

P-01

Electrochemical reduction of CO₂ in ionic liquids using catalytic graphene-metalloporphyrin systems

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It is a highly desirable goal to convert CO₂ into fuel precursors such as carbon monoxide, ethylene, methanol or formic acid at low overpotentials. CO₂ electrochemical reduction is one way to achieve these goals.

Most of CO₂ reduction research done until now uses combined systems of aqueous media and metal electrodes, and involves adsorption mechanisms. However, the well known high-energy CO₂^{•-} radical anion formation (-1.9V vs. NHE) which is the rate limiting step, in addition to the presence of a competitive HER (Hydrogen Evolution Reaction) leads to low selectivity CO₂ reduction. These, combined with a relative low solubility of CO₂ in aqueous electrolytes are major drawbacks of this reduction path.

Another approach to CO₂ reduction uses Co(II)/Co(I) porphyrin redox couples as catalysts, based on a mechanism that is believed to involve binding of the CO₂ to the reduced metalloporphyrin. Cobalt porphyrins were investigated as homogeneous catalysts for the reduction (in both aqueous and non-aqueous (organic) media) and were found to be effective. Additionally, graphene/metalloporphyrin systems have been studied with regard to oxygen reduction reaction, using graphene as an electron supplier. Our group showed recently the use of this system with regard to water splitting which is one aspect of artificial photosynthesis. This system is a good candidate as a catalyst for another aspect of artificial photosynthesis: CO₂ reduction. Nevertheless, the study of the couple Co(II)/Co(I) porphyrin in aqueous media is problematic because of the H₂O reduction potential which is in close vicinity.

Using imidazolium based ionic liquids as electrolytes instead of H₂O solves part of the problems mentioned above. EMIM ethyl sulfate ionic liquid is used in the present research. The imidazolium cations form a stabilized intermediate complex (ion pairing) with the CO₂^{•-} radical anion, (which leads to a lower overpotential by decreasing the energy barrier for the CO₂ reduction). The sulfate containing anions make the ILs hydrophobic and more stable (compared to ILs with PF₆ and BF₄ anions, usually used in CO₂ reduction studies). This in addition to their high CO₂ solubility and selectivity make them good medium candidates in trying to find an efficient system for CO₂ reduction.. Results concerning the use of graphene/metalloporphyrin systems for the catalytic reduction of CO₂ in Emim Ethylsulfate will be presented.

P-02

A One-Pot Anodic Thiocyanation of Alkenes

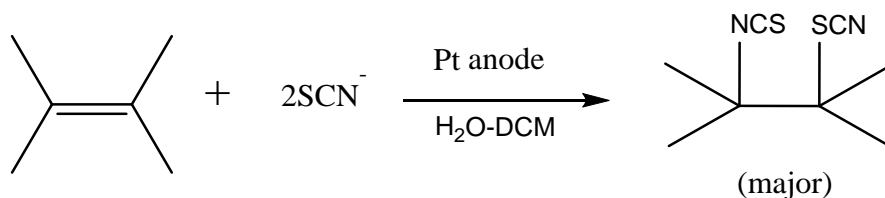
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Electrochemical thiocyanation of alkenes was studied in an undivided cell using a one-pot, two phase medium (water-dichloromethane), and employing a constant current electrolysis (CCE). The aqueous phase promotes the oxidation of thiocyanate anions and the organic phase is utilised to dissolve the alkene substrate and stabilise the electro-generated thiocyanogen ($\text{SCN})_2$ which is unstable in aqueous media. Thiocyanogen exhibits pseudo-halogen properties and reacts favourably with alkenes under acidic conditions (H_2SO_4). Thiocyanation was first implemented on a model alkene, the symmetric 2,3-dimethyl-2-butene. The major product is a mixed di-addition of thiocyano and isothiocyano groups to the double bond of the substrate (Scheme). Other minor products involve addition of two thiocyano groups, one thiocyano and one hydroxy group, and a trace amount of one thiocyano group and a hydrogen atom.



It is noteworthy that upon using a one phase of aqueous acetonitrile, the formation of the 2-hydroxy, 3-thiocyano derivative becomes predominant.

Structure-property relationship in integrated cathode materials for lithium rechargeable batteries

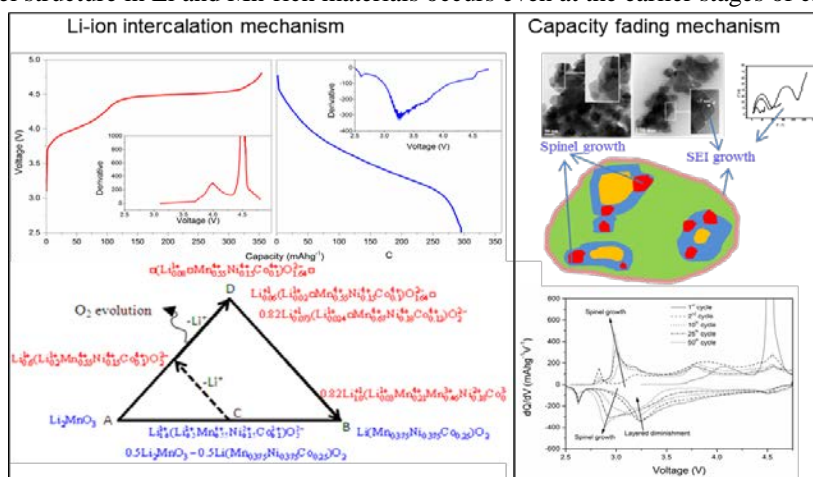
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We have demonstrated that the lithium ion intercalation/deintercalation mechanism in lithium and manganese rich oxide based integrated cathode materials is a complex process and the electrochemical performance of these cathode materials depends on various interrelated parameters. Through extensive structural and electrochemical characterization, we have found that (i) a significant structural change occurs during first cycle accompanied with the evolution of lattice oxygen, (ii) a relatively slower and continuous structural transition occurs during repeated cycling that leads to a layered-spinel intergrowth structure (iii) an electronically insulating solid electrolyte interface layer grows with repeated charge-discharge cycling (iv) the capacity of the composite cathodes is dependent on the Li_2MnO_3 domain size. We have established also an unusual *cross-over* phenomenon in the galvanostatic cycling profiles of the composite cathodes which is associated with the interplay of the cycling induced voltage decay due the layered-to-spinel like phase transformation and the increase in polarization due to the rise in charge transfer resistance after the “*cross-over voltage*”. The phase transformation is associated with migration of manganese ions to the lithium layer while the Li-extraction. An interesting finding is that a transformation from layered to spinel structure in Li and Mn-rich materials occurs even at the earlier stages of charge.



P-04

The role of surface chemistry in carbon electrodes for Li-Oxygen systems

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The study of the Li-Oxygen system is still struggling to answer the question: are there any stable cathodes and electrolyte solutions for ORR and OER application? We believe more and more that a "stable" solvent for Li-oxygen systems is not known yet. Our focus now is to reduce the amount of electrolyte solution decomposition and carbon corrosion during operation. To reduce of the over-potential of the OER is an obvious way, using electro-catalysis or redox mediators. The problem is that severe side reactions occur in most systems during the ORR. Here we can reduce side effects by forcing a fast precipitation of Li-peroxide. The side reactions occur by reactions between the oxides formed in solution phase, before precipitation as solid Li_2O_2 . Solid Li-peroxide is much less reactive than the oxides in solution phase. What can help to mitigate the side reactions are possible modifications of the carbon cathodes that promote a fast precipitation of solid Li_2O_2 .

We present herein our ongoing work on the effect of the carbon cathodes surface on the Li- O_2 cell performance. As mentioned above the carbon cathode is one of the problems leading to cell failure. With the understanding that carbon is the most used material for Li- O_2 applications we are trying to see whether or not modification of the carbon surface can lead to a better stability of both cathode and electrolyte solutions. These results include two types of carbon, a reduced carbon (hydrophobic) and an oxidized carbon (hydrophilic).

P-05

Imaging of Ink-Jet Printed Multi-Enzyme Micro-Arrays on Glass by Scanning Electrochemical Microscopy

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Bioelements arrays are difficult to produce using lithography technology due to the high temperatures required for most processes. When implementing printing technology to produce enzymatic arrays, the high temperatures may damage the biocomponent, mostly reducing its catalytic activity significantly, sometimes to the point of inactivity.

Since ink-jet printing can be carried out at room temperature, harnessing this technology enables us to fabricate enzymatic micro-arrays. The printing process is performed using Omnijet 100 inkjet printer (Unijet, Korea) equipped with Dimatix piezoelectric print heads. This approach posed several challenges. The composition of the ink was optimized after carefully studying the different parameters affecting the printing process: the enzymes are integrated into the ink, containing various other components to control the surface tension, density, viscosity and other properties of the ink. Post printing, the array ought to be immobilized to prevent leaching of the enzyme. The immobilization procedure requires maintaining the initial properties of the enzyme intact. The stability of the enzymes and their corresponding activities should be preserved in their immobilized form. We were able to obtain arrays composed of different enzymes immobilized onto the same substrate using ink-jet printing, while maintaining their catalytic activity.

In this work we present a study of the enzyme activity and their influence and/or complementing activity, monitored by scanning electrochemical spectroscopy (SECM). The main feature of SECM is its ability to generate a controlled flux of electroactive species close to an interface. This allows charge transfer processes as well as electroactivity and morphology of the interface to be studied.

The SECM enables to locally study the activity of the enzymes, the interaction between them, if any, and the dependence of this interaction on the distance between the immobilized enzymes printed drops on the surface.

Briefly, different compositions of the enzymes glucose oxidase, invertase and horseradish peroxidase were printed on aminated glass surfaces. The enzymes were immobilized using glutardialdehyde post printing. SECM images were acquired while applying a constant potential very close to an enzyme modified glass surface, in a solution containing the enzymes' appropriate substrates, obtaining an effect on the current (resulting from the oxidoreductase nature of the enzymes involved).

This work shows great promise toward developing enzyme based logic gates and even biosensors.

P-06

Electrodeposition of graphene oxide on electrodes and their application in electrochemical energy devices

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The future use of renewable energy depends largely on the ability to store part of it for later demands. The energy can be stored in energy carriers (e.g. hydrogen) or as charge (capacitors, batteries).

Graphene unique properties (large surface area, high conductivity, chemical resistance and high possible modification) make it one of the best candidates as hydrogen storage material and an ideal material in the fabrication of ultracapacitors. These depend on its structure and chemical derivatization.

Graphene chemical composition can be controlled by different methods. Electrochemical ones allow controlling the amount and type of graphene functional groups and other features such as conductivity, capacitance and hydrophilicity.

Graphene oxide, which is an oxidized version of graphene was casted on glassy carbon electrodes and then subjected to reduction at the potential range $-1.2 \div -1.7V$ (vs Hg/HgO). After reduction, the graphene showed a pseudo capacitance behavior with an average value of 68F/g. At more cathodic potentials, the total capacitance decreased by ~20%. In addition, we measured the hydrogen storage performance of these electrodes by galvanostatic charging and discharging, and measured a value of about 100mAh/g.

Graphene can be electrodeposited on conductive supports by reduction of a graphene oxide aqueous emulsion. The decrease in the amount of the graphene oxidized functional groups leads to decrease of the concentration of its hydrophilic groups and consequently to its deposition. We electrodeposited graphene oxide onto glassy carbon electrodes and examined the electrochemical properties of the coated films in 1M KOH solution. These were found to be similar to those of the electrochemically reduced films of cast graphene oxide. The stability of the cast and electrodeposited graphene films is being examined.

P-07

Ru-Co-Se Novel Pt-free Catalysts for Oxygen Reduction in Fuel Cells and Metal Air Batteries

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Oxygen reduction reaction (ORR) plays a key role in electrochemical energy conversion systems, in particular, in fuel cell and metal-air batteries cathodes. Platinum is considered the state of the art catalyst for ORR in acidic fuel cells. However high cost and long term stability shortcomings stimulate the quest for alternative materials. Ru chalcogenides and more specifically RuSe compounds were investigated in the past demonstrated high ORR activity of as well as high tolerance towards methanol contamination, which is crucial in direct methanol fuel cells (DMFC).

In order to further decrease the Ru content and enhance the ORR rate we synthesized Ru-Co-Se materials with several Ru to Co molar ratios, applying different synthetic routes. The materials were characterized by XRD, Raman, EDS and their ORR catalytic activity and kinetic parameters were determined by rotating disk ring electrode (RRDE). It was found that Ru_3CoSe_2 shows a comparable electroactivity with Ru_2Se which has the highest activity known so far (figure 1).

is the most Ru based catalyst was attained (see figure 1). The performance of these catalysts was also measured at pH=7 in order to determine their electroactivity as a potential cathode material for bio fuel cells.

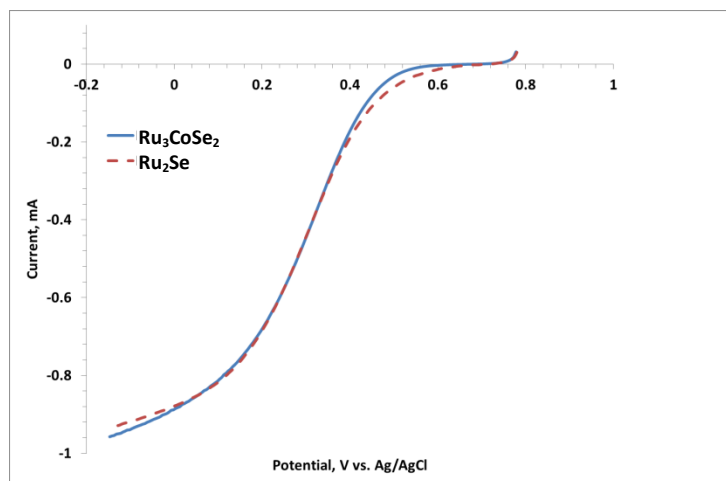


Figure 1. Current vs. Potential curves obtained from RDE measurements of oxygen reduction reaction on Ru_2Se and Ru_3CoSe_2 ($0.5\text{M H}_2\text{SO}_4$, scan rate = 2mV/sec , 1800 rpm).

Advanced Multiphase Silicon-Based Anodes for High-Energy-Density Li-Ion and Li-air Batteries

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Given that lithium-ion and lithium-air batteries are the preferred choice for EVs and plug-in applications, the focus is on improving their safety and performance. New, higher-capacity materials are required in order to address the need for greater energy density, longer cycle life and safer high-power operation. Silicon offers the highest gravimetric capacity as an anode material (e.g. $\text{Li}_{22}\text{Si}_5$: nearly 4,200mAh/g). The lithium-rich silicon compounds have high melting points and their higher working potentials (vs. Li) eliminate the possibility of metallic-lithium deposition due to overcharge. Silicon is the second-most abundant element in the earth's crust, and it is environmentally benign. Unfortunately, Si-based electrodes typically suffer from large volume changes (up to 420%) during insertion and extraction of lithium. This is followed by cracking and pulverization of silicon, which in turn, leads to the loss of electrical contact, unstable SEI and eventual capacity fading.

The methods of attachment of silicon nanoparticles to multi-wall carbon nanotubes (MWCNT) were developed with the purpose of creating silicon anodes supported by a strong, rigid and high-electrically-conducting matrix. Encapsulation of silicon nanoparticles by hard carbon is achieved by the pyrolysis of styrene-butadiene rubber (SBR) or sucrose (SCR). In addition, SiNi powder was synthesized by an electroless method and then pyrolysed under the same conditions, in order to improve the electronic conductivity of the anode.

We have found that SCR shows promise as a carbon precursor in the pyrolysis of multiphase silicon nanoparticles. ESEM, TEM, EELS and XPS tests indicated the formation of silicon nanoparticles wrapped by MWCNT and coated by nanometer-thick amorphous carbon.

Electrochemical analysis shows that Li/LiPF₆ EC:DEC/Si-C-MWCNT cells with anodes composed of about 40% silicon exhibited a de-intercalation capacity of 500mAh/g_{Si} after 1120 cycles. Stable capacity of 1000mAh/g_{Si} is obtained with the capacity-limited cycling mode.

The SiNi-C-MWCNT anode showed lower capacity in the 0.3MLiTFSi-PYR14TFSI IL electrolyte, but improved capacity retention, high faradaic efficiency and power capability (25μm anode, 1mg/cm² loading). We believe that boron-doped silicon, enriched by nickel silicide, silicon carbide compounds and attached to MWCNT, improve the electronic conduction.

P-09

Ohmic to Overlimiting Ion-Current Rectification Inversion in Funnel-Shaped Nanochannels

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An electrolyte filled, funnel-shaped nanochannel is shown to exhibit ion-current rectification inversion above a threshold of an externally applied DC voltage corresponding to the Ohmic to overlimiting current transition. Previous experimental studies have examined ion-current rectification at either low-voltages (Ohmic region) for conical nanopores/funnel-shaped nanochannels or at high-voltages (over-limiting region) for straight nanochannels having asymmetric entrances/microchannel chambers. In the current study we experimentally demonstrate new phenomenon of ion-current rectification inversion over the entire range of voltages. This inversion occurs because the intrachannel ion concentration-polarization (CP - depletion/enrichment) phenomenon, responsible for Ohmic rectification, is reversed by interaction with the opposite external CP, which develops above the threshold voltage.

P-10

Electrochemical Reduction of Indium Tin Oxide (ITO): Prevent and Use

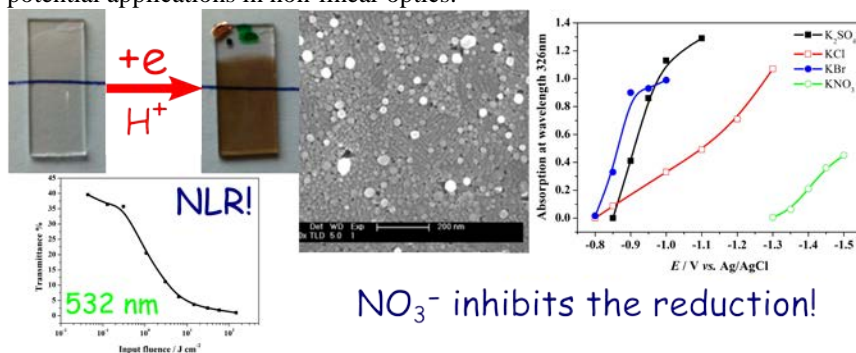
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Indium tin oxide (ITO) is widely applied as a transparent conductive electrode material. One main issue in the applications of ITO is its stability. Specifically, it is known that ITO undergoes electrochemical reduction at cathodic potentials, leading to the irreversible deterioration of its conductivity and transparency. In this work, we systematically investigated the influence of different solution parameters such as pH, ions and their concentration on the electrochemical reduction behaviour of ITO. The visible light absorbance of ITO at 326 nm was used as a measure of the reduction, and the reduced ITO samples were characterized by SEM, XRD and XPS. We observed that the onset potential and kinetics for the reduction of ITO is sensitive to the pH and anions of the solution. The reduction of ITO is favoured at low pH, because protons are involved in the reduction process. **NO₃⁻ ions are found to significantly inhibit the reduction of ITO**, although the reason is still unclear. The potential at which ITO starts irreversible reduction (turns dark) varies between -0.85 V and -1.6 V (vs. Ag/AgCl) depending on the solution conditions. The results suggest that **researchers should be extremely cautious when applying cathodic potential on ITO and referring the reduction potential to literature. Moreover, we turned the “negative” results into useful applications. The electrochemically reduced ITO shows non-linear optical properties, and the transmittance can be tuned by deposition conditions such as potential and time.** The optimized samples shows 50% of the maximum transmittance with the input fluence of 1 J/cm² (incite light 532 nm). The reduced ITO has good adhesion to the glass substrate, suggesting that it may have potential applications in non-linear optics.



NO₃⁻ inhibits the reduction!

Ni_xCo_yO_z Catalyst for ORR and OER for Sodium Air Battery

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Sodium -air batteries recently have been being studied as an alternative for lithium oxygen ones. In spite of lower theoretical specific energy (1980Wh kg⁻¹ of sodium vs. 3600Wh kg⁻¹ of lithium), abundance of sodium provides an advantage for its usage as a metal anode over lithium. Sodium-air batteries have similar reversibility problem of electrode reactions as lithium-air batteries. In order to solve this problem, a mechanism of O₂ reduction and evolution reactions (ORR and OER) must be understood, and an appropriate catalyst must be employed.

In this work, we studied ORR and OER in PEGDME500-based electrolytes, in the presence of Na⁺ ions, with and without catalyst application. For that purpose, two kinds of Ni_xCo_yO_z catalysts were synthesized by electroless method. The first one was synthesized on Black pearl particles, using Pt as an initiator of the synthesis, and the other one without using Black pearl and Pt. Glassy carbon electrode was coated by the catalysts, with loading of ~70μg/cm², and then tested in ORR and OER processes.

It was found that the both catalysts didn't influence reduction potential, but increased reduction current. In addition, the both catalysts shifted oxidation potential towards more positive values, which indicates increased rate of chemical disproportionation of NaO₂ to Na₂O₂ in the presence of the catalysts.

Electrodeposition of an Asymmetric Film Using Langmuir and Langmuir-Blodgett Techniques

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Asymmetric films play an important role in modern water-treatment membrane technology. The most selective membranes for water purification are based on asymmetric films. In our research we explored new, alternative ways for the preparation of asymmetric films by the Langmuir and Langmuir-Blodgett (LB) techniques.

In the first studied system a monomolecular Langmuir film of 1,2-polybutadiene (1,2-pbd) was prepared [1]. Mono and multilayers of 1,2-pbd were characterized with different techniques. The LB formed disorganized layers, which gradually blocked the permeation of different species with increased number of layers. Impedance spectroscopy (IS), gave us a tool to prove the "skin" structure of the formed multilayer. The thickness of the films was ca. 4–7 Å per layer. Furthermore, we took advantage of the reactivity of the double bond of the LB films and graft-polymerized acrylic acid on top of the 1,2-pbd layers.

In our next study [2], the octadecyltrimethoxysilane (ODTMS) Langmuir monolayer was prepared in the air-water interface and then was attached to the bulky polymer of sol-gel in situ in a Langmuir trough. The tetramethoxysilane (TMOS) was predissolved in the water subphase and the attachment of it to the dense Langmuir film was performed by electrodeposition. The horizontal touch (HT) electrochemistry was used in order to induce the sol-gel polymerization from the interface, containing the ODTMS Langmuir monolayer. The resultant asymmetric layer consisting of a thin hydrophobic ODTMS Langmuir film connected to a bulk hydrophilic sol-gel was studied in situ and ex situ using different techniques such as HT CV, HT AC impedance, SEM, TEM and water contact angle. This method can be used as an interesting alternative approach for asymmetric films construction for different purposes.

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P-13

Solid State Oxidation of Copper Nanoparticles. A Plasmonic Perspective.

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Copper nanoparticles (Cu NPs) represent an inexpensive alternative to more the expensive gold and silver plasmonic NPs, particularly in systems which could require extensive plasmonic surface layers, as in plasmonic solar cells or metal enhanced fluorescence, as well as in (photo)catalysis, conductive inks and as antibacterial agents. However, Cu NPs suffer from oxidation and corrosion processes which preclude some of these applications.

We proposed to evaluate the use of Localized Surface Plasmon Resonance (LSPR) measurements for studying the oxidation kinetics of NPs. Cu NPs were deposited by a chemical deposition method on glass substrates, and their oxidation kinetics was studied by LSPR during their thermal annealing at intermediate temperatures (100-170°C). The NP structures at different oxidation stages were evaluated by SEM and TEM, while compositional analysis was performed by GIXRD.

At the experimental conditions, Cu NPs form an initial Cu₂O layer which finally leads to hollow Cu₂O NCs due to a nano Kirkendall effect (NKE). An increase in LSPR extinction intensity, followed by a decrease is observed during the oxidation process.

A phenomenological adaptation of the Valensi-Carter model of metal oxidation was produced in order to consider cases where the fast Cu⁺ diffusion through the Cu₂O layer, compared to O²⁻, leads to oxide formation on both Cu₂O interfaces (*i.e.*, the NKE). Using the conversion fractions (δ) provided by the kinetic model, simple Mie scattering theory on core-shell particles was used to describe the optical properties of the system obtaining an acceptable qualitative description of the observed behavior.

P-14

Ab initio study of cathode materials for lithium ion batteries

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Mixed transition metal layered oxides ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM_{xyz})) and olivine phosphates are very attractive cathode materials for Lithium-ion batteries. However, NCMs likely have a complex in-plane transition metal (TM) ordering due to different charges associated with these. In this work, we study various transition metal ordering patterns and the effect of Al doping in NCM 523. Furthermore, we study the classical and quantum Li diffusion paths in Olivine phosphates. All the potential energy calculations were performed using Density Functional Theory (DFT) as implemented in the Vienna *ab-initio* simulation package (VASP)¹.

Our results suggest that by substituting the Mn-ions with Al^{3+} in the most preferred configuration, Al^{3+} is surrounded by one Mn, one Co and four Ni ions (Fig. 1b.). This configuration possesses the lowest energy when compared with other Mn substituted arrangements. In the most preferred Co-ion substituted configuration (Figure 1(c)), Al^{3+} is in a $(\sqrt{3} \times \sqrt{3}) \text{R}30^\circ$ type of motif. In the lowest energy Ni ion substituted configuration, Al^{3+} is surrounded by one Co, two Mn and three Ni ions (Fig. 1d.). The preference of Al substitution on TMs follows the order $\text{Ni} > \text{Co} > \text{Mn}$.

To study the Nuclear Quantum Effects⁴ (NQE) on Li and Na diffusion in LiFePO_4 and NaFePO_4 , respectively, classical and quantum minimum energy paths are obtained using the nudged elastic band (NEB) method and a novel path-integral based three dimensional wavefunction method.

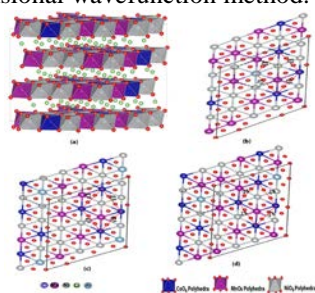


Figure 1

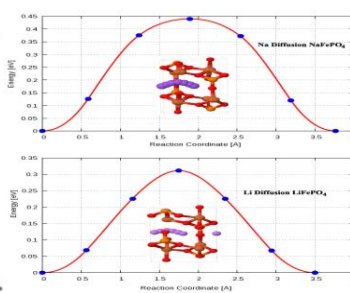


Figure 2

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Solar Absorptive Coating for High Temperature Receivers of Modern Solar Power Systems and Stirling Engines

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Efficient photo-thermal conversion of solar energy requires effective surface adsorptive coatings in the wavelength range between 0.3 and 2.5 μm . Solar absorptive coatings developed up to now characterized with excellent adsorptive characteristics, however, only at operation temperature below 500°C. Operation in atmospheric conditions at temperature above 500°C significantly reduces efficiency of solar absorption. The higher temperature and longer operation is the lower efficiency of solar adsorption.

New generation of adsorptive coating with efficient solar adsorption above 650°C for long term operation was developed in our laboratory. For coating formation we used the micronized Co oxide powders with spinel structure, Al oxide and glass frit. The coating can be deposited on substrate surface by electrochemical co-deposition or spraying.

The procedure of coating fabrication includes several consecutive steps: a) texturing substrate surface (in our case Ni alloy was used as substrate); 2) deposition of the metal oxides and glass frit composition; 3) high temperature treatment for coating bonding to the metal surface. Foam like high temperature solar coating obtained by this procedure is characterized with good solar absorption (~94-95%) and excellent thermal and corrosion resistance. It was established by aging test performed at 750°C for 1105-hr exposure in air atmosphere (BSII ltd.). No coating exfoliations and delamination were detected after high temperature exposure in air environment.

Electrochemical Deposition of Self-Assembled Monolayers and Hydroxyapatite on Orthopedic and Dental Implants Made of Titanium and its Alloys

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Calcium phosphate (CaP) coatings are commonly used for implant fixation. The most commonly used method for producing coatings nowadays is Plasma Spraying, however electrodeposition of these coatings has recently been gaining momentum.

Very few studies reported Self-assembled monolayers (SAMs) which were used as seed layers for the growth of synthetic CaP coatings on metal substrates from solutions resembling body fluids (1-2). Ordinarily, the end group of the monolayer is chosen based on mimicking the biomineralization process *in vivo*. Consequently, several SAMs have been studied; yet, an active discussion is ongoing in the scientific community regarding which SAM is most beneficial. Moreover, to the best of our knowledge, SAMs have never been studied in regards with CaP electrodeposition, which is the novelty of the presented work.

Our study presents electrodeposition of CaP under near-physiological conditions on SAMs covered titanium. We found that different SAMs covered surfaces electrodeposited with CaP exhibit different surface morphologies, while maintaining the same phase content and level of crystallinity. The latter may have substantial influence on the performance *in vivo* – lower crystallinity results in higher solubility, and possibly – enhanced osseointegration on the short term. The use of different SAMs resulted in different values of adhesion strength.

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Monitoring Low Concentrations of Hg(II) in Water Using Gold Nanoparticles

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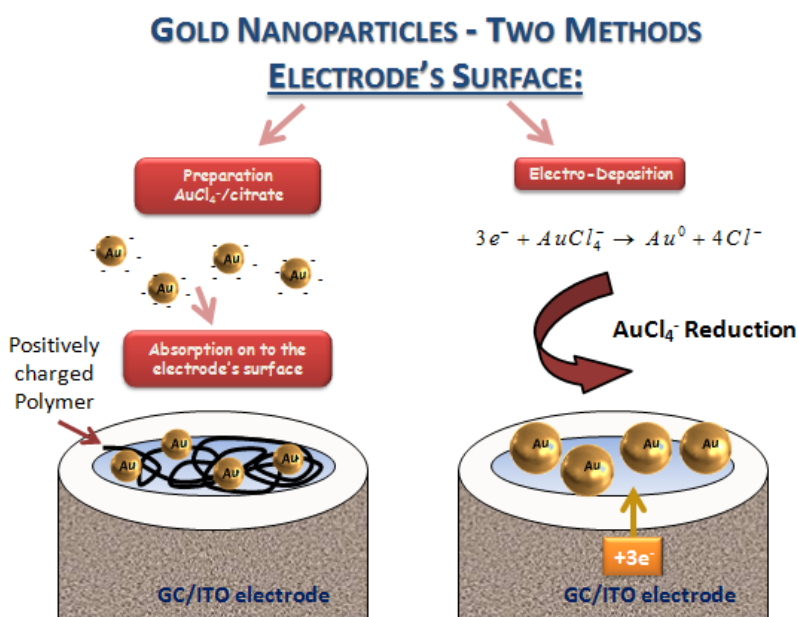
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Water is the most basic source of life for all known creatures and covers nearly 70% of the earth's surface. Mercury is a heavy metal that contaminates the water and is often accumulated throughout the food chain, thus posing a serious threat to the environment, animals and humans by causing damage to the brain, heart, kidneys, lungs and the immune system.

The aim of our research is to develop a simple and reliable sensor for very low levels of mercury in aquatic systems (ppt). This is achieved by modifying both glassy carbon (GC) and indium tin oxide (ITO) electrodes with gold nanoparticles (AuNPs). The determination of Hg on a glassy carbon and ITO electrodes gives sharp anodic peaks; however, these signals are not always reproducible, presumably due to the roughness and inhomogeneity of the surface. Hence, AuNPs are expected to serve as nucleation sites for the reduction and deposition of mercury.

We have tested two approaches for depositing AuNPs onto an electrode surface. The first involves the preparation of AuNPs dispersed in a solution as a result of reducing AuCl_4^- in the presence of citrate. Both electrodes, i.e. GCE and ITO are dipped into a solution of a positively charged polymer, polyethylenimine (PEI). This is followed by the electrostatic attachment of the AuNPs onto the modified electrodes. The second method comprises the electrodeposition (reduction of) of AuCl_4^- on the electrode. The figure below shows both approaches schematically.

Detection of Hg(II) is carried out using both anodic stripping voltammetry (ASV) and cyclic voltammetry (CV). The sensor is planned to be applied in real-world aquatic systems for monitoring the levels of mercury.



P-18

Ionic interaction in citrate electrolyte for deposition of Re-Ni alloys and the mechanism of deposition process

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Coatings of rhenium and its alloys are interesting for high temperature and electronic applications as well as in catalysis [1]. The coatings of Re-Ni alloys were electrodeposited with high (up to 93 %) Faradaic efficiency (FE), while the FE for deposition of pure Re did not exceed 7 % . Although the catalytic effect of Ni in the mechanism of induced co-deposition of Re in citrate electrolytes was shown [2], simultaneous electrodeposition of Re and Ni facilitated by interaction of perrhenate, nickel and citrate species in the electrolyte could not be excluded [3].

The aim of the present work is to shed further light on the mechanism of induced co-deposition of Re-Ni alloys from electrolytes containing citrate. We studied the deposition of Re-Ni in stagnant and stirred electrolytes of different compositions at different deposition times and pH. The observed features of the process were considered in terms of simultaneous Re and Ni deposition as a result of weak ionic interaction in electrolytes. The interaction of perrhenate ion and nickel - citrate complex in the electrolytes was studied using Conductometry, UV-Vis and Raman spectroscopy.

The FE of the deposition process and the composition of the deposits were determined. Increasing the concentrations of either the nickel or the perrhenate ion in the electrolytes was shown to enhance the rate of deposition of the Re-Ni alloy. The process is influenced by mass transport and deposition conditions. No evidence of the existence of perrhenate complexes with other components of the electrolyte was found. The increased deformation of the perrhenate ions with increasing molar ratio of nickel-citrate complex / perrhenate ion was clearly shown by Raman spectroscopy. Hence, a weak interaction is definitely observed, which is enough to distort the shapes of the perrhenate ion and nickel - citrate complex, thus enhancing the deposition rate of the Re-Ni alloy. The induced co-deposition is believed to be a catalytic process, including the stage of simultaneous reduction of perrhenate ion and nickel - citrate complex, which influences each other by weak interaction.

[1] A. Naor, N. Eliaz, E. Gileadi, S.R. Taylor, Properties and applications of rhenium and its alloys, *The AMMTIAC Quarterly* 5(1) (2011) 11

[2] A. Naor, N. Eliaz, and E. Gileadi, Electrodeposition of rhenium–nickel alloys from aqueous solutions, *Electrochim. Acta* 54 (2009) 6028

[3] O. Berkh, N. Eliaz, and E. Gileadi, The Initial Stages of Electrodeposition of Re-Ni Alloys, *J. Electrochem. Soc.* 161(5) (2014) D219

TiH₂ BM as a Substrate Material for Platinum Nano-Catalyst in PEM Fuel Cells

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Polymer Electrolyte Membrane Fuel Cells (PEMFC) is one of the leading low cost technologies for automotive applications. Platinum catalyst is the active material in the cathode which is posing the greatest challenge towards commercialization of PEMFC. Some of the main reasons relate to limited stability over time of Pt/C particles at high potentials (above 0.6V) and oxidizing environment. The automobile industry set as a target of 5000 hours of continuous work of the cell to be achieved in the next following years.

Many studies have shown that the degradation mechanism is caused by the carbon corrosion and the Pt particles agglomeration and dissolution¹.

In this research, the TiH₂ was examined as a Platinum support material prepared by BM (ball milling) synthesis at different milling times (2-8 hours). Preliminary results have shown that TiH₂ possess some unexpected properties including low resistivity, high BET surface area, thermal stability in oxidizing O₂ atmosphere and good stability in high concentration of acid solution and high potentials. In addition, TiH₂ is nontoxic and inexpensive material.

From obtained electrochemical results it appears that higher reduction current and onset reduction potential were observed in the nano-particles that were milled for shorter times. This is probably attributed to the larger surface area of these particles and their smaller size. SEM images of the commercial and the ball milled particles show some of the effects of the milling in terms of particle size and agglomeration. XRD measurements assure the fact that there are changes in the lattice parameters and crystal structure probably due to the lack of homogenization in the ball milling process². ECSA of the Pt/TiH₂ BM was lower than Pt/TiH₂ Commercial one probably due to better dispersion of the latter. From thermal analysis it has been seen that decomposition temperature shifts to lower values with respect to smaller particle size that was obtained². Another important issue that is related to the ball milling process is the hydrogen content in the milled particles that was lower compared to the commercial ones.

¹Xingwen Yu , Siyu Ye, Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC, Part II: Degradation mechanism and durability enhancement, of carbon supported platinum catalyst, Journal of Power Sources 172 (2007) 145–154.

²V. Bhosle, E.G. Baburaj, M. Miranova, K. Salama, Dehydrogenation of TiH₂, Materials and Engineering A356 (2003) 190-199.

Nitrogen doped vertically aligned carbon nanotube carpets: An effective oxygen reduction catalyst in alkaline medium

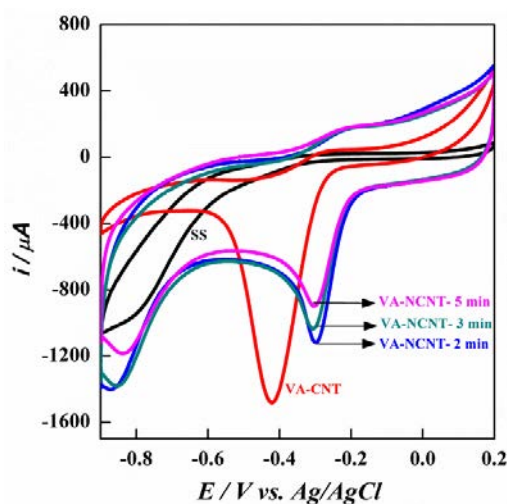
Asaf Cohen¹, Palaniappan Subramanian¹, Alex Schechter*¹, Daniel Nessim², Eti Teblum²

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A simple and rapid procedure to prepare nitrogen-doped vertically aligned carbon nanotube carpets (VA-NCNTs) is reported. The VA-NCNTs were obtained by nitrogen plasma treatment of vertically aligned multi-walled carbon nanotube carpets (VA-CNTs) grown on stainless steel substrate by chemical vapour deposition. This novel electrochemical interface reduces oxygen in lower over potential under basic condition (onset of -0.12 V vs.Ag/AgCl at pH 13) when compared to untreated VA-CNTs condition (onset of -0.22 V vs.Ag/AgCl at pH 13). The robustness of these nanostructures and ease of formation makes VA-NCNTs a promising non-platinum oxygen reduction catalyst that could be employed during real time alkaline fuel cell operation.



POSTER SESSION

- P-01 Electrochemical reduction of CO₂ in ionic liquids using catalytic graphene-metalloporphyrin systems,**
A. Nissim^[1], E. Korin^[2], I. Zilbermann^[1], A. Bettelheim^[2]
[1] Nuclear Center NEGEV, POB 9003 Beer Sheva, Israel
[2] Department of Chemical Engineering, Ben – Gurion University of the Negev, Beer – Sheva, Israel
- P-02 A One-Pot Anodic Thiocyanation of Alkenes**
A. Levi, J.Y. Becker
Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva 841050
- P-03 Structure-property relationship in integrated cathode materials for lithium rechargeable batteries**
C. Ghanty^a, S.B. Majumder^b, B. Markovsky^a, D. Aurbach^a
^a*Department of Chemistry, Bar-Ilan University, Ramat Gan, Israel-52900*
^b*Materials Science Centre, IIT Kharagpur, India-721302*
- P-04 The role of surface chemistry in carbon electrodes for Li-Oxygen systems**
D. Sharon, D. Hirshberg^{*}, M. Efri, A. Frimer and D. Aurbach,
Department of Chemistry Bar Ilan university, Ramat Gan 52900
- P-05 Imaging of Ink-Jet Printed Multi-Enzyme Micro-Arrays on Glass by Scanning Electrochemical Microscopy**
E. Gdor, S. Shemesh, S. Magdassi and D. Mandler
Department of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel, 91904
- P-06 Electrodeposition of graphene oxide on electrodes and their application in electrochemical energy devices**
H. Avraham^{1,2}, E. Korin², A. Bettelheim²
¹*Nuclear Research Center NEGEV, POB 9003 Beer-Sheva, 058-6419044*
²*Ben Gurion University – NEGEV, Chemical Engineering Department*
- P-07 Ru-Co-Se Novel Pt-free Catalysts for Oxygen Reduction in Fuel Cells and Metal Air Batteries**
H. Teller, S. Rosenfeld, and A. Schechter, *Department of Biological Chemistry, Ariel University Ariel, 40700, Israel*

- P-08 Advanced Multiphase Silicon-Based Anodes for High-Energy-Density Li-Ion and Li-air Batteries**
K. Goldshtein¹, K. Freedman¹, Dan Schneier¹, D. Golodnitsky^{1,2}, and E. Peled¹
1 – School of Chemistry; 2 - Wolfson Applied Materials Research Center, Tel Aviv University, Tel Aviv, 69978
- P-09 Ohmic to Overlimiting Ion-Current Rectification Inversion in Funnel-Shaped Nanochannels**
L. Rosentsvit and G. Yossifon, *Faculty of Mechanical Engineering, Micro- and Nano-Fluidics Laboratory, Technion – Israel Institute of Technology, Technion City 3200000, Israel*
- P-10 Electrochemical Reduction of Indium Tin Oxide (ITO): Prevent and Use**
L. Liu^{1,2}, S. Yellinek¹, I. Valdinger¹, D. Mandler^{1,*}
¹*Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
²*School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore*
- P-11 Ni_xCo_yO_z Catalst for ORR and OER for Sodium Air Battery**
E. Faktorovich Simon¹, M. Goor, R. Hadar, Diana Golodnitsky, Emanuel Peled, *School of Chemistry, Tel Aviv University*
Tel Aviv University, Orenshtein building 206
- P-12 Electrodeposition of an Asymmetric Film Using Langmuir and Langmuir-Blodgett Techniques**
M. Hitrik, D. Mandler and O. Lev, *Institute of Chemistry, the Hebrew University of Jerusalem, Jerusalem 91904, Israel*
- P-13 Solid State Oxidation of Copper Nanoparticles. A Plasmonic Perspective.**
M.D. Susman, A. Vaskevich, I. Rubinstein, *Department of Materials and Interfaces, Weizmann Institute of Science, 234 Herzl St., Rehovot 76100, Israel*
- P-14 *Ab initio* study of cathode materials for lithium ion batteries**
M. Dixit, H. Engel, M. Kosa and D.T. Major, *Department of Chemistry and the Lise Meitner-Minerva Center of Computational Quantum Chemistry, Bar-Ilan University, Ramat-Gan, Israel*
- P-15 Solar Absorptive Coating for High Temperature Receivers of Modern Solar Power Systems and Stirling Engines**
N. Sezin, D.Starosvetrsky and Y. Ein-Eli, *Department of Materials Science &Engineering, Technion-Israel Institute of Technology, Corrosion and Applied Electrochemistry laboratory*

P-16 Electrochemical Deposition of Self-Assembled Monolayers and Hydroxyapatite on Orthopedic and Dental Implants Made of Titanium and its Alloys

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P-17 Monitoring Low Concentrations of Hg(II) in Water Using Gold Nanoparticles

N. Ratner and D. Mandler, *Institute of Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel*

P-18 Ionic interaction in citrate electrolyte for deposition of Re-Ni alloys and the mechanism of deposition process

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P-19 TiH₂ BM as a Substrate Material for Platinum Nano-Catalyst in PEM Fuel Cells

Y. Moshe, O. Krichevski, A. Schechter, *Department of Biological Chemistry, Ariel University Ariel, 40700, Israel*

P-20 Nitrogen doped vertically aligned carbon nanotube carpets: An effective oxygen reduction catalyst in alkaline medium

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P-21 Electroless Local Deposition of Anisotropic Metal Nanoparticles Using Scanning Electrochemical Microscopy (SECM)

R. Fedorov, D. Mandler, *Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

P-22 Novel 3D Electrochemical Touch-Sensor for Cell and Tissue Diagnostics

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¹*Department of Physical Electronics, Tel-Aviv University,*

²*Department of Molecular Microbiology and Biotechnology, Tel-Aviv University*

- P-23 Anodic Oxidation of N-Acylazacycloalkanes in Methanol**
T. Golub and J.Y. Becker, Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, 8410501, Israel
- P-24 Study of spin-orbit coupling and its impact on magnetism in olivine-type $\text{LiCo}_{1-x}\text{Fe}_x\text{PO}_4$ cathode materials: Insight from first principles**
V. Singh, M. Kosa, Y. Gershinsky, D. Zitoun, D.T. Major*
Department of Chemistry and the Lise Meitner-Minerva Center of Computational Quantum Chemistry and the Institute for Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel
- P-25 Impedance Spectroscopy Analysis of SOFC using Evolutionary Programming**
Z. Drach, S. Hershkovitz, S. Baltianski, Y. Tsur, *Department of Chemical Engineering, Technion- Israel Institute of Technology Technion, Haifa 32000, Israel*
- P-26 Electrochemical Determination of Low Levels of Uranyl by a Vibrating Gold Microelectrode**
Yael Peled^{1,2}, Haim Tobias² and Daniel Mandler¹
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²Chemistry Department, Nuclear Research Centre-Negev, Beer Sheva 84190, Israel

Novel 3D Electrochemical Touch-Sensor for Cell and Tissue Diagnostics

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3D integration allows vertical stacking of electronic, electrochemical, and other micro-system technologies. In this work we present a novel concept combining flexible electrochemical sensor with a unique 3D architecture allowing measurement in contact, or in close proximity with a tested target on one side of the sensor while the electrical interface is on the opposite side. Such device, designed for biomedical systems, offers some unique measurement opportunities compared to the conventional 2D electrodes.

The flexible chip consists of a biocompatible substrate comprises of an electrochemical cell with two gold electrodes (working and counter) and an Ag/AgCl quasi-reference electrode. The metal electrodes are fabricated by conventional electroplating and patterning methods. The electrical communication between the bio-chip front and backside was enabled by through-hole via contacts fabricated by cast molding. The via-contacts were filled with conductive PDMS containing 60 wt% graphite powder.

The chip performance was verified by two methods: a. electrochemical characterization of the redox behavior of ferricyanide/ferrocyanide couple in a cyclic voltammetry analysis and b. electrochemical detection of an enzyme-substrate interaction. The 3-D sensor exhibited stable voltammetric signatures in repeated tests. This approach paves the way to perform direct, non-invasive diagnostics performed on top of an exposed cell layer for both *in-vivo* and *in-vitro* applications.

[1] R. Popovtzer, A. Natan, Y. Shacham-Diamand, J. Electroanal. Chem. 602 (2007) 17.

[2] S.Vernick, A. Freeman J. Rishpon, Y. Niv, A. Vilkin, Y. Shacham-3D like. Proper column and margin measurements are indicated.

Anodic Oxidation of N-Acylazacycloalkanes in Methanol

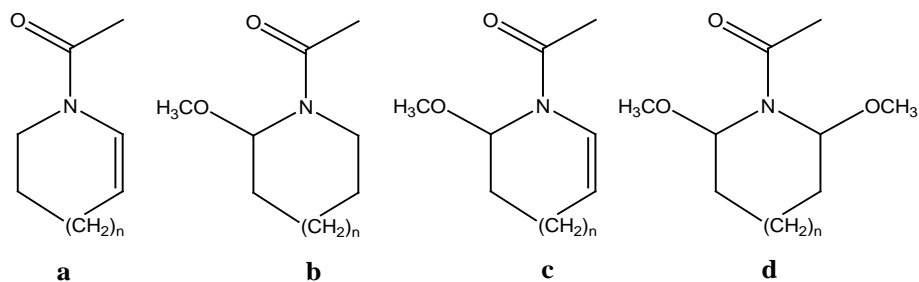
Tatiana Golub and James Y. Becker

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Anodic oxidation of N-monoalkylamides in the presence of nucleophiles such as water, alcohol or carboxylic acid, affords the respective α -hydroxy, -alkoxy or -carboxy derivatives as final products [1]:



The present work describes the electrochemical properties of three cyclic amides of the type N-acylazacycloalkanes (5-, 6- and 7-membered rings) by cyclic voltammetry in acetonitrile and preparative electrolysis in methanol. In principle these three cyclic amides can undergo a double functionalization. The outcome at C anodes under various electrochemical conditions (current density, electricity consumption and supporting electrolytes) indicates that four major products were formed by all three substrates: cyclic eneamide (**a**), α -methoxy, cyclic α -eneamide (**c**), α -methoxy- (**b**) and α,α -dimethoxy (**d**) cyclic amides (Scheme). Their relative ratio was found to be highly dependent on the nature of the electrolyte used and current density [2]. A plausible mechanism of formation of products will be discussed.



Scheme. Type of products (n=0, 1, 2)

1. H. Lund, M. M. Baizer, Eds., "Organic Electrochemistry: an Introduction and a Guide", 3rd ed, Dekker, New York, 1991, pp. 602-603.
2. T. Golub, J. Y. Becker, Anodic Oxidation of N-Acylazacycloalkanes in Methanol. *J. Electrochem. Soc.*, 160 (7), G5 (2013).

Study of spin-orbit coupling and its impact on magnetism in olivine-type $\text{LiCo}_{1-x}\text{Fe}_x\text{PO}_4$ cathode materials: Insight from first principles

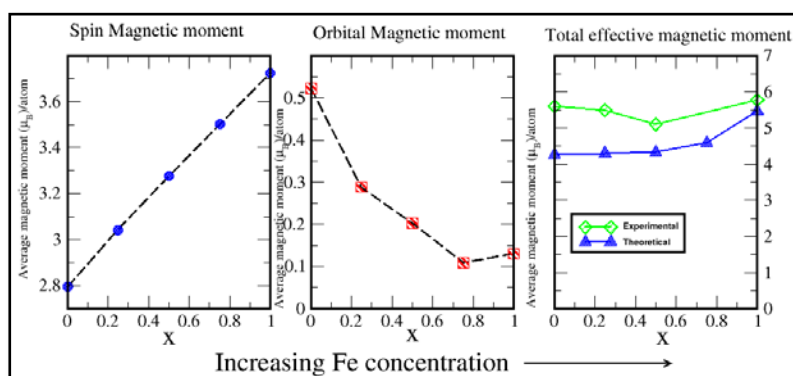
Vijay Singh, Monica Kosa, Yelena Gershinsky, David Zitoun, Dan Thomas Major*

Department of Chemistry and the Lise Meitner-Minerva Center of Computational Quantum Chemistry and the Institute for Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 52900, Israel

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Current research in the field of lithium-ion batteries focuses on the improvement of energy-density and power-density. One possible solution to increase the battery performance is the use of high voltage cathode materials with a large charge and cycling capacity. LiCoPO_4 (LCP) olivine is an interesting candidate as a high voltage cathode material for lithium ion cells due to its high working potential (4.8V vs Li/Li^+). However, poor electronic conductivity and the low Li-ion diffusion coefficient put a constraint in its practical application. On the other hand, LiFePO_4 (LFP) is today a mature material and its properties have been largely optimized, therefore opening the door to its commercial exploitation.

In the recent year, the attention of the scientific community is focusing the possible advantage of forming mixed olivine materials, obtained by substitution of Fe in LCP or Co in LFP. This might open the door to large improvements in the energy- and power density performance. In the view of the above, we have studied olivine type $\text{LiCo}_{1-x}\text{Fe}_x\text{PO}_4$ compounds using first principle theory, where $x=0.00, 0.25, 0.50, 0.75, 1.00$. All calculations were performed using density functional theory (DFT) implemented in the Vienna Ab-initio simulation package (VASP). Some of the initial results will be discussed here. For example, we have found that in the LCP system, Co^{2+} exhibits strong orbital moments, which significantly get quenched by the substitution of Fe in the place of Co. This may lead to a quality improvement in the electronic conductivity of the LCP. Therefore, the primary focus of the present work will be the role of the spin-orbit coupling (SOC) and its impact on the magnetism of Fe substituted LCP. This study may help to engineer an effective cathode material for use in the field of lithium ion battery.



Electrical and Electrochemical Microsensors using Molecularly Imprinted Polymers (MIP)

Tehila Shahar, Daniel Mandler*

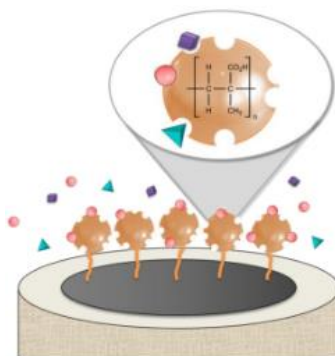
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The essence of this project is to develop microsensors with improved selectivity based on molecularly imprinted polymers (MIPs) integrated in either a microelectronic transducer on silicon or as an electrochemical sensor by electrode modification. The selective binding of different model compounds alters the interfacial physical properties in the case of the electronic sensor, i.e. conductivity and/or impedance, and is thus the basis of signal transduction. In the electrochemical sensor, the electroactive analyte will be detected via voltammetric analysis methods, i.e. cyclic voltammetry and linear sweep voltammetry.

The development of the chemical interface involved in the recognition event requires the synthesis of MIPs by radical polymerization of acrylic precursors in the presence of the template, e.g. Sudan or catechol derivatives. The MIPs are prepared as spherical nanoparticles in order to enlarge the surface to volume ratio, which improves electron transfer and enhance recognition site accessibility, thus increasing the signal obtained. To fully understand the system, various experimental parameters such as cross linker and solvent type and concentrations, solution volume and vessel shape, were examined. Consequently, particles size and polydispersity can be controlled, resulting in a minimal diameter of 10 ± 1 nm. To confirm the presence of the analyte inside the MIPs, the MIPs were washed to remove the template, and then examined by numerous characterization techniques, such as XPS, visible absorption, FTIR and Raman spectroscopy. The selective uptake of the analyte is currently examined. Finally, the chemical interface was coupled with microelectronics and electrochemical interfaces by immobilization of the MIPs particles onto the substrate, for example, using silane chemistry in the case of silicon surfaces.

We intend to optimize the MIP sensor in terms of sensitivity, selectivity, time response, range of linearity, reproducibility (precision) and accuracy.



Schematics of the MIP integrated electrochemical sensor

Electrochemical Determination of Low Levels of Uranyl by a Vibrating Gold MicroelectrodeYael Peled^{1,2}, Haim Tobias² and Daniel Mandler¹¹The Institute of Chemistry, the Hebrew University of Jerusalem, Jerusalem 91904, Israel²Chemistry Department, Nuclear Research Centre-Negev, Beer Sheva 84190, Israel**Abstract**

In this work we report on the development of a new approach for the electroanalytical sensing of uranium(VI) in aqueous solutions. Uranium commonly exists in aqueous solutions in the form of its oxo ion, uranyl ($\text{U}^{\text{VI}}\text{O}_2^{2+}$). The detection of uranyl has been accomplished by us through its deposition upon reduction by two electrons to the insoluble UO_2 using a bare disk gold macroelectrode and anodic stripping voltammetry (ASV). This gave unsatisfactory detection limit of *ca.* $1 \cdot 10^{-5}$ M uranyl. Moreover, the evolution of hydrogen bubbles blocked the electrode surface as a result of water reduction at negative deposition potential (-0.7 V *vs.* Ag/AgCl). Hence, we used a bare gold microelectrode of 25 μm diameter on which the uranium precipitated at negative potential (-1.2 V). The results were encouraging due to enhanced mass-transport that increased substantially the current density; however, the sensitivity was still insufficient (*ca.* $1 \cdot 10^{-6}$ M uranyl). To improve the detection limit, we have introduced a vibrating microwire as a working electrode in ASV. The vibration reduces significantly the diffusion layer (~ 2 μm) during the deposition step and therefore increases the amounts of UO_2 deposition. Vibration of the microelectrode was achieved by attaching a standard speaker (1 W, 8 Ω) to the working electrode. Using a 5 min deposition time, -1.2 V deposition potential and vibrating the electrode at frequency of 250 Hz and amplitude of 6 V, a detection limit of *ca.* $1 \cdot 10^{-9}$ M of uranyl was achieved.