TALK 1

Electrodeposition as an universal tool for making metallic surfaces slippery

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A simple, nontoxic and inexpensive method to prepare mechanically robust surfaces that repels a variety of liquids and solids has immediate relevance in many industrial applications. Unwanted interactions between liquids and surfaces are currently a limiting factor nearly everywhere liquids are handled or encountered. Most state-of-the-art liquid repellent surfaces are modeled after lotus leaves, which are known to exhibit superhydrophobicity and self-cleaning. Despite over a decade of research, these surfaces are still plagued with problems that restrict their practical applications.

Recently, the slippery liquid-infused porous surfaces (SLIPS) technology was introduced by our group. SLIPS technology is inspired by the *Nepenthes* pitcher plant and provides unique capabilities that are unmatched by any other liquid-repellent surface technologies. SLIPS surfaces function under high pressure conditions, instantly self-heal imperfections, provide optical transparency, repel ice nucleation, and are ultra-repellent to pure and complex fluids such as blood, crude oil, and brine. They also repel solids such as ice and wax. These properties allow the slippery surfaces to be used in a wide variety of applications and environments. Moreover, the slippery surfaces can be constructed from a broad range of simple, inexpensive materials without the need for specialized fabrication facilities.

Here we used a stainless steel, which is widely used in biomedical, household and industrial equipment, surgical instruments, kitchen appliances, transport and architecture, as a substrate. We use an inexpensive and environmentally friendly electrodeposition process to form a thin layer of nanostructured tungsten bronze. Such films are mechanically robust and can be functionalized to increase its hydrophobicity, ideal for integration with SLIPS technology. Moreover, electrochemical deposition provides various control parameters for optimization of the film morphology. We will present that slippery stainless steel surfaces can be optimized to repel simple and complex fluids, reduces ice formation, accelerates frost removal and prevent adhesion of biofilms.

Water Splitting by Artificial Photosynthesis Using Iron Foam Photoanodes Coated with Catalytic Self-Assembled Graphene-Manganese Porphyrin Structures.

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Photoelectrochemical (PEC) water splitting, also called artificial photosynthesis, is one way to produce clean hydrogen using solar energy to split water into oxygen and hydrogen gases. The main challenge in PEC field deals with low current densities of the photoanode. Today's conventional approaches to increase current densities are directed towards improving semiconductor (e.g. hematite) properties, increasing the active surface area of the electrode and adding known water splitting co-catalysts.

The present work deals with the characterization of porous iron foams as photoanodes, instead of the mostly used planar transparent electrodes. The iron foams can be coated by a thin hematite layer by a simple heat treatment procedure. The performance of these electrodes is significantly increased by doping with silicon, Co(II) ions, and macrocyclic catalysts. The iron foams electrodes yield efficient photocurrents for water splitting in the range of ~ 0.2-0.4 mA/cm² at 1.23 V vs. NHE.

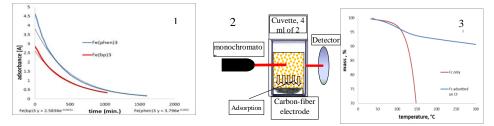
Anionic carboxylic-rich graphene oxide (CGO) and cationic Mn(III) tetrakis(N-Methyl-4-Pyridinium) porphyrin (MnTMPyP) form self-assembled leaflike structures. These are obtained through electrostatic and π - π stacking interactions, as indicated by the red shift of the metalloporphyrin Soret band throughout the 6-12 pH range. When exploited for the photoelectrochemical oxidation of water, CGO-MnTMPyP films on iron/hematite foams exhibit substantial activity as evidenced by the current density (0.54 mA/cm² at 1.23 V vs. NHE) and IPCE (9.0 % at 1.43 V vs. NHE) measured at pH 10.

Metal Organic Complexes as Redox Candidates for Carbon Based Pseudo Capacitors

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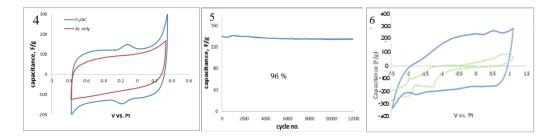
We present metal organic complexes (MOC) as a new type of redox active materials for pseudo capacitors. The consept of this work is the suitability if aromatic ligand to bond strongly to the graphitic-like activated carbon electrode. Additionaly, the MOC have the ability to preduse pseudocapacitance in both anodic (ligands) and cathodic (metals) sides.

The adsorption of three iron complexes, Ferrocene (Fc), iron-tris-bipyridin and irontris-phenanthroline (Ferroin) with different size of aromatic ligands on activated carbon electrodes was done in several methods. In the wet rout we could measure the degree of adsorption via UV-vis photospectroscopy (Fig. 1,2). We approved that the strength of the bond increases with the size of the carbonaceous ligand. Thermo Gravimetric Analysis of the composited electrodes confirmed our approach (Fig. 3).



The dry method for adsorption was done by vapoting the complex on activated carbon fibers (ACF) electrodes.

After optimization, high specific capacitance was measured with composite activated carbon electrodes containing ferrocene (143 F/g) in neutral aqueous solutions (Fig. 4,5) and ferroin (315 F/g, Fig. 6) in non-aqueous solutions. The latter systems exhibit a 370% gain in capacity due to the adsorption of the redox compound on the surface of the activated carbon electrodes. These systems demonstrated very good stability during more than 12,000 cycles and also exhibited high rate capability.



Li-S cathodes with extended cycle life by sulfur encapsulation in disordered micro-porous carbon powders

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Sulfur cathodes have excellent theoretical properties for use as positive electrodes in rechargeable lithium batteries, but lack long-term stability required of practical secondary battery systems. To deal with this issue, high capacity Lithium-Sulfur cathodes were prepared through sulfur impregnation of disordered micro-porous carbon powders that have high surface-area. By using microporous carbon as a matrix for sulfur cathodes and lithium nitrate as an additive to the electrolyte solution, that suppresses the shuttle phenomena in Li-sulfur batteries, we managed to achieve a reversible capacity of over 500mAh/g for 1000 cycles with a Columbic efficiency approaching 100% throughout cycling. The influence of the volume of the electrolyte solutions in Li-S cells was further evaluated by analyzing their voltage profiles during cycling.

Aluminum Activation in Ionic Liquids

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Abstract

Aluminum (Al) is the third most abundant element (after oxygen and silicon) and the most abundant metal in Earth's crust. Al is quite remarkable as it holds a low density and it has the ability to resist corrosion due to the passivation phenomenon. Structural components made from Al and its alloys are vital to the avionic and aerospace industry and are important in other areas of transportation and structural materials.

Aluminum is covered with a pristine passivating oxide (Al₂O₃), which protects Al from corrosion in a relatively wide range of pH and potentials. This passivating film is vulnerable in both highly acidic and basic environments, leading to rapid corrosion reactions. Due to its passivating nature and the naturally grown oxide film, Al metal is being used in Li ion batteries as a cathode current collector, enabling the operation of the batteries up to a potential of 4.5 V. The theoretical gravimetric capacity of Al metal is 2.98 Ah/g and its volumetric capacity is as high as 8.1 Ah/cm³. For the sake of comparison, Li metal holds capacities of 3.86 Ah/g and 2.06 Ah/cm³, respectively. The challenge we are currently facing is whether it is possible to use Al metal as an anode in a battery for Post Li-ion era? Al-air cells are well known and the challenges in activating Al in alkaline media are quite substantial (corrosion, water uptake, interaction with the environment...). In the presented work our initial results on activation of Al metal in ionic liquids will be discussed, without compromising its corrosion resistivity.

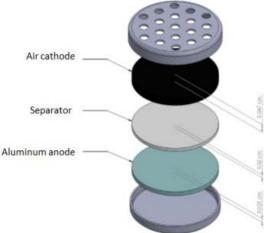
Talk 6 Novel Aluminum Air Ionic Liquid Based Battery

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The changing and expanding needs in the energy market, ranging from power grid energy storage systems to portable power sources, dictates the development of efficient, inexpensive, and high performance battery systems. These advanced electrochemical systems should better deal with the challenges posed by the nascent green economy and non-oil based transport systems. One of the promising avenues for achieving these goals is the development of battery systems based on aluminum (Al) and its alloys as anodes. The main advantages of such systems are the low equivalent weight of Al, its high natural abundance in the earth's crust, (leading to a rather low price), and its safety characteristics. In addition, Al and its by-products are non-toxic and environmental friendly. Aluminum battery systems cover a wide range of applications; from field-portable emergency power supply to remote power applications and batteries for transportation. Theoretically Al contains approximately one-half the energy content of gasoline per unit weight (8,100 Wh/kg for Al-air and 13,000 Wh/kg for gasoline) and three times the energy per unit volume (21,870 Wh/l for Al-air and 9,700 Wh/l for gasoline). Currently, the best practical utilization of gasoline for automotive applications can reach approximately 1,700 Wh/Kg and for aqueous Al-air batteries the values are 300-500 Wh/Kg. Nevertheless, the utilization of Al-air batteries as a sustainable energy storage device is hampered by some severe problems. High corrosion rate of the Al anode in aqueous alkaline solution is of great concern in terms of Al utilization and safety. On the other hand, Al surface activation is somewhat problematic in nonaqueous electrolytes, limiting substantially the possibility to utilize any power output. In this study, a newly developed non-aqueous Al-air battery is presented. The battery configuration utilizes 1-ethyl-3-methylimidazolium oligo-fluorohydrogenate $(EMIm(HF)_{2,3}F)$ room temperature ionic liquid (RTIL). The battery shows the ability to sustain current densities up to 1.5 mA/cm², producing a capacity of 140 mAh/cm² and thus, utilizing above 70% of the theoretical Al capacity. This is equivalent to an outstanding energy densities of 2,300 Wh/Kg and 6,200 Wh/L. Al₂O₃ is detected at the air electrode as the battery discharge product, being the main cathodic reaction of oxygen reduction coupled with Al ions migrated to the air electrode.

* Equally contributed to the presented study



Talk 7 FIRST-PRINCIPLES CLASSICAL AND QUANTUM STUDY OF CATHODE MATERIALS FOR RECHARGEABLE BATTERIES

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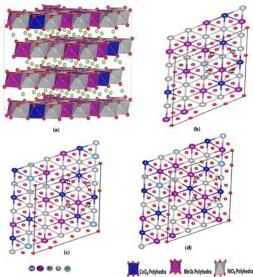
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Reducing our dependence on fossil fuels is one of the greatest challenges facing our society today. A move toward efficient alternative energy sources is of primary concern and requires significant scientific and technological advances. Rechargeable batteries, and in particular Li-ion batteries, constitute one of the most promising renewable energy sources. Due to the higher energy densities, lithium ion batteries are now being pursued intensively for large scale applications such as electric vehicles. In particular, lithium transition metal phosphate compounds, LiMPO₄ (M=transition metal), and Ni-rich layered compounds, are promising cathode materials.¹

Crucial features of Li-based batteries, such as high energy densities, high power density, and good safety features may readily be defined in terms of microscopic quantities, thus facilitating their theoretical prediction using state-of-the-art modeling techniques. Especially, density functional theory (DFT) is a popular quantum mechanics based approach to tackle solid state problems. This serves as a relatively inexpensive, yet powerful research tool which might significantly reduce the time needed to identify promising materials. In order to understand the behavior of mixed transition metal materials such as LiMPO₄, M = [Fe,Mn, Co], and LiM'O₂ M'=[Ni, Co, Mn], we have carried out a series of studies in which the effect of the cathode material composition on cell potential, the electronic and magnetic structure, and stability was addressed. Experimental redox potentials and magnetic properties are in line with our calculations, suggesting that mixed systems exhibit binary system properties. Additionally, we address the question of the nature of lithium ion mobility in cathode materials. To this end, we employ a novel method for solving the three-dimensional wavefunction for a lithium-ion, based on a DFT potential. Surprisingly, we find that lithium displays significant nuclear quantum behavior. This is in contrast to the classical behavior of sodium, which is a much heavier ion.

References:

 Osnis, A.; Kosa, M.; Aurbach, D.; Major, D. T. A systematic first-principles investigation of mixed transition metal olivine phosphates LiM_{1-y}M'_yPO₄ (M/M'=Mn, Fe, Co) as cathode materials. J. Phys. Chem. C 2013, 117, 17919–17926.



Determination of Hydraulic Power Losses in Vanadium Redox Batteries Based on Experimental Analysis of Electrolyte Flow through Carbon Felt of Electrodes

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Energy generation from alternative technologies, such as wind turbines (WT) and solar photovoltaic (PV) has been greatly increased in the past decades. Significant output power fluctuations are typical for non-conventional sources having negative impact on total grid reliability and energy costs. The possible solution for preventing named shortcomings is to integrate alternative power sources with energy storage systems (ESS).

Vanadium Redox Flow Battery (VRB) represents a significant opportunity for future ESS. Main expectations of VRB relate to its prolonged service life, outstanding dynamic response and flexible controllability during charge/discharge processes. Nevertheless, VRB suffers of relatively significant hydrodynamic problems that are related to the need of a constant electrolyte pumping through battery cells. The typical cell of VRB consists of two compartments (positive and negative) divided by a proton exchange membrane (PEM). The electrolyte flow across electrodes made carbon felt. It is chosen for electrode's material due to its ability to provide intensive electrochemical reaction owing enlarged external surface and thus a sufficient current (power). The principal volume of electrolyte is stored in two separated external tanks, and it's pumped through both cell's compartments. There are two essential reasons of electrolyte pumping through battery cells. The first one is the restricted solubility of vanadium species in sulfuric acid and as a result, low energy density of electrolyte. The enlarged electrolyte volume may be located outside of the cells only and has to be pumped into the cells by an external mechanical force. Indeed, separation between electrolyte volume and power cells is one of the most significant features of the VRB, which defines the independence and modularity of power (kW) and energy (kWh) ratings. The second reason for electrolyte pumping is the need to diminish concentration polarization effects on the electrode surface that lead to increased internal voltage drop, inferior output and abated battery efficiency. The higher is electrolyte flow the lower are losses due to polarization effects (battery resistance). However, large flow rate increases hydrodynamic losses. Consequently, providing high efficiency of electrochemical reactions by increasing electrolyte flow is accompanied by additional pumping losses. That is why an optimal control of the hydraulic system, may be achieved using correct description of hydrodynamic properties of a carbon felt and accurate representation of battery output power versus electrolyte flow speed and battery State-of-Charge.

Special investigations regarding hydrodynamic properties of carbon felt and influences of electrolyte flow rate on battery output power and internal electrical losses were carried out in the present work. It was confirmed that the structure of carbon felt may be represented as a porous media where electrolyte flow is described by Darcy law. The coefficients of hydraulic felt resistance were obtained. In addition, internal battery resistance as the main reason for electrical losses was described as functionally dependent on electrolyte flow rate and battery State-of-Charge.

The present research work offering a novel approach to development of optimal VRB pumping system. This approach is based on a correct description of hydrodynamic felt properties and battery internal electrical resistance.

High Quality Metallic Grid Preparation on Large Area ITO-Coated Plastic Substrates

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ITO-coated plastic substrates have a variety of applications in solar energy conversion systems, optoelectronic devices, touch panels, flat-panel displays and others. ITO is one of the most used materials for these applications. However, conductivity of ITO is not enough to produce efficient large area devices. The problem can be solved with high conductivity metallic grids embedded in ITO. We propose the electrochemical method for such metallic grids preparation.

We have developed a new electrochemical method to deposit different metals and alloys (e.g. silver, copper, nickel, cobalt) on large area ITO-coated glass and plastic substrates in order to substantially diminish the sheet resistance. Our method is noted by a very high adhesion and Ohmic contact to the ITO. The thickness of metallic layers can be easily controlled, and it can reach few microns without deterioration of adhesion to ITO. The sheet resistance of ITO-PET can be decreased more than in 75 times: from 45 down to 0.6 Ohm/sq and lower by electrodeposited silver or copper meshes. The electrodeposited metallic layers possess dense structure, and therefore relatively low specific resistance.

120 mm*120 mm samples of copper and silver meshes on ITO-PET with sheet resistance of 0.85 Ohm/sq, a uniform metal lines thickness and excellent metal adhesion to ITO were prepared. The width of metallic lines can be smaller than 25 μ m. Optical transmission of ITO with electrodeposited copper or silver meshes diminishes less than 10% in comparison with an initial ITO.

The electrochemical metal plating is the method which is widely used in industry, in high volume production. This method is roll-to-roll compatible (for flexible, plastic based substrates), relatively low cost, high speed and can be performed under ambient conditions. It is direct method, no expensive metal inks are required. Patterning of ITO-PET before the metal electrodeposition was performed by gravure printing with a low cost resist which can be easily removed after electrodeposition.

Based on sol-gel electrophoretic deposition we further developed insulating coating of the metallic grid to avoid electric shorts. This process is performed from transparent solutions under an applied electric field and results in transparent or slightly opaque dense uniform conformal metal oxide coatings on top of metallic layers.

The Effect of Lithium Bis(oxalate)borate and Vinylene Carbonate on the Surface Chemistry of Lithium Ion Battery Electrodes

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Lithium ion battery (LIB) electrodes operate in severe regimes that cause electrolyte breakdown, resulting in the formation of electrode films. On graphitic anodes, this film, the solid-electrolyte interphase (SEI), is extremely important because it protects the graphite from exfoliation during cycling. At cathodes, a stable film can protect the electrolyte from further breakdown that increases cationic resistance through film growth during cycling. SEI films should be stable, as thin as possible, and conductive towards lithium. In recent years much attention has focused on the use of additives such as lithium bis(oxalato)borate (LiBOB) and vinylene carbonate (VC) which can stabilize these SEI films at both electrodes. Our goal is to characterize the films formed from these additives, exploring the organic electrochemistry of LiBOB and VC additives.

Fig. 1 depicts dependence of impedance spectra of an NCM 111 electrode, at 30 $^{\circ}$ C, with standard 3:7 EC:EMC, 1 M LiPF₆, electrolyte and electrolyte with 0.25 wt % LiBOB, and 2 wt % VC added. The impedance spectra show a strong dependence on the composition of the electrolyte as well as the cycle number.

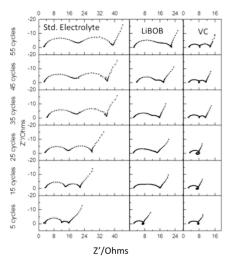


Figure 1: Impdance spectra of different electrolyte systems using std. electrolyte and electrolyte with the additives LiBOB and VC. The cycle number that each spectra was taken is marked on the left of the figure (bottom up).

DEVELOPMENT AND CHARACTERIZATION OF A POLYMER-IN-CERAMIC

BATTERY MEMBRANE

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Ion conducting membranes play a key role in all batteries. The membrane must have high ionic conductivity (either by intrinsic ion-conducting pathways or by soaking in the electrolyte) and electrochemical compatibility with anode and cathode materials. In this work, we report on recent achievements in the development of thin-film hybrid composite polymer-in-ceramic electrolytes for applications in planar- and 3D-battery configurations. The method of electrophoretic deposition (EPD) was used to fabricate the mesoporous membranes. TGA, TOFSIMS, ESEM and AC-impedance tests were used for the characterization of the films. We found that the relative content of polyethylene oxide and $LiAlO_2$ in the membrane depends on the type of solvent, voltage and composition of the suspension. Films deposited at 50V are smoother, conformal and more uniform than those prepared at 100, 150 and 200V. TOFSIMS positive-ion-species images showed that, with increase in concentration of ceramic powder in the suspension, the deposition of PEO occurs predominantly between the LiAlO₂ agglomerates. The ionic conductivity of the novel mesoporous composite membrane with impregnated 0.3M LiTFSI-PYR₁₄TFSI ionic liquid electrolyte is comparable to that of commercial battery separators. The membrane follows the complex contours of the electrodes conformally and provides strong mechanical integrity of the battery. Polymer-in-ceramic membrane is able to prevent high-temperature thermal runaway and significantly improve battery safety, which are important issues in both micro- and macro-battery applications We believe that the composite membrane is likely to serve as a prototype of polymer-inceramic solid electrolyte and to replace liquid electrolytes in lithium/air and lithium/sulfur batteries for high-power, high-energy applications.

Acknowledgement

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Electrochemical Direct diagnosis of Cancer and Monitoring of Anti-Cancer Drug Efficacy

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The feasibility of utilizing miniaturized biosensor for cancer diagnosis and treatment efficiency utilizing the electrochemical distinction of cancerous cells activity will be described.

First we demonstrate a multiplexed amperometric biosensor for colon cancer diagnosis based on the difference in the amperometric signal between cancerous and normal epithelia, relying on the observed down-regulation of Alkaline Phosphatase (AP) enzyme secretion by the cancerous cells. Detection of AP activity enabled to distinguish cancer tissue from healthy tissues, according to the expression level of the enzyme. Moreover, we offer the possibility of sampling small volume biopsies rather than cell cultures thus eliminating the need for pre-treatment and strenuous preparation steps.

This system was also applied the detection of colon cancer cells response to differentiation therapy. We have design and built a novel electrochemical 'lab on a chip' system that contains an array of nano volume electrochemical cells on a silicon chip. The efficacy of each of the differentiation inducing agents was evaluated through electrochemical detection of the cellular enzymatic activity level. The results demonstrate the ability to evaluate simultaneously multiplex drugs effect on miniature tumor sample (~15 cells) rapidly (5 min) and sensitively, with quantitative correlation between the cancer cell number and the induced current.

In addition, a new electrochemical method of detecting and diagnosing melanoma based on melanoma biomarker was developed and its feasibility demonstrated. The method is based on an electrochemical biosensor platform comprised of a special biochip and device, performing a multi-channel amperometric detection of the enzymatic activity of tyrosinase, an enzyme biomarker of melanoma. The newly developed biosensor platform is able to electrochemically detect tyrosinase activity in fresh biopsy samples.

This bioelectrochemical detection method is rapid, yielding results within minutes from biopsy removal. Using "as is" biopsy samples, without pre-treatment, simplifies the process, saves time and reduces cost and labor dramatically.

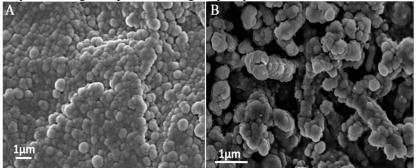
In conclusion, electrochemical biosensors as cancer diagnostic tools present exciting opportunities and may pave the way towards decentralized clinical applications

Core-Shell Cu-Si Nanowire Embedded Si Thin Film As Anode Materials For Lithium Ion Batteries

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Silicon is considered as one of the most promising anode materials for next generation lithium ion batteries owing to its highest known theoretical capacity of 4200mAh/g [1-2]. However, the lithiation and delithiation induced huge volume change and intrinsic poor electrical conductivity severely hinder the commercialization of Si [3]. In this work, Core-shell Cu-Si nanowire embedded Si thin films were fabricated onto Cu current collector through Cu nanowire slurry casting, annealing, and magnetron sputtering, subsequently. The copper nanowire connected either with copper current collector or with each other, forming a continuous electrical conductive network. Meanwhile, copper nanowire could function as mechanical support, and effectively mitigate or release the volume change induced stress built in Si during cycling. Its porous nature enhance the opportunity of contact between Si and electrolyte. The coreshell nanowire embedded Si film exhibits an impressive reversible capacities of 2560 mAh/g and an initial coulombic efficiency of 81%, and good cyclability and rate capability, indicating their promise as high capacity Li-ion anodes.



SEM image of Si thin film (A) and core-shell Cu-Si nanowire embedded Si films (B)

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Electrochemical characterization of the photovoltaic cells by using the new LED kit from Metrohm-Autolab.

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Dye-sensitized solar cells (DSSC), a viable alternatives to the silicon based photovoltaic devices, are currently subject of intense research in the framework of renewable energies as a low-cost photovoltaic (PV) device. Electricity generated from a PV produces zero emissions, is modular, and can produce energy anywhere the sun shines. The standard characterization technique of a PV device consists in the determination of the DC Current-Voltage curves under different incident light intensities. Alongside DC characterization methods, it is also possible to analyze the behavior of these devices using electrochemical impedance spectroscopy (EIS).

In this presentation, the new LED kit from Metrohm Autolab will be presented with the possibility of applying the specific techniques used for the characterization of the DSSC: i-V characteristics, electrochemical impedance spectroscopy (EIS), Intensity Modulated Photocurrent Spectroscopy (IMPS) and Intensity Modulated Photovoltage Spectroscopy (IMVS).

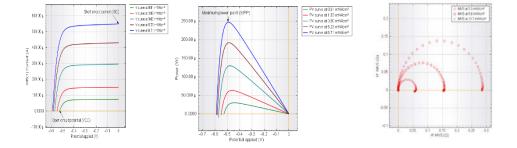


Figure 1 – Examples of i-V plot (left), power plots (middle) and IMVS plots measured on the same sample, at different light intensities by using the Autolab LED kit.

Multi-Cage Mixed-Conductor Matrix (MCMC) Encapsulating Li₂S as Cathode for Lithium/Sulfur Batteries

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The lithium/sulfur battery has many attractive properties. In addition to a high theoretical energy density of about 2600 Wh/kg, it is made of relatively low cost and environmentally friendly materials. However, it has several disadvantages resulting from the solubility of lithium polysulfides in the battery electrolyte. These include self-discharge, short cycle life and too-low coulombic efficiency.

In this talk, a novel approach to the formulation of nano-materials as highly stable and long-cycle-life cathodes for lithium/sulfur batteries will be presented. Our design involves the encapsulation of lithium sulfide nanoparticles in a mixed-conductor multicage (MCMC) matrix with unique properties. The desired structure encapsulates each particle within a protective cage, to match the maximal volume of the particle. These cages consist of compounds with mixed ion-electron-conduction properties and are substantially free of pores. This unique structure enables good conductivity of lithium ions as well as electrons through it, allowing for high-rate electrochemistry while preventing leakage of polysulfides to the electrolyte. To fabricate such a structure, we employ simple, cost-effective methods and materials which could easily be applied as an industrial process. Preliminary results collected from the cycling of coin cells, having 1 to 4 mAh/cm² of sulfur, over a voltage range of 1.5 to 2.8 V, show very stable capacities and very high coulombic efficiency, close to 100%. The high coulombic efficiency clearly indicates a strong depression of the shuttle current that results from the solubility of polysulfides in common lithium/sulfur batteries.

Liquid-Free Lithium-Oxygen Battery

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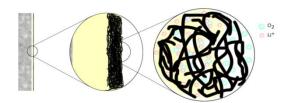
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Non-aqueous Li-O₂ batteries are considered as most advanced power sources, albeit they are facing numerous challenges concerning almost each cell component. Herein, we diverge from the conventional and traditional liquid-based non-aqueous $Li-O_2$ batteries to a solid polymer electrolyte (SPE) Li-O₂ system, operated at a temperature higher than the melting point of the polymer electrolyte, where useful and most applicable conductivity values are easily achieved. The proposed SPE-based Li-O₂ cell is compared to glyme-based Li-O₂ cells through potentiodynamic and galvanostatic studies, showing higher cell discharge voltage by 80mV and most significantly, a charge voltage lower by ~400mV. The solid state battery demonstrated a comparable discharge specific capacity to glyme-based Li-O2 cells when discharged at the same current density. The discharge products were identified as lithium peroxide by XRD analysis and FT-IR combined with quantitative ¹H and qualitative ¹³C NMR spectroscopies identified lower molecular PEO as the main degradation products, as well as in-chain ester and formates in negligible amounts. The results shown here demonstrate that safer PEO-based Li-O2 battery is highly advantageous and can potentially replace liquid-based cells contingent upon further investigation. While safety is a prime concern in Li-metal based battery, it is of greater challenge once a viable Li-O₂ battery development is being considered. A polymer-based system, which is liquid electrolyte-free, seems to be another and important step towards resolving this issue.



Scheme 1. Schematic representation of Li-O₂ battery comprised of lithium anode (grey), P(EO)₂₀LiTf electrolyte (yellow) and CNT air-cathode (black).

Study of Ethylene-Glycol-Based Electrolytes for High-Temperature Sodium-Oxygen Battery

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The sodium/air redox couple has the potential to deliver a pronounced step change in the specific energy of batteries (1690Whkg⁻¹ including the weight of O_{2} , assuming Na₂O as the discharge product). This is particularly important for electric-vehicle (EV) applications. The main problem of using an alkali-metal anode is the formation of metal dendrites on battery charge. These dendrites could cause internal short circuits and constitute serious safety issues, including that of thermal runaway.

We have recently proposed the novel approach of a molten-sodium/air battery. Operating the battery at above the melting point of sodium (97.8°C), in addition to eliminating dendrite formation, could accelerate sluggish cathode reactions, lower cell impedance and minimize interference by water vapor and CO_2 .

While current studies have shown progress in the development of room-temperature Na/O_2 batteries with the use of a diethylene glycol dimethyl ether (DEGDME)-sodium triflate mixture, the low flash point of DEGDME (57°C) makes it unsuitable for high-temperature applications. In this report we evaluate the performance of tetra(ethylene glycol) dimethyl ether (TEGDME) and poly(ethylene glycol) dimethyl ether (PEGDME), which are more suitable for future molten-sodium/oxygen batteries, operating in the medium- to high-temperature range. While a first-discharge capacity of up to 800mAh/g has been observed, the oxygen cell exhibits degraded performance over the following cycles. Electrochemical characterization of the Na/O₂ system, with the use of conductivity measurements, EIS and cell cycling tests, will be reported. Chemical and structure analysis of the discharge products with the use of EDS, XRD and SEM, will be addressed.

Current-Voltage Relations and Defect Distribution in Metal₁|Mixed Ionic Electronic Conductor|Metal₂ Devices

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Devices based on mixed-ionic-electronic-conductors (MIECs) are a subject of many experimental and theoretical investigations. Devices of a simple form: $metal_1 | MIEC | metal_2$ are of interest because they show unique I-V relations which do not fit the classical theory of solid state devices where the ionic conductivity is neglected. The measurements on such type of devices show hysteresis, crossing of I-V curves and memory, which may be exploited to design new types of nonvolatile computer memory. The current-voltage (I-V) relations and charged defect distributions are calculated numerically for a metal₁|MIEC|metal₂ device. The mixed ionic electronic conductor (MIEC) is a thin film that changes its conductivity under a high driving force. The MIEC considered contains one type of mobile donors (or acceptors) and conducting electrons (or holes). Under an applied voltage the mobile donors redistribute and the I-V curves show hysteresis and a sharp change in the current derivative, dI/dV, both in our experiment (Figure 1) and in our calculation. We denote the latter effect as quasi-switching. We show that the donor distribution and the I-V relations depend on the following device parameters: the MIEC film thickness, the contact potentials between the MIEC and the metal electrodes, the mobility ratio of donors and electrons and the electrodes impedance for material exchange with the surroundings. The I-V relations also depend on the operation conditions: the waveform and frequency of the applied voltage and the chemical composition of the surroundings. The model assumes a constant temperature, i.e. the stated effects are obtained in the absence of heating by the current. We also show that the I-V curves may cross if an asymmetry in the device design or working conditions exists.

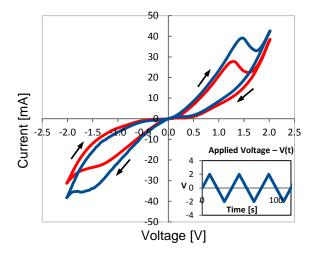


Figure 1 Experimental I-V relations in Au $|MoO_{3-x}(200nm)|$ Au device at temperature- 47 °C. The applied voltage of periodic triangular waveform is show in the inset in the lower right corner. The I-V curve exhibits hysteresis and quasi-switching (rapid changes in dI/dV) behavior. The I-V curve doesn't cross itself as indicated by the arrows on the graph.

Concentration Polarization and Electroconvection in Heterogeneous Permselective Systems

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The passage of an electric current through a permselective medium (membranes or nanochannels) under an applied electric field is characterized by the formation of ionic concentration gradients which result in regions of depleted and enriched ionic concentration at opposite ends of the medium, i.e. concentration polarization (CP). Understanding the effects of 3D geometric field focusing effects on CP in realistic three dimensional and three layers system (i.e. microchannel-permselective medium-microchannel device) is of much importance in the growing field of electrokinetics and nanofluidics. In our previous works[1,2], under the assumption of local-electroneutrality and negligible convection, we derived analytical solutions for the ionic concentrations and electric potential distributions for an electrolyte undergoing CP in one and three layers systems. In particular, we studied the effect of system heterogeneity (i.e. 2D and 3D cases, in contrast to the 1D, characterized by a non-equal permselective medium and microchamber cross-sections) on the current-voltage curves and the concentration profiles. We shall experimentally verify these theoretical predictions by studying a system made of a nanoslot array (Fig.1)

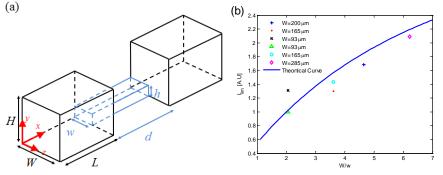


Fig.1: (a) Schematics describing half a single 3D unit periodic cell consisting of a straight permselective medium connecting two opposite symmetric microchambers. (b) Normalized measured limiting currents compared to theory as a function of the heterogeneity W/w.

Talk 20 Structural and Electrochemical Evidence of Layered to Spinel Phase Transformation of Li and Mn Rich Layered Cathode Materials Upon Cycling

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Abstract

In recent years, there is an increasing interest in Li and Mn rich layered materials of the xLi₂MnO₃.(1-x)LiMO₂ (M=Mn, Co and Ni) type as cathodes for Li-ion batteries because these materials can provide high capacities that may approach the maximum limit for LiMO₂ materials, namely 300 mAh g^{-1} [1-3]. Layered Li and Mn rich cathode materials of the xLi[Li_{1/3}Mn_{2/3}]O₂.(1-x)LiMn_{1/3}Ni_{1/3}Co_{1/3}O₂ (x=0.2, 0.4, 0.6) were synthesized by a self-combustion method, characterized by XRD, SEM, HRTEM and Raman spectroscopy and studied as positive electrode materials for Li-ion batteries. The cathode material with x=0.6 exhibits an initial high discharge specific capacity of 270 mAh g⁻¹ at C/10 rate in galvanostatic charge-discharge cycling, which decreases to 220 mAh g⁻¹ after 50 cycles. It also exhibits a high rate capability as compared to other composites. Structural studies using the electron diffraction technique with TEM and spectral studies by Raman spectroscopy indicate continuous structural changes upon cycling that include formation of a spinel phase. The electrochemical impedance spectra recorded at various potentials present evidence of a substantial increase in the charge-transfer resistance at potentials higher than 4.4 V during charge and also at potentials lower than 3.8 V during discharge. The chemical diffusion coefficient of Li⁺ ions in these materials was calculated to be around 10^{-13} cm² s⁻¹ and it reaches a minimum near 3.3 V from PITT studies. The minimum value of the diffusion coefficient of Li⁺ around 3.3 V potential can be explained as resulting from the formation of spinel phase upon cycling. The results will be discussed.

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