gum arabic, iodide ions, sulfuric acid, synergistic effect

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Effect of Sulfur Bridge in Phenolic Schiff Base on the Corrosion Inhibition of Mild Steel in Acidic Medium

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The effect of newly synthesized Schiff bases was investigated on stainless steel X52 corrosion in 1M hydrochloric acid using electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) and Tafel polarization measurements. Our findings showed that 2,5-DHDPs have the Maximum inhibition among the tested Schiff bases, the inhibition efficiency was increased following increased concentration of the Schiff bases. Polarisation curves revealed that the Schiff bases acted as anodic inhibitors. The inhibitor performance was strongly associated to the type of functional groups on the benzene ring and sulfur bridge. The adsorption process was solely spontaneous and follows Langmuir adsorption isotherm model. The thermodynamic parameters K_{ads} and ΔG_{ads} are calculated and discussed. The surface morphologies examination using SEM/ EDX and AFM of mild steel corroborates the existence of thin protective layer of inhibitors on the surface of metal. Quantum chemical calculations were employed to supply mechanistic insight into role of the sulphur bridge on the corrosion inhibition and adsorption behaviour of the studied Schiff bases.

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Keywords: Schiff base, inhibition, DFT, Corrosion.

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Effect of Heat Treatment on Electrodeposited Sn NWs in Anodic Alumina Oxide Templates

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Tin nanowires are considered to be very interesting material for several applications, such as gas sensors, anodes in Li-ion batteries, catalysts etc. In all of these applications, the increase of the surface area is one of the most widely used approaches for enhancing their performance [1]. The aim of this study is to develop a simple and cost effective process for the production of vertically aligned tin nanowires attached to a tin film, with high surface area and mechanical stability after the removal of the AAO template. For the synthesis of Sn nanowires template assisted electrodeposition in anodized aluminium oxide porous membranes (AAO) was applied, as it is one of the most effective techniques with significant technical and economic advantages, such as simplicity, low cost, and the ability to operate at low temperature and in different electrolytes media. Anodised aluminium oxide (AAO) membranes were fabricated by one step anodization of aluminium in 0.3M oxalic acid. Two types of AAO templates were fabricated with the same mean pore diameter of $\approx 100\text{nm}$ and pore length $\approx 15\mu\text{m}$ and $\approx 8\mu\text{m}$, subsequently. Tin nanowires were electrolytically deposited from a commercial acidic tin electrolyte. After the filling of the AAO pores with tin nanowires, the electrodeposition continues until the entire surface is coated with a tin film. The tin film works as mechanical support for the nanowires after the removal of the AAO template [2]. As heat treatment is known as an efficient approach for relaxation of stresses caused by electrodeposition [3], a series of heat treatment experiments in the range of 120 to 210 $^{\circ}\text{C}$ (while nanowires were still embedded in the AAO template) was applied in order to investigate the effect of heating on the mechanical stability of tin nanowires and as a consequence to their surface area. Electrochemical measurements were applied in order to evaluate the surface area moderations between the as deposited and heat treated tin nanowires. A series of analytical techniques were applied in order to define the structural and morphological characteristics of tin nanowires (X-ray Diffraction, Field Emission Microscopy and TEM).

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Keywords: electrodeposition, tin nanowires, AAO template, heat treatment, surface area

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Optoelectronic Properties of a Metallo-poly(3,4-ethylenedioxythiophene) Derivative

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In this study we disclose electrochromic properties of an poly(3,4-ethylenedioxythiophene) derivative (PEDOT-Ru) which was synthesized through electrochemical polymerization of an EDOT derivative anchored with [Ru(bpy)2pytri]2+ complexes through alkyl chain. At neutral state the polymer ($E_g=1.84$ eV) revealed multiple absorptions (317, 414- 445, 582 nm) stemming from $\pi-\pi^*$ (bpy), MLCT, $\pi-\pi^*$ (PEDOT) transitions, respectively. Voltammetry and spectroelectrochemistry studies revealed that the anodic behavior of the polymer was determined by the redox and optical properties of both the conjugated backbone and the Ru complex, whereas the cathodic behavior of the polymer was mainly dominated by Ru complex. Thus, it was observed that presence of non-conjugated spacer between the metal center and conjugated backbone provided multichromic and ambipolar nature to PEDOT-Ru. The optical contrast, switching time and coloration efficiency values of the polymer were calculated as 46.24 %, 2.52 s and 365.22 cm²/C, respectively. The polymer exhibited multichromic behavior within a wide range of potentials (-2,6 V to 1,6 V), displaying green, yellow and light blue colors which are explicated different from pristine PEDOT.

This work was financially supported by the National Science Foundation of Turkey (TUBITAK Project No: 215Z400)

DRAFT

Keywords: Ambipolar; Electrochromism; 3,4-Ethylenedioxythiophene; Metallopolymer, Multichromic

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

The Effect of Tin and Cobalt Coordination Compounds on Nickel-Free Black Coatings

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²Timay&Tempo, Turkey

Plating can alter the chemical and physical properties of metal surface and results in various appearance. In order to obtain desired properties different metals and their alloys are being plated. Gold plating is often used for passivation of the metal surface or to get cheap metals to give look of gold. Ruthenium plating is also popular because of its shiny black color. But it is too expensive to use it as shiny black coated buttons for coats and jeans. Black Nickel coating was used as cost effective alternative, but many people are allergic to nickel. Therefore, nickel-free black tin cobalt alloy plating are being used widely [1-3].

Potentiostat and Hull-cell test were used to determine the best condition of the bath composition for tin-cobalt alloy. The potential range in which the alloy electrodeposition process could be carried out in a solution containing CoSO₄, SnSO₄, and complexing agents was determined by CV. Surface topography and coating composition were analyzed used SEM and EDX. The crystal structure of coatings were determined from powder X-RAY diffraction data. The addition of glycine has improved black color formation but lead to increase in cobalt concentration in the coating.

We thanks to Ondokuzmayıs University and Timay&Tempo for their support.

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Keywords: nickel-free black tin cobalt alloy, Coating, Coordination compounds

**Electrochemical Material Science
(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)**

Recent and Traditional Electrochemical Techniques Used in Corrosion

Ambrish SINGH

Southwest Petroleum University, China

The use of electrochemical techniques in corrosion is very important as it helps to understand the mechanism at the electrode surface in a particular solution. Electrochemical impedance spectroscopy (EIS) is the most traditional method used in electrochemistry to determine the electrode behavior. Electrochemical impedance spectroscopy provides valuable information about the Nyquist, bode and phase angle plots together. EIS was used to determine the efficiency of some corrosion inhibitors in the corrosive solution. Micro- electrochemical methods such as scanning electrochemical microscopy (SECM), and scanning vibrating electrode (SVET) were used to detect the localized electrochemical behavior of the different metal samples. Various concentration of inhibitors were used to detect the changes in the electrochemical nature. These variations in presence of inhibitors were used to calculate the inhibition efficiencies of the inhibitors. The study was carried on using recent techniques including electrochemical frequency modulation (EFM) and electrochemical frequency modulation trend (EFMT). Further, the polarization tests (Tafel, and linear polarization resistance (LPR)) were done to determine the corrosion rate and inhibition efficiency of the inhibitor.

In this presentation I will talk about the traditional method electrochemical impedance spectroscopy (EIS) with examples !! Then I will talk about Micro-electrochemical techniques like SECM and SVET !! Further I will talk about recent electrochemical techniques using electrochemical frequency modulation (EFM) and EFMT !! How these techniques are being used to monitor corrosion !!

Authors are thankful to the Sichuan 1000 Talent Fund, financial assistance provided by the Youth Scientific and Innovation Research Team for Advanced Surface Functional Materials, Southwest Petroleum University number-2018CXTD06 and open fund project number-X151517KCL42.

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Keywords: Corrosion, EIS, Tafel, Inhibitor; EFM; SECM

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

The Electrochemical and Immersion Corrosion Tests of Metallic Materials in Highly Corrosive Medium

Tansu GÖYNÜK, Mertcan BAŞKAN

ROKETSAN, Turkey

The corrosion behavior of AISI 304, AISI 316 stainless steels and 5xxx, 6xxx series aluminum alloys has been evaluated in highly corrosive acid solution using weight loss, metallographic examination and electrochemical polarization. Corrosion rate derived from the weight losses indicated the occurrence of increased corrosion rates of stainless steels with increasing immersion time. An increase of corrosion rate with immersion time was also observed for 6xxx series aluminum alloy but with lesser extent than stainless steels. However, 5xxx series aluminum alloy showed a decrease of corrosion rate with immersion time, suggesting the formation of a protective oxide layer on their surfaces. Quite the contrary, the corrosion rate derived from the Tafel plots and immersion tests was higher for 5xxx series aluminum alloy compared to stainless steels and 6xxx series aluminum alloy. Pitting formation at stainless steels, 6xxx series aluminum alloy surfaces and formation of protective oxide layer on 5xxx series aluminum alloy, observed from metallographic examination, are enough to explain electrochemical and immersion corrosion test results.

DRAFT

Keywords: corrosion, pitting corrosion, electrochemical polarization, immersion corrosion test

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Hydrogen Nanobubbles at Roughness-controlled Platinum Surface

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Naritaka KOBAYASHI, Seiichiro NAKABAYASHI**

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As the standard hydrogen electrode (SHE), IUPAC recommends to use a platinum with an extremely rough surface (i.e. platinized platinum). Since the rate of the equilibrium reaction ($2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$) is very rapid on the platinized platinum surface, SHE gives the stable electrode potential. On the other hand, possible influence of nanobubbles on the electrode potential should be taken in account, because the fabrication of SHE exactly follows the procedure of the nanobubble formation. We thus examined surface roughness dependency on the hydrogen nanobubbles formed at the electrochemically controlled platinum electrodes.

To confirm the formation of hydrogen nanobubbles on the electrochemically controlled platinum electrode, we used atomic force microscopy (AFM). Pt (111) facet formed on platinum bead was immersed in 0.1 M sulfuric acid solution and observed. AFM images depict cyclic formation and/or dissolution of the hydrogen nanobubbles according to the electrode potential cycling. The formation and dissolution of the hydrogen nanobubbles were synchronized with the potential cycling. The hydrogen nanobubbles appeared at the edge potential of the hydrogen formation, but they disappeared in the hydrogen oxidation potential. The hydrogen nanobubbles tend to form on surface step preferentially. In holding electrode potential at hydrogen adsorption potential, the amount of hydrogen nanobubbles was estimated as the amount of charge required to oxidize hydrogen nanobubbles. These nanobubbles density were compared between three platinum electrodes with different in surface roughness. The first one is Pt (111) electrode which has an atomically flat surface. The second one is platinum polycrystalline (poly- Pt) which has a lot of steps and edges. Third one is platinized platinum which has an extremely rough surface. The nanobubble density were depend on the surface roughness. The density at Pt (111) and platinized platinum surfaces are much lower than that of at poly- Pt surface. Thus, the maximum density was obtained at the moderately rough surface. The nanobubble formation was suppressed at atomically flat and extremely rough surface. Because of the suppression of the hydrogen nanobubble formation on platinized platinum, the possible potential fluctuation is minimized at the standard hydrogen electrode, which reconfirmed the validity of IUPAC recommendation.

Keywords: platinum catalyst; nanobubble; AFM; standard hydrogen electrode

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Determination of Corrosion Initiation Sites on TiN Coated Steels and Their Propagation with Ferroxyl Test and AC Impedance Measurements

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Corrosion protective properties of nitride based hard ceramic coatings produced depends on the inherent defects such as porosities, voids, pinholes, and macro droplets (MP). Many studies have been focused on the improvement of corrosion resistance of these coatings via several approaches. However, long-term corrosion behavior and control mechanism of corrosion properties hasn't been fully investigated.

In this study, we aimed to investigate the main mechanism that determine the long-term corrosion behavior of TiN coatings deposited on IF steel substrates by cathodic arc physical vapor deposition (CA-PVD). To achieve this aim ferroxyl test is applied to determine initial number of defects that extends to the substrate. After determining the initial sites and number of defects at a specific area, the marks that appear on the surface after ferroxyl tests are washed away thoroughly. Then the same sample is subjected time dependent AC impedance measurements for following up the extension of corrosion that takes place on the substrate. After each time duration specific areas of the samples were subjected to ferroxyl test to follow up the extension of the previous defects. Results of the study clearly showed that although the initial number of defect sites that extend to the substrate does not change, polarization resistance of the samples decreased which indicated an increase in the area of the corrosion sites. SEM follow up of the time dependent defects after opening their mouths with ultrasonic probe, clearly showed that only the area below the defect sites increased with increasing immersion time.

The results of this investigation clearly showed that sole electrochemical measurements are not enough for determining the corrosion protective nature of coatings because electrochemical experiments does not give information about the distribution of defects that extends through the coating to the substrate. Additional tools such as ferroxyl or salt spray tests are required for having a realistic picture of defect distribution and their contribution to corrosion.

The authors acknowledge the scientific and technological research council of Turkey-TÜBİTAK (project no. 117Z906) for their financial support.

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Keywords: magnetic nanoparticles, IMAC, protein purification, phosphate adsorption

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Multiscale Correlative Electrochemical Multi-Microscopy: Building an Understanding of Electrochemical Interfaces from Single Entities Upwards

Patrick UNWIN

University of Warwick, United Kingdom

Electrodes used in electrochemistry, with applications in electrocatalysis, energy storage, sensor technologies and corrosion, show heterogeneity and complexity on a range of length scales. The activity of these electrodes is often determined by old classical macroscopic electrochemical techniques that provide an average response of an electrode and are unable to detect and analyze spatially heterogeneous fluxes that govern the electrode response. We propose new approaches to study electrochemical and electrocatalytic phenomena, whereby the activity of an electrode is visualized by electrochemical microscopy in the form of “activity maps” and “activity movies”, and these quantitative data are then related to co-located electrode structure from complementary high-resolution microscopy and spectroscopy techniques applied in the same area of the electrode. This new age of correlative electrochemical multi-microscopy seeks to relate electrode structure to activity clearly and unambiguously. This contribution will discuss the use of nanoscale scanning electrochemical cell microscopy (SECCM) and scanning ion conductance microscopy (SICM) for the acquisition of electrochemical activity-electrode topography maps, coupled with a wide range of microscopy techniques, spanning electron microscopy and electron backscatter diffraction, micro-Raman spectroscopy and atomic force microscopy to pinpoint particular active sites in the same area. This is a general platform for investigating electrochemical interfaces, and illustrative examples of this approach will include: layered materials (2D and 3D), structurally and/or compositionally heterogeneous surfaces such as polycrystalline metals and conducting polymers, and ensemble electrodes comprising of nanoparticles on an electrode support surface, with applications in electrocatalysis and energy storage (batteries).

A key thesis of our work is that electrochemistry of complex electrode surfaces can be broken down and studied as a set of simpler “single entities” (e.g., individual steps, terraces, defects, crystal facets, grain boundaries, single particles). The resulting nanoscale understanding of reactivity can then be used to create scalable models for electrochemical interfaces that will ultimately facilitate the rational design of functional (electro)materials.

Countless talented people at Warwick and elsewhere have contributed to our work in this area and will be acknowledged in the presentation.

General Molecular Electrochemistry

(Structural and mechanistic aspects of electrode processes of inorganic, organic and organometallic compounds and reactions)

Electrochemical Behavior of Cycloalkylidenehydrazide and 4-Aza1-thiaspiro[4.5]decan-3-one Derivatives of Imidazo[2,1-b]thiazole

Hayati CELIK¹, Busra ARICI¹, Demet KOSE¹, Ayse Gokcen KILIC¹, Melek Sirin BAYMAK², Nuray ULUSOY³

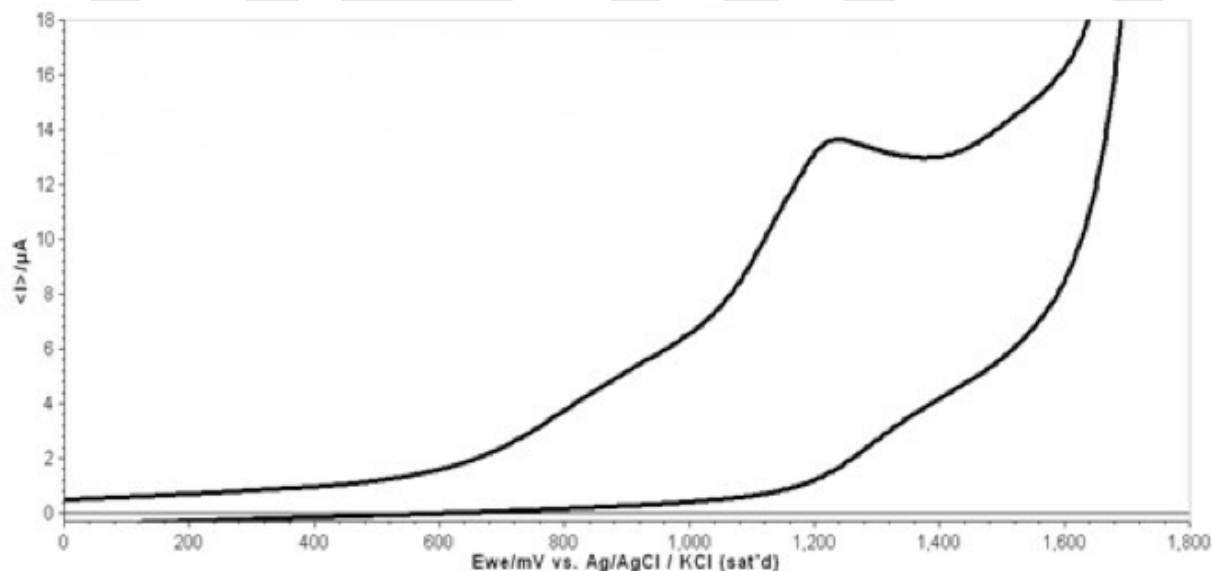
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The biological and chemical activity of imidazothiazoles and their derivatives have received great interest due to the potent immunomodulating drug called levamisole, which contains 2,3,5,6-tetrahydro-6-phenylimidazo[2,1-b]thiazole. It has been shown that these group of compounds have antimicrobial activity [1]. Likewise, the presence of thiazole ring in compounds have shown wide range of biological activities that are reported to display antimicrobial and antimycobacterial properties in the literature [2]. Furthermore, newly synthesized N2-cycloalkylidene-(6-phenyl/4-chlorophenylimidazo[2,1-b]thiazol-3-yl) acetic acid hydrazides were shown antituberculosis activity against Mycobacterium tuberculosis H37Rv [2].

For every analytical method it is of importance to understand the nature of chemical and physical processes involved in the procedure used. Merely when such processes and their sequence are elucidated it is specifically possible to show and perhaps forecast the influence of other components in the studied matrix on analytical results. Such understanding of reaction schemes or mechanisms is also important in electroanalytical processes, which often involve a complex sequence of chemical and physical steps. Therefore, electrochemical behavior of these compounds was determined and tried to correlate with biological activity. In the electrochemical part, oxidation mechanism was elucidated by using cyclic voltammetry (see Figure) with a glassy carbon electrode in aqueous buffer solution pH between 3 and 11. It was observed that peak potentials were function of acidity of the solution. Electrooxidation mechanism is suggested based on experimental data. Further studies on electrochemical reduction mechanism are currently under investigation.



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Keywords: oxidation, electrochemistry, mechanism, Cyclic voltammetry, polarography

**General Molecular Electrochemistry
(Structural and mechanistic aspects of electrode processes of inorganic, organic and organometallic compounds and reactions)**

Transition Metal Complexes with Redox Active Diimine Type Ligands: Synthesis, Structures, Electrochemical and Catalytic Properties

Artem GUSHCHIN

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In modern chemistry, an important place is occupied by coordination compounds of transition and non-transition metals with redox-active ligands. In particular, diimine ligands of the bis-(imino)acenaphthenes class (abbreviated, bian) are attracting increasing interest. A key feature of these compounds as strong π -acceptor molecules is their ability to reversibly accept up to four electrons and exchange them reversibly with a metal center, which leads to the implementation of multi-step redox processes and can be used in multi-electron activation of small molecules and catalytic reactions based on redox transformations.

This paper presents the results on the use of diimine-type compounds (dpp-bian, bpy, phen) for the preparation of complexes of early and late transition metals. The synthesis of new compounds, their molecular and electronic structure, magnetic and electrochemical properties, and catalytic activity in oxidation reactions of organic substrates and carbon dioxide reduction are discussed [1-3].

This work has been supported by the Russian Foundation for Basic Research (Grants No. 19-03-142, 18-33-20056 and 18-03-00155)

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Keywords: transition metals, redox active ligands, diimines, synthesis, electrochemistry, catalysis

Physical Electrochemistry

(Experimental, theoretical and computational aspects of electrochemistry, alone or in conjunction with other methods)

EIS and XPS: Two Powerful Techniques for Probing Electrowetting on Dielectric (EWOD) Phenomenon

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Electrowetting on dielectrics (EWOD) is a process of changing the contact angle of a liquid droplet sitting on a dielectric covered conducting electrode by application of external electric field(s). Spreading of a liquid drop under an electric field can be observed on both dielectric coated and conductive surfaces, however, the dielectric layer prevents the passage of faradaic current and eliminates the possibility of electrolysis during the process. Hence, larger amplitudes of contact angle changes are achieved. This activation can be realized under both DC and AC fields with variable frequency. In fact, it has been reported that the contact-angle hysteresis are smaller in AC than DC, which is why AC is preferred in many applications. We have employed both conventional Electrochemical Impedance (EIS) and unconventional in-situ X-ray photoelectron spectroscopic (XPS) techniques to investigate several low molecular weight liquid drops sitting on dielectric covered planar electrodes, while imposing both DC and AC (square-wave) with varying frequencies between 10-1 – 105 Hz. Chemical and Electrochemical information derived from both techniques will be compared and contrasted.

DRAFT

Keywords: EIS, XPS, Electrowetting

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Influence of Sulfurization Parameters on the Photoelectrochemical Response of CZTS Based Thin Films

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²University of Virginia, United States

Cu₂ZnSnS₄ (CZTS) is a promising, environmentally friendly and earth-abundant absorber material for photovoltaic applications [1]. Electrodeposited Cu-Zn-Sn (CZT) metallic precursors were grown from acidic or basic electrolytes and underwent gas-phase sulfurization, resulting in CZTS based layers. In order to understand the influence of sulfurization parameters on structure and properties, first we studied the effect of sulfur amount incorporated into the metallic precursor deposited from an acidic solution. Then, we investigated the effect of sulfurization time on the formation of CZTS layers from metallic precursors deposited from an alkaline solution. Lastly, we examined the influence of sulfurization temperature on the phase purity of CZTS layers formed from metallic precursors deposited from both acidic and alkaline solutions.

The quality of the layers was investigated with EDS, SEM, Raman spectroscopy, X-ray diffraction and photoelectrochemical (PEC) measurements as a function of sulfurization parameters. We found that there is a correlation between the improved phase purity and PEC response of the CZTS layers for all the sulfurization parameters. The highest PEC response is observed as 0.99 mA/cm², occurring for the film grown from acidic precursor and 0.4 mA/cm² for the film formed from alkaline precursor.

This work was financially supported in part by the NSF grant CMMI #1131571. BU was funded by the Republic of Turkey Ministry of National Education.

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Keywords: CZTS, electrodeposition, photoelectrochemical measurement, Raman Spectroscopy, semiconductors

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Ceria Supported Nickel(0) Nanoparticles: Highly Active Hydrogen Evolution Catalysts

Elif DEMIR ARABACI, Ahmet M. ÖNAL, Saim ÖZKAR

Middle East Technical University, Turkey

With the increasing concern over global warming and increased fossil fuel depletion, the urgency of developing renewable energy sources, associated energy transformation and storage technologies are greatly important issue for today's world [1]. One of the most promising ways to overcome this fundamentally and practically important challenge is to produce hydrogen from water splitting, which has attracted much interest of researchers. Therefore, the development of low-cost, easy-to-prepare new efficient catalysts has been the main aspect of the research [2]. From the 3-d group materials, manganese, cobalt and nickel compounds are comprehensively investigated with attention-grabbing electrochemical properties [3]. In this study, nickel metal was used to modify electrodes and the stabilization of Ni NPs was achieved by supporting them on the surface of suitable material which is cerium oxide (CeO₂). By examining high resolution TEM images in the Figure 1a-b, the size and dispersion of nickel nanoparticles on the surface of ceria was found. TEM images exhibit the existence of nickel nanoparticles with the particle size in the range 2.5-6.5 nm on the surface of ceria powder. The mean diameters of Ni NPs on the surface of ceria was found to be 4.39 ± 1.2 nm. Electrocatalytic activity of NiO/CeO₂ catalyst on GCE was tested in H₂ evolution from water electrolysis at 25°C in acidic solution. The resulting polarization curves are shown in Figure 1 together with those obtained for bare GCE, CeO₂-GCE, for comparison. NiO/CeO₂ modified GCE exhibits relatively high electrocatalytic activity for HER while the bare GCE and CeO₂-GCE show almost no catalytic activity in the same electrolyte solution. The onset potential of NiO/CeO₂ modified GCE appears at 35 mV and demands overpotentials of 40 and 64 mV to drive 10 and 20 mA.cm⁻² catalytic current densities, respectively. The activity of NiO/CeO₂ modified GCE in HER is comparable with the reported electrocatalysts such as Ni₂P (η = 130 mV at 20 mA.cm⁻²) [4], Ni@Pd/PEI-rGO (η = 90 mV at 10 mA.cm⁻²) [5], NiSe nanoflakes (η = 217 mV at 10 mA.cm⁻²) [6].

Figure 1. TEM images of NiO/CeO₂ (3.90% wt. Ni) at 20 nm magnification (a–b), Polarization curves of the NiO/CeO₂ sample on GC electrode, bare GCE and CeO₂-GCE in 0.5 M H₂SO₄ solution at a scan rate of 5 mV/s (c).

We thank to the METU Central Laboratories for the TEM and ICP-OES analyses.

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Keywords: Hydrogen evolution reaction, water splitting, energy.

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Synthesis and Electrochemical Polymerization of New D-A-D Monomers Based on Fluorinated Benzothiadiazole Acceptor Unit

Deniz ÇAKAL, Yalçın BOZTAŞ, Ahmet M. ÖNAL

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Electronically conducting polymers constitute an important class of active materials for widespread applications such as sensors, photovoltaics, electrochromic devices, light emitting diodes, and field-effect transistors due to their tunable characteristics like high conductivity, flexibility and processability. In this regard, 3,4-ethylenedioxythiophene (EDOT) bearing polymers are highly attractive materials for polymer-based conducting materials. Previously reported polymer containing EDOT – Benzothiadiazole scaffolds (PE2BTD) revealed good electrochromic behaviours such as high optical contrast, fast switching time, high coloration efficiencies and high redox stabilities [1-3]. In the light of this finding, in our study, two new D-A-D type monomers, namely 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (E2BTD-F) and 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-5,6-difluorobenzo[c][1,2,5] thiadiazole (E2BTD-2F) were synthesized via Stille Coupling reaction. Electrochemical and optical properties of D-A-D type monomers and their corresponding polymers were investigated by cyclic voltammetry in a mixture of acetonitrile and dichloromethane containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte and the results were reported in Table 1.

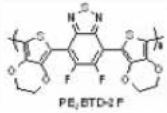
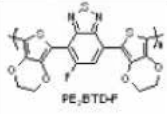
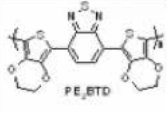
Polymers	$E_{ox,m}$ (V)	$E_{ox,p}$ (V)	λ_{max} (nm)	$\Delta\%T$	CE (cm ² /C)	E_g^a (eV)	t_s^b (s)	Color at neutral state	Color at oxidized state
 PE ₂ BTD-2F	1.38	1.07	390, 570	15, 17	265, 307	1.68	0.7, 0.7	Navy purple	Reddish brown
 PE ₂ BTD-F	1.18	0.90	400, 630	27, 26	203, 406	1.50	0.5, 0.4	Transparent blue	Transparent gray
 PE ₂ BTD	0.92	0.1	430, 750	42, 23	497, 664	1.32	0.5, 0.3	Green	Transparent light blue

Table 1. Electrochemical and optical properties of monomer and polymers.

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Keywords: Conducting polymers, D-A-D approach, fluorinated benzathiadiazole, EDOT

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Copper-immobilized Platinum Films for the Effective Reduction of Nitrate in a Low Conductive Medium: Mechanism, Adsorption Thermodynamics and Stability.

Mohammad HASNAT

Shahjalal University of Science and Technology, Bangladesh

The electrocatalytic reduction of NO_3^- and its intermediate NO_2^- in neutral medium was performed at Cu- Nano particles immobilized Pt surface. The voltammetric investigations showed that bare Cu electrode has a little effect on nitrate reduction reactions (NRR). Whereas, an enhanced catalytic effect (i.e. a positive shift of the peak potential and an increased reduction current) was obtained when Cu NPs were immobilized onto the Pt surface. The NRR process occurred via a two-step mechanism at the Pt-Cu surface with the transfer of 2 and 6 electrons, respectively. The results were further validated by chronoamperometry (CA) investigations. In the present work conditions, the NRR proceeded via a simple adsorption-desorption mechanism following a Langmuir isotherm with an adsorption Gibbs free-energy of ca. $-10.16 \text{ KJ.mol}^{-1}$ (1st step) and ca. $-10.05 \text{ KJ.mol}^{-1}$ (2nd step). By means of a Pt | Nafion | Pt-Cu type reactor without any supporting electrolyte, bulk electrolysis was performed to identify the step products. It was found that after 180 min long electrolysis, 51% of NO_3^- was noticed to convert into intermediate NO_2^- . This percentage decreased to 30% in CO_2 buffered condition. However, when a tri-metallic Pt-Pd-Cu was employed as a cathode, all of the evolved NO_2^- could successfully be converted into NH_3 and N_2 . In contrast to reported works concerning Cu electrodes, the as-prepared Pt-Cu catalyst in this study showed no apparent surface poisoning as confirmed by its stability after excessive CV runs as well as successively extended electrolysis.

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Keywords: Voltammetry, Nafion, Electrolysis

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Removal of Weak Electrolyte by Electromembrane Process

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Ege University, Turkey

Electrodeionization (EDI), also known as continuous deionization (CDI), is a novel hybrid separation process combining ion-exchange resins with ion-exchange membranes in one unit [1]. Electrodeionization (EDI) removes ionizable species from liquids using electrically active media and an electrical potential to effect ion transport [2].

In this work, EDI was applied for the removal of silica (SiO₂) from aqueous solutions. The effect of applied voltage, feed flow rate, and conductivity of Na₂SO₄ in the electrode compartment on the removal of SiO₂ investigated. The micro flow cell (MFC) was used in the experiments. The cathode and anode compartments of the cell are separated from the central compartment with the Selemion AHT (anion exchange membrane) and CMD (cation exchange membrane) membranes. The effective areas of the membranes inside the cell are 10.2 cm².

According to the results the concentration of SiO₂ decreased from 5 mg/L to 0.2 mg/L with the EDI system when a 40 V of voltage was applied to the EDI cell.

This study was supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK) (Project Number: 117 Z 718). We are especially grateful to AGC Engineering Co., Ltd. (Japan) for providing membranes and Purolite Int. Co. for supplying ion exchange resins samples.

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Keywords: Electrodeionization, Ion exchange membrane, silica

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Kolbe Electrolysis of Levulinic Acid

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In the purpose of the sustainability, bulk production of bio-derived chemicals has increased for last decade with the aid of developed new technologies in processing biomass. Within the variety of biomass derived chemicals, Levulinic acid (LVA) is of interest of both academia and industry due to its potential to be functionalized further into valuable chemicals. It is a platform chemical produced from biomass hydrolysis and it has been investigated to convert to valuable chemicals such as fuel additive or polymer precursors. The purpose of this study is to increase the energy density of LVA via decarboxylation. Kolbe electrolysis is the decarboxylation reaction of carboxylic acids that end-up in dimerization reaction of keto alkyl radical. As side products, keto alkyl can further react with hydrogen radical or can involve second oxidation reaction leading to formation of carboxylate ion and hence esters or alcohols.

In this study, electrochemical oxidation of Levulinic acid to higher energy density chemicals such as 2-butanone, 2,7-octanedione is investigated over Platinum (Pt) and Glassy Carbon (GC) electrodes. The reactions were held in a three-neck bottle undivided electrochemical cell operated via Autolab PGSTAT302N Potentiostat. Constant voltage experiments were carried out by application of potential of 2.5 V and 5.0 V in potassium hydroxide and sodium methoxide in methanol medium. Cyclic voltammetry analysis showed that addition of Levulinic acid hinders the oxidation of methanol and irreversibly oxidizes to further products mainly 2-butanone and 2,7-octanedione. Preliminary results showed that Pt electrode is selective (60 % mole) to 2,7-octane, whereas, GC is selective (65 % mole) to 2-butanone. This is due to the GC entraps the keto alkyl radical and may increase the probability of the reaction with the hydrogen radical leading to formation of 2-butanone. Pt | KOH | Pt system exhibits highest coulombic efficiency (93%).

DRAFT

Keywords: Levulinic acid, Kolbe electrolysis, Decarboxylation

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Formation of Contact Charges on Polymer Surfaces in Triboelectric Generators

Bilge BAYTEKIN, S. Doruk CEZAN, Hasan Tarik BAYTEKIN

Bilkent University, Turkey

Triboelectric generators, devices that harvest the surface electric potential developed when two dielectric surfaces come into contact, have attracted attention in recent years as a means of retrieving energy from everyday events. Current literature is booming with numerous types of triboelectric generators, yet the underlying mechanism of charge formation is still unclear. Indeed, the mechanism of tribocharge generation on dielectric surfaces upon contact is one of the few scientific questions that remained unanswered for millennia. Here we will present, a new theory including bond-breaking of surface polymer chains for creation of the tribocharges, and the ramifications of these events in generation of the observed signals in triboelectric generators. Firstly, the microscopic (Kelvin Probe Force Microscopy and Magnetic Force Microscopy) and chemical analyses proving the existence of bond breakages on polymer surfaces will be shown. Next, the surmised mechanism (involving the role of the species formed after bond-breaking) for the unexpected bipolar charge generation of the time-resolved contact and separation events during a first-time time-resolved tapping of the two surfaces will be displayed. We believe these results will help not only to increase the efficiency of the triboelectric generators but also to understand the elementary mechanisms of tribocharging of polymers.

This work was supported by Scientific and Technological Research Council of Turkey (TÜBİTAK) under project number 214M358. BB acknowledges BAGEP 2016 award. HTB acknowledges Marie Skłodowska-Curie fellowship with project number H2020-MSCA-IF-2015_707643.

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Keywords: triboelectric generators, static charging, tribocharging, polymers

General Session

(Any electrochemical topic in the broad umbrella of Electrochemistry not covered by any of the above titles.)

Photoelectrochemical Tests for Catalytic Activity of Soluble Photosensitizers Towards Photooxidation of Phenols

**Shahid Ullah KHAN¹, Stanislav TRASHIN¹, Yuliya S KOROSTEI²,
Tatiana V DUBININA², Sammy W VERBRUGGEN¹, Karolien DE WAELE¹**

¹University of Antwerp, Belgium

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Photocatalysis represents an exciting and one of the most promising research area in various applications such as waste water purification¹, environmental friendly organic synthesis², energy conversion³ and air purification. A number of new photosensitizers have been recently synthesized for photocatalytic applications⁴. Among them phthalocyanines are one of the attractive candidates whose photocatalytic activity need to be evaluated. Highly soluble phthalocyanines and their analogs were tested as prospective photosensitizer.

In this work we developed a new method to test the photoelectrocatalytic activity of photosensitizers in methanol via the use a simple batch cell, a LED laser and a conventional potentiostat. The method is based on coupling photooxidation of hydroquinone (HQ) in the presence of oxygen and simultaneous electrochemical reduction of oxidized products at an electrode. This process forms an electrocatalytic loop (ECcat mechanism) allowing to perform kinetic studies in short term without complications related to long term experiments such as oxidative photo-degradation of both photosensitizers and singlet oxygen traps by reactive oxygen species (ROS). Our method can be used for the screening of photosensitizers in solution without getting aggregated and investigating the effects of different parameters on photosensitizer's activity for their application in water treatment, photodynamic therapy, singlet-oxygen based organic synthesis and photoelectrochemical detection of phenols.

Financial support by ERA.Net RUS Plus Plasmon Electrolight project (RFBR No. 18-53-76006 ERA) is gratefully acknowledged.

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Keywords: (Sub)phthalocyanine, photosensitizer, photoelectrocatalysis, phenols, amperometry

POSTER PRESENTATIONS

Analytical Electrochemistry

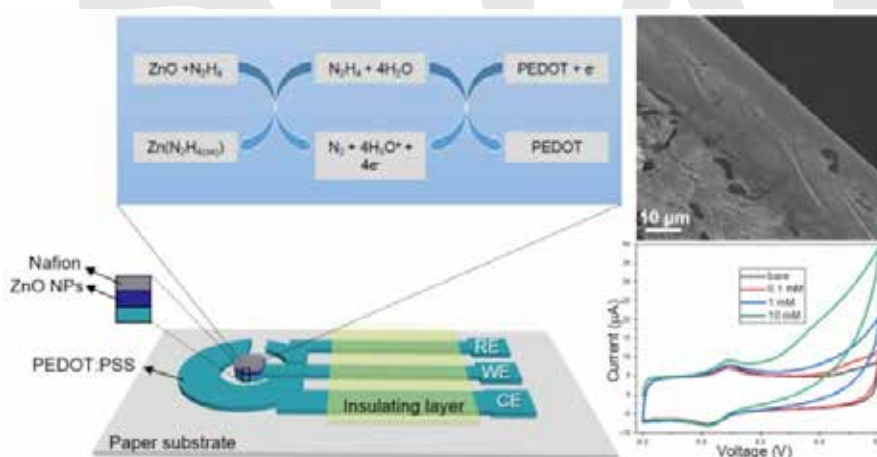
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)

Fully Inkjet-printed Hydrazine Sensor Based on ZnO Nanoparticles-modified PEDOT:PSS Electrode on Paper

Tutku BEDUK, Eloise BIHAR, Khaled Nabil SALAMA

King Abdullah University of Science and Technology, Saudi Arabia

In this work, we have developed a sensor device on a paper substrate by using inkjet printing technology which is a convenient method that allows controlled deposition of a variety of electronic materials in a customized geometries at low temperatures. Most electrochemical hydrazine sensors lack of portability and need expensive electrodes, which makes essential to build simple, user-friendly, cheap electrochemical setup and design portable sensor devices. Here we have used conducting polymer poly(3,4 ethylenedioxythiophene) doped with polystyrene sulfonate, (PEDOT:PSS) as a counter, working, and reference electrodes of the sensor. As the recent studies have shown that the use of nanomaterials to fabricate electrochemical-based sensors have improved the sensing performance due to increasing the surface area and catalytic ability for oxidation reactions, we have utilized ZnO nanoparticles deposition onto the working area by inkjet printing method to improve sensing ability of the fabricated sensor device. Hydrazine sensing performances of the printed sensor was evaluated before and after modifying the working electrode of the device by inkjet printed ZnO nanoparticles. The enhanced electron transfer, sensitivity, stability and electrocatalytic activity of printed sensor after ZnO nanoparticle modification indicates that the fabricated device has good and selective sensing ability towards hydrazine. This fully printed, easy to fabricate device exhibits high sensitivity, a linear response in the concentration range of 0.01 -10 mM, and lower detection limit ($\sim 6 \mu\text{M}$) towards hydrazine. Other features include a highly reproducible, fast fabrication process, stability, and selectivity.



Keyword: electrochemical detection, hydrazine, chemical sensor, inkjet printing

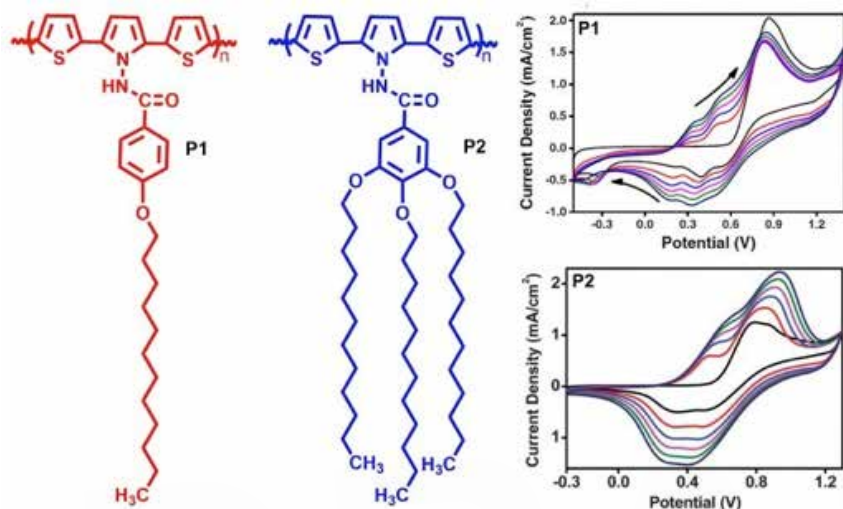
Analytical Electrochemistry

(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)

Soluble 2,5-Di(2-thienyl)pyrrole Based Conducting Polymers: Optical, Electrochemical and Electrochromic Properties

Metin Ak, Tugba SOGANCI

Pamukkale University, Turkey



While most of the conductive polymers are insoluble and infusible, their solution processable derivatives are more desirable for preparing large size flat panel display and solid state applications because they are compatible with low cost, large area manufacturing process [1,2]. Recently, increased attention has been focused on the synthesis of soluble and processable conducting polymers due to interest in their potential application. For this purpose, solution-processable fluorescent conjugated polymers (P1 and P2), consisting of electron rich 2,5-dithienylpyrrole and dodecyloxybenzamide have been electrochemically synthesized [3,4]. These soluble conducting polymers have well-defined and reversible redox processes in the ACN/LiClO₄. Moreover, synthesized polymers have showed multielectrochromic behavior: blue in the oxidized state caesious in the intermediate state and greenish in the neutral state. Also the copolymers consist of EDOT and soluble monomers have been synthesized by cyclic voltammetry. Copolymer films have superior electrochromic and electrical properties when compared with a homopolymer. Furthermore, the fluorescence features of the monomers and the polymers were investigated. Synthesis of these new type solution-processable and fluorescent conducting polymers is an alternative to the conventional synthesis of soluble conducting polymers which allows the direct application of the conductive polymer to any desired surface for potential technological applications.

This work was supported by BAGEP Award of the Science Academy

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Keyword: conducting polymers; electrochromic, soluble polymer

Analytical Electrochemistry

(Experimental and theoretical aspects of electroanalytical processes.

Electrochemical sensor devices and the methods used therein)

Electrochemical Monitoring of Label Free BRCA Hybridization by Single Use Caffeic Acid Modified Electrode

Merve ISTEK, Erdem MUTİ

Aydın Adnan Menderes University, Turkey

A novel caffeic acid modified disposable pencil graphite electrodes were developed for the electrochemical determination of breast cancer gene sequence (BRCA) hybridization. Amino labeled DNA probe was used to benefit from the interaction between the amino group and the carboxyl groups in caffeic acid. 44% signal enhancement in guanine oxidation signal was obtained by caffeic acid modified electrode compared to the bare electrode. Besides, these probes exhibited high selectivity towards its complementary DNA sequences (target). Hybridization between probe and target (BRCA1) was studied to evaluate the selectivity of the probes for complementary, non-complementary and mismatch sequences. The selectivity was also tested in the presence of a mixture containing the target and one base mismatch BRCA sequences in the same ratio (1:1). It can be said this probe can select its complementary from the mixture.

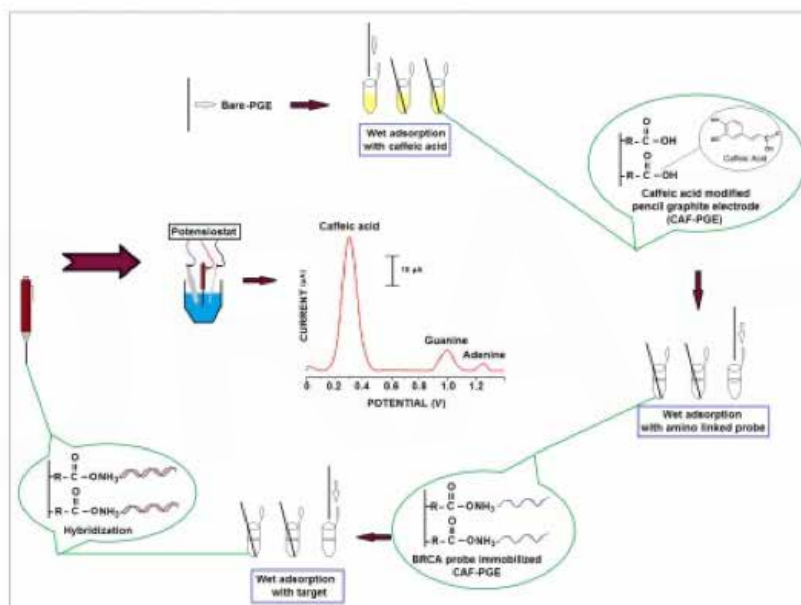


Figure 1: Experimental scheme for electrode preparation and the electrochemical detection process.

Authors acknowledge the financial support from Turkish Scientific and Technological Research Council (TUBITAK Project No: 114Z103).

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Keyword: BRCA, caffeic acid, electrochemical detection, modified electrodes, single-use sensors

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Electrochemical Monitoring of the Interaction Between Anticancer Drug Bendamustin and DNA

Aylin EROL, Mithican MUTİ

Aydin Adnan Menderes University, Turkey

Investigation of drug–DNA interactions is significant for understanding the mechanism of interaction, drug development process and for the design of specific DNA-targeted drugs. Intercalating occurs when an aromatic ring of the drug is embedded among the base pairs in nucleic acid duplex, which enhances the distance amid the base pairs. Belonging to the structural features of both the molecule and DNA, several molecules indicate more than a single interaction mode with DNA [6-8]. Between interaction of drug and DNA, intercalation is the most common ways to link directly and selectively. Intercalating occurs when an aromatic ring of the drug is embedded among the base pairs in nucleic acid duplex, which enhances the distance amid the base pairs. Belonging to the structural features of both the molecule and DNA, several molecules indicate more than a single interaction mode with DNA

The aim of this study is to investigate Bendamustin-DNA interaction and the effect of antioxidant on this interaction. Disposable, inexpensive, easy handle electrodes were used in this study to investigate interaction of bendamustin and DNA electrochemically. Bendamustin is an anti-cancer drug which is used for the treatment of one or more type of leukaemia.

Electrochemical behavior of bendamustin was investigated by using cyclic voltammetry. The interaction between anticancer drug, bendamustin and fish sperm double-stranded DNA (dsDNA) was investigated by using differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) techniques. The effect of antioxidant on the interaction of bendamustin and DNA was investigated in the absence and presence of caffeic acid.

Aydin Adnan Menderes University Scientific Research Projects FEF19007

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Keyword: Bendamustin; drug-DNA interaction; antioxidant; caffeic acid; electrochemistry.

Analytical Electrochemistry

(Experimental and theoretical aspects of electroanalytical processes.

Electrochemical sensor devices and the methods used therein)

Electrochemical Investigation of the Effect of Caffeic Acid on the Oxidative Damage Caused by UV Rays

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DNA damage and genetic mutation caused by UV rays can result in skin cancer. Therefore, it is very important to design biosensors for the early, simple and inexpensive detection of DNA damage caused by UV rays. In this study, a new biosensor was designed to determine the DNA damage caused by UV rays and how the damage will change in the presence of caffeic acid was investigated electrochemically.

When the DNA is damaged by oxidative action, some changes are occurred in DNA. These changes can be expressed as the breaking of the chain and the decrease in oxidation signal of the DNA bases. These changes can be determined by using Electrochemical Impedance Spectroscopy and Voltammetry techniques. In this study, first, 50 ppm single strand DNA solution (calf thymus DNA, ctssDNA) was kept under UV lamp at a current time by using UV-Vis Spectrophotometer in the presence and absence of caffeic acid. Disposable pencil graphite electrodes were dipped in the vials containing DNA solution before and after damage in the absence and presence of caffeic acid. Differences of the charge transfer resistance (R_{ct}) of these DNA solutions were measured by EIS and the oxidation signals of DNA bases (Guanine and Adenine) was measured both before and after interaction with UV rays. By determining the level of prevention of DNA damage caused by UV rays of caffeic acid, it is hoped that the use of cosmetic products supported by caffeic acid in people who are exposed to UV rays will bring useful results in preventing skin cancer.

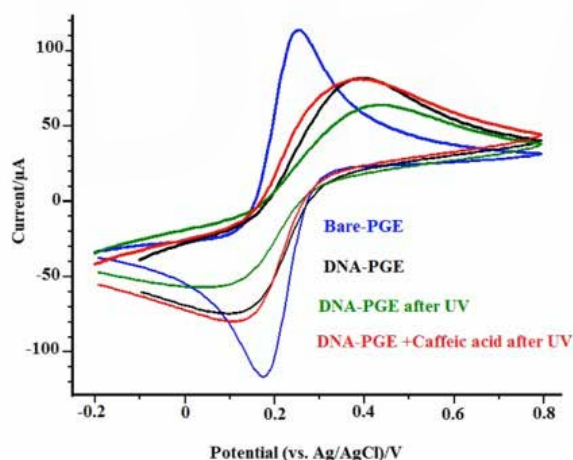


Figure 1: Cyclic voltammogram of 2.5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ system containing 1 M KCl

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Keyword: UV radiation, cancer, DNA damage, caffeic acid, electrochemistry

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Salophen Type Schiff Bases as a Novel Sensing Ionophore for Potentiometric Applications

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²Giresun University, Turkey

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Salophen templated Schiff bases have been synthesized, characterized, probed electrochemically and explored as a novel sensing ionophore in the form of a PVC membrane as selective potentiometric sensor for analytical monitoring of different metal ions. Schiff base 2,3-bis(salicylaldimino)pyridine (H₂IF) based sensor exhibits very good selectivity and sensitivity towards Cu²⁺ over a wide variety of cations. The sensor has a linear response to Cu²⁺ with a detection limit of 6.3×10^{-8} M and displays a Nernstian slope (29.14 ± 0.6 mV/dec). Schiff base N,N'-o-phenylene-bis(3-methoxysalicylideneimine) based sensor exhibits Near-Nernstian response to Pb(II) within a wide concentration range (1.0×10^{-7} to 1.0×10^{-2} M), with a slope of 28.88 mV/dec and a lower detection limit of 8.6×10^{-8} M. All fabricated sensors exhibit a fast response time ($t_{95\%} = 10$ s) and the lifetime of the sensors are limited to 16 weeks. The fabricated sensors were applied successfully for the monitoring of metal ions in real samples. It was experimentally demonstrated that the Salophen templated Schiff bases can be applied as a novel sensing ionophore for the potentiometric applications.

This work was supported by Scientific Research Projects Foundation (BAP) of Ondokuzmayıs University. Project no: PYO. FEN.1904.14.004

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Keyword: Schiff bases, potentiometric sensor

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Electrochemical Detection of Carbon Nano-materials

Jun Hui PARK

Chungbuk National University, South Korea

We have demonstrated electrochemical detection of carbon nano-materials (e.g., graphene oxide) on an ultramicroelectrode (UME) in aqueous solution using carbon nano-materials collision events. The collision phenomena are detected by monitoring a current-time transient. To attract the carbon nano-materials to the UME surface, an electric field was developed near the UME using a redox reaction. As model systems, outer sphere redox probe and inner sphere redox probe reactions were tested respectively. With an outer sphere reaction probe, amperometric current measurements showed a staircase current response after attachment of carbon nano-materials on the UME surface. The magnitude of the staircase current is given by the stepwise increase in current, which can provide insight into the size distribution of the carbon nano-materials colliding with the UME. In the presence of higher concentrations of carbon nano-materials, multiple collision events happened sequentially on the UME. In this case, an increasing current trend, rather than a single staircase current, was observed. The overall current increment for a given time is a measure of the concentration of carbon nano-materials in solution. By using this method, carbon nano-materials in an aqueous solution can be sensitively detected and/or accumulated.

DRAFT

Keyword: single particle collision, collision, nanoelectrochemistry

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Electrochemical Study of Blocking Behavior of Microsphere in Aqueous and Organic Solution

Yeji KANG, Byung-kwon KIM

Sookmyung Women's University, South Korea

The microbeads, uniform polymer particles, are usually used in personal care and biotechnology. They are easily modified by various functional group, which makes the beads have different properties, such as protein affinity and fluorescent expression. It can be useful in biotechnology, but hazardous in environmental systems. Therefore, fast and easy detection of microbeads in various condition is important. In previous studies, various particles have been detected by electrochemical analysis method. Thus the electrochemical method is proper to detect and find out properties of microbeads. Therefore, the electrochemical behavior in two type of solutions with same redox molecules are studied. These are performed by chronoamperometry measurement with ultramicroelectrode(UME). The experimental results show different signals according to the type of solution. In this study, we tried to find out the reason of these different behavior in two type of solutions.

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, and ICT (NRF-2018R1C1B6008668), and also supported by the BK21 plus program through the National Research Foundation (NRF) funded by the Ministry of Education of Korea.

DRAFT

Keyword: Electrochemistry, Collision, Blocking behavior, Microsphere

**Analytical Electrochemistry
(Experimental and theoretical aspects of electroanalytical processes.
Electrochemical sensor devices and the methods used therein)**

Red blood Cell Detection Using Single-entity Electrochemistry

Byung-kwon KIM

Sookmyung Women's University, South Korea

In the field of electrochemistry, researches on single particle detection, called collision or nano-impact methods, are actively conducted. These research methods have recently been renamed as single-entity electrochemistry.[1] This single-entity electrochemistry can measure several important scientific information at the individual particle level that can not be measured in conventional electrochemistry. We can obtain important information of single particles about concentration, size, diffusion coefficient, electrophoresis, etc. through single-entity electrochemistry. Single-entity electrochemistry allows the measurement of a variety of materials, from hard particles (metal nanoparticles, dielectrics, etc.) [2] to soft particles (cells, bacteria, proteins, etc.). [3] In this study, we introduce a new method to detect red blood cells (RBCs) in blood. [4] When the RBCs collide with the ultramicroelectrode (UME) while measuring the oxidation current of the high concentration ferrocyanide ion (Fe(CN)_6^{4-}), the current signal to be measured immediately decreases. We can measure the concentration of RBCs using the number of collisions of RBCs on UME surface. Moreover, the size (i.e., volume) of RBCs can also analyzed by magnitude of the stepwise decreasing current value. We used this method to analyze the number and volume of RBCs present in real human blood, which was in good agreement with the analysis method used in the hospital.

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, and ICT (NRF-2018R1C1B6008668), and also supported by the BK21 plus program through the National Research Foundation (NRF) funded by the Ministry of Education of Korea.

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Keyword: Red blood cell, Single-entity electrochemistry, Collision, Nano-impact, Detection

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**Synthesis of Different Transition Metals Doped Battery Grade Nickel Hydroxide
Cathode Materials and Investigation of Their Electrochemical Properties**

Emre Yusuf GÖL, Ahmet AYTEKİN, Ecem Ezgi ÖZKAHRAMAN

Izmir Institution of Technology, Turkey

Nowadays, energy and energy requirement start to become more and more an important topic in the world. To meet this requirement, studies have focused on synthesis of battery grade nickel hydroxide (Ni(OH)_2) as a cathode material. Nickel hydroxide is an important positive electrode material used in the batteries such as Li-ion, and Ni-MH [1]. This cathode material has two different form; one is $\alpha\text{-Ni(OH)}_2$ and the other is $\beta\text{-Ni(OH)}_2$ [2]. In this study, we synthesized nickel hydroxide by using urea decomposition method. 0.1 mole $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 mole urea ($\text{CH}_4\text{N}_2\text{O}$) were dissolved in distilled water and stirred for 10h at 95°C. Formed Ni(OH)_2 was filtered and washed with hot distilled water, and then dried at 80°C in the oven. We doped Ni(OH)_2 with different transition metal such as Co, Zn, Cu, Al, Fe and Mn. The study exhibits that doped- Ni(OH)_2 is better than undoped $\alpha\text{-Ni(OH)}_2$ as electrochemical performance, specific capacity, and good stability. Here, all electrochemical properties were measured by using Cyclic voltammetry (CV). Synthesized materials were characterized by SEM, XRD, BET.

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Keyword: Cyclic voltammetry, battery, specific capacitance, energy storage

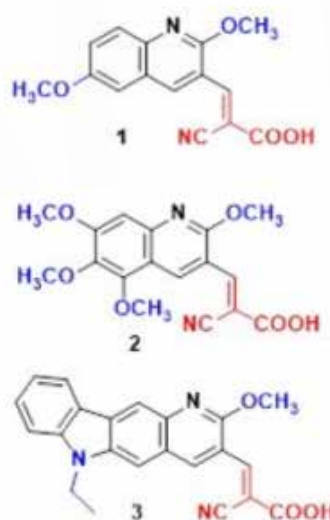
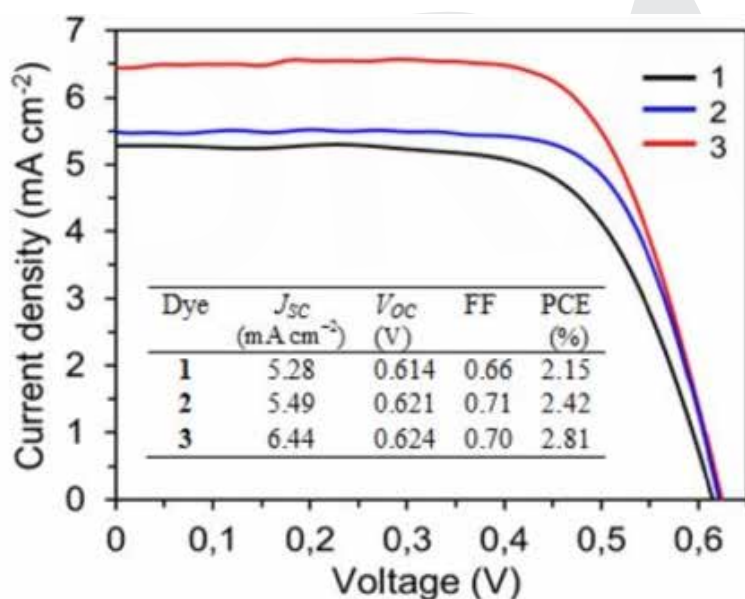
Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Quinoline Based Organic Dyes for Dye-Sensitized Solar Cells

**Yavuz DERİN, Seda Nur ÜLÜŞ, Barış Seçkin ARSLAN, Emre GÜZEL,
Ahmet TUTAR, Mehmet NEBİOĞLU, İlkay ŞİŞMAN**

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In this study, quinolone based metal-free organic dyes containing different electron donor groups were synthesized for dye-sensitized solar cells (DSSCs). These compounds bearing methoxy (1) trimethoxy (2) and carbazole (3) were synthesized starting with aniline and carbazole derivatives through acetylation, Wilsmeier Haack formylation and Knoevenagel condensation reactions [1]. The effect of electron donor alternation on the optical, electrochemical and the photovoltaic properties is systematically investigated. Compared to dyes 1 and 2, dye 3 shows a broader absorption spectrum due to the stronger electron donating nature of carbazole group, which is an advantageous spectral property for light harvesting of the solar spectrum [2]. The electrochemical studies indicate that dye 3 oxidized much easier than the others due to stronger electron donating ability of carbazole group, which is consistent with the spectral changes. All the highest occupied molecular orbital (HOMO) levels of dyes are more positive than the redox potential of I⁻/I³⁻ (0.4 V vs. NHE), ensuring fast regeneration of the oxidized dyes for DSSCs. The lowest unoccupied molecular orbital (LUMO) levels of dyes are much more negative than the conduction band of TiO₂ (-0.5 V vs. NHE), suggesting that the electron injection process of the dyes into the conduction band of TiO₂ is energetically favorable [3]. The DSSC based on dye 3 shows a short circuit photocurrent of 6.44 mA cm⁻², an open circuit voltage of 0.624 V, and a fill factor of 0.70, corresponding to an overall conversion efficiency of 2.81% under simulated AM 1.5G irradiation. The photovoltaic performance of dye 3 is better than those of dyes 1 and 2, indicating carbazole is a promising electron donor group for metal-free organic sensitizers in DSSCs.



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Keyword: Quinoline, Organic Dye, Dye-Sensitized Solar Cells

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

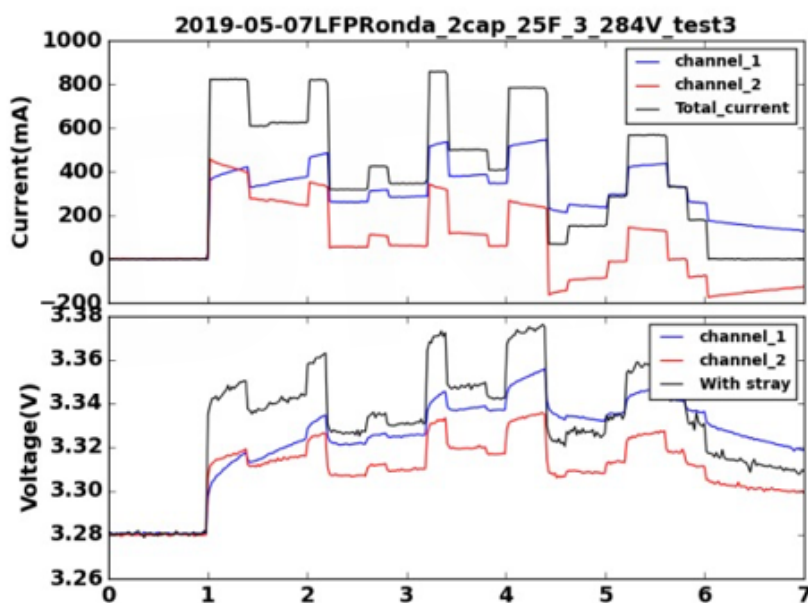
Modelling of Parallel Connected Hybrid Energy Storage System

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In electrochemistry, batteries and supercapacitors are significant elements, and they have different properties from each other. Batteries have higher specific energy than supercapacitors, which enables high amount of storage for a long time; whereas supercapacitors have higher specific power than batteries, which leads to charge or discharge in a short time. Since these two properties -specific energy and specific power- are important for an energy storage system, if these can be combined in one system properly then the system become more efficient in various application of electrochemistry. These combined systems are called Hybrid Energy Storage System (Stacks). In order to make stacks systems, one needs to understand all physical and electrochemical properties of both components completely and as well as figure out the voltage behaviour and current distribution of the each system.

In this work, supercapacitor and battery are connected in a parallel and the behaviour of systems is understood by taking some measurement and analysed them. In order to do this, firstly symmetric systems, which are two identical batteries and two supercapacitors, are studied. After these systems understood very well, then asymmetric systems, which are battery and supercapacitor connecting in parallel, are studied. As a result of all experiments and data, the Hybrid Energy Storage System will be modelled for parallel connection of battery-super capacitor.



The purpose of the current work is to develop an algorithm to understand parallel combinations of supercapacitors and batteries. Ultimately, design guidelines to find the best combination will be determined using the framework of the Zero Free Parameter Modelling algorithm.

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Keyword: Battery, Supercapacitor , Hybrid System, Modelling

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Bioinspired Vanadium Compounds as Robust Flow-Battery Active-Materials

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Modern electrical grids, especially those comprising energy from intermittent, renewable sources such as wind and solar, require storage. Non-aqueous redox flow batteries (NRFB) are a promising technology to meet this growing need. Compared to their aqueous counterparts, they have the potential to approach the energy density of lithium-ion systems, while maintaining the advantages of flow systems, including decoupled scaling of power and energy ratings and thermal stability.

Despite the promise of NRFB, fundamental technical obstacles have limited their application thus far, including low solubility and instability of active-materials. To address these issues, we have developed an active material based on a family of molecules that is naturally occurring and produced biologically. These compounds are analogues of Amavadin, which is found in mushrooms of the *Amanita* genus. Biosynthesis of this molecule evolved to bind vanadium selectively and with the highest stability ever reported, using a unique, tetradentate, bis-carboxylato- η^2 -hydroxyimino- motif. Ligand-substitution is suppressed, shutting down a major mechanism of decomposition. In this way, natural selection serves as a toolkit for molecular design, elucidating a scaffold for optimized NRFB active materials.

Herein we present a suite of electrochemical and spectroelectrochemical data demonstrating this bioinspired active material, which we call VBH₂⁻, is oxygen-tolerant and is extremely stable, even in the presence of water. Bulk oxidation and reduction are tightly coupled to formation of the vanadium(v) and vanadium(iv) species. We also demonstrate that a strategy of modifying the counter cation of VBH₂⁻ can maximize solvent-solute stabilization while simultaneously destabilizing the lattice, facilitating high concentration and providing its own supporting electrolyte. Finally, we present a strategy to increase open-circuit voltage without compromising stability.

Keyword: Electrical Grid, Energy Storage, Battery, Batteries, Electrolyte

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

**An Improved Pre-Lithiation of Graphite Anodes Using Through-Holed Cathode and Anode Electrodes
in a Laminated Lithium Ion Battery**

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In order to remove irreversible capacity exhibited by graphite anodes at first charging process, pre-lithiation was applied to the anodes which were laminated with cathodes and separator sheets. Through-holes were formed in the anodes and cathodes. By contacting the anodes with Li metal which was attached beside the laminated cell, the pre-lithiation process to the graphite anodes was started. After pre-lithiation for a limited period of time, the pre-lithiated capacity was balancing among the pre-lithiated graphite by contacting among the anodes. The cells composed of through-holed anodes and cathodes were tested in charging/discharging cycle and removal of the irreversible capacity which can be observed at the first charging/discharging cycle was confirmed. The anodes which were treated with appropriate pre-lithiation charge and balancing period successfully could decrease irreversible capacity from 7 to 1% and the cells exhibited stable 100% of targeted capacity. In this study, practical pre-lithiation process to decrease the irreversible capacity could be proposed.

DRAFT

Keyword: Li ion battery, Through-holed structured electrodes , Pre-lithiation, Pico-second pulsed laser **Electrochemical**

Energy Storage and Conversion

(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Graphene for Energy Conversion and Storage Systems

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Graphene, as a unique, single-atom thick layered structure of carbon, can be utilized for various applications especially for energy including fuel cells, batteries and supercapacitors. The previous reports have revealed that graphene and its derivatives with spectacular theoretical electrical, and mechanical properties could be used as highly efficient electrodes in various energy related applications. Nevertheless, the crucial role of graphene-based materials in providing the reliable solid-state support for fuel cells, Li-air and Li-ion batteries should be explored.

Polymer electrolyte membrane (PEM) fuel cells are attractive for portable, stationary and automotive applications while there are still challenges because of cost and durability issues. Especially, platinum (Pt) nanoparticles, used as catalyst in PEM fuel cells, have high cost, performance and durability problems and low abundance as well. Catalyst support materials are of great importance in regulating the properties of catalyst nanoparticles such as shape, size, and dispersion. Carbon black, the most commonly used commercial catalyst support, has several limitations which cause the degradation of catalyst activity and performance. The use of graphene as the catalyst support due to its high surface area, high conductivity and chemical stability, could lead to an improvement in both catalytic activity and catalyst utilization in PEM fuel cells [1]. The deposition of metal nanoparticles on graphene layers results in formation of a heterogeneous catalyst system which further leads to decrease in metal catalyst consumption, and leaching, while increasing the catalytic activity via high charge mobility of the graphene-based support. In the present work, graphene nanoplatelets, reduced graphene oxide, functionalized graphenes and various hybrids of graphene have been employed as the catalyst support. Graphene supported Pt nanoparticles were prepared by means of impregnation-reduction, microwave-assisted deposition, photocatalytic deposition, supercritical carbon dioxide deposition, surfactant assisted deposition methods. Highly dispersed and uniformly decorated 2-3 nm Pt nanoparticles with significantly better electrocatalytic activity and fuel cell performances compared to commercial carbon black nanoparticles were achieved [1,2].

Graphene based materials are also promising candidates for energy storage applications such as Li-ion and Li-air batteries, especially when used as a substrate for metal oxides, because of their high theoretical capacities. We aimed to simultaneously enhance the electronic and ionic conductivities of the active material in the anode by adding graphene as a conductive component. For a stronger attachment, titania nanotubes are hydrothermally grown on nitrogen doped graphene oxide (NrGO) sheets in an aqueous medium. This novel 3D architecture resulted in a reduction of conductive additive components, such as carbon black, and enhanced the overall performance of the anode [3]. Moreover, cerium oxide-based catalysts were decorated on NrGO in order to achieve structures with stable capacity for Li-air batteries.

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 696656 (Graphene Flagship) and The Scientific and Technological Research Council of Turkey (TÜBİTAK) No 115M659

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Keyword: graphene, fuel cell, battery, catalyst support, electrodes

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Conversion of Carbon Dioxide to Formic Acid over Cu₆Sn₅ with a SnO₂ Shell Layer

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A novel ordered intermetallic compound of carbon-black-supported Cu₆Sn₅ nanoparticles (Cu₆Sn₅ NP/CB), in which Cu₆Sn₅ has a NiAs-type structure, was successfully prepared through a wet chemical method using lithium triethylborohydride as a reducing agent. The XRD measurements confirm the formation of NiAs-type ordered intermetallic Cu₆Sn₅. XPS and STEM-EDS measurements allowed us to confirm the Cu₆Sn₅ structure, and the surface of the intermetallic Cu₆Sn₅ was found to be covered by SnO₂, indicating that a core-shell structured intermetallic compound (i.e., Cu₆Sn₅ core/SnO₂ shell) had formed. The Cu₆Sn₅ NP/CB material exhibited a faradaic efficiency of 65.3% at 0.6 V for HCOO⁻ formation via electrochemical CO₂ reduction, which is superior to those of the Cu NP/CB and Sn NP/CB samples. From the XAFS measurement, we determined the Sn-Sn distance in the SnO₂ on the surface of the Cu₆Sn₅ NPs, and the key factor affecting the high selectivity was found to be the 4.9% compressive strain of the SnO₂ shell layers on the Cu₆Sn₅ compared to that of the Sn NP/CB sample.

The authors are grateful to Dr. Toshiaki Ina for help with QXAFS measurements at the BL01B01 beamline of the SPring-8 facility (Proposal No. 2019A1316).

DRAFT

Keyword: Intermetallic compounds, Core-shell structure, Electrochemical reduction of CO₂

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Carbide-derived Oxide/carbon Hybrid Materials for use as Lithium-ion Battery Anodes

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To enable a more sustainable future based on more efficient technologies, global efforts are ongoing to develop advanced energy storage devices and materials with high energy density and efficiency. As such, lithium-ion batteries (LIBs) are widely used, for example, for portable electronics or electric vehicles. For next-generation LIBs, it is necessary to further increase the energy density and power density by designing new and improved electrode materials. Along this line of work, vanadium trioxide (V₂O₃) is a promising anode material for LIBs that has remains, so far, poorly investigated. The state of the art assumes that the performance of V₂O₃ is limited by its volume change during galvanostatic charge/discharge process, and its low electronic conductivity, thus, resulting in poor cyclic stability. To overcome the limited performance of bulk V₂O₃, there has been a focus on hybrid electrode architecture, which employs a nanoscopic chemical blending of the metal oxide phase with carbon, and the resulting materials provide improved electrochemical performance. Our work has shown the versatile nature of carbides as precursors for the design of nanohybrids of metal oxides and carbon. In this work,[1] we introduced one-step thermal treatment synthesis of V₂O₃/carbon core/shell hybrid materials by using VC and NiCl₂·6H₂O in an inert gas atmosphere. Decomposition of NiCl₂·6H₂O etches vanadium out of the structure of VC, leaving behind nanoporous carbide-derived carbon with incomplete graphitic ordering. In addition, the process concurrently creates rhombohedral V₂O₃ by oxidation of VC. We compared the materials resulting from thermal chloro-oxidation with commercially available rhombohedral V₂O₃ (com-V₂O₃) mixed with the same amount of carbon regarding LIB applications. Our V₂O₃/carbon hybrid material shows a reversible specific capacity of 187 mAh/g at 0.01A/g, which is higher than com-V₂O₃ (126 mAh/g). Cyclic performance stability measurements show an almost complete loss of capacity of com-V₂O₃ after 50 cycles; in contrast to this, the V₂O₃/carbon hybrid material shows a performance increase during the first ten cycles and a low rate of decay afterwards. Post-mortem analysis of the electrode material indicates no significant structural changes of the rhombohedral V₂O₃ but a decreased degree of graphitic ordering of the carbon phase. Thereby, the initial performance increase can be explained per the improved ability of more disordered carbon to contribute to the charge storage capacity. After all, our work clearly shows that V₂O₃ should not be dismissed per volumetric constraints but may enable stable performance as an anode material for LIB applications.

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Keyword: core/shell, hybrid materials, lithium-ion batteries

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Coral-Like Manganese Oxide Decorated Cotton Fabric Electrodes for Wearable Supercapacitors

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In today's modernized world, where the global energy crisis became a critical bottleneck for technology development, renewable energy reservoirs, which are constantly replenished and will never run out, have opened the way to a whole new perspective on energy security [1]. No need to say, developing highly-efficient energy storage systems to store the harvested energy and rendering it to the consuming system, is of critical importance to generate high performance renewable energy systems. Supercapacitors gaining benefits from high energy and power densities alongside fast charge/discharge capability and remarkable cyclic stability stand out among the rest of energy storage systems [2]. In response to growing demands of smart wearable electronics for a variety of applications from fashion sport-wears to military camouflage and healthcare devices, flexibility in power sources have been emerged [3]. Having prime impact on the foldability, mechanical strength, and stability of the wearable supercapacitors, substrates play a pivotal role in developing wearable supercapacitors. Remarkable instinctive characteristics including highly porous structure as well as eco-friendly feature make cotton fabrics as a part of human lives from making cotton cloths to generating renewable and green energies at a low price. Decoration of 3D hierarchical arrangements of cotton fibers with electrically conductive materials resulted in highly porous structures having the merit of not only remarkable electrochemical properties, but also superior flexibility which can overcome the mechanical cracking and failure of active materials within bending or wrapping [3]. Among a large variety of conductive materials, transition metal compounds are at the leading edge of the emerging field of renewable energies [1]. Their unique pseudo-capacitive features make these materials superior and indispensable in modern wearable energy storage devices. Not only high theoretical capacitance, but eco-friendly feature makes manganese dioxide (MnO₂) as the most promising pseudocapacitive electrode material in comparison with any other precious transition metal oxides, which are not available in abundance [2]. Regarding the profound impact of specific surface area of electrodes on energy storage mechanism, mesoporous architecture of active materials, which enlarges the electroactive surface area and also provides ample open channels for electrolyte diffusion, is of prime importance to enhance the capacitive performance of fabricated electrodes [4]. Herein, innovative high performance binder-free wearable electrodes were fabricated via a one-pot hydrothermal method in which commercial cotton fabrics were directly decorated by coral-like MnO₂ nanostructures. The prepared electrodes not only exhibit remarkable specific capacitance, but also represent remarkable rate capability. The fabricated electrodes, therefore, seem to be a potent candidate for practical applications in the future high performance wearable electronics. All-in-all, the prepared wearable electrodes receive the benefit of high specific capacitance, remarkable rate capability and long-term cycle life in 3M KOH aqueous electrolyte, providing compelling evidence on its remarkable electrochemical performance.

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Keyword: Coral-Like Manganese Oxide; Commercial Cotton Fabric; Wearable Supercapacitors

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Synthesis of Nickel Hydroxide Powder for Secondary Ni-Zn Batteries

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Nickel-based materials such as nickel hydroxide have been widely used as electrode materials in Nickel-Cadmium, Nickel-Metal Hydride and a few other batteries due to their high electrochemical performances. However, there are several problems specifically related to nickel hydroxide. One of them is tendency of Ni electrode to swell or expand while charging especially during overcharge portion of the cycle that reduces battery life. Another problem is the low capacity of nickel electrode after charging at high temperatures. Since morphology plays an important role in electrochemical activity of the material and it is the main factor which cause these problems, studies have been focused on investigating parameters that effect morphology. The main purpose of this study is to synthesise nickel hydroxide (Ni(OH)_2) powder with different morphologies for Nickel-Zinc (NiZn) batteries using chemical precipitation method. In this study, the effect of Ni(OH)_2 morphology on performance of Ni electrodes in NiZn batteries was investigated with respect to temperature, pH and aging time.

DRAFT

Keyword: nickel hydroxide powder, Ni electrode, NiZn battery

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Comparative Study of Silanized-rGO/Pd Nanocomposite Film Prepared by Different Methods as Advanced Electrocatalyst for Hydrogen Evolution Reaction

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The sustainability of hydrogen production is essential for the hydrogen economy. The electrochemical hydrogen evolution reaction is a well-studied electrochemical reaction which requires highly efficient and low-cost catalysts to lower the required overpotential and energy consumption. The palladium (Pd) is regarded as a low-cost alternative metal to the Pt as electrocatalysts for hydrogen evolution reaction because of its higher electrocatalytic activity and stability. Moreover graphene based materials such as reduced graphene oxide (rGO), has been studied intensively because of its straight forward, scalable, low-cost synthesis, mechanical and electrical properties.

The graphene oxide modified by 3-aminopropyltriethoxysilane (APTES) to react the amino groups of the APTES with carboxylic acid groups in graphene oxide, then the Schiff base (Sch) reaction was conducted to form imine groups on the composite in this study. After the modification the rGO/APTES/Sch composite film decorated with Pd nanoparticles with two different methods. The structural characterizations of the composites were achieved by SEM, EDX and FT-IR spectroscopy.

The electrochemical performances of rGO/APTES/Sch/Pd nanocomposite films prepared with different methods were examined by using cyclic voltammetry, Tafel polarization curves and electrochemical impedance spectroscopy techniques in acidic medium.

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DRAFT

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Modeling the Effects of Grid Design, Grid Size and Lug Position of The Lead Acid Battery to Reduce Lead and Obtain Better Battery Performance

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The aim of this study is improving the grid design of lead acid battery in order to increase lead acid battery performance by obtaining more uniform distribution of the current and the potential. 3D mathematical grid models have been investigated according to the size of grid frame, the lug position on grid frame, the wire density of grid and the grid thickness to understand the effects of grid on the lead acid battery performance. Therefore, considering the modelling by using Comsol Multiphysics, the production cost and the time can be saved since the results of mathematical model provides us an idea before the experimental test.

In the light of this study, the basic grid design of lead acid battery has been modelled by taking into account the thermodynamic and the kinetic effects of the battery under certain conditions. Later, the new grids design have been obtained by comparisoning the wire density and the lug position, also the capacity and the cycle tests have been started. If the simulation results and the experimental results have matched, the new grid designs can be used for the production. This model provides us the better performance of lead acid battery with more uniform the potential and the current distribution and the lead reduction with the new grid design, therefore the cost has been reduced.

This work was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK), Grant No: 3160706

DRAFT

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

The Effect of Varying Tin (Sn) Content in Lead-Calcium (Pb-Ca) Based Alloys on Grid Corrosion

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The Pb-Ca based lead acid battery positive grids are critical components in terms of battery life, since corrosion takes place primarily at the positive grid. Lead acid batteries operate by reductions and oxidation reactions. As a result of these reactions PbSO₄ passive layer is formed. PbSO₄ passive layer has high electrical resistance and it can cause premature capacity loss on battery. Pb-Ca alloys have small particle size, so it is vulnerable to active material cracking. To solve this problem different Pb-Ca based alloys have been prepared. Several ratios of tin (Sn) was added to the positive grid alloy. In this study, the effect of PbSO₄ passive layer in lead, calcium, tin (Pb-Ca-Sn) based alloys on grid corrosion is investigated. Different alloy combinations are produced under Argon atmosphere and in air in the laboratory scale induction furnace. The electrochemical properties of anodic films are obtained by using potentiostat. Polarization resistance and cyclic voltammetry measurements are performed to determine the corrosion rate and the redox capacities, respectively.

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DRAFT

Keyword: Lead acid battery, Corrosion, Electrochemistry, Cyclic Voltammetry, Polarisation Resistance

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Li⁺ transport Number of Solid Poly (ethylene oxide) Composite Electrolyte Containing Nano-sized MOF-5

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Ondokuz Mayıs University, Turkey

Since ethylene oxide (EO) units of polyethylene oxide (PEO) have a high donor number for Li⁺, lithium salts can be dissolved in PEO towards complex formation with Li⁺ ion and forms polymer electrolytes by forming coordination sites for Li⁺ migration [1, 2]. However, Li ion conductivity of PEO electrolytes is pretty low at room temperature (10⁻⁶—10⁻⁷ S cm⁻¹). In order to increase ionic conductivity of PEO, highly crystalline nature of PEO should be distorted since Li ions mostly travel throughout the amorphous region of PEO [2]. The transference number can be defined as the ratio of electric current derived from the cation to the total electric current. A transference number close to 1 can reduce concentration polarization of electrolytes during charge–discharge steps and results higher power density [3, 4]. In this study, nano sized metal organic frameworks (Zn₄O(1,4-benzenedicarboxylate)₃ metal-organic framework, MOF-5) were synthesized in the presence of triethylamine (TEA) via consecutive combination of ultrasound (US) and microwave irradiation (MW) methods and employed as solid nanoadditive in the composite polymeric membrane of Li-ion batteries [5]. The prepared nanocomposite polymer electrolytes (NCPEs) based on a poly(ethylene oxide) (PEO) network with lithium bis(trifluoromethane) sulfonimide (LiTFSI) and nano sized MOF-5 are mechanically robust and thermally stable up to 270 °C, and provide appreciable ionic conductivity on the order of 0.1 mS cm⁻¹ at 60 °C. At room temperature, Li⁺ transport number increased to 0.3 with the addition of MOF-5 which suggests that MOF-5 acts as an anion receptor in the nanocomposite electrolyte. In order to prove the anion stabilization by MOF-5, the interaction energy calculations between MOF-5 and bis(trifluoromethanesulfonyl) imide (TFSI) anion were performed by density functional theory (DFT).

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Keyword: Li battery, Li⁺ transport number, polyethylene oxide, nanocomposite, electrolyte, nano-sized MOF

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

ZnS Electrodeposition on an ITO Substrate to Obtain a Solar Cell Material

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In recent decades, solar energy is considered as the most promising renewable energy. Thus, a significant interest has been given For the development and manufacturing solar cell materials able to absorb visible light, nontoxic and low cost. In this study, we focused on Zinc Sulfide (ZnS) as a new photoactive material. We deposited ZnS on a substrate of ITO (indium tin oxide) electrochemically. The ZnS was synthesized using a bath composed of a solution mixture of which essentially sodium citrate with an acidic medium (pH 3.5-4.5). The experimental conditions of the various tests have been optimized. Indeed, the study of electrochemical behavior by cyclic voltammetry allowed to determine the potential suitable of ZnS ZnS electrodeposition. Structural and microstructural characterization (Raman spectroscopy and XRD) and morphological observation (MO and MEB / EDX) of the deposits obtained found that the composition, the optical and the electrical properties of these deposits are dependent on the synthesis conditions (the applied potential, the concentration and the composition of the supporting electrolyte).

DRAFT

Keyword: ZnS, ITO, Solar cells, Electroplating, Characterization techniques, Observation techniques

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Comparative Study of the RRO for Two Lanthanum Nickelate Materials $\text{La}_{1,98}\text{Sr}_{0,02}\text{Ni}_{0,99}\text{Co}_{0,01}\text{O}_{4\pm\delta}$ (LSNC001) and $\text{La}_{1,95}\text{Sr}_{0,05}\text{Ni}_{0,95}\text{Co}_{0,05}\text{O}_{4\pm\delta}$ (LSNC005).

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University of Mohamed Seddik Ben Yahia-Jijel, Algeria

The reaction of reduction of oxygen is one of the most important reactions in the cathode of batteries metal-air and especially on the Zinc-air batteries.

This cathodic reaction have an unknown mechanism and a low kinetics For this reason recent researches have develop a new type of material that can ameliorate the operation of this type of batteries.

In this study we are going to do a comparative study between two material and estimate the effect of doping material of Nickélates on the reaction of reduction of oxygen.

The two material are preparing with the same method which is the citrat method and the powders have being characterizes by using X-Ray diffraction and XPS to examined the surface statement as tow physicochemical method, the electrochemical characterization have been by using the lineair voltammetry to evaluate the current of reaction and know the number of step of the oxygen reaction and also we use the impedance spectroscopy ,this study has been in a basic middle and by using a rotating Disk with varying the rotating speed.

DRAFT

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Carbon-based Lanthanum Nickelate Materials $\text{La}_{2-x-y}\text{Nd}_x\text{Pr}_y\text{NiO}_{4+\delta}$ ($x = 0, 0.3$ and 0.5 ; $y = 0$ and 0.2) as a Bifunctional Electrocatalyst for Oxygen Reduction in Alkaline Media

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The kinetics and mechanism of Oxygen Reduction Reaction (ORR) in alkaline medium are studied on lanthanum nickelate materials $\text{La}_{2-x-y}\text{Nd}_x\text{Pr}_y\text{NiO}_{4+\delta}$ ($x = 0, 0.3$ and 0.5 ; $y = 0$ and 0.2) using the electrochemical technique of the rotating disk electrode in a 0.5 M solution of NaOH. The oxide powders are synthesized by the citrate-nitrate method. Structural and surface characterizations are performed by X-ray diffraction (XRD) and X-ray photo-electron spectrometry (XPS), while the morphology is studied by scanning electron microscopy (SEM). Electrochemical studies are carried out by linear voltamperometry, cyclic voltamperometry and impedance spectroscopy. The doped and undoped electrocatalyst composites ($\text{La}_{2-x-y}\text{Nd}_x\text{Pr}_y\text{NiO}_{4+\delta} / \text{C}$), made of the rare earth nickel oxides mixed with carbon black (Vulcan XC-72(C)) are deposited as a thin layer on a glassy carbon substrate. At room temperature, the undoped electrocatalyst $\text{La}_2\text{NiO}_{4+\delta}$ material shows single step kinetics unlike the doped materials. The doping by the rare-earths Nd or/and Pr significantly enhances the electrical conductivity of the electrode under air and the diffusion of oxygen. On the other hand the steric hindrance between the atomic oxygen orbital [π -orbital (O_2) - π -orbital (O_2)] and the [d_{z^2} -orbital (Ni) - π -orbital (O_2)] influence the training model of the liaison [$d_{z^2}(\text{Ni})$ - π (O_2)] . The structure, oxygen adsorption and oxidation states of the catalyst elements have a large influence on the mechanism and kinetics of the ORR. The LNNO_3/C and LNPN_5/C electrocatalysts have better electrocatalytic performances, which allow them to be used as a bifunctional electrocatalyst for the reduction of oxygen in alkaline media.

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Keyword: ORR Process, MIEC, Impedance Spectroscopy, XPS analysis, Electrocatalyst materials.

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)
Electroactivity of MWCNTs/Ni nanocomposite Film on Hydrogen Evolution**

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The demand of green energy is a major goal for researchers in this century. There are many ways to develop green energy but, among various forms of green, safe and sustainable energy, hydrogen is considered as the best one due to its abundance and no pollution. Because of the production of hydrogen from water is inexpensive and pollution free; hydrogen is a very promising renewable fuel generated from water. Moreover, hydrogen has higher energy density than the fossil fuels.

Among carbon supports, carbon nanotube is a desirable candidate as a support material due to its great specific area, high electrical conductivity and excellent chemical stability. Multiwalled carbon nanotubes (MWCNTs) films and their composites are regarded as promising materials for hydrogen evolution reaction (HER), can significantly improve HER activity. Also, nickel (Ni) is regarded as a low-cost alternative metal to the Pt and Pt group metals as electrocatalysts for hydrogen evolution reaction.

In this work, multiwalled carbon nanotubes were applied on the pencil graphite electrode (PGE) and decorated with Ni nanoparticles. The structural characterization of the electrode surface was investigated by scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDS). The catalytic activity of the MWCNTs-Ni nanocomposite film was investigated for electrocatalytic hydrogen evolution reaction in acidic medium. The electrocatalytic activity of the composite electrode was studied by cyclic voltammetry, Tafel polarization curves and electrochemical impedance spectroscopy. When the MWCNTs were combined with Ni, the MWCNTs-Ni composite film exhibited excellent HER performance

DRAFT

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Ti-based Active Materials for Negative Electrolytes of Aqueous Redox-flow Batteries

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The necessity of intermittent renewables' integration into the electrical grid has been distinctly proven. Achieving this principle requires assuring the energy demand and energy supply balance by introducing dependable and inexpensive energy storage systems. Redox-flow batteries are among most scalable and most stable energy storage technologies for this large-scale applications and are greatly dependent on the chemistry of the active materials within the electrolytes. Titanium as the second most abundant Transition metal in Earth's crust could be assumed as a promising candidate for an inexpensive active material in the negative electrolyte of the redox-flow batteries. Moreover, some titanium complexes show reasonable solubilities in aqueous solutions even at near neutral pH, resulting in reasonable charge storage densities and non-toxic systems. Furthermore, their redox potentials can be quite low [1], allowing to reach high cell voltages. The aim of this study was to find and introduce a favorable titanium-based active material for the anolyte of redox flow battery paired with different redox (mostly Iron based) couples in the positive electrolyte. Accordingly, a wide range of complexing agents was employed for titanium species. Different pH environments were investigated as effective factors for introducing the optimized state of battery stabilization.

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DRAFT

Keyword: Redox-flow battery, Titanium-based, Active material, Anolyte

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Lithiated Nafion Ion Exchange Membranes for Li-S Batteries

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Lithium-sulfur (Li-S) batteries exhibits the highest theoretical energy density of 2600 Wh.kg⁻¹ among the rechargeable batteries. In addition, resources of sulfur and Li are abundant and inexpensive [1]. However, Li-S battery chemistry is still hindered by some basic obstacles for practical applications. One of the obstacles is caused by the solubility of lithium polysulfides (Li₂S_n, 4 ≤ n ≤ 8, intermediate charge/discharge products) in the organic electrolytes [2]. During the discharge process, the dissolved lithium polysulfides transport from the cathode to the lithium anode induce a so-called “shuttle effect”, which causes the loss of the active sulfur materials and lowers the coulombic efficiency [3]. Nafion which is a perfluorinated sulfonate ionomer is used in a wide variety of electrochemical and chemical applications due to its excellent temperature and chemical stability [4]. When Nafion is lithiated, it has the potential to transport only Li⁺ ions and prevent the polysulfide anions’ shuttle effect because of its special structure [2].

In this work, lithiated Nafion (Li-Naf) ion exchange membrane was produced as both electrolyte and separator for Li-S batteries. Sufficient quantity of LiOH was added to %5 Nafion (Naf) solution and ultrasonicated for 4 hours. Then, Naf and Li-Naf solutions are poured into the smooth casting molds. After that they were dried in a vacuum oven at 80 oC for 12 h and cured at 120 oC for 12 h.

Produced Naf and Li-Naf film membranes were characterized by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) analyses. Optical properties of membranes were investigated via fourier transform infrared spectroscopy (FT-IR). To evaluate the thermal stabilities, thermogravimetric analyzes (TGA) were performed. Electrochemical impedance spectroscopy (EIS) technique was applied for produced Li-Naf membrane. Also electrochemical performance of Li-Naf membrane assembled in CR2032 cell was investigated with battery tester device.

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Keyword: Nafion, ion exchange membrane, electrolyte, Li-S batteries

Electrochemical Energy Storage and Conversion (Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)

Development of High Capacity Cathodes for Li-S Batteries

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Lithium batteries are widely used energy storage devices for mobile phones, notebooks, electric vehicles (EVs), hybrid electric vehicles (HEVs). With increasing energy demand, the interest in research on energy storage devices with higher energy density and longer cycle life rises [1]. Lithium-sulfur (Li-S) batteries have very advantageous features in meeting these demands such as high capacity and energy density. Its theoretical capacity is 1675 mAh g⁻¹ and specific energy density is 2600 Wh kg⁻¹ [2]. However, applications of Li-S batteries have some problems, including insulating nature of sulfur, formation of high soluble lithium polysulfides and its shuttle effect, deposition of insulating Li₂S₂ and Li₂S on the anode surface [3]. One of the measures taken to reduce the impact of these negative problems is to develop cathode structures. The design of new carbon materials with three-dimensional architectures as a cathode matrix has received great interest [4].

In this work, laminar structured S-rGO-CNT cathodes was produced as free-standing papers to develop high-capacity Li-S batteries. Here, rGO structure improves electronic conductivity and acts as a buffer to accommodate volumetric expansion of sulfur together with CNTs. The aim of this work is to benefit from the synergistic effect of the hybrid structure of rGO and CNT. Therefore, sulfur particles were deposited on the layers of rGO and CNTs from Na₂S₂O₃·5H₂O precursor by a reduction process using HCl solution. For this purpose, the suspension stirred by ultrasonication was filtered by vacuum filtration to yield free-standing, flexible and binderless paper cathodes. Produced S-rGO-CNT cathodes were characterized by field emission scanning electron microscopy (FESEM), energy dispersive x-ray spectrometer (EDS) and x-ray diffraction (XRD). Electrochemical performance of the CR2032 button cells was measured with MTI BST8-MA Battery Analyzer at room temperature in the range of 1.5-3.0 V at 0.1C rate and under a constant current density. Cycling voltammetry (CV) study of the cathode was performed with OrigaFlex OGF500 model OrigaLys ElectroChem SAS device at a scan rate of 0.1 mVs⁻¹ in the potential range of 1.5–3.0 V.

This work is supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK) under the contract number 118M265. The authors thank the TÜBİTAK-MAG for their financial support.

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Keyword: S-rGO-KNT cathodes, laminar structure, free-standing papers, Li-S batteries

**Electrochemical Energy Storage and Conversion
(Batteries, fuel and solar cells/electrolyzers, electrochemical capacitors)**

Synthesis and Electrical Properties of $\text{LiMn}_{2-x}\text{Al}_x\text{O}_4$ Cathode Material for Li-Ion Batteries

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The lithium manganese spinels have been studied widely and become the most prospective cathode material for lithium-ion batteries in recent years. In this paper, Al - doped LiMn_2O_4 was prepared by a sol-gel procedure. $\text{LiMn}_{2-x}\text{Al}_x\text{O}_4$ ($0 \leq x \leq 0.3$) were determined from X-ray powder diffraction method (XRD) using Rietveld analysis . The SEM micrographs of the samples show that the size of the modified particle is larger than that of unmodified material, so electrons can be easily transported between the particles. The electrical measurements show that the performances and characteristics of Al - doped LiMn_2O_4 electrode material are better than those of LiMn_2O_4 . Hence, the $\text{LiMn}_{2-x}\text{Al}_x\text{O}_4$ material is a good cathode material for lithium batteries.

DRAFT

Keyword: Lithium manganese spinels, Lithium batteries, cathode material, Electrical Properties, Scanning electron microscopy SEM, X-ray diffraction DRX

Electrochemical Engineering and Process Technology

Fabrication and Evaluation of a Micro-sensor Array Chip for Personalized Medicine of Sickle Cell Disease

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Sickle cell disease is a common inherited blood disorder that leads to major morbidity and early mortality. In order to increase sickle cell treatment efficiency, it is necessary to directly measure the concentration levels of the administered drugs in serum or blood and to establish pharmacokinetics profiles to generate individualized dosing plans. (a) We are developing a low-cost and simple test for rapid quantification of the FDA approved drug hydroxyl urea in biological samples, in order to improve the way the dosing is established and the treatment is monitored.

The main challenge of in-situ analysis of unlabeled redox-active molecules in biofluids is the interference from other redox molecules generating overlapping electrochemical signals (e.g., uric acid, ascorbic acid). We modified the sensing microelectrode with 5 different materials (chitosan hydrogel, alginate hydrogel, molybdenum sulfide, tungsten sulfide, and carbon nano-dots) that allows tuning the partial selectivity of each of the electrode in the array towards hydroxyl urea while decreasing the influence of the interfering molecules.

The selective modification of 32 microelectrodes generates electrochemical interfaces with different properties allowing generating multiple electrochemical signatures corresponding to the drug hydroxyl urea. The physical properties of each electrodeposited material differ, thus generating variable specificity toward the analytes and the interfering redox molecules. The complex variability of the electrochemical signal in the presence of interfering redox active molecules is analyzed via principal component analysis. The determination of hydroxyl urea is possible in finger pricked volumes of a synthetic serum (10-20 micro-L) via the characteristic oxidation peak of hydroxyl urea observed with differential pulse voltammetry at 0.65 V vs Ag/AgCl. The selective functionalization of the 32 microelectrodes also enables the quantification of hydroxyl urea levels in biological samples of sick children with sickle cell disease.

The authors thank the Ilse Katz Institute for Nanoscale Science & Technology for the help in Microfabrication and material characterization. We thank the Cincinnati children hospital and Ben Gurion University BG3C Pediatric Medical Device Initiative for funding. The authors also thank the Marcus family donation which support Dr. Cazelles via the Water Science Fund of the Ben-Gurion University of the Negev.

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Keyword: Multielectrode array (MEA), personalized medicine, finger pricked blood analysis

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

The Effects of Perpendicular Magnetic Field and Current Density on the Electrodeposition of Zn-Ni Coatings

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20 august 1955, Algeria

The electrodeposition of Ni-Zn alloy from aqueous solutions is classified as anomalous co-deposition, according to the Brenner definition [1].

Current density is an experimental parameter suitable to include the effect of the magnetic field; because the value of current density occurs on the morphology and texture of the deposits. The influence of the magnetic field may appear at low current densities. It can be considered that the influence of magnetic induction is greater than that of electric fields.

Zinc-nickel alloy coatings were electrodeposited on stainless steel substrates in chlorinated acid medium at two current densities of -20 and -40mA/cm², without and with perpendicular magnetic field for two amplitudes 0,5 and 1T. A reverse effect is observed during the application in the two current densities (-20et -40mA/cm²); however the coating Zn-Ni is smoother and uniform at the low current density.

The electrochemical, morphological and structural characterizations presented allowed us to:

-Define an electrolyte for the preparation of a zinc-nickel or perpendicular field alloy with good physical properties, by controlling the applied field intensity. For concentrations greater than 15 %, the co-deposits become more noble than the steel substrate following a dezincification process[16].-Comparing the DRX, it is observed that the preferred orientation of phases γ and δ depends not only on the magnetic field, but also on the composition of the bath and the density of the applied current. One can conclude an inverted effect when applying the field in both intensities (-20 and -40mA/cm²); However the Zn-Ni deposit is smoother and, a reverse effect can be concluded when applying the field in both intensities (-20 and -40mA/cm²).

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Keyword: Magnetic field; current density, Zn-Ni; chloride

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Applications of Nanocatalyst Hybrite Systems for Direct Methanol Fuel Cells (DMFCs)

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Nanotechnology has recently been applied to direct methanol fuel cells (DMFCs), one of the most suitable and promising options for portable devices. It also provides clean energy solutions to many applications and may have a profound effect on energy generation, storage and utilization. Therefore, understanding differences in energy states and transport mechanisms of nanostructures compared to macrostructures is vital¹. DMFC are an extremely promising power source for portable applications due to its simple handling and processing of fuel. Hence, extensive studies on DMFCs have been carried out, mainly aiming at improving its poor performance. The performance of DMFCs and polymer electrode membrane fuel cells (PEMFCs) are dramatically dependent on the electrocatalytic activity of the precious metals such as platinum and its alloys dispersed on suitable supporting materials. The improvements are necessary with a motivation of lowering of the amount of precious metal required for economic reasons mainly for applications such as generators for electric vehicles². Decreasing the amount of catalyst could be achieved by reducing the size of particles. Carbon nanotubes are of interest for composite materials because of their good electronic - mechanical properties and high stability. Conducting polymers also have been studied extensively due to their intriguing electronic -redox properties and applications in many fields³. By this sense, the synthesis of hybrid materials consisting carbon nanotubes (CNT) with polyaniline matrix (PANI) for the fabrication of PANI-CNT composite supports is an interesting approach to improve the properties of electrocatalyst materials because composite structure may exhibit improved characteristics than the corresponding individual counter parts⁴. Hence, the current research was focused on the preparation of Pt and Pt-binary or ternary metal nanoparticles decorated by polyaniline (PANI) -functionalized multi-wall carbon nanotube composites (fMWCNTs) and its activity in the methanol electrooxidation. Cyclic voltammetry was used throughout the study. The modified structures were characterized by SEM, EDX, TEM and Raman. The fabricated electrodes showed comparable catalytic performance and long-term stability towards methanol electrooxidation in acidic media with the corresponding nanoparticles modified by various composites. Finally, comments were revealed on the effectivity differences between ordinary and nanostructure systems⁵.

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Keyword: Methanol oxidation, nano particles, carbon nanotubes, platinum

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Investigation of The Electrochemical Machining Process for Ti-6Al-4V And Stainless Steel

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Traditional manufacturing methods are not generally appropriate for machining at micro-scale. Physical contact between the workpiece and the tool materials during machining is a severe problem in many operations. Electrochemical machining method is a non-traditional machining process to remove material from the workpiece by electrochemical dissolution. A smooth surface with tight tolerances can be achieved by this non-conventional method without deteriorating the mechanical properties of the material. Electrochemical machining of Ti-6Al-4V and stainless steel (Grade 304) were investigated in this study. Surface roughness and weight loss of materials were recorded during electrochemical machining experiments, which were conducted using stationary workpiece for stainless steel and rotating workpiece for Ti-6Al-4V. It was observed that material removal strongly depends on the applied voltage, electrolyte concentration and flow and anode-cathode distance.

DRAFT

Keyword: electrochemical machining, Ti6Al4V, titanium alloy, stainless steel.

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Optoelectronic Properties of Ru(II) Complex Tethered Poly(2,5-dithienylpyrrole)Derivatives

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The materials that combine the conductivity of conductive polymers and the optical and electrochemical properties of metal complexes form a new kind of conjugated polymer class (metallopolymer). The ruthenium coordination complexes of the bipyridine derivatives form an important group of materials owing to their electroactivity and electrochromic properties. Here in, synthesis of novel transition metal (Ru) complex tethered conducting polymers based on 2,5-dithienylpyrrole (SNS-Ru) was achieved through electrochemical polymerization in the presence and absence of EDOT. Both homopolymer and copolymer exhibited multiple reversible redox behavior and multichromism due to the two different electroactive components (conjugated polymer and transition metal complex) which were separated by a spacer group. Optoelectronic properties of both polymers was observed to be the superimposition of both electrochromes where this ambipolar homopolymer displayed brick red, yellow, green, gray colors upon amplification of applied potential. The copolymer, on the other hand, displayed distinctive color variations from dark brown, brown, yellowish green, green to blue underlining the forcefulness of copolymerization in fine-tuning the color of polymers.

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DRAFT

Keyword: Ambipolar; 2,5-Dithienylpyrrole; Electrochromism; Metallopolymer

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Electrodeposition of Zn Coatings Reinforced with SiC Nanoparticles

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Zinc coatings are most popular anticorrosive protection of steel construction. Zinc due to its physicochemical properties, location in electrochemical series and low cost is a great alternative to other kinds of corrosion protective materials. Javanbakht et al. observed positive influence of reinforcement of Zn matrix by SiC nanoparticles resulting in shifting of corrosion potential values towards more electropositive range. Reported Zn-SiC composites were deposited at pulsed current conditions and electrolyte was additionally stirred to ensure homogenous distribution of reinforcing particles in electrolyte volume [1]. Properties of composite coatings depend of numerous factors such as: current density, bath composition, concentration and size of reinforcing phase, presence of brighteners, temperature and stirring intensity [2]. Kinetics of ceramic particles incorporation process is influenced also by type and size of reinforcing particles. Positive effect visible in increase of particles incorporation rate is usually observed at increased particles concentration but concentration increase resulting in particles coagulation [3]. Application of ultrasounds during electrolysis may result in decrease of susceptibility of particles for aggregation influencing homogenous distribution of reinforcing particles in metal matrix. Homogeneity of layers guarantee an increase of microhardness values as well as abrasion resistance [3].

Main objectives of performed studies were focused on the development of technology for sonoelectrochemical coating of composite anticorrosive Zn films reinforced by SiC nanoparticles and optimization of synthesis parameters towards their functional properties. Investigations were performed with the use of modified commercial acidic electrolyte. Optimization of composite coating process was performed under current controlled conditions (constant current, pulsed current) without and at the presence of ultrasounds agitation. Coatings deposited at pulsed current as well as constant current conditions were characterised towards their composition, structure, reflectivity and morphology. An influence of ultrasounds as well as current conditions on coatings deposition rate, current efficiency was also investigated.

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Keyword: Zn-SiC composites, electrodeposition, sonoelectrochemistry

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Towards Cr(VI) Free Corrosion Resistant Coatings via Comparing Salt Spray Corrosion Tests (ASTM B117) with Electrochemical Impedance Spectroscopy and Accelerated Cyclic Electrochemical Techniques (ACET)

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Most commonly, anti-corrosive performance of organic coating systems would be tested in accelerated tests such as salt spray (ASTM B117), humidity chamber or tests with similarly exaggerated exposure conditions. Corrosion reactions are electrochemical in nature, but corrosion process as a whole involves both electrochemical driving forces and physical phenomenon such as solubility and mass transfer. Therefore accelerated exposure tests for corrosion are not exactly accelerated; rather they are arbitrary corrosion tests in which industry accumulated some experience. Results from these tests are evaluated visually. Although progress of rust, cathodic delamination, blistering and adhesion loss can be qualitatively evaluated, these tests cannot provide a quantitative assessment of coating performance.

With electrical impedance spectroscopy (EIS), it can be possible to evaluate coating condition directly and quantitatively. This can be done on the fresh, as well as exposed coatings. Using accumulated knowledge on the correlation between accelerated tests and real world performance, similar correlation can be constructed between EIS and accelerated exposure tests. While this is a useful technique it still relies on accelerated tests and can take long time, even up to months in some cases¹.

Accelerated cyclic electrochemical techniques (ACET) can be described as both fusion of EIS and accelerated exposure tests. ACET cycle starts with an initial impedance measurement and after that coating subjected to a DC voltage followed by a relaxation period. Finally, again an impedance measurement was performed (Figure 1). The constant DC voltage causes deterioration of the coating system, which expresses itself as the difference between the EIS measurements. In relaxation period voltage and current is measured, behaviour of coating during this period gives data on the adhesion. ACET cycle performed until a reasonable deterioration of the coating is achieved.



Figure 1 Accelerated cyclic electrochemical technique cycle

Corrosion protection with organic coatings is proved mainly through barrier effect of the coating and chemical corrosion suppression with anticorrosive pigments. Currently Cr6+ anticorrosive pigments can be considered to give highest anticorrosion performance but their usage is rather precarious, Cr6+ is a known carcinogen². In this study, an epoxy based primer with Cr6+ is used as benchmark, effects of Cr6+ on the corrosion resistance of coating system and Cr6+ free alternative anti corrosive chemistries were investigated. Corrosion of organic coating system was evaluated using salt spray test and EIS. ACET is also used on the coating system, viability of ACET as a total or partial replacement for the accelerated tests is discussed.

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Keyword: organic coating, corrosion, electrical impedance spectroscopy, hexavalent chromium, ACET

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Synthesis and Study of the Thermo-mechanical and Morphological Properties of Composite Materials Based on Unsaturated Polyester Reinforced with Perlite and Electrochemical Behavior in NaCl Medium

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La présente étude vise à fabriquer un matériau composite UPR / perlite. En effet, une charge minérale à base de perlite a été utilisée comme charge renforçante pour la résine de polyester insaturé (UPR). Ce matériau composite est synthétisé par addition de différentes charges de perlite (1 à 5 phr - parties pour cent parties de résine) de différentes tailles (jusqu'à 50 μm et moins de 50 μm) à l'UPR. Au début, une étude d'optimisation et les propriétés mécaniques et thermiques sont réalisées. Les matériaux UPR / perlite ont augmenté jusqu'à 4 phr de charge de perlite. Cependant, une charge de perlite plus élevée a entraîné une diminution de ces propriétés. De plus, un degré de réticulation plus élevé a été atteint. Les thermogrammes DSC ont montré que le pic exothermique est décalé à des températures plus élevées, ce qui suggère que la perlite a retardé la réaction post-polymérisation.

Enfin, une étude électrochimique du comportement du matériau composite UPR / perlite est réalisée en milieu salin à l'aide de techniques stationnaires et transitoires.

DRAFT

Keyword: Unsaturated polyester resin, materials composites, NaCl3%, thermal analysis, electrochemical techniques

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Synthesis, Spectral Characterization, Electrochemical and Electrocatalytical Properties of Copper Complex of a Potentially Bidentate NO Schiff Base Ligand Derived from 2-(4-methoxyphenyl) Ethylamine and 2-hydroxybenzaldehyde

Ouennoughi YASMINA, Bouzerafa BRAHIM

University Ferhat Abbas Setif- 1, Algeria

The synthesis of copper complex of Schiff base derived from condensation reaction of 2-(4-methoxyphenyl)ethylamine) and 3,5-dichloro-2-hydroxybenzaldehyde was reported in methanolic solution. Its spectroscopic, electrochemical and electrocatalytical properties have been studied and well discussed. As for the spectroscopic methods, this complex was characterized by several techniques such as elemental analyses, FT-IR, UV-Vis and EI-MS. The elemental analyses confirm that the stoichiometry of the copper complex is of type CuL_2 . The electrochemical behavior of the $Cu(II)$ complex were studied using cyclic voltammetry. As indicated by cyclic voltammetry, the copper complex undergo redox processes involving the metal redox pairs $Cu(III)/Cu(II)$ or $Cu(II)/Cu(I)$. The redox property of the $Cu(II)$ complex was also investigated by electrochemical method using cyclic voltammetry. The electrocatalytical properties towards reduction of alkyl halides such as have been examined.

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DRAFT

Keyword: Metal-Schiff base complexes, spectroscopic methods, Cyclic voltammetry electrocatalytical properties.

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

The Influence of the Anodizing Temperature on the Anti-corrosion Properties of the Aluminum Alloy

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Two-step aluminium anodizing is widely used to prepare oxide films with a highly-ordered porous structure through the whole thickness. Temperature is an important thermodynamic parameter which is able to accelerate chemical reactions and mass-transport and, thus, could be suggested as an effective tool to control the growth rate of anodic alumina [1].

In this study, electrochemical experiment was conducted to select the optimal surface modification temperature to have excellent corrosion resistance in a marine environment using 5083 aluminum alloy because it is a highly reactive and corrosion-sensitive metal in a corrosive environment such as sea water [2,3]. The results obtained showed that the anodizing treatment makes it possible to obtain a sealed oxide layer whose thickness increases with decreasing temperature. The formation of this layer on the surface of the alloy significantly improves its resistance to corrosion induced by chloride ions. This improvement, due mainly to the high compactness and the stability of the obtained oxide layer, which has played the role of physical barrier against aggressive agents, is becoming more and more remarkable with the increase in the treatment duration of anodizing and decreasing the temperature of the electrolyte.

DRAFT

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Keyword: Anodization, Aluminum alloy, Corrosion, Temperature, Marine environment

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Physicochemical, Electrochemical and Theoretical Study of Some Organic Compounds as Corrosion Inhibitors of Mild Steel in 1M HCl

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University of Jijel, Algeria

Steel is used in many applications: marine industry, refining, chemical processing, metal processing, oil production etc. because of its mechanical strength, its good conductivity, its ease of manufacture, its low cost and especially its wide availability. However the main problem of steel is its low resistance to corrosion, it is easily attacked and solubilized in acid solutions, which are widely used in the industry for various purposes. Corrosion prevention plays an important role in the field of scientific research. In this context, researchers and industrials work together to develop an alternative and innovative solution to prevent metals and alloys from corrosion. The use of inorganic and organic inhibitors is one of the best methods due to their cost effectiveness and ease of application in industry.

In this work, we synthesized and characterized by physicochemical and electrochemical techniques some organic compounds in order to study their inhibitory efficiency of mild steel in hydrochloric acid solutions.

An electrochemical study by monitoring the evolution of the free potential (OCP) as a function of time, the plot of the polarization curves and electrochemical impedance was conducted. The effect of concentration and temperature have also been studied. These studies confirm the inhibitory power of corrosion of these organic compounds. Quantum DFT parameter analysis and Monte Carlo molecular dynamics simulation confirm that amines have a strong protective effect against steel corrosion. A correlation between the experimental study and the theoretical study has been established.

Finally, the different results obtained in this study through the three different approaches are in good agreement with each other and provide a complete picture and a complete study of the phenomenon studied to better counter and find an appropriate solution to a problem that affects the economy and the environment.

DRAFT

Keyword: organic compounds, mild steel, inhibitor, polarization curve, DFT, Monte Carlo.

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Cu-SiC Thin Films as a Photocathode for the Photoelectroreduction of CO₂

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Research Center on Semiconductor Technology for Energetic, Algeria

CO₂ reduction into fuels has become an increasingly active area in energy research over the last several years. The present work is developing artificial photosynthesis technologies that use visible light to convert CO₂ and water into value-added product. In this study, SiC loaded copper particles (Cu-SiC) thin films were elaborated, characterized and studied for photoelectrochemical (PEC) reduction of CO₂ into methanol under visible light ($\lambda > 470$ nm) irradiation. The SiC thin films were deposited via sputtering method followed by a vacuum evaporated of Cu particles on the surface of SiC thin films. photocathode characterization was done by Scanning electron microscopy (SEM), UV-vis absorption spectra, and VMP3 station. Linear sweep voltammetry (LSV) was employed to evaluate the photocatalytic activity of the prepared photocathode under visible light ($\lambda > 420$ nm) irradiation for CO₂ reduction reactions. SEM results indicated that the Cu particles were well dispersed on the SiC thin film surface. The band gap energy of the Cu-SiC catalyst was 1.8 eV. The flat band potential was calculated using the Butler relation and was found at ~ -0.46 V vs Ag/AgCl. During LSV, the onset potential was shifted positively (~ 100 mV) under the light-on condition than the dark condition in CO₂ saturated solution suggests an increase in photocurrent and occurrence CO₂ photoreduction reaction. The PEC performance of Cu-SiC photocathod showed an increased methanol formation under visible light irradiation

DRAFT

Keyword: CO₂ reduction; Photoelectrochemical; visible light; Cu-SiC photocathode; methanol

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Anticorrosion Properties of Zn₃(PO₄)₂/Ppy Coatings on Steel

Yeldana BAKHYTZHAN, G.s RAKHYMBAY, Y.n YESSALY, A ARGIMBAYEVA, B BURKITBAYEVA, A TURLYGAZIEVA

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Electrochemical polymerization of conductive polymers is the most convenient and simple method of obtaining coatings on the surface of metals. In the process of synthesis, it is possible to control the properties of the obtaining films [1-2]. In the work, polypyrrole composite zinc-phosphate coatings on mild steel grade St3 were successfully synthesized. Electropolymerization of polypyrrole occurs with the previous passivation of the surface of the steel with a tartrate protective layer. The corrosion properties (film resistance and corrosion rate) of the synthesized coatings with the composition Zn₃(PO₄)₂/polypyrrole were determined by two methods, linear voltammetry and impedance spectroscopy. These results were used to analyze the protective effect of the obtaining film, LV (97%) and EIS (80%). The morphology of the synthesized coatings was also investigated. According to the results of scanning electron microscopy, polypyrrole shows a globular morphology of various sizes. The deposition of polypyrrole on the surface of zinc phosphate, leads to the formation of a homogeneous and compact sediment and, consequently, leads to an increase in the protective properties of this coating.

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Keyword: electropolymerization, film, polypyrrole, corrosion, steel

Electrochemical Material Science

(Electrochemical synthesis, processing, surface treatment, corrosion, passivation)

Electrochemical Synthesis of Poly(aniline-co-o-anisidine) on Steel and their Anticorrosion Properties

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Al-Farabi Kazakh National University, Kazakhstan

For many decades, corrosion has been one of the key scientific problems, the solving of them can save enormous material and financial resources. One of the alternative corrosion inhibitors are conductive polymer films, which are distinguished by non-toxicity, high stability, ease of synthesis and environmental safety [1,2]. The main goal of this study was to create high-performance polymer coatings to protect steel from corrosion. To achieve this goal, the poly(aniline-co-o-anisidine) (PAOA) copolymer was successfully direct electrosynthesized on a steel (St3) electrode from solutions of oxalic and phosphoric acids, and their protective properties were studied using potentiodynamic polarization and electrochemical impedance spectroscopy in 3.5% NaCl. The morphology of the obtained polymer films was investigated by scanning electron microscopy (SEM), according to which they homogeneously covered the surface of steel and had a dense structure. The results of X-ray spectral analysis showed the presence of phosphate ions in the film, which play the role of an alloying anion. The results of the potentiodynamic polarization measurements showed that the PAOA coatings provided more effective corrosion protection to steel and inhibition efficiency for it was 98.8%. The Electrochemical Impedance Spectroscopy (EIS) results are in good agreement with the potentiodynamic polarization measurements. EIS measurements indicated that the coating resistance (R_{coat}) and corrosion resistance (R_{corr}) values for PAOA coatings was much higher than of bare steel electrode. This study reveals the poly(aniline-co-anisidine) coating has excellent corrosion protection properties and can be considered as a potential coating material to protect St3 against corrosion in chloride medium.

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DRAFT

Keyword: Corrosion protection; Steel; Electropolymerization; Conducting polymers; Electrochemical Impedance Spectroscopy

General Molecular Electrochemistry

(Structural and mechanistic aspects of electrode processes of inorganic, organic and organometallic compounds and reactions)

Bottom-up Cu Electrochemical Filling of Wafer Level TSV for MEMS 3D Integration

Alper Kaan SOYDAN, Dilek IŞIK AKÇAKAYA, Haluk KÜLAH

Middle East Technical University, Turkey

3D packaging technology enables production of compact, light weight and robust MEMS devices saving space and resources. Through silicon vias (TSV) permit integration of separate devices by electrically connecting them to a low volume package. While, TSV technology have been available for long, distinct constraints of materials and methods (via first, via last) used in MEMS fabrication processes lead to different requirements and production flows. In this study, development of the wafer level TSV fabrication process flow and electroplating wafer holders for the 3D MEMS device integration has been described. TSV structures with 100 μm diameter width and 350 μm depth were etched into Si wafers utilizing Bosch Process with a deep reactive ion etching system (DRIE). SiO_2 as electrical isolation layer, Cr and Au layers as adhesion and seed layers were coated, respectively. Due to its high conductance and availability, Cu was selected as the filling material. For Cu electroplating process, ECSI Fibrotools (ElectroChemical Systems, Inc.) setup was used to empirically find out the critical parameters of the void-free filling. Two bottom-up wafer level ECD TSV filling methods were investigated: (i) carrier wafer seed layer usage for the pulse timing of the current source, then (ii) via sealing seed layer for the determination of the additive ratios. For the both methods, special bottom-up electroplating wafer holders were designed and manufactured. Range of pulse duty cycles from 0.1 to 0.9 were experimented using commercial sulfuric acid based Cu solution (Transene) without additives. After determining the duty cycle as 0.8, leveler, suppressor and accelerator additives were included for the increased TSV filling quality. Void free filling process obtained with the via sealing and bottom-up ECD method. Wafers were diced and SEM investigation for the cross sections were carried out to observe the success of the proposed methods.

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme under grant agreement No 682756.

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Keyword: Through silicon vias, copper electroplating, additives, MEMS processes

**General Molecular Electrochemistry
(Structural and mechanistic aspects of electrode processes of inorganic,
organic and organometallic compounds and reactions)**

Development of New Metal-free Organic Materials Based on Anthracenyl-Bridged TPA-Mono-, Bis-thienothiophene Dyes: Potential Photosensitizers for Efficient Dye-Sensitized Solar Cells

Adewale ADELOYE

Umaru Musa Yar'adua University, Nigeria

To date, a number of new π -conjugated aromatic and heteroaromatic functional material systems have been investigated as photosensitizers for dye-sensitized solar cells (DSSCs) among which include thiophene or thienothiophene as π -bridges with remarkable solar cell efficiency. The design of these new metal-free dyes often gives special attention towards compound rigidity, extended π -conjugation and condensed-polycyclic structure leading to unique electronic properties such as conductivity, high field effect mobility and tunable stacking in the solid state that affect the deactivation of the excited states.

With the aim to investigate the structure-performance relationship of the dyes in the cell, we designed a small library of structures involving an anthracenyl-bridge functionality connecting two arms of acceptor group, π -bond linkage, and the donor group as represented in the model Dye-1. This allowed us to elongate the conjugation thereby lowering the band gap and enlarge the absorption spectra. In particular, the incorporation of anthracene is expected to function as upconversion material to increase the efficiency of single band gap solar cells beyond the Shockley Queisser limit. We present the spectroscopy, photophysical, electrochemical, DFT and solar conversion efficiency of the photoactive materials.

The author will like to thank the mangement of Umaru Musa Yar'adua University for sponsorship

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Keyword: dye-sensitized solar cells, anthracene, metal-free dyes, photophysical, electrochemical, DFT studies

General Molecular Electrochemistry

(Structural and mechanistic aspects of electrode processes of inorganic, organic and organometallic compounds and reactions)

Cu(II) and Ni(II) Tetradate Schiff Base Complexes Containing N-substituted Pyrrole: Synthesis, Electrochemistry and Electrocatalytical Properties in Homogeneous and Heterogeneous Media

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We have initiated the synthesis of original pyrrole-M(II)-Schiff base complexes derived from 6-[3'-(N-pyrrol)propoxy]-2-hydroxyacetophenone and 1,2-diaminoethane. The electrochemical behavior has been investigated in acetonitrile solution using cyclic voltammetry. These pyrrolic Ni(II) and Cu(II) complexes were electropolymerized onto glassy carbon (GC) and indium tin oxide (ITO) electrode surfaces. The electropolymerization was performed also in acetonitrile of pyrrolic moieties by cyclic voltammetry. The modified electrodes were electrochemically and morphologically characterized and their electrocatalytic properties in homogeneous and heterogeneous phases have also been investigated. The efficiency of the electrochemical polymerization was investigated as a function of several parameters such as the nature of the electrode material, the number of voltammetric scans, and the scan rate dependence. The electrodeposited poly(pyrrole) films onto ITO surface were characterized by atomic force microscopy (AFM). The electrocatalytic performances of the copper complex seem to be more efficient towards the electro-oxidation of isopropyl alcohol than any other kinds of alcohols such as methanol, ethanol and benzyl alcohol. As for the nickel complex, its poly(pyrrole) matrix, containing Ni(II) centers, was found to have good catalytic properties towards the electro-reduction of iodobenzene. The electro-reduction of carbon dioxide was also examined for both complexes.

DRAFT

Keyword: Schiff base complexes, electropolymerization, electrocatalytic properties, atomic force microscopy.

**General Molecular Electrochemistry
(Structural and mechanistic aspects of electrode processes of inorganic,
organic and organometallic compounds and reactions)**

Supercapacitive Properties of h-BN doped Gel Polymer Electrolyte

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It is well known that electrolyte is a crucial part of supercapacitor but traditional liquid electrolytes have usually some disadvantages such as leakage and corrosion. Though these problems have been tackled by replacing liquid electrolytes with solid polymer electrolytes, the application of solid polymer electrolyte in a high-performance supercapacitor is greatly limited due to its low ionic conductivity [1-3]. To achieve both advantages of the liquid electrolyte and solid electrolyte, the gel polymer electrolytes (GPEs) were proposed. A novel hexagonal boron nitride (h-BN)-doped poly (vinyl alcohol)-sulfuric acid (PVA-H₂SO₄) gel polymer electrolyte (GPE) was fabricated through a simple solution-mixing/casting method. These GPEs electrolyte were characterized using FTIR, DSC, and dielectric-impedance spectroscopy. The polymer electrolyte showed an ionic conductivity of $\sim 1.38 \times 10^{-2} \text{ Scm}^{-1}$ at 20°C. Moreover, a symmetric supercapacitor, with carbon nanofiber as electrodes and the hBN-PVA-H₂SO₄ gel polymer as electrolyte was designed. Electrochemical performance studies demonstrated that hBN-PVA-H₂SO₄ GPE had a maximum electrode specific capacitance (Cs) of $\sim 90 \text{ Fg}^{-1}$. The h-BN doped GPEs, with excellent performance and a simple method are promising materials for the future generation of high performance supercapacitors.

Acknowledgements We would like to thank ERANET-INCOMERA programme supported by Scientific and Technological Research Council of Turkey (TUBITAK) 1509-International Industrial R&D Projects Grant Programme with Project Number 9160035

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Keyword: gel polymer electrolyte, boron nitride, ionic conductivity, supercapacitor

General Molecular Electrochemistry

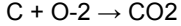
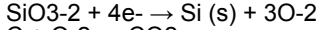
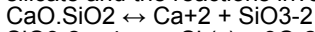
(Structural and mechanistic aspects of electrode processes of inorganic, organic and organometallic compounds and reactions)

Molten Salt Electrolysis as an Alternative for High Si Content Fe-Si Alloy Production

Oğuz Kaan COŞKUN, Servet I. TIMUR
Istanbul Technical University , Turkey

Fe-Si alloys are widely used in electrical applications due to their exceptional soft magnetic properties. Electric motors and transformers are among the most common use cases. In order to obtain the low hysteresis losses that is required by the applications mentioned above, 6.5 wt.% Si content is the optimum. However, when those high concentrations are attempted, B2 and D03 ordered phases are observed leading to catastrophic decrease of ductility of the material. This decrease in ductility prevents the thin sheet production which is a requirement in applications such as transformers, by conventional rolling techniques. Many different production methods have been proposed to obtain high Si content in Fe-Si alloys such as chemical or physical vapor deposition, hot dipping and thermos-mechanical recipes. In all of those methodologies, the starting material is 3 wt.% Si containing steel. Firstly, Si is deposited on the surface; afterwards, diffusion annealing is conducted to obtain homogeneous concentration throughout the cross-section. In this study, using inexpensive, environmentally friendly and earth-abundant SiO₂ as precursor with a water-soluble CaCl₂ electrolyte which has no or less disposal problems, high Si content Fe-Si alloys have been tried to be produced starting from the low carbon none-alloyed steel after whatever the geometry it is given. By this, it is shown that this method can be an alternative in Fe-Si production and can solve the industrial problem mentioned above.

In experimental system, graphite crucible is polarized anodically and the substrate (1018 steel) cathodically. The experiments are conducted at 1200oC to avoid diffusion blocking effects of ordered phases by staying above the critical temperature for ordering, for 10 minutes. SiO₂ solubility in CaCl₂ is increased by CaO addition, via the formation of calcium silicate and the reactions involved in the system is given below.



Furthermore, it is claimed in the literature that CaO addition increases reaction kinetics of the system by increasing O²⁻ concentration, which needs to be transported from cathode to the anode so as to realize anodic reactions. The cyclic voltammetry (CV) of the CaCl₂+CaO+SiO₂ electrolyte system is given in Figure 1.

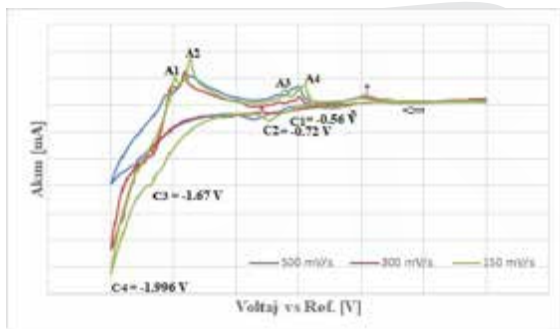
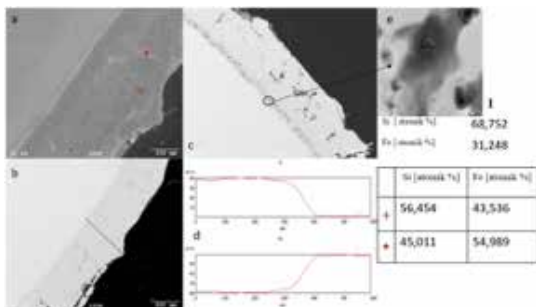


Figure 1 : The voltammograms of CaCl₂ + CaO + SiO₂ electrolytes with different scan rates [1100oC, (-2, +1) V voltage domain, Reference and counter electrode : Graphite, Working electrode: W wire].

This CV study shows that SiO₂ can be reduced in a two-step reduction reaction:



The Fe-Si formed after electrolysis at 500 mA/cm² current density for 10 minutes at 1200oC results in the layer given in Figure 2. The average thickness of Fe-Si is 400 µm.



Şekil 4.11 : The scanning electron microscope image formed out of secondary and back-scattered electrons a. 200x secondary, b. 100x back scattered, c. 100x back scattered, d. çizgi-EDS result, e. 5000x back scattered.

Physical Electrochemistry
(Experimental, theoretical and computational aspects of electrochemistry,
alone or in conjunction with other methods)

Ultrafast Cyclic Voltammetry and Spectroelectrochemistry of Conducting Polymers

Hamza KAHRI, Burak ULGUT

Bilkent University, Turkey

Since they were discovered [1], conducting polymers have attracted much interest in the field of electrochemistry due to their original properties such as an ease of synthesis, flexibility and moderate band gap [2]. In cyclic voltammetry the current response is resulting from the redox reactions of the electroactive species that can travel the length of the diffusion layer. The redox processes in conducting polymers are complex, this is can explained by the difficulty of getting all necessary experimental information especially for short time-scales/high sweep rate. By increasing the rate at which a triangular potential is applied, the length of the diffusion layer can be adjusted such that only the electron transfer occurs without the counter ion diffusion required for electroneutrality. In order to obtain fast kinetics information about the redox behavior of conducting polymer, we have used ultrafast cyclic voltammetry to investigate heterogeneous electron transfer kinetics decoupled from the counter ion transport. By using a broadband UV-vis spectrometer during an ultrafast cyclic voltammetry experiment allow us to understand the effects of ion transport in color switching times of electrochromic devices to improve their performance.

H.K thanks to the Scientific and Technological Research Council of Turkey (TUBITAK) for the fellowship.

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DRAFT

Keyword: Ultrafast cyclic voltammetry, electrochromism, spectroelectrochemistry, conducting polymers.

Physical Electrochemistry

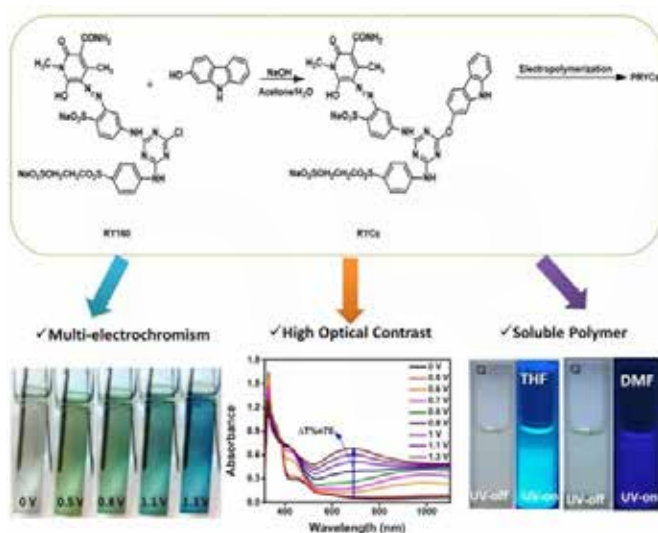
(Experimental, theoretical and computational aspects of electrochemistry, alone or in conjunction with other methods)

Processable Multipurpose Conjugated Polymer Based on Reactive Yellow 160 and 2-hydroxycarbazole

Merve GÜZEL, Metin AK

Pamukkale University, Turkey

In recent times, the synthesis of soluble and processable conductive polymers has attracted great interest owing to their potential application[1,2]. In this work, the super structured multi-functional monomer (RYCz) containing Reactive Yellow 160 with 2-hydroxy carbazole was designed and successfully synthesized. The RYCz was confirmed by $^1\text{H-NMR}$ and FTIR. Electropolymerization of RYCz was carried out by using cyclic voltammetry in acetonitrile (ACN) and in the binary solvent system including acetonitrile (ACN)/ boron trifluoride diethyl etherate (BFEE). The obtained polymers have been compared in terms of their electrochemical, electrochromic and colorimetric properties. While the oxidation potential of RYCz was 1.03 V at ACN, this value decreased to 0.87 V when BFEE was added to the medium. Their color varied from transparent in the neutral state to aquamarine in the oxidized state. Also, fluorescence features of the monomer and polymer were investigated. The PRYCz film has been found to be soluble in both THF and DMF. According to ACN, the PRYCz film prepared in ACN/BFEE solution has been showed excellent electrochemical and electrochromic properties such as high stability (92%), high coloration efficiency ($678 \text{ cm}^2/\text{C}$) at 690 nm and high optical contrast (70%). The results showed that the electrochemical and electrochromic properties of PRYCz film prepared in ACN/BFEE solution are more efficient than those prepared in ACN solution.



Authors gratefully thank the PAUBAP 2018FEBE051 project.

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Keyword: electrochemical polymerization; soluble polymer; coloration efficiency; optical contrast

Physical Electrochemistry

(Experimental, theoretical and computational aspects of electrochemistry, alone or in conjunction with other methods)

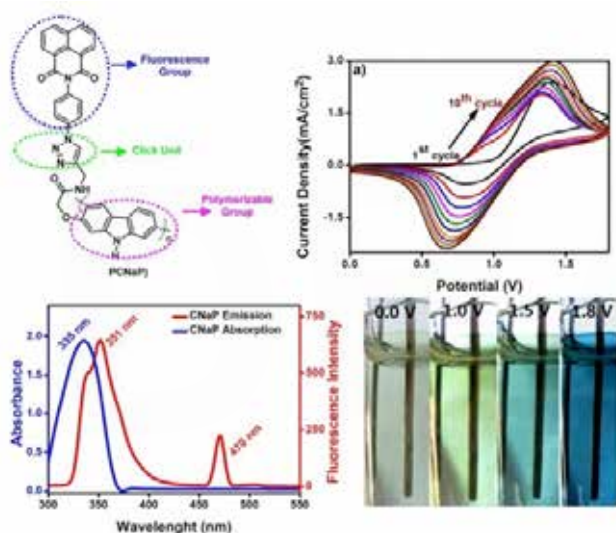
Synthesis and Electropolymerization of Naphthalimide Clicked Carbazole Derivative

Fatma ÇOBAN¹, Metin AK²

¹Burdur Mehmet Akif Ersoy University, Turkey

²Pamukkale University, Turkey

Conducting polymers (CPs) have drawn considerable attention because of their unique optical and electrical properties. Due to these properties, they have widely used in applications such as chemosensors, light-emitting diode (OLEDs), organic photovoltaic cell (OPV), organic thin-film transistors (OTETs), biosensors, etc [1-3]. In this study, multifunctional naphthalimide carbazole derivative (CNaP) was successfully synthesized with reaction of 2-((9H-carbazol-2-yl)oxy)-N-(prop-2-yn-1-yl)acetamide and 2-(4-azido-phenyl)-1H-benzo[de]iso-quinoline-1,3(2H)-dione via click chemistry. CNaP monomer was characterized via FT-IR, ¹H-NMR, ¹³C-NMR techniques as well as fluorescence and electrochemical measurements. The electrochemical polymerization of the CNaP monomer was performed on ITO glass in ACN:BFEE(2:1) (v/v) with a scan rate of 150 mV/s by cyclic voltammetry. PCNaP film revealed multielectrochromic behavior (transparent, yellow, green, blue colors) at different potentials. PCNaP had a good optical contrast (41% at 693 nm) and fast switching time (1.92 s, at 693 nm). The novel clicked, fluorescent, polycarbazole-derived conducting polymer has the potential to be used for many different applications such as electrochromic devices, electrochemical/optical sensors, and fluorescence imaging applications.



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