Plenary Lecture 1:

CHARGE TRANSFER MECHANISMS IN ION-CONDUCTING MATERIALS

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Electrochemical energy storage systems are of major interest owing to their potential to fulfil a major role in today's worldwide efforts to decarbonize the energy and mobility sectors. In particular, secondary batteries running on alkaline and alkaline-earth anodes are characterized by a high specific energy and power and an extensive cyclability [1]. The main bottleneck in the widespread of this technology is the development of suitable ion-conducting materials (ICMs) able to provide a sufficient ion conductivity, an appropriate chemical and electrochemical stability, and high compatibility with all the other functional materials used in the assembly of the device [2].

Ion conductivity in ICMs occurs *via* a number of different processes, of which the predominant are attributed to: i) the charge migration of ions between coordination sites in the host materials; and ii) the increase of conductivity due to relaxation phenomena involving the dynamics of the host materials [3-5]. Ions efficiently hop to new coordination sites only when their occupying domains concurrently relax *via* reorganizational processes, which are generally coupled with relaxation events associated with the host matrix dynamics. All these phenomena are easily detected and clearly described by the broadband electrical spectroscopy (BES) technique [6].

In this lecture, an overview will be given on the results of the application of BES in the study of the charge transfer mechanisms of a variety of ICMs, including: (i) hybrid and polymer electrolytes based on alkaline and alkaline-earth ions [7,8]; (ii) ionic liquid-based electrolytes for multivalent metal batteries [9]; and (iii) solid-state ceramic electrolytes for Li^+ ion conduction (Figure 1) [10].

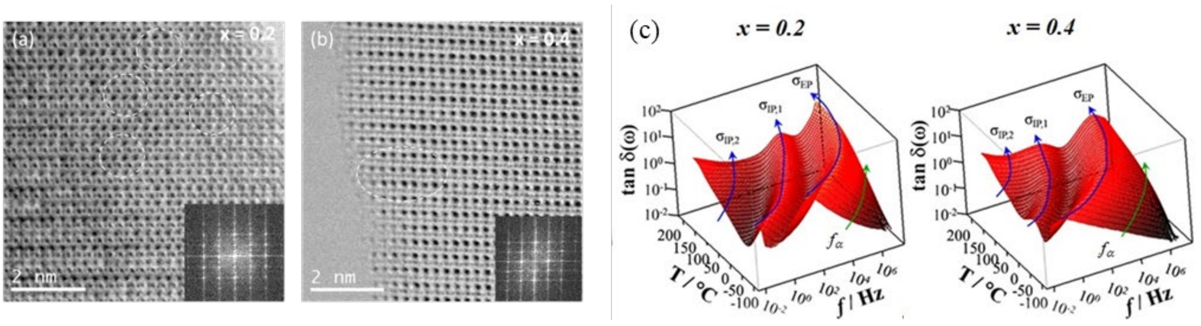

Figure 1. Annular bright field scanning TEM images of $La_{1/2+1/2x}Li_{1/2-1/2x}Ti_{1-x}Al_xO_3$ perovskite crystals of the x = 0.2 (a) and x = 0.4 (b) compositions, in the [110] projection. Electric response of the perovskite crystals determined by means of BES (c) [10].

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Acknowledgments

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Keynote Lecture 1:

Decoupled Water Splitting for Green Hydrogen Production

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Green hydrogen produced by splitting water molecules into hydrogen and oxygen using renewable sources is expected to play a major role in the transition to carbon neutral economy, serving as an energy carrier that can facilitate the penetration of an higher share of intermittent renewable energy, the decarburization of hard-to-abate industrial sectors (e.g. industrial processes which require high-grade heating or rely on hydrogen as a feedstock) and the cross-sectorial coupling (linking power, gas and other energy vectors or energy intensive commodities and replacing them in their respective usages). The baseline technology for green hydrogen production is called water electrolysis, where renewable power is applied to break the chemical bonds in water molecules and produce hydrogen and oxygen simultaneously at two electrodes, cathode and anode, in alkaline or acidic solution. The coupled generation of hydrogen and oxygen at the same time in the same cell presents a safety risk, since the mixture of the two is highly flammable. Therefore, a membrane and sealing are used to isolate the electrodes from each other, which complicates cell construction and requires maintenance, both increasing the production cost of green hydrogen. In addition, severe (20-30%) energy losses, mostly due to the difficult reaction that evolves oxygen, increase the cost of energy in this energy intensive technology. These drawbacks present challenges for wide scale adoption of green hydrogen.

To overcome these challenges, we developed an alternative technology that decouples the generation of hydrogen and oxygen into two consecutive stages (time separation), or two cells (space separation), avoiding the need for membrane and sealing. In addition, we divided the oxygen evolution reaction, a difficult electrochemical reaction that requires four electrons to generate an oxygen molecule on a single atomic reaction site, into two sub-reactions that occur on four sites, thereby enabling easier reactions and reducing most of the losses in water electrolysis. An ultrahigh efficiency of nearly 99% was demonstrated at lab scale, and we expect reaching 95% at system scale. To bring this transformative concept to reality we established H_2Pro, an Israeli company that aims to provide green hydrogen at scale based on our innovation.

Keynote Lecture 2:

Development of Electrochemical Activity Descriptor for PGM-free ORR Catalysts

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The activity of Pt-group metal (PGM)-free ORR catalysts, has been increasing significantly in the past decade, and reached a level where it is comparable with Pt-based catalysts, proving their viability. Nowadays, the advancement in their development matured to the point where their stability and durability under fuel cells operating conditions must be determined, and the activity of the catalyst must be studied in-situ in order to monitor the catalyst performance in real time. While the advancement in activity is impressive, the next necessary improvement, durability, is impeded by the lack of a procedure that is specific towards the catalyst's activity, and informative with respect to its degradation rate during fuel cell testing, undermining the ability of understanding durability issues. Currently, the degradation of the catalyst is described quantitatively by using the Tafel region of polarization curves. While an indispensable measurement, it is not specific towards the processes that the catalyst undergoes, as its output is influenced by many factors, such as pore structure, membrane conductivity, and especially, the activity of various active sites. This lowers the usefulness of this method, as it is not specific towards any active site in particular, limiting any inferences on possible routes that may be taken towards understanding and mitigating the catalyst's degradation. Hence, there is a critical need to develop new analytical tools that have high specificity towards different aspects of the catalyst's performance.

With Pt-based catalysts, this problem is easily solved using an electrochemical activity descriptor that is specific to the active site: electrochemical active surface area (ECSA). This descriptor, which can be determined during an accelerated stress test (AST), helps quantify the degradation of Pt-based active sites, and has been playing an important role in the development of durable PGM ORR catalysts.

In this work, Fourier-Transform Alternating Current Voltammetry (FTacV), was used as a method for describing the PGM-free ORR catalyst degradation in-situ fuel cells. FTacV has shown great applicability in unraveling complex mechanisms and in discerning low signal faradaic reactions from high capacitive currents and noise. It is backed by an extensive theoretical background. Recently, FTacV has been used to probe the electron transfer in surface bound catalysts and enzymes, providing invaluable information on the electron transfer mechanisms that underpin the electrocatalytic reactions, thus, enabling further development of the catalysts and better understanding of these reaction.

In this talk we will present the use of FTacV as an electrochemical, catalyst-specific method for following the PGM-free degradation during fuel cell operation. For the first time, FTacV was employed during the operation of a polymer electrolyte membrane fuel cell before, during, and after stability tests. FTacV was found to be a highly sensitive technique to follow the activity of electrochemically active species, opening the path towards the accurate quantification of electrochemical active site density (EASD) of PGM-free ORR catalysts.

Session A: Analytics and Modeling
Chair Dr. Barbara Kazanski Traubin (ACEJ)

Invited Lecture 1:

Dramatic electrochemical tuning of the plasmonic spectrum of a metal nanoparticle on a mirror

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Enhancement of electric fields in the nanometric gap between plasmonic nanostructures is widely exploited for sensing, enhanced spectroscopies and photochemistry. Plasmonic properties of nanostructures with ultranarrow gaps, such as nanoparticles (NPs) on a flat metal surface (a mirror), have attracted much attention in recent years [1]. We studied the effect of electrochemical control on the plasmonic properties of single Au and Ag NPs on a mirror. We found that the coupled plasmonic resonance can be reversibly tuned over a range of tens of nanometers, more than an order of magnitude higher than expected based solely on capacitive charging of the NPs.

Our experimental system consisted of single Au or Ag NPs (50 nm – 100 nm) adsorbed on a self-assembled monolayer (SAM) of either polyelectrolytes, cysteamine (CEA) or ethanedithiol (EDT) deposited on an atomically flat 100nm thick Au electrode prepared by template stripping. The NPs were either bare (prepared by H_2 reduction) or citrate-stabilized. The NP-modified electrode was immersed in a basic solution.

Dark-field microspectroscopy revealed several bands in the plasmonic spectrum of individual NPs on the mirror electrode (Fig. 1A). Variation of the electrode potential generated a very large, though reversible shift of the lowest-energy band, attributed to the NP-mirror coupled plasmon. A plot of the peak position vs potential displayed an S-shaped behaviour resembling a phase-transition (Fig. 1b). This remarkable result was not observed with individual NPs deposited on HOPG electrode, and can therefore be attributed to a dramatic modulation of the coupling between the particles and the mirror with electrode potential.

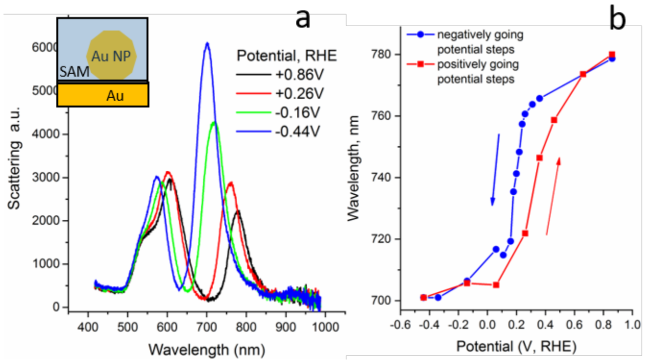

Figure 1. Scattering spectra (a) and variation of the spectral position of the coupled plasmon peak (b) of bare AuNP (ca. 60 nm) on CEA/Au electrode. Inset in (a): Scheme of NP on the mirror.

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Oral Presentation 1:

Oxygen adsorption and ORR activity on catalytic surfaces: a theoretical investigation

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The adsorption of oxygen is a key factor in many processes and reactions. This is especially true for electrodes in metal-air batteries and fuel cells. To model oxygen adsorption on catalytic surfaces, we applied Density Functional Theory (DFT) as a useful tool to obtain the proper adsorption site and oxygen binding energy (OBE).

In the first part of the talk I will show the results for adsorption of oxygen on several surfaces involving transition-metal carbide surfaces (TMC, TM = Ti, V, Zr, Nb, Mo, Hf, TaC [1,2]), metal oxides (MnO_2 [3]) and Pt-based materials (Ru/Pt [4]). I will demonstrate that that during the simulations the O_2 molecules break down and bind to the surface hollow TM sites in TMC systems, which correspond to the ABC stacking, except for α-MoC(001) and Mo_2C, on which AB stacking happens [1]. We obtained a clear trend for OBE, which becomes smaller with the increase of TM d-band occupation for (111) surfaces, and a direct correlation between the surface energy of the TMC(111) and the OBE. We also found good correlation between the experimentally measured oxidation potential of several TMCs and our calculated OBE.

In the second part of the talk, I will show the effect of ruthenium coverage on the oxygen reduction reaction (ORR) and surface activity of a Pt-based catalyst. We found a decay of the ORR activity with increasing Ru coverage on Pt(111) surface, which is in a good agreement with the experimental measurements of the ORR activity [4]. The investigations presented here provide a deeper understanding of the effect of structure and compound of different materials on oxygen adsorption and ORR kinetics for metal-air batteries and fuel cells applications.

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Oral Presentation 2:

Machine Learning in Modeling Properties of Ionic Liquids

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Ionic liquids (ILs) possess a unique combination of physicochemical properties that make them extremely important in the development of clean and sustainable materials for electrochemical energy storage and conversion devices, especially as electrolytes in Li-ion, Na-ion, Li-air, Li-S, all-solid-state, dual-ion and other types of batteries, as well as supercapacitors [1-2]. The importance of the ability to perform quantitative predictions of various properties of ILs using quantitative structure-property relationships (QSPR) models necessitates the understanding of which modern machine learning (ML) methods in combination with which types of molecular descriptors are preferable to use for this purpose.

We report a large-scale benchmarking study of QSPR models built by combining three traditional ML methods and seven different architectures of neural networks (NNs) with five types of molecular descriptors to predict six important physical properties of ILs: density, electrical conductivity, melting point, refractive index, surface tension, and viscosity [3]. The models are built using datasets consisting of 407 to 1204 ILs composed of diverse organic and inorganic ions. QSPR models for predicting the properties of ILs at eight different temperatures are built using multi-task learning. For each of the properties, the best combinations of ML methods and molecular descriptors are identified. A unified ranking system is used to rank and prioritize different ML methods and molecular descriptors. It is shown that on average: (1) nonlinear ML methods perform much better than linear ones; (2) NNs perform better than traditional ML methods; (3) NNs with attention-based Transformer architectures, which are actively used in natural language processing (NLP) and other fields of artificial intelligence (AI), perform better than other types of NNs due to the advanced ability to analyze SMILES text strings encoding chemical structures of ILs. The resulting models can be applied both to predict the properties of new ILs and to design ILs with the desired set of physical properties.

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Oral Presentation 3:

Structural dynamics of solid ionic conductors

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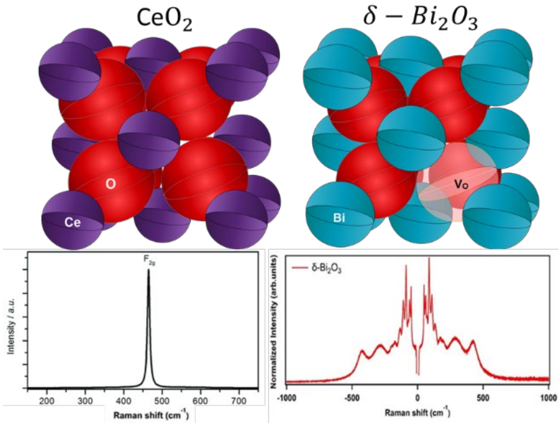
Solid ionic conductors are commonly crystalline compounds in which electric current is carried by charged atoms. Since the current requires a mass transfer of the conducting ions, the rest of the atoms presumably remain in place to maintain a crystallographic structure. In this presentation, I will show how the structural dynamics influence the properties of selected solid ionic conductors, change local structure and symmetry, and thus contribute to the ionic conductivity.

Our research group uses a state-of-art custom-built Raman spectroscopy system to study structural dynamics and anharmonic effects. By applying modern experimental and computational techniques, we can detect relaxational and anharmonic motions of the ions, which were previously considered immobile. These discoveries contribute to a deeper understanding of the basic ionic conductivity mechanism of some important materials in the field of solid-state electrochemistry.



Oral Presentation 4:

Electro-Oxidation of Methyl Formate on $Pt_3Pd_3Sn_2$ alloy: A DFT Study

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Hydrogen storage, safety and transport are the biggest challenges in PEMFC commercialisation. Therefore, methyl formate (MF) has been considered as an attractive alternative fuel due to high energy density, low toxicity, and ease in storage and transport. However, the lack of an efficient anodic catalyst is preventing the wide implementation of the direct methyl formate fuel cell (DMFFC). Herein, a first-principle density functional theory (DFT) calculation was performed to study the MF electro-oxidation on the surface of $Pt_3Pd_3Sn_2$ alloy. The main goal of this study is to provide a fundamental details for the thermochemistry and kinetics of MF oxidation. Our results show that the role of Sn and Pd to facilitates more active sites utilization, and synergistically improve the kinetics of electrochemical reaction.

Session B: (Photo)Electrocatalysis and Sensors
Chair Prof. Brian Rosen (TAU)

Invited Lecture 2:

Coupling Enzymes with Electrodes for Biosensing, Biofuel Cells or Biomass to Electricity Devices

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Interfacing enzymes and electrodes is a key challenge for the construction of amperometric biosensing and biofuel cell devices. Here I will present novel methods for the construction of amperometric biosensing devices for glucose or lactate using bioengineered oxygen insensitive enzymes.[1,2] I will further discuss methodologies to enable direct or mediated electron transfer process using full or partial expressed enzymatic structure. The developed bioanodes were further coupled with bilirubin oxidase biocathodes for the construction of biofuel cell devices. Lastly, I will show how cellulose biomass can be directly converted into electrical energy by coupling cellulase complex enzymes with biofuel cell/ or photo biofuel cell devices.[3]

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Oral Presentation 5:

Enhanced Photocatalytic Activity of Cs4PbBr6/WS2 hybrid Nanocomposite

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Photocatalytic processes are among the prime means for mitigating the pollution caused by toxic effluents. In this context, photocatalysis presents a promising path and undergoing rapid evolution. Halide perovskites (HPs) became promising candidates due to the negative conduction band minimum and the low work function, which is necessary for dye degradation and hydrogen generation. Interestingly, HPs performance significantly improves by introducing transitional metal dichalcogenides (TMDs) as a co-catalyst, which enables suppressed charge recombination. Here we investigate the photocatalytic performance of Cs_4PbBr_6/WS_2 hybrid nanocomposites towards organic dye degradation under visible light illumination. We find that the hybrids of Cs_4PbBr_6/WS_2 nanotubes (NT) and Cs_4PbBr_6/WS_2 nanoparticles (NP) significantly increase the degradation rate of methylene blue (MB) compared to pristine Cs_4PbBr_6 nanocrystals and WS_2 nanostructures. Specifically, ~98% of dye degrades after 90 minutes, which is a ~15% improvement compared to previous reports on similar composites. The results of transient absorption measurements reveal charge transfer from Cs_4PbBr_6 to WS_2. This finding, along with additional optical measurement, implies that the boosted photocatalytic performance of the nanocomposites is induced by reduced carrier recombination. Our findings pave the way for the implementation of Cs_4PbBr_6/WS_2 nanocomposites as superior photocatalysts.

Oral Presentation 6:

Multiple Application of Ag-Pt-CFFCs for Water and Wastewater Treatment

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The rapid growth of human population and industry results in the high generation of environmental pollutants, some of which could be recovered and reused in different industries, others should be properly degraded before being released to the environment to secure human, animal, and ecosystem health.

Recently, a new catalytic process named Capacitive-Faradaic Fuel Cells (CFFCs) was proposed by us. The CFFCs are comprised of granules of activated carbon with nanosize platinum crystals. The CFFCs are used in a two-step process of hydrogenation and oxygenation reactions to treat the water or wastewater. Hydrogenation or oxygenation reactions (Eq. (1) and Eq. (2)) are achieved by recirculation of the water through the CFFCs loaded column reactor while introducing a steady flow of hydrogen gas or air to the column respectively.

(1) $H_2 \rightarrow 2H^+ + 2e^-$ $E^0_r = 0.0$ V (vs SHE) (2) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^0_r = 1.23$ V

By properly grouping these half-cell reactions in each step to a thermodynamically spontaneous full reaction it is possible to achieve selective separation and degradation of pollutants. For example, we showed that a selective separation of silver from electronic waste leachates is possible by hydrogenation of Ag^+ ion to Ag^0 and its deposition on the CFFCs (Eq. (3)). Next, the full recovery of silver and regeneration of CFFCs is obtained by oxygenation of the Ag^0 back to Ag^+ (Eq. (4)).(1)

(3) $2Ag^+ + H_2 \rightarrow 2Ag^0 + 2H^+$ (4) $4Ag^0 + O_2 + 4H^+ \rightarrow 2H_2O + 4Ag^+$

A different application of the CFFCs that was studied by us is the selective separation of chloride ions from acidic wastewater for acid reuse. In this process, first silver is hydrogenated on the CFFCs as shown in Eq. 3 to create Ag-CFFCs. Next, the acidic wastewater containing Cl^- is recirculated through the Ag-CFFC column and air is introduced. This results in separation of Cl^- from the wastewater by oxygenation of Ag^0 crystals to Ag^+ and the immediate deposition and formation of AgCl crystals on the CFFCs via Eq. 5. Next, a separate portion of water is recirculated while hydrogen gas is introduced to the column to regenerate the Ag-CFFCs via Eq. 6.(2)

(5) $4Ag^0 + O_2 + 4H^+ + 4Cl^- \rightarrow 2H_2O + 4AgCl$ (6) $2AgCl + H_2 \rightarrow 2Ag^0 + 2Cl^- + 2H^+$

A third application of Ag-Pt-CFFCs is proposed for the posttreatment of homogeneous Ag^+-Peroxydisulphate advanced oxidation process (AOP). Residual concentration of Ag^+ and peroxydisulphate (PDS) are left in the treated water after degradation of the persistent organic pollutants (POPs) via the AOP. This treated water is recirculated through the CFFCs column with hydrogen gas to degrade residual oxidant (PDS) (Eq. 7) and deposit the silver onto the CFFCs (Eq. 3). Next, silver recovery and its reuse in the AOP is obtained by oxygenation reaction (Eq. 4).

(7) $S_2O_8^{2-} + H_2 \rightarrow 2SO_4^{2-} + 2H^+$

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Oral Presentation 7:

Benchmarking Various Metal-oxides as Electrocatalysts for the Aqueous Alkaline Dehydrogenation and Oxidation of Benzylamines to Nitriles and Imines

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The anodic electrochemical oxidation of amines (AO) in aqueous media is attracting major interest from groups working on fuel cells and electrochemical water splitting as it offers a more cost-effective option to the rather sluggish electrochemical oxygen evolution reaction (OER).

Not only does OER requires more net energy spend, therefore increasing the total cost of hydrogen production, but the formation of oxygen also has no added value and the catalyst usually suffers from decomposition due to the high energy requirement of OER. On the other hand, AO requires lower energy resulting in more cost-effective hydrogen production, and its products imines (via oxidation) and nitriles (via dehydrogenation) are widely used in the pharma and agrochemical industries.

First-row transition metal oxides such as nickel-, iron-, and cobalt oxides are widely explored as suitable catalysts for AO. Although impressive strides toward understanding the underlying principles of AO in Ni-based catalysts were made, the mechanistic pathway of AO and the knowledge to design other metal-based electrocatalysts are rather unclear.

Herein we present a simple hydrothermal synthesis of Ni, Fe, Co sulfides grown on Ni foam which are later converted *via* electrochemical conversion to metal-oxides which allows us to examine and benchmark various metals as suitable electrocatalysts for benzylamine dehydrogenation and oxidation. The bond free energy values, impedance, kinetic, surface, and performance studies reveal that the Ni-based electrocatalyst has the highest selectivity and activity for nitrile formation ($4e^-$ dehydrogenation pathway) while the others can offer a slightly better activity for imine formation ($2e^-$ oxidation pathway) which helps us to reveal the structure-activity relations of various metal oxides in AO.

Oral Presentation 8:

Electrocatalytic nitrogen reduction to ammonia performance of the RuO_2 nanoparticles under ambient condition

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Designing a suitable electrocatalyst is highly challenging but desirable for efficient electrochemical ammonia synthesis from nitrogen. Herein, the Ruthenium oxide (RuO_2) catalyst explored for the first time as an efficient catalyst for electrocatalytic nitrogen reduction reaction (NRR) under ambient conditions. The ruthenium oxide nanoparticles exhibited an ammonia production rate of 16.5 µg h^{-1} cm^{-2} with an FE of 0.26 % at -0.15 V vs. RHE in N_2 saturated 0.1M KOH. On the other hand, only an ammonia production rate of 6.8 µg h^{-1} cm^{-2} with 0.19% FE at -0.15 V vs. RHE is realized for Ru nanoparticles under similar operating conditions. About 58% higher NRR rate is observed for RuO_2 compared to Ru black which is attributed to the in-situ formation of oxygen vacancies (OVs) on RuO_2 under cathodic applied potentials, which provides a facile adsorption sites for N_2. X-ray diffraction analysis of the electrode fabricated with RuO_2 after NRR analysis evidenced the presence of distinguished diffraction peaks corresponding to the metallic Ru in addition the diffraction peak of RuO_2 which supports the in-situ formation of such catalytically active vacancy/defects on RuO_2 during the electrocatalytic NRR. During the electrochemical stability analysis, a stable ammonia production was achieved for 2 and 5h for RuO_2 and Ru black, respectively with minor changes in the FE. The present study demonstrating the crucial role of oxides in achieving the higher NRR activity pave the way for designing various RuO_2 based electrocatalyst through effective modification for ambient condition electrochemical NRR application.

Session C: Environmental electrochemistry: water splitting and CO2 electroreduction processes

Chair: Dr. Tomer Zidki (AU)

Oral presentation 9

Nano-Encapsulation: Overcoming Conductivity Limitations by Growing MOF Nanoparticles in Porous Carbon Enables High Electrocatalytic Performance

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Among methods employed for carbon capture, electroreduction of CO_2 offers not only reducing CO_2 levels but also the possibility of recycling it into commodity chemicals. However, the most efficient catalysts for this reaction are precious metals. In order to achieve cost-effective processes, other elements should be used. Transition-metal atoms coordinated in metal-organic frameworks (MOFs) exhibit high performance as electrocatalysts. However, the isolating nature of MOFs limits their utilization as electrocatalysts. We have grown MOF nanoparticles inside porous carbon instead of mixing the MOFs with conducting carbons. The incorporated MOF nanoparticles show improved properties than MOFs mixed with carbon, proving the strong electronic interactions in the composites. The encapsulated MOF nanoparticles demonstrate high electric conductivity while preserving their original crystallinity. When used as electrodes in CO_2 electroreduction, the MOFs provide high electroactive coverage of 155 nmol cm^{-2}. Moreover, in CO_2 saturated electrolytes, the composites exhibit excellent electrochemical performance, including a small onset potential (-0.58 V) and large reduction currents (-17 mA· cm^{-2} at -1.0 V), considerably higher than usually reported for MOF-based beyond CO electroreduction. Importantly, the composite is able to produce valuable hydrogenated chemical commodities, including formic acid.

Oral presentation 10

Layered electrodeposited catalyst for 'Hydrogen on demand system'

Shany Hershkovitz, Ya'ara Shaham, Karina Gavrilenko, Michael Karchemny, Oshik Adler & Dana Baram

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Hydrogen is playing a critical role in the global energy mix. But traditional hydrogen such as compressed hydrogen gas or liquified hydrogen, require complex infrastructure and cumbersome, costly safety measures, while suffering from lower energy density. The current commercially available fuel cell systems use compressed hydrogen tanks (350-700 bar) which is a major safety hazard in various application and emphasizes the need for a hydrogen on-demand system.

Electriq~Global is an innovative Israeli start-up company which focuses on generating on-demand Hydrogen from solid inorganic hydrogen carrier (SIHC) and water. The hydrogen production is elevated by immersing a highly active catalyst in the water, as part of a robust-designed patented system. Surpassing compressed or liquified hydrogen, Electriq's hydrogen storage solution exceeds 9% storage density at 99.999% hydrogen purity.

The catalyst developed by Electriq~Global, is assembled using electrodeposition method in explicit conditions. Using a stainless-steel support, the catalyst has a layered structure which enhances its mechanical properties and longevity. The catalyst's high activity derives from its close packed nanoclusters that increase its surface area and the crack free exterior ensures its resilience and durability.

We present a catalyst characterized by SEM-EDS, XPS, TOF-SIMS and 3D-profilometer. It is based on non-precious and available materials and manufactured by a commonly used procedure. We demonstrate its performance and durability with our state-of-the-art generator, the 'Moses 3kW PowerPack', which is comparable by size and power to the Honda 3kW EU3000iS petrol generator. It demonstrates how Electriq's zero-emission power can be used when needed with a simple release system.

Oral presentation 11

Combined nanofiltration and advanced oxidation processes with bifunctional carbon nanomembranes

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Wastewater reclamation is becoming a top global interest as population growth and rapid industrialization pose a major challenge that requires development of sustainable cost-effective technologies and strategies for wastewater treatment. Carbon nanomembranes (CNMs)—synthetic 2D carbon sheets—can be tailored chemically with specific surface functions and/or physically with nanopores of well-defined size as a strategy for multifunctional membrane design. Here, we explore a bifunctional design for combined secondary wastewater effluent treatment with dual action of membrane separation and advanced oxidation processes (AOP), exploiting dissolved oxygen. The bifunctional membrane consists of a CNM layer on top of a commercial ultrafiltration membrane (Microlon™) and a spray-coated reduced graphene oxide (rGO) thin film as the bottom layer. The CNM/support/rGO membrane was characterized by helium ion and atomic force microscopy, FTIR, XPS with a four-point conductivity probe, cyclic voltammetry, galvanostatic measurements, and impedance spectroscopy. Combined treatment of water by nanofiltration and AOP was demonstrated, employing a unique three electrodedead end filtration setup that enables concurrent application of potential and pressure on the integrated membrane. For the model organic compound methylene blue, oxidation (by the Fenton reaction) was evaluated using UV-vis (610 nm). The rejection rate and permeability provided by the CNM layer were evaluated by dissolving polyethylene glycol (400 and 1000 Da) in the feed solution and applying pressure up to 1.5 bar. This demonstration of combined membrane separation and AOP using an integrated membrane opens up a new strategy for wastewater treatment.

Oral presentation 12

Activating a Keggin Polyoxometalate as an Electrochemical Water Oxidation Catalyst by Entrapping it in a Sol-Gel Matrix

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Water oxidation is considered the bottleneck process for water splitting, an efficient and cost-effective method for a sustainable future in moving toward green energy. Polyoxometalates (POMs), a class of molecular metal oxides, have been well studied and explored in electro/photchemical water oxidation catalysis for over a decade.[1-3] The high solubility of POMs in water and stability of POMs mostly in acidic to neutral pH leads to the limited use of these compounds under homogenous conditions. Different approaches have been used in the last few years to prepare heterogeneous POM-based water oxidation catalysts (WOCs) by incorporating organic moieties forming an organic-inorganic hybrid. The other approach and well studied in this regard are encapsulating POM in the sol gel matrix.[4-5] Heterogenization of POMs using sol-gel method aids in recyclability and structural stability of POM under electrochemical conditions. Thus, we have used this approach to encapsulate a Keggin POM, $K_6[Co_{12}W_{12}O_{40}]$ ($E_{Co(III)/Co(II)} = 1.02$ V *vs.* NHE, pH 7) in the sol-gel matrix to prepare the working electrode for water oxidation at low pH (2). The prepared electrode is robust and stable, which could achieve electrochemical water oxidation at the current density of 2 mA/cm^2 for an overpotential of 300 mV.

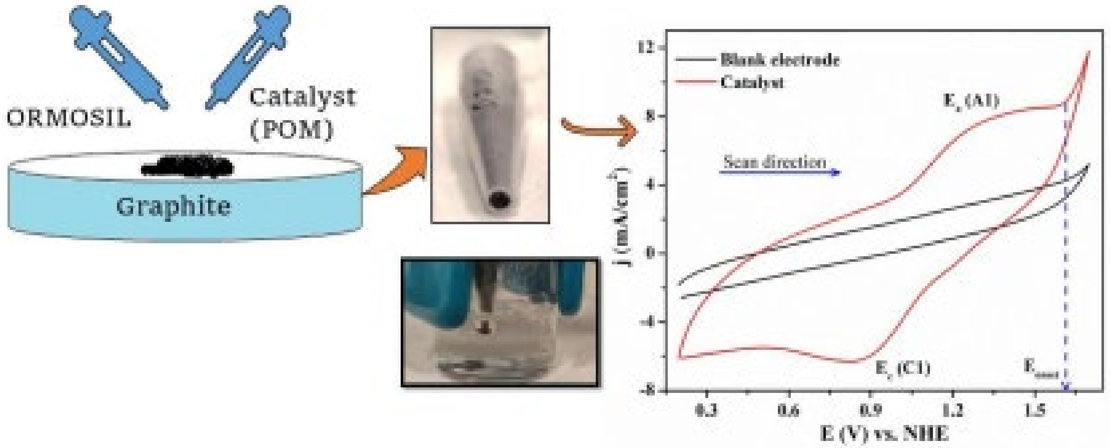

Figure 1. Pictorial representation of the formation of the electrode using the sol-gel method and its corresponding cyclic voltammetry plot compared with the blank electrode at the scan rate of 100 mV/s in 0.1 M $NaClO_4$ pH 2.

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Oral presentation 13

Kinetic Analysis of the Oxygen Reduction Reaction Electrocatalysis Using Advanced Transient Voltammetry

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The widespread commercialization of polymer electrolyte fuel cells requires decreasing the prices of its components. A promising route is the replacement of the ubiquitous platinum-based catalysts for the oxygen reduction reaction (ORR) by earth-abundant metal catalysts such as the FeNC catalysts. Although still debated, a growing consensus in the field is that the active sites of these catalysts structurally resemble the iron-based macrocycles such as iron-porphyrins and iron-phthalocyanines, with an iron coordinated by several nitrogen atoms constituting the active center. This hypothesis has been strengthened by recent findings showing a correlation between the number of electro-reactive active sites and the catalytic activity towards the ORR by in-situ spectroscopic and electrochemical methods. The electrochemical nature of the active sites enables the utilization of electroanalytical methodologies to investigate various properties of the catalyst, such as the durability, stability, and catalytic activity. Quantitatively, the catalytic activity is measured as the turnover frequency (TOF), which is the number of catalytic cycles occurring on each site per a given time. The TOF depends on the kinetic and thermodynamic properties governing the catalytic reaction, which are modelled as the rate and equilibrium constants of different elementary steps. Quantitative knowledge of the kinetic and thermodynamic constants is desirable as they enable a fuller picture of the catalytic cycle and can relate the material properties of a catalyst to various aspects of the reaction mechanism, shedding light towards possible avenues for obtaining more active catalysts. In this talk I will present our work on quantitively determining the kinetic and thermodynamic parameters of the ORR by combining advance transient voltammetry measurements with a detailed microkinetic model. Multiple-frequency Fourier transformed ac voltammetry measurements are used to probe the catalysis of the ORR on a model catalyst, iron-phthalocyanines, showing the applicability of the methodology towards electrochemically active catalysts. The generated harmonics are then analyzed, and the parameters extracted are a fitted to the kinetic current, reviling intricate relations influencing the TOF of the ORR.

Session D: Materials design: From Synthesis to Coating
Chair: Prof. Daniel Mendler (HUJI)

Invited Lecture 3:
Critical Percolation Threshold for Solvation Site Connectivity in Polymer Electrolytes Mixtures

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To address the tradeoff between mechanical strength and Li^+ conductivity in Poly(Ethylene Oxide) (PEO)-based electrolytes, a rigid nonconductive polymer is frequently added to the electrolyte via blending or copolymerization. The ionic conductivity of mixed PEO electrolytes is generally lower than that of unmixed PEO electrolytes. The suppressed ionic conductivity is attributed to the reduced segmental mobility and connectivity of the conductive PEO cites. Most experimental systems make it difficult to decouple the two mechanisms and accurately examine their impact on conductivity. We compare two symmetric polymer mixtures (50:50 wt%): a miscible polymer blend PEO/PMMA and a disordered block copolymer (BCP) PEO-b-PMMA, both with the same amount of Li salt. Because their chemical and physical properties are the same, changes in ionic conductivity can be attributed solely to local changes in PEO network connectivity. We discover that the mixtures' immediate Li^+ solvation sites (<5 Å) are identical to those of unmixed PEO electrolytes. The presence of non-conducting PMMA near the PEO, on the other hand, causes local concentration changes at longer range scales. The BCP is more mixed than the blend electrolyte at these length scales, resulting in a factor of two drop in conductivity. To that end, we propose a quantitative computational model that considers Li^+ transport within and across PEO clusters at the appropriate length scales. This new understanding of network connectivity in polymer electrolyte mixtures is critical for the design of future multiphase polymer electrolyte systems.

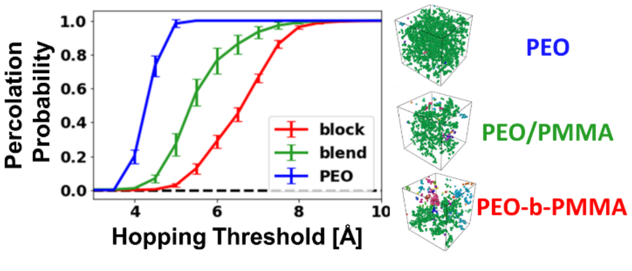

Figure.1 Representative configurations of percolated clusters polymer electrolyte mixtures

Invited Lecture 4:

The Versatility of CVD to Synthesize 2D Nanostructures: Carbon Nanotubes and Transition Metal Chalcogenides for Electronic and Electrochemical Applications

Prof. Daniel Nessim

Bar Ilan University

Since the excitement about graphene, a monolayer of graphite, with its 2010 Nobel Prize, there has been extensive research in the synthesis of other non-carbon few/mono-layers exhibiting a variety of bandgaps and semiconducting properties (e.g., n or p type). The main approaches to deposit few/monolayers on a substrate are: (a) bottom-up synthesis from precursors using chemical vapor deposition (CVD) or (b) top-down exfoliation (liquid or mechanical) of bulk layered material. Using a Lego approach of superposng monolayers, we can envisage the fabrication of heterojunctions with original electronic behavior.
Here we show a combined bottom-up and top-down approach where (a) we synthesize in one step high yields of bulk layered materials by annealing a metal in the presence of a gas precursor (sulfur, phosphorous, or selenium) using chemical vapor deposition (CVD) and (b) we exfoliate and deposited few/mono-layers on a substrate from a sonicated mixture of our material in a specific solvent. It is interesting to note that, besides the structure being 2D layered, the properties of the nanomaterials synthesized slightly differ from the materials with the same stoichiometry synthesized using conventional chemical methods (e.g., solvothermal).
In this talk, we will discuss the chemical synthesis, the very extensive characterizations, and the lessons we learned in making multiple metal sulfides (Cu-S, Ag-S, Ni-S), metal phosphides (Ni-P, Cu-P), and metal selenides (Ag-Se, Cu-Se, W-Se, Mo-Se). We will see how we integrated these new materials into electrochemical devices and sensors.

Oral presentation 14

Molten-State Synthesis of Nickel Phosphides for Electrochemical Applications

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Prof. Yair Ein-Eli,[b] Prof. Menny Shalom[a,*]
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A straightforward, benign, and scalable molten-state synthesis of nanoscale nickel phosphides is demonstrated, utilizing low-cost precursors, namely $Ni(NO_3)_2 \cdot 6H_2O$ and triphenylphosphine (PPh_3)[1]. The new method offers an alternative to common solvothermal and gas-solid phosphidation synthetic methods, allowing tunable phase composition of the produced nanoparticles, along with significant simplification of synthesis method and equipment.

Combined analytical and computational methods were used to elucidate the high-temperature reaction mechanism indicating that the reaction propagates through favored Ni-P bonding and consecutive cleavage of phenyl–P bonds of PPh_3. Intermediate formation of metallic nickel nanoparticles, originating from ligand-to-metal charge transfer, as calculated by DFT and observed by XRD, was found essential for *in-situ* production of phosphides.

We took advantage of this simple and controllable method to investigate the correlation between phase composition of the products (different Ni/P ratios) and their activity as electrocatalysts for hydrogen evolution reaction (HER) and as anode-materials in Li-ion batteries. The materials studied herein exhibit a clear composition-activity trend for both HER and Li-ion batteries (LIBs), providing high performance, which are comparable to nickel phosphides produced by other common methods. Ni_3P products were found favorable as HER electrocatalysts, with 145 mV overpotential at 10 mA/cm^2, and Ni_2P products are favored as LIBs anode materials, with 206 mAh g^{-1} capacity; both with high morphological and electrochemical stability.

This new simple synthetic path, along with the elucidation of the high-temperature reaction mechanism, offer new possibilities for the synthesis and design of low-cost catalytic materials with

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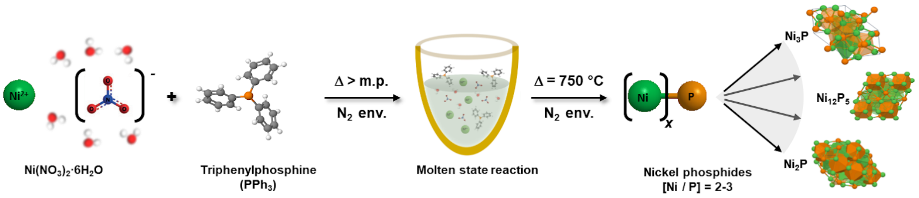
[1] R. Geva, M. Shalom *et al*, *J. Mater. Chem. A,* **2021**, 9, 27629-27638.

a wide variety of single and multi-component transition-metals.



Scheme 1 Illustration of nickel phosphides synthetic route involving a direct thermal reaction between nickel nitrate and triphenylphosphine in molten state

Oral presentation 15:

Laser induced all nanocarbons hybrid electrodes with improved conductivity and flexibility

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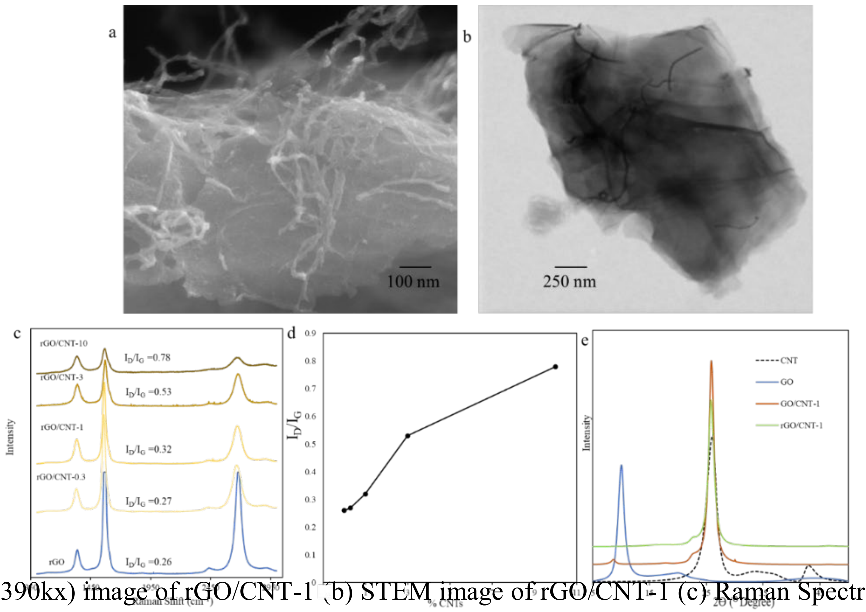
Laser processing of nanocarbon films emerges as the preferred technique to prepare carbon-based electrodes. A great effort focuses on exploiting this fast, sustainable, and cost-effective method on a broader range of nanomaterials. This study describes the laser-induced production of rGO/CNT composites and their application as flexible electrodes. Conductive carbonized films were imprinted on a flexible substrate by laser-carbonization. The composites formation is supported by a detailed microstructural and chemical analysis, which confirms the structural integration of rGO with CNTs. Electrodes containing CNTs exhibit 7.5-fold increase in conductivity compared to only rGO electrodes. Importantly, when the electrodes are bent, the conductivity retention of the composite is significantly superior compared to the only rGO electrodes. Upon bending, the change in conductivity is lowered from 0.62 to 0.19. Furthermore, when used as electrodes in flexible supercapacitor devices, the composites with CNTs show 98.45 % retention in specific capacitance while maintaining structural integrity. In contrast, rGO electrodes without CNT addition deform upon bending and retain only 63.88 % of the relaxed specific capacitance.



(a) SEM (390kx) image of rGO/CNT-1 (b) STEM image of rGO/CNT-1 (c) Raman Spectroscopy of laser-reduced rGO/CNT-1, I_D/I_G ratio dependence with the number of CNTs. (d) XRD of GO/CNT-1 films.

Oral presentation 16:

Templated electrodeposition of nanowires arrays: influence of natural convection

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Nanowires (NWs) are almost one-dimensional nanostructures with aspect ratio reaching 1000 and even more. They are of great interest to researchers because of unique physical and chemical properties and their applications in electronic, optical, magnetic and biological devices [1,2]. The templated electrodeposition method is most widely used for obtaining of arrays of NWs [3]. The obvious advantages of this method include simplicity of implementation, as well as the ability to control the length, diameter, and morphology of NWs. However, an important problem of templated electrodeposition is the high lengths dispersion of the formed NWs. Features of mass fluxes in the system defined by convective and diffusion processes are ones of the main causes of this problem. Thus, the investigation of the influence of natural convection during electrodeposition in an electrochemical cell on the length distribution of the formed NWs is an extremely important task.

35 μm nanoporous anodic aluminum oxide (AAO) films obtained by two-step anodizing aluminum (0.3M $H_2C_2O_4$, 40V, 1±1 °C) was used as template for electrodeposition of NWs. A 2 nm Cr/ 120 nm Au film serving as working electrode was deposited by magnetron sputtering onto bottom side of the AAO template. Copper was used as the nanowire material. In addition to their wide application, copper NWs are deposited with a high current efficiency, and hydrogen evolution does not lead to significant changes in their morphology. Electrodeposition was carried out from a solution containing 0.1 M $CuSO_4$ and 0.1 M H_2SO_4 (pH = 1.08) in potentiostatic mode in a three-electrode electrochemical cell. During electrodeposition the electrolyte was constantly agitated by magnetic stirrer with the rate of 100 rpm.

The values of pore diameter on top and bottom sides of AAO template were 58 ± 5 and 46 ± 1 nm, respectively, the porosity was about 28%. According to the cyclic voltammetry (CVA), it was found that copper is electrodeposited in the kinetic mode at overvoltage of -0.0 – -0.2 V and in the diffusion mode at -0.3 – -0.6 V relative to the equilibrium potential of copper deposition in this solution (0.31 V). The limiting diffusion current was about 2.8 mA/cm^2. The first NWs reached the template surface in the diffusion mode of electrodeposition after 500 s.

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Session E: Energy & Storage
Chair: Prof. Doron Aurbach (BIU)

Invited Lecture 5:

Suppression of Electrode Material Degradation by Using Surface Modifications Techniques

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Powering most currently used portable devices, batteries ushered electronics into a new era of mobile energy, directly supporting and influencing our daily lives. However, the ever-increasing demand for energy storage devices with improved performances and is challenging the scientific community to develop new chemistries and morphologies of ***electrode materials (EM)*** to move ***beyond current technology*** toward electrochemical storage devices with higher energy density, superior power performance and significantly extended stability.

Understanding fundamental degradation mechanisms of EMs, and their mitigation strategies, are challenged by constraints of the liquid electrolyte environment and the complexity of electrode/electrolyte interphase formation, namely the solid electrolyte interphase (SEI) layer which forms, grows, and changes (on the electrode interface) with battery usage. Accordingly, the research community is increasingly seeking new pathways to understand and control battery degradation, including new diagnostic and characterization methods as well as mitigation strategies (e.g., electrode surface treatments, electrolyte additives and artificial SEI layers).

In my talk I will demonstrate how surface modification of EMs, significantly suppress the degradation of the battery components (e.g. electrodes, and electrolyte) and facilitates long-term stability of the electrochemical device.
I will demonstrate how in our lab, we modify the surface of the EMs by either thin protection layer applied on its interface (using atomic/molecular layer deposition- M/ALD), or by surface reduction of high voltage cathode materials. I will farther show how we monitor *In-Operando* the degradation of the electrode\electrolyte interface using online electrochemical mass spectroscopy (OEMS), and will demonstrate the efficacy of our coating strategy in suppressing the degradation pathway of the Ems.

Oral Presentation 17:

Understanding highly complex electrochemical systems for energy applications

Yevgeny Rakita [a,b,g,*], James L. Hart [b], Partha Pratim Das [c] , Sina Shahrezaei [d] , Daniel L. Foley [b] , Suveen Nigel Mathaudhu [d,e] , Stavros Nicolopoulos [c] , Mitra L. Taheri [b] , Simon J. L. Billinge [f,g]

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With the growing complexity in structure and composition of functional materials, and particularly those in use in electrochemical systems, we often find ourselves puzzled when trying to correlate a structural description of the system with a certain property, for example, ionic or electronic conductivity. Complete modeling of the structure becomes increasingly difficult and often lead us to compromise and describe a material system, such as an electrode interface, in an average way that is too simplistic to explain measured properties. In this talk, I will introduce the Scanning Nano-Structure Electron Microscope (SNEM) [1] conception for mapping the evolution of structural correlations and the correlation lengths. Among many structural features that can be extracted from SNEM, I will focus on mapping the chemical short-range order, which corresponds to a local chemical environment that affects ionic and electronic transport. Particularly, I will focus on an amorphous alloy that interfaces with a crystalline system, similar to what one may find around at the interface between the electrode and the electrolyte, or across a solid electrolyte. SNEM, together with a data-driven analysis approach, reveals the structural variability across a 100 nm thick laminated multicomponent complex chemical system, and by doing so, allows asking new questions that link structural descriptors and functional properties in energy systems.

[1] Y. Rakita et al., ‘Mapping Structural Heterogeneity at the Nanoscale with Scanning Nano-structure Electron Microscopy (SNEM)’, 2021, arXiv:2110.03589

Oral Presentation 18:

Assessment of confined water in electrodes for energy storage by EQCM-D

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The need for advanced electrodes capable to store a large amount of energy and yet providing fast charging rates accelerated the search for new electrochemically active compounds. In this regard, the use of 2D structures, open framework structures, and organic electrodes is gaining momentum in recent years. Unlike conventional intercalation compounds utilized in Li batteries which can host only lithium, these structures by most, are not limited by the size or the valance of the inserted ions. Hence, they are considered to be highly attractive candidates for ‘beyond lithium’ energy storage as well. These compounds have unique frameworks which contain confined water molecules either as part of their crystalline structure, trapped between the electrode layer, or in adsorbed form. The presence of the confined water has a significant influence not only on the physical parameters of the electrodes but also on their charge storage mechanism and their electrochemical performance. The existence of water in the electrodes may facilitate the insertion of multivalent ions by screening repulsive interactions with the host atoms from one hand but can occupy active insertion sites from the other. Hence it is necessary to develop effective methods that enable evaluation of the H_2O dynamics in electrode structures upon their polarization. In this lecture, the use of electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) for real-time assessments of water fluxes at operated electrodes will be presented. Two demonstrative studies related to the effect of the inserted/extracted water on the charging mechanism and the performance of Ti_3C_2 (MXene) electrodes, and organic anodes (polyimide) will be described as well.

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Oral Presentation 19:

Ultralow Platinum Loading for Redox Flow Battery by Electrospinning

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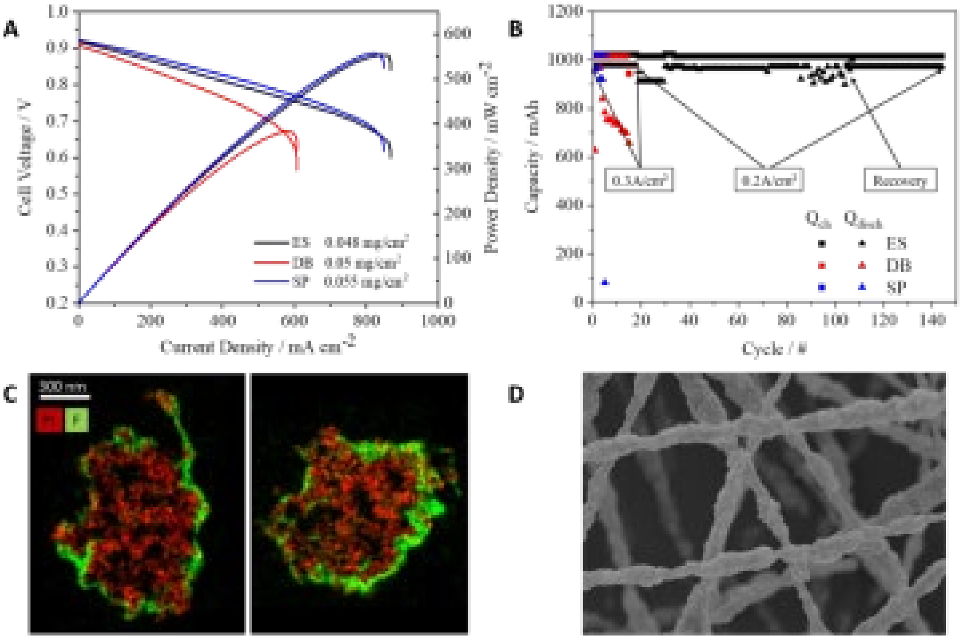
Performance, durability, safety and cost of catalytic materials are fundamental parameters in every electrochemical system, especially for very long-term storage solutions. The acidic environment in Hydrogen Bromine Redox Flow Batteries (HBRFB), which targets tens of thousands of hours in durability, makes the challenge even more acute.[1] The first and main effort was to explore the lower limits in catalyst loading for two of the most active precious group metals (PGM) – platinum and iridium (each of them individually and in bimetallic catalyst). The catalyst has been structurally characterized and lab-scale redox-flow cell have been cycled with a decreasing loading of PGM for the three different types of catalyst (Pt, Ir, PtIr). The carbon support and polymeric coating on the Pt catalyst enable dramatic reduction of 57% in platinum loading (0.36mgPt/cm^2) while keeping a high discharge power loading of 1.56W/mg$_{PGM}$.

Although the impressive reduction, PGM loading in RFB is still in order of magnitude higher than in Fuel Cells (FCs). Electrospinning, as a well-known technique for nanoscale polymer fibers production, was used to create catalyst-polymer mat cathode for H_2/O_2 FC. Better distribution of the Pt/C particles and the Nafion binder in the nanofibers (400-800nm fiber diameter) allows higher electrochemical active surface area and improved ionic conductivity during FC operation.[2]In order to test this method in RFB, catalyst coated membrane (CCM) with electrospun catalyst was fabricated. The electrospun (ES), sprayed (SP) and Dr. Blade coated (DB) electrodes were compered in initial polarization (fig. A) and for cycling durability (fig. B). ES shows high performance and durability over more than 140 cycles at minimal platinum loading of 0.048mg/cm^{2}and maximal power loading of 11.5W/mg$_{PGM}$. XPS and XRF measurements for the used catalytic layer showed that the platinum is still available, in contrast to the SP&DB electrodes, whose catalyst was unseen after few hours of low performance operation. The accepted structure of Nafion coated fibers (fig. C) limits bromides corrosion of the catalyst, improves the electrode stability and enables an effective recovery during long term operation.

kobby



(A) Polarization comparison between coating methods; (B) cycling durability comparison of HBRFB; (C) STEM-EDS cross-section elemental map of a single catalyst fiber and (D) SEM image as-spun fiber mat.

Acknowledgements

The research has been funded by the Ministry of Science, Technology and Space (MOST).

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[2] W. Zhang and P. N. Pintauro, *ChemSusChem*, 4, 1753 (2011).

Oral Presentation 20:

Li Batteries Cathode Material Stabilization Using ALD Synthesis of ACEI for Medical Applications

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Medical devices use non-rechargeable lithium batteries in critical applications to patients, either lifesaving (implantable cardiac defibrillator ICD etc.) or life preserving (cardiac pacemaker etc.). Such devices have stringent requirements on functionality and costs. The complex electrochemistry in Lithium batteries employed today in medical devices leads to fast degradation, and the need to replace the battery in a surgical procedure.

The dominant primary ICD batteries are cells with Li metal as the anode and Silver Vanadium Oxide (SVO) as the cathode. The main degradation mechanism of this type of battery is the dissolution of the cathode. Ions released from the cathode deposit on the anode, causing an increase in impedance and restricting power for needed therapeutic shock in case of an emergency. One way to mitigate this is the creation of an artificial CEI layer on the cathode side, to mitigate its degradation.

Atomic layer deposition (ALD) enables uniform coating by thin films, even on surfaces with challenging topography. A model system for artificial CEI is Al_2O_3, mostly due to its ease of synthesis by ALD. This work focus on synthesis of thin Al_2O_3 layers using ALD for primary Li batteries. Here we present preliminary results regarding the synthesis, characterization and electrochemistry of SVO batteries.

Keynote Lecture 3:

Increasing the Cycle Life of Silicon-Anode Lithium Ion Battery and Lithium Metal Battery

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Because of their higher energy density, compared to graphite-anode lithium-ion batteries (GLIB), rechargeable lithium-metal batteries (LMB) and silicon-anode lithium ion battery (SLIB) have been considered as the most attractive next-generation energy-storage systems (ESS). A promising approach to improving LMB performance, that has gained interest in recent years, is the use of anode-free lithium-metal batteries (AFLMB). Such battery configuration enables elimination of the problem of using excessive amounts of lithium in LMBs, hence increasing the specific energy of the battery. Furthermore, silicon is a low-cost and environmentally friendly material, and is the second most abundant element in the Earth's crust. Its theoretical capacity of 4200mAh g^{-1}, is an order of magnitude greater than that of graphite. Nevertheless, the main and most important challenge with both systems is the short cycle life. This work explores the beneficial effects of integrating metal-oxide nanoparticles (MONPs) into the liquid electrolyte of these systems. It was found that the addition to the electrolyte of low concentrations (0.1 to 5%) of MONPs significantly improves coulombic efficiency (CE), capacity retention (CR) and the SEI properties. In both cases, the cycle life was more than doubled.

Keynote Lecture 4:

Rechargeable batteries for electromobility, challenges and reality.

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Electro-mobility is the major challenge today in the field of electrochemical power sources. However, we encounter too many unsupported promises, too much noise! Examples: Many publications on ‘novel’ nano-materials, not suitable for practical battery applications. Nanomaterials may mean high surface area and pronounced side reactions. For instance - thousands of papers on conversion reactions anodes (nanomaterials), none of them show performance at elevated temperatures, why? Also nano-materials have puffy structure (difficult to process into electrodes). A lot of words (recently also conferences) on “ beyond Li-ion batteries”. Beyond…

for what purposes? Hard to see what can be relevant for electrochemical propulsion beyond Li-ion batteries (except fuel cells). There are too many unsupported promises on very high energy density, fast charging.. where are the limits? In fact, the only relevant partner to Li ion batteries for electro-mobility may be H_2/O_2 fuel cells, which are becoming highly relevant power sources because hydrogen can be stored in EVs at high pressure. The main theme of this presentation is to examine what is the true horizons for advanced Li ion batteries that can promote the electro-mobility revolution. The limiting factor in Li-ion batteries in terms of energy density, cost, potential, durability and cycling efficiency are the cathode materials used. The most promising cathode materials for advanced Li-ion batteries are Li and Mn rich layered oxides ,$Li_{1+x}[MnNiCo]_{1-x}O_2$ (providing specific capacities > 250 mAh/g, but at high voltages) and lithiated transition metal oxides, $Li[NiCoMn]O_2$ compounds, in which the main transition metal is nickel. As the amount of Ni in the latter cathode materials is higher, the specific capacity is higher as well, yet can be extracted at relatively low potentials (< 4.3 V vs. Li) which do not endanger the anodic stability of the electrolyte solutions used in these batteries. For instance, the specific capacity of $LiNiO_2$ cathodes can reach 240 mAh/g upon charging up to 4.3 V. However, as the content of Ni is higher, these cathode materials are less stable mechanically, thermally and electrochemically. We will explain the problems and will demonstrate solutions for them. Using judicious doping and/or surface coating, it is possible to fully mitigate detrimental situation with both classes of cathode materials. After gaining enough experience, it is possible to develop computational routes that can suggest optimal doping and coating processes. This presentation reports about our ongoing work in the field. We can conclude that developing advanced Li-ion batteries, fully suitable for long-range electric vehicles, is real, practical and fruitful. Traditional graphite anodes may be sufficient, however, there are some developments related to silicon containing anodes that deserve discussion in this presentation. The use of Li metal anodes in rechargeable batteries can increase further their energy density, on the account of durability & safety. Li-sulphur and Li-NCM batteries can be suitable for propulsion of unmanned vehicles (like drones) where some compromise between very high energy density and safety features can be justified. The presentation will discuss some interesting examples. Finally, in order to develop EVs working at zero-fault level in terms of safety features, it may be justified to give-up high energy density and use Li ion batteries comprising graphite and $LiFePO_4$ electrodes. We will examine briefly such an option as well.

Plenary Lecture 2:

NMR Studies of Concentrated Aqueous Electrolytes

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Aqueous electrolytes present a safe and inexpensive alternative to those based on organic solvents. The discovery by Suo, et.al.,[1] that high salt concentration (> 10M) in water yields a solvation structure that increases the both the electrochemical stability window well beyond the 1.3 V water electrolysis window and the Li^+ transference number has spurred much interest in these systems. Nuclear magnetic resonance has proven to be a valuable tool to characterize solvation structures and transport properties of electrolytes. We present here results in collaboration with the U.S. Army Research Lab (Kang Xu, et.al.) and the University of Maryland (Liumin Suo, Chunsheng Wang, et.al.) on LiTFSI in water, up to 21 M. Despite the high macroscopic viscosity of these super-concentrated solutions, nanoscopic heterogeneity provides a mobile pathway for ~ 40% of the Li^+ ions.

Extensions to non-lithium chemistries are also described. Motivated by potential application in aluminum ion batteries, we investigated $Al(OTf)_3$ in water, up to 3.6 M, in collaboration with the U.S. Army Research Lab (Glenn Pastel, Kang Xu, et. al.) and Pacific Northwest National Lab (Karl Mueller et.al.). Among several findings that suggest serious performance challenges, we find that the diffusing Al-containing species are closer to monovalent than trivalent.

Finally, in collaboration with Fudan University (Ziyue Li, Fei Wang), we have studied concentrated water phosphoric acid solutions envisioned for proton-based batteries that can operate at low temperature. The observed conductivity maximum at 5.9 M concentration is attributed to a change in solvation structure, in addition to the usual trade-off between viscosity and carrier concentration.

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Keynote Lecture 5:

Electrochemical performance of MXene-based catalysts at positive potentials

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Transition metal carbides have been widely studied as replacements for carbons as catalyst supports in electrochemical systems. Since the discovery of MXenes in 2011, research into their use in electrochemical systems has attracted much attention since most MXenes are two-dimensional transition metal carbides. MXenes therefore allow for the simultaneous exploitation of the electrochemical properties of transition metal carbides together with those of two dimensional materials. While their activity in many systems shows promise, MXenes are far less durable compared to their bulk metal carbide counterparts, and restricting their degradation is an area of ongoing research. The overwhelming majority of degradation studies are done at potentials below the reversible hydrogen electrode. Here, we study the degradation mechanisms and performance of the titanium-based MXene, Ti3C2Tx, at potentials higher than the reversible hydrogen electrode, in an effort to improve the durability of MXene-based electrodes for a wider array of electrochemical applications while not sacrificing their activity.

Poster Presentations-Catalysts & Redox Reactions

PC1

Preparation of Biocompatible Ceramic Coatings on Titanium Implants by the MAO Method in Molten Salt

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Titanium implants are an integral part of surgical practice in traumatology and orthopedics for various purposes[1]. Meanwhile, cases of implant rejection are common, and the rate of new bone growth on the untreated titanium surface is low. The rate of recovery of the patient directly depends on the regeneration rate of body tissues, which is determined by the behavior of cells at the site of surgery. One of the proposed solutions is using bioactive coatings that improve the biocompatibility of implants and cell proliferation and adhesion.

As a bioactive coating can be applied, hydroxyapatite is usually used, similar to bone tissues' properties and chemical composition.

One of the most advanced coating technology is micro arc oxidation in an aqueous electrolyte, which makes it possible to form products from titanium with bioactive oxide layers. However, this technology has several significant disadvantages: the impossibility of processing large-sized items due to electrolyte heating, high currents and voltages, the low current output of the oxidation process, decomposition of electrolyte components in the process, electrophoresis, etc.

An alternative solution can be the use of nitrate salts[2] instead of an aqueous electrolyte. The advantages of this process include energy efficiency, simplicity of technological execution, the ability to process large-sized parts, a high output current, the absence of unwanted side processes, high protective and bioactive properties of the coatings and etc.

In this study, the coating of titanium oxide-containing apatite nanoparticles was formed by MAO. The effect of current and voltage at a specific frequency on the formation of the oxide coating on the morphology, chemical, and phase composition, was studied. The biocompatibility of the created coating was studied by contact angle (CA) measurements. The potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS) studied the anti-corrosion properties of untreated and oxide-coated alloys.

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PC2

Electronic and Size Effects of Molecular Catalysts on Homogeneous and Heterogeneous HER

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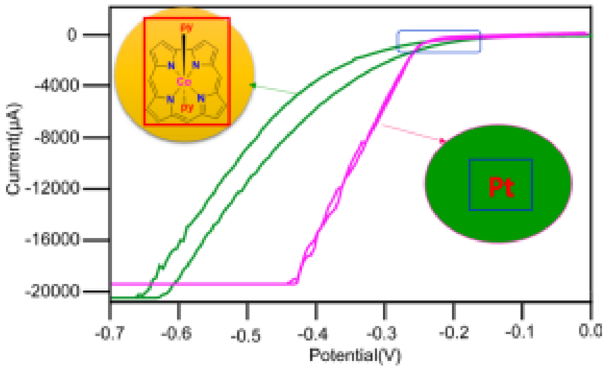
One most urgent and challenging need of this era is to design suitable alternatives for non-renewable energy sources. Hydrogen-based fuel cell are the best choice, but the main problem is the low abundance and high cost of Pt, which is still the most efficient catalyst and most expensive component of fuel cells. Thus, the feasibility of hydrogen economy depends on the design of efficient catalysts based on earth abundant metals. In the present investigation, we have analyzed Co corroles with different electron withdrawing substituents and sizes for electrocatalytic proton reduction. The smallest derivative (cor)Co^{III}(py)2 with only H atoms on the macrocycle (depicted in the Figure), provided the best catalytic activity and highest faradaic efficiency under the application relevant heterogeneous conditions. Surprisingly, its onset potential is more positively shifted than those of the much more electron-poor complexes; and pleasingly quite close to that of Pt (at -10 mA/cm^2). Accompanying mechanism-of-action investigations exposed a new pathway in which protons are activated by singly rather than doubly-reduced (cor)Co^{III}(py)2.



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PC3

Laser Processed Magnetite Nanoparticles Embedded on rGO Composites for Efficient Electrocatalytic Oxygen Evolution Reaction

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Fabricating earth-abundant, highly-active catalysts in a scalable and cost-effective method for OER is vital and challenging. Recently, laser processing has emerged as a promising route to obtain micron-thick films of highly graphitic carbons. The laser approach enables a one-step synthesis of highly-dispersed nanoparticles under ambient temperature and pressure conditions. In this work, we fabricate magnetite- reduced graphene oxide (rGO) composite electrodes demonstrating promising OER catalysts. The level of graphetization can be controlled by tuning laser parameters and the precursors' thickness. The detailed chemical, structural and morphology characterization and electrochemical measurements were investigated. With only five atomic percentages of metal, the designed magnetite-rGO electrocatalyst lowered the overpotential by 40 mV at 10 mA cm^{-2} with a smaller Tafel value (63 mV dec^{-1}). Moreover, our studies demonstrate that magnetite-rGO nanocomposite is a stable OER electrocatalyst with only 13.5 % activity reduction after 10 hours of chronoamperometric operation. This work combines an efficient nanocomposites fabrication method with important implications for energy-related applications.

PC4

Transition metal Chalcogenide Catalysts For Ammonia Electro-Oxidation: A Study On Activity And Selectivity

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On tackling the problems of green house gases along with serving the global energy demand, selective oxidation of ammonia to nitrogen has shown remarkable potential over the years. Ammonia is carbon free and has high energy density of 11.5 MJ/L compared to that of liquid hydrogen (8.5MJ/L) and compressed hydrogen (4.5MJ/L at 690 bar and 15˚C) [1]. Low vapour pressure of ammonia (8-10 bar) allows for its easy storage and it is the second most produced substance in the world next to sulfuric acid with wide distribution which makes it a potential fuel for the future. In the efficient conversion of ammonia to electricity in fuel cell technologies, such as portable power sources, a major challenge is the identification of a suitable catalyst that can selectively oxidize NH_3 to N_2 at low over potentials, and ambient pressure and temperature, at high rates.

Transition metal chalcogenides have been explored as catalysts in the field of water splitting, CO_2 reduction, N_2 reduction and as ammonia sensors [2] but have not yet been studied as catalysts for ammonia oxidation. This study focuses mainly on copper based chalcogenides, (CuS and CuSe) as catalysts for selective electro-oxidation of NH_3 to N_2. The catalysts were synthesized and characterized using PXRD and SEM-EDS. Electrochemical techniques such as cyclic voltammetry, linear sweep voltammetry and chronamperometry has been used to analyze the activity and stability of the catalysts. Copper sulphides were found to be more active towards ammonia oxidation (5.4mA/mg) compared to copper selenides (1.5mA/mg) (in a solution of 0.1M KOH and 10mM NH_3 at 20mV/s). Though the CuS catalyst lost its activity with time, it was found that an electrochemical treatment with Na_2S helped in regaining partial activity. Hydrazine and nitrogen were detected as byproducts of ammonia oxidation reaction using mass spectrometry. Nitrite was also detected in solution using UV-Vis spectrometry.

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PC5

Application of Molecular Catalysts for the Oxygen Reduction

Reaction in Alkaline Fuel Cells

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The development of precious group metal-free (PGM-free) catalysts for the oxygen reduction reaction is considered as the main thrust for the cost reduction of fuel cell technologies and their mass production. Within the PGM-free category, molecular catalysts offer an advantage over other heat-treated PGM-free catalysts, owing to their well-defined structure, which enables further design of more active, selective, and durable catalysts. Even though non-heat-treated molecular catalysts with exceptional performance have been reported in the past, they were rarely tested in a fuel cell. Herein, we report on a molecular catalyst under alkaline conditions: fluorinated iron phthalocyanine (FeFPc) supported on cheap and commercially available high surface area carbon - BP2000 (FeFPc@BP2000). It exhibits some of the highest activity reported for molecular catalysts under alkaline conditions in half-cells and fuel cells.

In addition, we used iron phthalocyanine (FePc) in fuel cell as a model for the catalytic active site in pyrolyzed PGM-free catalysts and applied electrochemical technique – Fourier transform alternating current voltammetry (FTaCV) for in-situ quantification of site density. We could show that FTaCV can be used as analytical tool for accurately detection and quantification of the catalytic center in pyrolyzed catalysts.

PC6

Electrochemical Reduction of Hydrazine by Metallocorroles

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Fossil fuels are the main source of energy for a long time already, but also the main cause for air pollution and emission of greenhouse gasses.[1] This induces the large need for developing alternative and green power devices.[2] Recent developments in alkaline fuel cells increased the interest in hydrazine oxidation, which can offer high theoretical voltage of 1.56 V, carbon free emissions and easy transportation.[3] The hydrazine oxidation reaction (HzOR) is a multi-electron and multi-proton process, proceeding best in alkaline media: $N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$, $E^0 = -0.33V$ vs RHE at pH = 14. Electrocatalysts are required to make this reaction efficient and directed towards formation of molecular nitrogen. Various precious metals catalyze HzOR effectively, however, their low earth abundance and high cost motivate electrochemists to search for alternatives such as Ni, Co, Cu and Fe.[3,4] Molecular catalysts can be adsorbed on porous carbon substrates for such purposes; and indeed porphyrins and phthalocyanines were reported since 1980 as electrocatalysts for hydrazine oxidation.[5,6] Corroles, also from the porphyrinoid family, are also useful electrocatalysts for reduction of protons, oxygen and carbon dioxide, water oxidation, and most recently also for hydrazine oxidation.[7] To increase the scope of molecular catalysts for heterogeneous hydrazine oxidation in alkaline conditions, we now focus on cobalt and iron corroles that contain very different-in-size substituents: pentafluorophenyl, trifluoromethyl, and hydrogenrole. After adsorption on Vulcan XC-72R and BP2000, we got improvement of the catalysis relative to the carbon as is, with onset potential of 0.4V vs RHE (pH = 14) and higher current than reported with iron corroles.[7] The reactions proceed by a four-electron path, as required for fuel cells, indicated by strong nitrogen gas evolution.

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PC7

Performance Optimization of Hydrogen Generating Disposable Pouch Membrane Electrode Assembly using 1D MATLAB Simulation

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Abstract

The hydrogen fuel cell is a promising technology due to its familiar advantages such as high efficiency, no product (only water), and easy oxygen availability. However, its applications are limited by the assembly weight and availability of hydrogen for applications related to portable and airborne devices. In this study, a self-hydrogen generating device (Figure 1) from hydrolosys of metal hydrid powder using water molecules present in the surrounding humidity is studied using a 1D steady-state MATLAB model.

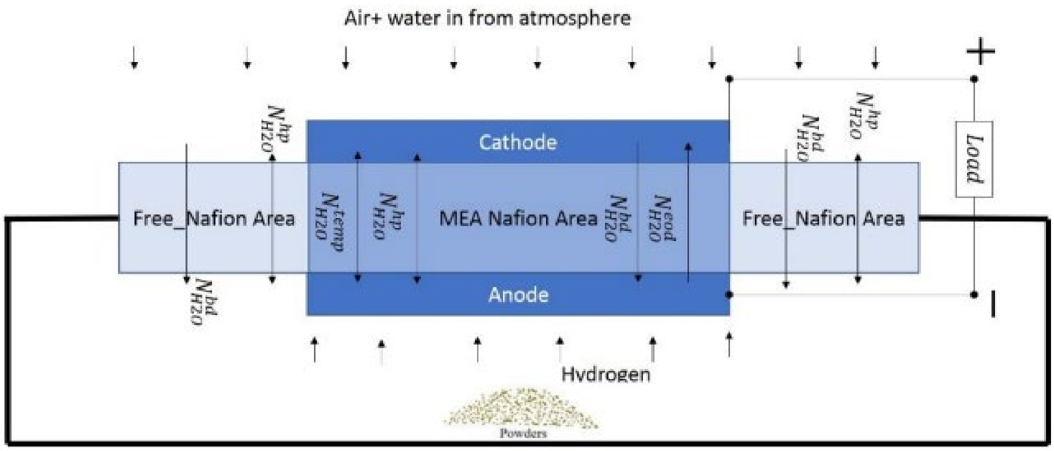

Figure 1: Schematic diagram of the device

The model developed here has distinguished features such as air & hydrogen breathing electrodes, estimation of water flow through the membrane, hydrogen production & storage combined with physical parameters to predict system performance. It is also used to investigate the effect of operating parameters such as pressure, temperature and humidity on the polarisation curve. This study shows that water transport across the membrane plays a crucial role in improving power density and hydrogen generation. The model is compared with experimental analysis for validation, and system parameters such as free membrane area, electrode area and membrane thickness are optimized for robust performance.

PC8

Production of ceramic coating on Ti-6Al-7Nb with bioactive and antibacterial properties by Plasma Electrolytic Oxidation

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Titanium and its alloys (Ti - 6Al - 7Nb) are widely used in medicine, such as hip and cardiological joint replacement, dental and body implants, due to its corrosion resistance, low cytotoxicity, and good mechanical properties. However, the osseointegration process is prolonged due to it’s inertness to biological tissues and fluids. Sometimes, the biological systems rejects the implant and causes infectious, inflammation and other immunostimulations[1]. To increase bioactivity and eliminate bacterial infection, various methods and compositions used for surface modifications. One of the most promising methods for surface modification with the possibility of introducing bioactive and antibacterial components is micro arc oxidation in molten salts[2]. Precursors of hydroxyapatite (HA) and copper nanoparticles introduced into the coating as bioactive elements and antibacterial agent respectively. The combined use of hydroxyapatite allows the formation of structures that mimic the composition of the bones of the body, increasing the osseointegration of implants. When a potential difference is applied, a ceramic coating formed on the surface of the substrate, consisting of titanium oxides, HA, and copper oxides. In turn, the antibacterial agent inhibits the formation of a bacterial biofilm and destroys bacteria's cellular structure[3].

In this work, a titanium oxide coating layer created, contains hydroxyapatite and copper nanoparticles. The surface morphology, chemical and phase composition have been studied. Corrosion resistance and the effect of bioactive solution (Hanks solution) on surface morphology analyzed. Furthermore, the antibacterial activity of the Cu nanoparticles introduced into the coating examined on *Staphylococcus aureus* and *Escherichia coli*.

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PC9

Miniature and Light Fuel Cell Energy Pack based on Hydrolysis with Atmospheric Humidity

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Abstract

In this study, we present a novel light, portable, disposable, self-regulated and easily operated small energy pack, with a theoretical energy density of 1500 Wh/kg. The energy pack is based on hydrogen production from a chemical reaction of Lithium Aluminum hydride (LiAlH4) and water vapor extracted from the air humidity. The produced hydrogen is utilized to generate electrical power using an on-board fuel cell exposed to oxygenated air. The LiAlH4 powder is placed in a small plastic bag which has a window of a Nafion membrane (Figure 1). The Nafion is used both as a selective membrane allowing water vapor to enter the bag and reacting with the

LiAlH4, and as the reactant barrier and protons conductor of a membrane electrode assembly (MEA) with a catalyst for the reaction of the produced hydrogen with the outside oxygen and to generate electricity and water.

In the study we examined the effect of working conditions (e.g. ambient temperature and humidity) and system design (Nafion membrane size and thickness) on the hydrogen production rate, and the effect of MEA features on the obtained electrical power over time.

Four membrane types (with a thickness of 24.5-177 mm) and five membrane areas (1x1, 4x4x, 5x5, 6x6, 8x8 cmxcm) were examined. The experiments were conducted in a fixed temperature incubator (25.6°C) and the humidity was regulated by a humidifier (100% RH) (Figure 1a). Hydrogen production was measured using the water level in an upside-down graduated cylinder that was recorded using a GoPro camera. The reaction temperature was measured using a thermocouple. The chamber humidity and temperature were recorded using a data-logger. Each of the experiments lasts for up to 10 hours.

The effect of MEA features was examined under the same environmental conditions. We measured the obtained power over a resistor of 220Ω connected to the MEA electrodes (Figure 1b).

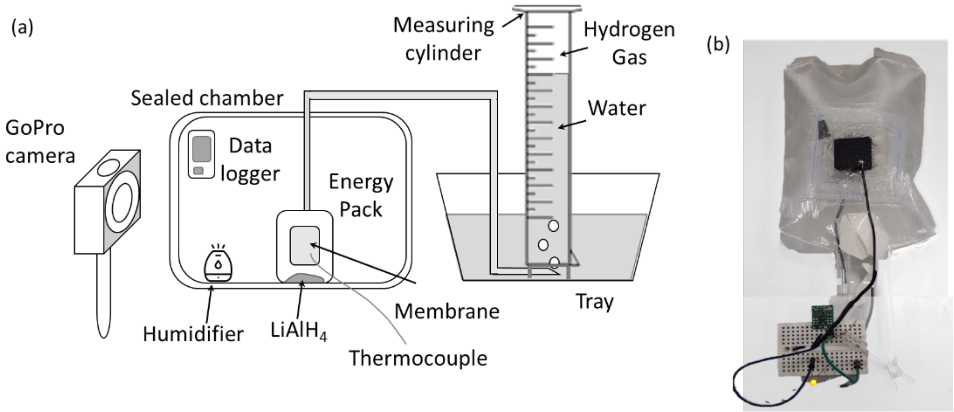

Figure 1: Descriptions of the first (a) and the second (b) experimental systems

PC10

Combined nanofiltration and advanced oxidation processes with bifunctional carbon nanomembranes

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Wastewater reclamation is becoming a top global interest as population growth and rapid industrialization pose a major challenge that requires development of sustainable cost-effective technologies and strategies for wastewater treatment. Carbon nanomembranes (CNMs)—synthetic 2D carbon sheets—can be tailored chemically with specific surface functions and/or physically with nanopores of well-defined size as a strategy for multifunctional membrane design. Here, we explore a bifunctional design for combined secondary wastewater effluent treatment with dual action of membrane separation and advanced oxidation processes (AOP), exploiting dissolved oxygen. The bifunctional membrane consists of a CNM layer on top of a commercial ultrafiltration membrane (Microlon™) and a spray-coated reduced graphene oxide (rGO) thin film as the bottom layer. The CNM/support/rGO membrane was characterized by helium ion and atomic force microscopy, FTIR, XPS with a four-point conductivity probe, cyclic voltammetry, galvanostatic measurements, and impedance spectroscopy. Combined treatment of water by nanofiltration and AOP was demonstrated, employing a unique three electrodedead end filtration setup that enables concurrent application of potential and pressure on the integrated membrane. For the model organic compound methylene blue, oxidation (by the Fenton reaction) was evaluated using UV-vis (610 nm). The rejection rate and permeability provided by the CNM layer were evaluated by dissolving polyethylene glycol (400 and 1000 Da) in the feed solution and applying pressure up to 1.5 bar. This demonstration of combined membrane separation and AOP using an integrated membrane opens up a new strategy for wastewater treatment.

PC11

Modeling Of Electric Field Distribution and Thermal Effects in Basal Cell Carcinoma (BCC) During E-biopsy

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BCC is the most common skin cancer, accounts for almost 75% of skin cancers. To confirm diagnosis, biopsy is essential, but it is time-consuming, costly and can cause pain, scars, and infections. Furthermore, only part of the malignant tissue is resected and classified. Recently, we developed new minimally invasive method for molecular profiling of BCC named e-biopsy with electroporation. In e-biopsy, non-thermal pulsed electric fields are delivered via a needle-shaped electrode which temporarily increase cell membrane permeability and creates nanopores in the cell membrane, that enables extraction of BCC specific biomarkers in vivo. As the technique is minimally invasive, multiple probing in different locations of the lesion and in the same procedure can be done. The objective of this work is to study various configurations of electrode designs and their impact of sampled tissue volume. We used the finite element method to study computationally the electric field distribution in BCC electrical model under different e-biopsy design parameters using Quick Field software. Electric field distribution was simulated in two different configurations. In configuration A, ground electrode was placed on BCC lesion, while in configuration B tumor size was smaller and ground electrode was placed outside of BCC radius, on healthy, adjacent skin tissue. The tested e- biopsy design parameters were electrode radius, penetration depth, gap between ground to electrode, ground radius and BCC electric conductivity. The model was validated experimentally with a potato phantom model. To study brain safety during e-biopsy, we also simulated, the electric field distribution in head layers from skin to brain applying various voltages.

Electrode distance from the ground, electrode radius, and electrode penetration depth and radius, majorly increased the electroporated volume in configuration A, B, and potato phantom model respectively. We also demonstrated in our model that brain tissue is safe during e-biopsy in facial areas.

Choosing design parameters is crucial for maximizing the BCC electroporated volume, as more molecules potentially extracted during e-biopsy. Device geometry should be built carefully to achieve maximum safety and electroporated tissue volume, during e-biopsy.

PC12

Exploring pi-SnS for photoelectrochemical water splitting

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SnS is a compound semiconductor whose constituent elements are earth abundant and relatively non-toxic. Orthorhombic SnS (α-SnS), the stable phase at room temperature, has a direct optical band gap of 1.3–1.5 eV, a high absorption coefficient, and high charge carrier mobility. α-SnS is known as an efficient cathode for photoelectrochemical water splitting, an environmentally friendly, sustainable approach to generate green hydrogen fuel. The newly discovered π-SnS phase, a metastable cubic phase which can be stabilized at room temperature by surface passivation, has similar optoelectronic properties along with a larger band gap (1.5-1.7 eV), p-type conductivity and higher electrical conductivity. I aim at comparing the performance of π-SnS and α-SnS phases, in the form of chemical bath deposited nanoparticles and thin films, as photocathodes for the

photoelectrochemical hydrogen evolution reaction (HER). Material characterization included XRD, UV-VIS, SEM, and TEM, and electrochemical characterization was done by cyclic voltammetry, linear sweep voltammetry, and chronoamperometry. This will demonstrate the relative advantages and disadvantages of π-SnS as a photocathode for HER.

PC13

Corrosion protective properties of aluminum alloys coated by PEO method

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Plasma electrolytic oxidation (PEO) is an electrochemical method which creates a protective anode layer on aluminium or other valve metals and their alloys. PEO method can significantly improve corrosion protective properties of metals and alloys. Now PEO coatings are widely applied in fields from the building construction industry to the satellites productions.

The usage of an electrolyte based on molten salts can significantly reduce energy costs, while the resulting protective layer of PEO method has a denser structure and fewer impurities [1]. The molten salts electrolyte was a eutectic composition of nitrate molten salts with a melting point about 220C.

Protective coatings on aluminum alloys obtained in these molten salts using PEO were studied by various methods from impedance spectroscopy, XRD and SEM. The changes in the protective layer after exposure for various times in sodium chloride solutions were studied. Using the analysis of images obtained by the SEM method we found the porosity of the protective layer, the distributions of the pore radius and characteristic sizes of the formed pits. The strong correlation of porosity with the density of pits was revealed.

Comparison of polarization curves on aluminum alloys with and without PEO coating shows that the corrosion currents are reduced by several orders of magnitude due to the coating, besides the corrosion potential shifts up to +1V. Using a fitting, the limiting diffusion currents through the coating layer were estimated by Levich-Kautetsky equation. It was shown that the occurrence of pitting does not cause complete dissolution of the protective layer to the bare metal; moreover, the dense undissolved part of the coating layer can even increase its ohmic resistance.

The effects of experiment conditions on the anodic and cathodic curves were investigated. It was found that stirring of the electrolyte reduces the rate of anodic dissolution. This can be explained by alkalinization of the surface due to the removal of hydrogen ions from the surface. In addition, the effect of oxygen concentration on the corrosion rate was studied and the dependence of the corrosion potential on the concentration of dissolved sodium chloride was found.

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PC14

Lactate Analysis using Flexible non-Enzymatic Electrochemical Sensor

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Lactate is a diagnostic biomarker for various physiological conditions, which is produced in all the tissues such as the brain, muscles and it is present in the blood, cerebrospinal fluid, and sweat. Monitoring lactate levels of a person at the point of care will enable personalized health monitoring; however, the available commercial lactate sensors mostly use enzymes as biorecognition elements, which suffer from limited stability. Here, we report a novel flexible electrochemical sensor for lactate detection in artificial sweat samples. The sensor was fabricated on a polyethylene terephthalate (PET) substrate with gold electrodes. The sensor consists of two disk working electrodes (‘WE1’ & ‘WE2’; 2 mm diameter), a reference electrode (‘RE’; 1 mm diameter), and an arc-shaped counter electrode (‘CE’) to maximize the symmetry around the working electrodes (Fig.1A). Electrochemical characterization of the modified electrodes showed increased faradaic current characteristics with a reversible Nernstian behavior (Fig. 1B). Lactate in the artificial sweat sample was detected using the reduced graphene oxide (rGO) and platinum black modified electrodes (Fig.1C, D). By providing an enzyme-free sweat sensor for lactate detection, we hope to establish the means to develop patches for real-time monitoring of stress.

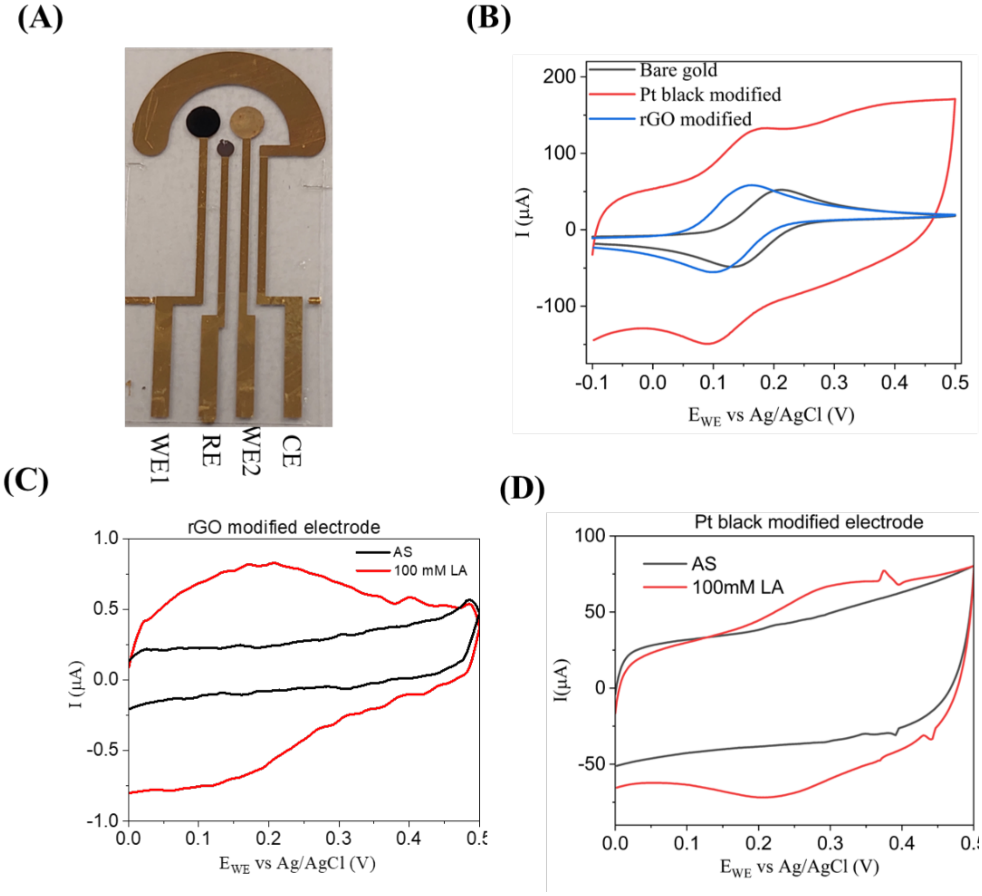

Figure 1. Lactate sensing using polyethylene terephthalate (PET)-based flexible electrochemical sensor. (A) Sensor design and (B) Cyclic voltammogram of bare gold, Pt black modified and rGO modified electrodes with 5 mM potassium ferrocyanide solution in 1M KCl (100 mV/s scan rate), cyclic voltammogram of lactate using (C) rGO modified electrode, and (D) Pt black modified electrode (100 mV/s scan rate).

PC15

Iron- Phthalocyanine Models the Active Sites Degradation in PEM Fuel

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Non-precious metal catalysts based on earth-abundant elements such as iron- and nitrogen-doped carbon materials have been deemed the most promising alternative to platinum-based catalysts for the oxygen reduction reaction in fuel cells. Despite tremendous progress in enhancing their activity, their usefulness as fuel cell catalysts remains in doubt due to their very short lifespan. The catalysts' unclear active-site structure has made it difficult to fully understand their degradation mechanisms thus far. In this work, we investigated the degradation mechanisms of a molecular model catalyst, iron-phthalocyanine (FePc), which has Fe-N_4 active sites similar to those seen in more active pyrolyzed Fe-N-C catalysts. Three primary demetallation mechanisms have been identified based on XPS and chronoamperometric studies. Various degradation pathways can be triggered by a combination of different iron oxidation states and oxygen species. The decay rates measured during stability tests can be used to determine what is causing the catalytic activity to deteriorate. As a result, this model can help better understand how Fe-N-C and other platinum group metal-free oxygen reduction reaction fuel cell catalysts degrade and mitigate these processes.

PC16

Hydrogen evolution reaction (HER) on Pt foil and Pt/C catalyst at near-neutral pH conditions

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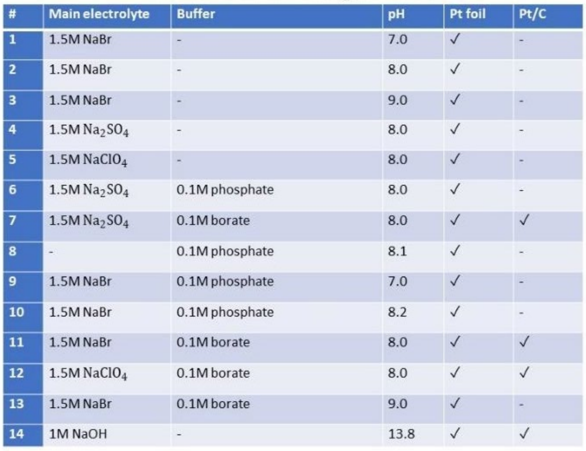
Hydrogen evolution is the core process of any water splitting technology (PEM or AEM electrolyzers, E-TAC water splitting, PEC water splitting, etc). In most of the commercialized electrochemical water splitters, HER does not represent the technology bottleneck due to its relatively fast kinetics, unlike the counterpart oxygen evolution reaction, at least on platinum-based electrocatalysts. However, at near-neutral pH conditions, even HER ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$) becomes the source of significant overpotential.

In our study we are aiming to investigate a set of electrochemical properties (along with the HER kinetics) on Pt foil and 40%Pt/Vulcan XC72 catalyst as the model cathode materials for bromide-based electrolytes of the brand-new water splitting concept we are currently developing.

Using a three-electrode electrochemical cell, we have studied pH effect on the HER kinetics and cyclic voltammograms (CVs) (#1-3; 9-11, 13-14, Table 1); effect of buffer on the HER kinetics and CVs (#2, 10-11, Table 1); anion effect on the HER kinetics and CVs (#2, 4-5, 7, 11-12, Table 1).

The pH effect on HER kinetics on Pt foil was shown to be negligible. The presence of the Br^- anions turned to suppress hydrogen and oxygen chemisorption on Pt, as well as the HER kinetics. However, only O-atoms adsorption is suppressed by Br^- presence in buffered solutions. The overpotential for HER on Pt foil at near-neutral pH conditions is dramatic, however even the use of Pt/C catalyst at high loading (0.5 mg cm^{-2}) in buffered Br$^-$ solutions reveal a negligible effect of the catalyst on the HER compared to Pt foil, unlike the positive effect observed in 1M NaOH (#14, Table 1).

Table 1. Solution compositions.



#	Main electrolyte	Buffer	pH	Pt foil	Pt/C
1	1.5M NaBr	-	7.0	✓	-
2	1.5M NaBr	-	8.0	✓	-
3	1.5M NaBr	-	9.0	✓	-
4	1.5M Na_2SO_4	-	8.0	✓	-
5	1.5M $NaClO_4$	-	8.0	✓	-
6	1.5M Na_2SO_4	0.1M phosphate	8.0	✓	-
7	1.5M Na_2SO_4	0.1M borate	8.0	✓	✓
8	-	0.1M phosphate	8.1	✓	-
9	1.5M NaBr	0.1M phosphate	7.0	✓	-
10	1.5M NaBr	0.1M phosphate	8.2	✓	-
11	1.5M NaBr	0.1M borate	8.0	✓	✓
12	1.5M $NaClO_4$	0.1M borate	8.0	✓	✓
13	1.5M NaBr	0.1M borate	9.0	✓	-
14	1M NaOH	-	13.8	✓	✓

PC17

Electrocatalytic and Photo-electrocatalytic Methanol Oxidation by Cobalt Carbonate

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Simultaneously boosting the electrochemical methanol oxidation reaction for direct methanol fuel cell is meaning full but challenging. Here, the $Na_3Co^{III}(CO_3)_3$ was deposited on Pt and Pd electrode surfaces by a chronoamperometric technique. The deposited $Na_3Co^{III}(CO_3)_3$ was characterized using various surface characterization techniques. The electrochemical and photoelectrochemical behaviour of the $Na_3Co^{III}(CO_3)_3$ precipitated electrode was studied using cyclic voltammetry and chronoamperometric techniques in KOH and Na_2CO_3 electrolytes for the methanol oxidation reaction. The $Na_3Co^{III}(CO_3)_3$ deposited on the Pt electrode showed enhanced current density in KOH/Na_2CO_3 media due to oxidation of methanol when compared to both bare Pt and $Na_3Co^{III}(CO_3)_3$ deposited on the Pd electrode. The $Na_3Co^{III}(CO_3)_3$ deposited Pt electrode performs high electrocatalytic oxidation and shows an anodic peak current density of 19.7 mA·cm^{-2} at 0.1 V vs. NHE.

Interestingly, the $Na_3Co^{III}(CO_3)_3$ deposited on the Pt electrode also shows a good photo-electrocatalytic response under UV-vis light irradiation. The anodic peak current density of methanol oxidation is about 22.9 $mA{\cdot}cm^{-2}$ under the light.

PC 18

Halogen-Hydrogen Bonding for the Synthesis of Active Carbon Nitride Materials

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Carbon nitride (CN) materials perform as photocatalysts for H2 production under sunlight irradiation. The most straightforward synthetic pathway towards CN materials is the thermal condensation of CN-containing precursors such as melamine. However, melamine tends to sublime and leads to unordered CN with very low surface area, poor charge separation, and limited light absorbance. Melem (2,5,8-triamino-tri-s-triazine, C6N10H6) one heptazine unit, the accepted repeating unit in CN-materials and an intermediate when synthesized from melamine.[1] The melem is known to form well constructed assemblies.[2]It is less prone to sublime than melamine due to increased $\pi - \pi$ interactions leading to better yields for the synthesis of CN-materials and better ordered CN. Here we show, that melem acts as a precursor to construct various carbon-nitride assemblies with different halogen acids, resulting in different morphologies and improved photocatalytic activity. While mixing melem with varying amounts of the other halogen acids in water, various supramolecular assemblies are formed. For example, the bromine and chlorine ions are known to interact with different nitrogen atoms of melamine,[3]and are assumed to do so with melem as well. After calcination and condensation, the different halides in varying concentrations alter the lead to different: morphologies, surface defect concentrations, specific surface areas and electron-hole conductive pathways, which in turn influence the photophysical properties of the resulting CN-materials, such as the absorption efficiency, band-gap energy, and position, as well as photoinduced charge carrier's lifetime and quantum efficiency. By studying different halogens and acid concentrations, the optimum acid concentration is found, and their structure-activity relations are elucidated.

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PC 19

Templated electrodeposition of nanowires arrays: influence of natural convection

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Nanowires (NWs) are almost one-dimensional nanostructures with aspect ratio reaching 1000 and even more. They are of great interest to researchers because of unique physical and chemical properties and their applications in electronic, optical, magnetic and biological devices [1,2]. The templated electrodeposition method is most widely used for obtaining of arrays of NWs [3]. The obvious advantages of this method include simplicity of implementation, as well as the ability to control the length, diameter, and morphology of NWs. However, an important problem of templated electrodeposition is the high lengths dispersion of the formed NWs. Features of mass fluxes in the system defined by convective and diffusion processes are ones of the main causes of this problem. Thus, the investigation of the influence of natural convection during electrodeposition in an electrochemical cell on the length distribution of the formed NWs is an extremely important task.

35 µm nanoporous anodic aluminum oxide (AAO) films obtained by two-step anodizing aluminum (0.3M $H_2C_2O_4$, 40V, 1±1 °C) was used as template for electrodeposition of NWs. A 2 nm Cr/ 120 nm Au film serving as working electrode was deposited by magnetron sputtering onto bottom side of the AAO template. Copper was used as the nanowire material. In addition to their wide application, copper NWs are deposited with a high current efficiency, and hydrogen evolution does not lead to significant changes in their morphology. Electrodeposition was carried out from a solution containing 0.1 M $CuSO_4$ and 0.1 M H_2SO_4 (pH = 1.08) in potentiostatic mode in a three-electrode electrochemical cell. During electrodeposition the electrolyte was constantly agitated by magnetic stirrer with the rate of 100 rpm.

The values of pore diameter on top and bottom sides of AAO template were 58 ± 5 and 46 ± 1 nm, respectively, the porosity was about 28%. According to the cyclic voltammetry (CVA), it was found that copper is electrodeposited in the kinetic mode at overvoltage of -0.0 – -0.2 V and in the diffusion mode at -0.3 – -0.6 V relative to the equilibrium potential of copper deposition in this solution (0.31 V). The limiting diffusion current was about 2.8 mA/cm^2. The first NWs reached the template surface in the diffusion mode of electrodeposition after 500 s.

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PC20

Joule-heating synthesis of free-standing transition metal phosphides based electrodes as electrocatalysts for CO_2 reduction reaction

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Transition metal phosphides (TMPs) have attracted great interest as high-performance, non precious heterogeneous (electro)catalysts for energy-related applications.[1] The incorporation of phosphorus into the metal structure imparts exclusive structural, electronic properties, and chemical stability. Although some TMPs can be synthesized through various synthetic pathways, including simple heating of a metal source with red phosphorus (RP) under vacuum conditions or an inert atmosphere using conventional furnaces, the process often consumes time and energy.

Here, we introduce a new strategy to synthesize TMPs *via* electrical Joule-heating and exemplify its advantages for electrochemical CO_2 reduction reaction (CO_2RR). Joule-heating-directed material synthesis technique is an innovative strategy to rationally design and synthesize high-quality materials such as ceramic materials in a facile, rapid, and controllable way.[2, 3] Typically, this method possesses elevated sample temperatures, resulting in fast kinetics and high heating rates. In this work, the Joule-heating-directed route is adopted to easily synthesize TMPs such as copper and nickel phosphides as self-standing electrodes for their utilization in CO_2RR electrochemical systems. To do so, a pressed pellet of precursors is sandwiched between two parallel Joule-heating carbon strips (*e.g.,* carbon cloth) that conformally wrap the pellet and act as radiation heaters with controllable temperatures as a function of the applied input power. This technique enables us to form TMPs-based electrodes that can be utilized directly as stand-alone electrocatalysts for efficient CO_2 reduction towards valuable products (e.g., alcohols and alkenes) with high selectivity and good faradaic efficiencies.

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PC21

Electricity generation in microbial fuel cell based on bacterial anode combined with kaolin

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Abstract

In a microbial electrolysis cell (MEC) that operates in wastewater (WW), the anode can be contaminated by non-exoelectrogenic bacteria, leading to a decrease in the hydrogen evolution reaction (HER) rate.

In this study, the electrochemical activity and chemical oxygen demand (COD) removal by an MEC based on *Geobacter sulfurreducens* (1 OD), which is encapsulated on the anode using alginate and chitosan or only alginate (AC-1 and A-1 bacterial anode, respectively), are compared with a non-immobilized anode. When acetate is used as the carbon source, the current density of the MEC based on the non-immobilized anode is 10.95 A m^{-2}, 15% higher compared to the immobilized bacterial anodes. When WW is used, the AC-1 bacterial anode yields the highest current density: 11.52 A m^{-2} at a potential of 0.2 V, 11 % and 29 % higher than the A-1 and the non-immobilized anodes, respectively. The AC-1 anode leads to a HER rate of 0.56 $m^3m^{-3}d^{-1}$ (at 0.5 V), COD removal of 75%, and composition of 92% *G. sulfurreducens*. SEM analysis shows a biofilm covered with a layer of (presumed) alginate. To our knowledge, this is the first study demonstrating an MEC based on an immobilized bacterial anode using alginate.

Keywords: Hydrogen, microbial electrolysis cell, immobilization, bio anode, alginate,

PC22

Carbon Supported Ternary Metal Catalyst $Pt_3Pd_3Sn_2$ for the Electrooxidation of Dimethyl Ether and Methyl Formate

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Dimethyl ether (DME) is a potential gas fuel in polymer electrolyte membrane fuel cells. DME offers higher energy density, lower toxicity, and minimum Nafion membrane crossover than the extensively investigated fuels (methanol and ethanol) [1]. However, the low activity of the state-of-the-art catalyst, PtRu, for DME oxidation, a limited understanding of the reaction mechanism, and blockade of the Pt active sites by CO_{ads} and $HCOO_{ads}$ formed at lower potentials hindered the application of the direct DME fuel cell. In this study, we have synthesized a highly active ternary metal catalyst supported on Vulcan XC72 carbon, $Pt_3Pd_3Sn_2/C$. From the DME Oxidation products analysis on this catalyst, we have seen the formation of methanol, CO_2, formic acid, and methyl formate (MF) and proposed a possible reaction mechanism accordingly [1]. We have reported a significant improvement in the catalyst electroactivity and site utilization through the oxidation of DME mixed with MF. DME and MF have different binding sites, confirmed from our density functional theory calculations, hence mixing them improved the surface coverage and anodic fuel utilization. Oxidative stripping of a monolayer DME+MF fuel adsorbed on the catalyst gave a higher oxidation charge ($Q_{DME + MF}$) than the summation of the charges provided by taking the two fuels separately (Q_{DME} + Q_{MF}). A fuel cell operated with a mixture of DME+MF anode fuel offered a higher peak power density (123 mW cm^{-2}) than DME (84 mW cm^{-2}) or MF (28 mW cm^{-2}) at the same anode fuel flow rate and working conditions (70 °C and ambient gas pressure).

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PC 23

Anchoring MoS_2 on Ethanol-Etched Prussian Blue Analog for Enhanced Electrocatalytic Efficiency for Oxygen Evolution Reaction

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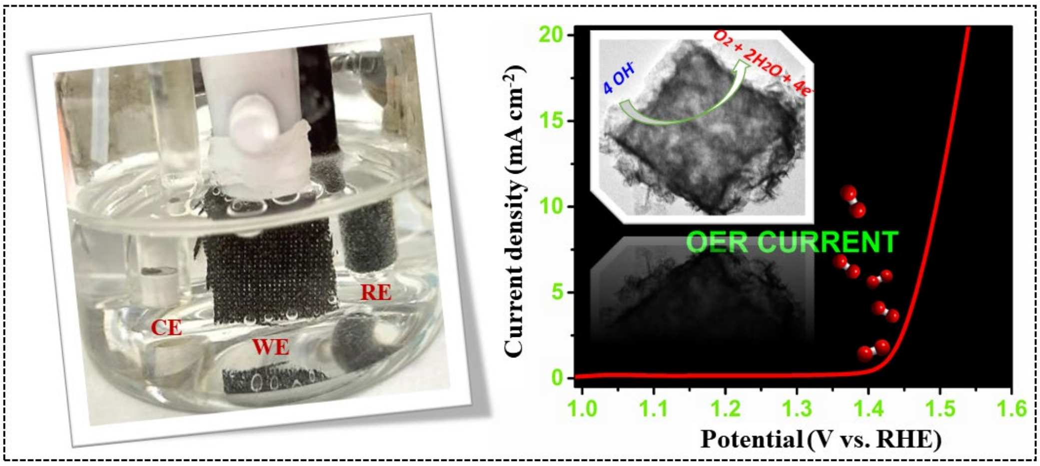
Controllable defects and interface engineering are promising routes for developing efficient noble-metal-free electrocatalysts for oxygen evolution reaction (OER), the bottleneck of overall water splitting. The presented work highlights the significance of blending the etching effect and decorative effects of molybdenum disulfide (MoS_2) on the edges and surfaces of Co-Fe Prussian blue analog (PBA) for the electrochemical OER process. We propose using an ethanol-water mixture as a mild etching agent to convert solid PBA nanocubes into hollow nanocages, without the need for a capping or stabilizing agent. The potent catalyst exhibits excellent OER activity, requiring an overpotential of only 340 mV (on GC) and 260 mV (on CC) to obtain a 10-mA cm^{-2} current density. The catalyst has a promising future owing to two structural advantages: a 3D void that increases the electroactive surface area to promote charge and mass transportation and active sulfur sites that promote high electrochemical activity. We can modify the structure of the Prussian blue analog and stimulate the slow OER kinetics by decorating these changed structures with MoS_2-based dichalcogenide materials for energy applications. This work set the stairs to rationally design PBA-based heterostructures for inexpensive electrocatalysts.



PC 24

Effect of Mn Doped Ni-Co Mixed Oxide Catalysts on Urea Oxidation

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Urea as a fuel for energy generation and storage has attracted increased attention, particularly in recent times, for it is stable, non-toxic, and abundantly available from nature. Urea possesses 10.1 wt% of hydrogen, which may be produced directly or indirectly.[1] Nevertheless, the electrochemical oxidation of urea is generally sluggish and considered to be an inefficient process.[2] However, inexpensive Ni-based catalysts have shown comparable urea oxidation activity to precious metals in an alkaline electrolyte, which steamed the use of this type of catalysts in Direct Urea Fuel Cell (DUFC) anodes. We investigated urea oxidation on a novel three-dimensional transition metal-based catalyst in the present study. The mixed oxide catalyst synthesized using manganese (Mn), cobalt (Co), and nickel (Ni) were NiO, Mn-doped NiO, Co_3O_4, Mn-doped Co_3O_4, $NiCo_2O_4$ and Mn-doped $NiCo_2O_4$, utilizing a simple precipitation route for a comparative urea oxidation study. It was found that the Mn-doped $NiCo_2O_4$ catalyst exhibited the highest urea oxidation activity of 45.88 mAcm^{-2} (at a potential of 1.30 V vs SHE), which is fifteen times higher than NiO and Co_3O_4 catalysts and twice that of bare $NiCo_2O_4$ spinel catalysts.

Chronoamperometry curves of the Mn-doped $NiCo_2O_4$ catalyst demonstrated stable urea oxidation for over 3 hours. The significantly higher mass activity of Mn-doped $NiCo_2O_4$ catalyst is attributed to the least nano-crystallite size, better dispersion of Ni nuclei onto the spinel crystal matrix, enhanced Ni electrochemical active surface area, and lower bandgap, as observed in this study, making it in the list of top 5 per cent catalysts used for urea oxidation till date.[3]

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PC 25

Heterogenous WOR by $Na_3[Ru_2(\mu\text{-}CO_3)_4]$ entrapped in a sol-gel matrix

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The production of hydrogen in a water-splitting process (WSP) is one of the most promising sources of alternative, environmentally friendly energy[1]. An important step in this process is the oxygen-evolution reaction, OER, which is typically conducted electrocatalytically, photo-catalytically, or electro-photo-catalytically [1].
The formation of O_2 from water requires a significant molecular rearrangement and is a challenging process, both kinetically and thermodynamically[1]. Thus, intense efforts are made to increase its efficiency[1], in order to increase the efficiency of the hydrogen-evolution reaction (HER) in the generation of alternative, green energy[1]. Many of the molecular water oxidation catalysts (WOCs) are based on ruthenium. Due to the ability of many of them to absorb light in the visible region which makes the potential for direct coupling of light absorbance to water oxidation[2].
In the current study, heterogeneous catalysis of water oxidation was studied by the single-stage entrapment process of the dimeric ruthenium complex $Na_3[Ru_2(\mu\text{-}CO_3)_4]$, in sol-gel electrodes. Initial results show that the $Na_3[Ru_2(\mu\text{-}CO_3)_4]$ complex entrapped in the electrodes is stable and recycled.
Using precursors, for the preparation of the sol-gel matrices, containing hydrophobic residues slows down the rate of diffusion determined electrochemically. Thus, the selected precursor has an influence on the electrocatalytic process rate. This result is important for controlling and monitoring the redox reaction, using various precursors as needed. Thus, optimizing the WSP helps expand hydrogen usage as a green and more available energy source.
It was found that a cathodic shift, of the oxidation potential, occurred in the presence of carbonate and in the heterogeneous system compared without carbonate (0.74 V and 0.80 V vs Ag/AgCl, respectively), therefore, the process is more efficient.

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PC 26

Improvement of the Electrochemical Performance of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ via Atomic Layer Deposition of Lithium-Rich Zirconium Phosphate Coatings.

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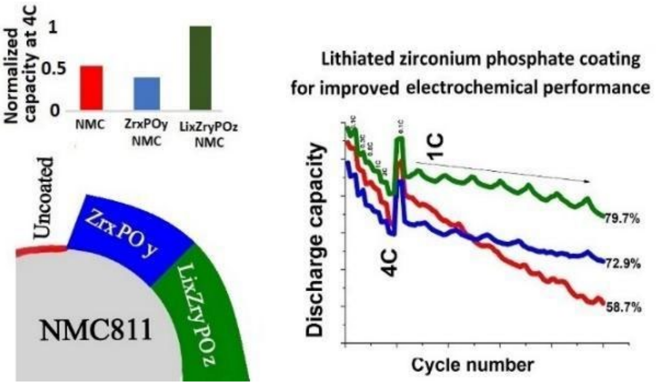
Abstract

Owing to its high energy density, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NMC811) is a cathode material of prime interest for electric vehicle (EV) battery manufacturers. However, NMC811 suffers from several irreversible parasitic reactions that lead to severe capacity fading and impedance build-up during prolonged cycling. Thin surface protection films coated on the cathode material mitigate degradative chemo-mechanical reactions at the electrode-electrolyte interphase, which helps to increase cycling stability. However, these coatings may impede the diffusion of lithium ions, and therefore, limit the performance of the cathode material at high C-rate. Herein, we report on the synthesis of zirconium phosphate Zr_xPO_y and lithium-containing zirconium phosphate ($Li_xZr_yPO_z$) coatings as artificial cathode electrolyte interphases (ACEIs) on NMC811 using the atomic layer deposition technique. Upon prolonged cycling, the Zr_xPO_y and $Li_xZr_yPO_z$ coated NMC811 samples show 36.4% and 49.4% enhanced capacity retention, respectively, compared with the uncoated NMC811. Moreover, the addition of Li ions to the $Li_xZr_yPO_z$ coating enhances the rate performance and initial discharge capacity in comparison to the Zr_xPO_y-coated and uncoated samples. Using online electrochemical mass spectroscopy, we show that the coated ACEIs largely suppresses the degradative parasitic side reactions observed with the uncoated NMC811 sample. Our study demonstrates that providing extra lithium to the ACEI layer improves the cycling stability of the NMC811 cathode material without sacrificing its rate capability performance.



The graphical abstract depicts the uncoated NMC811, NM811 ALD coating with Zr_xPO_y and $Li_xZr_yPO_z$. The electrochemical profiles show improved rate capability for $Li_xZr_yPO_z$ coated NMC811 over Zr_xPO_y coated NMC811 and uncoated NMC811. Both the with Zr_xPO_y and $Li_xZr_yPO_z$ coated NMC811 shows stabilized electrochemical performance.

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PC27

Assembly of a Metal-Organic Framework Membrane on Solid Electrocatalyst: Introducing Molecular-Level Control over Heterogeneous CO_2 Reduction

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Electrochemically active Metal-Organic Frameworks (MOFs) have been progressively recognized for their use in solar fuel production schemes. Typically, they are utilized as porous, platforms for tethering of large concentration of active molecular electrocatalysts. However, so far, the potential influence of their extraordinary chemical modularity on electrocatalysis has been overlooked. Herein, we demonstrate that, when assembled on a solid Ag electrocatalyst for CO_2 reduction, a non-catalytically active UiO-66 MOF acts as a porous membrane that systematically tunes the active site's immediate chemical environment at the molecular level, leading to a drastic enhancement of electrocatalytic activity and product-selectivity. Specifically, detailed electrochemical characterization shows that the MOF membrane improves catalytic performance through physical and electrostatic regulation of reactants' delivery towards the catalytic sites. Moreover, the MOF also stabilizes reactive catalytic intermediates *via* modulation of the secondary coordination sphere of the active site. The presented concept can be expanded to a variety of solid electrocatalyst and a wide range of proton-coupled electrochemical solar fuel reactions and provides new means for precise, molecular-level manipulation of heterogeneous electrocatalysis.

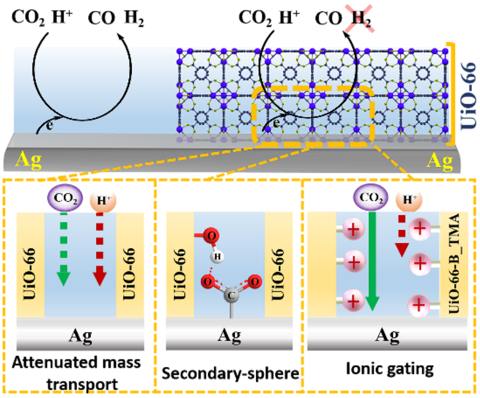

Figure 1. Molecular control over the electrocatalytic CO_2 reduction performance of Ag achieved by MOF membrane. Enhancement of CO selectivity due to the simultaneous operation of (a) mass transport attenuation, (b) secondary-sphere effect and (c) ionic gating.

Suggested Read:

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PC28

Fe–N–C Electrocatalysts in the Oxygen and Nitrogen Cycles in Alkaline Media: The Role of Iron Carbide[1]

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Iron- and nitrogen-doped carbons (Fe–N–C) are fast-rising stars in electrocatalysis. Fe-N-C drive reactions in the oxygen/water cycle (reduction and evolution of O_2, H_2O_2 and H_2), the nitrogen cycle (oxidation of hydrazine and urea, reduction of N_2 and NO_x), and the carbon cycle (CO_2 reduction). Yet the mechanisms by which Fe–N–C electrocatalysts operate are obscured by their compositional and structural complexity. Iron carbide (Fe_3C) is found in nearly all pyrolytic Fe–N–C materials, including the most catalytically active ones. Its role in catalysis remains murky, despite detailed investigations: some identify Fe_3C as a central catalytical component, while others maintain it is a useless by-product of the pyrolysis. The discussion is clouded by the challenge of preparing

Fe_3C-free control materials. We now report a direct investigation on the role of iron carbides to electrocatalysis in the oxygen and nitrogen cycles in alkaline media. We examine the typical Fe_3C phases found in pyrolytic Fe–(N)–C materials, by systematically assessing a broad range of particle sizes and carbon environments in five different Fe_3C-rich carbon materials. Then, we remove the Fe_3C by a non-oxidizing acid wash, allowing us to determine the true contribution of Fe_3C without destroying other sites. The carbide-rich and washed materials are tested as electrocatalysts towards the oxygen reduction reaction (ORR) and the hydrazine oxidation reaction (HzOR), two representative and important reactions in the oxygen and nitrogen cycles, respectively. Finally, DFT calculations of oxygen- and nitrogen-cycle reactions on bare Fe_3C corroborate and extend the experimental findings.

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PC29

Combinatorial Synthesis and Screening of a ternary NiFeCoOx library for the Oxygen Evolution Reaction

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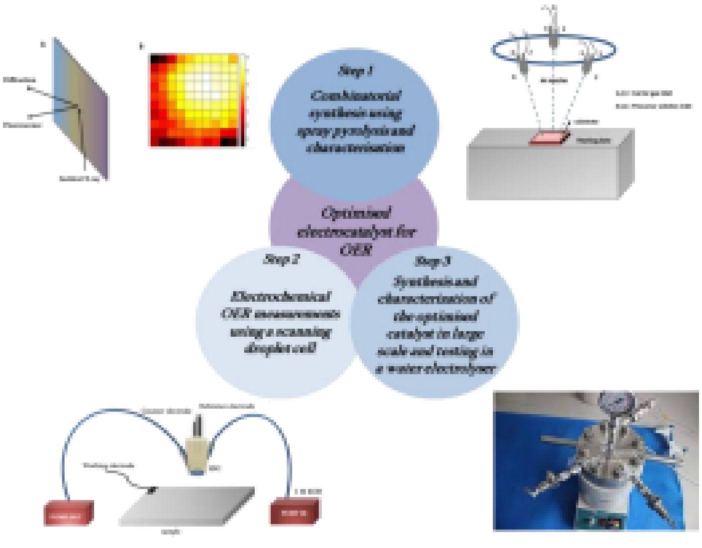
The rational design of an efficient catalyst for the Oxygen Evolution Reaction (OER) is critical to fulfilling the mission of hydrogen generation by water splitting. Nickel based systems are the most studied catalysts for OER in alkaline media. Higher order composition spaces hold great promise of improved electrocatalytic performance and doping other transition metals (Fe, Co, Al, Ce etc.) to nickel lattice is proven to enhance its activity.

Various multicomponent systems have been investigated so far for OER, although a systematic investigation is lacking and there are discrepancies as to which formulations make the best catalyst. Here, we perform a systematic investigation of a ternary Ni-Fe-Co oxide gradient library for OER, using a combinatorial approach. This approach allows a much faster investigation of a vast compositional space compared to the traditional step by step approach. Also, it enables a more reliable comparison of the various catalysts as they all experience the same process and measurement conditions. Combinatorial electrochemical screening using a scanning droplet cell (SDC) set up allowed the study of 98 different points in the compositional space of the trimetallic Ni-Fe-Co oxide library, which was used to deduce a composition-activity relationship. This study provides a foundation for broad exploration of other mixed-metal oxide combinations.



PC30

Orthogonal Design of Fe-N4 Active Sites and Hierarchical Porosity in Hydrazine Oxidation Electrocatalysts

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Hydrazine is a promising energy-dense fuel for alkaline fuel cells. To design efficient and affordable electrocatalysts for the hydrazine oxidation reaction (HzOR), one needs to control both the active site and the supporting scaffold. We now report a family of electrocatalysts for alkaline HzOR, consisting of atomically dispersed Fe-N_4 sites (as iron corroles of varying sizes) on hierarchically porous, electronically conductive carbon scaffolds that were prepared by self-templating from a novel barium based precursor. The orthogonal design of active sites and flow-enhancing scaffolds allowed the rational optimization of their combination, to achieve excellent HzOR activity. These catalysts demonstrate the utility and versatility of metallocorroles for electrocatalysis in the nitrogen cycle, as well as the importance of pore tuning for current density optimization.

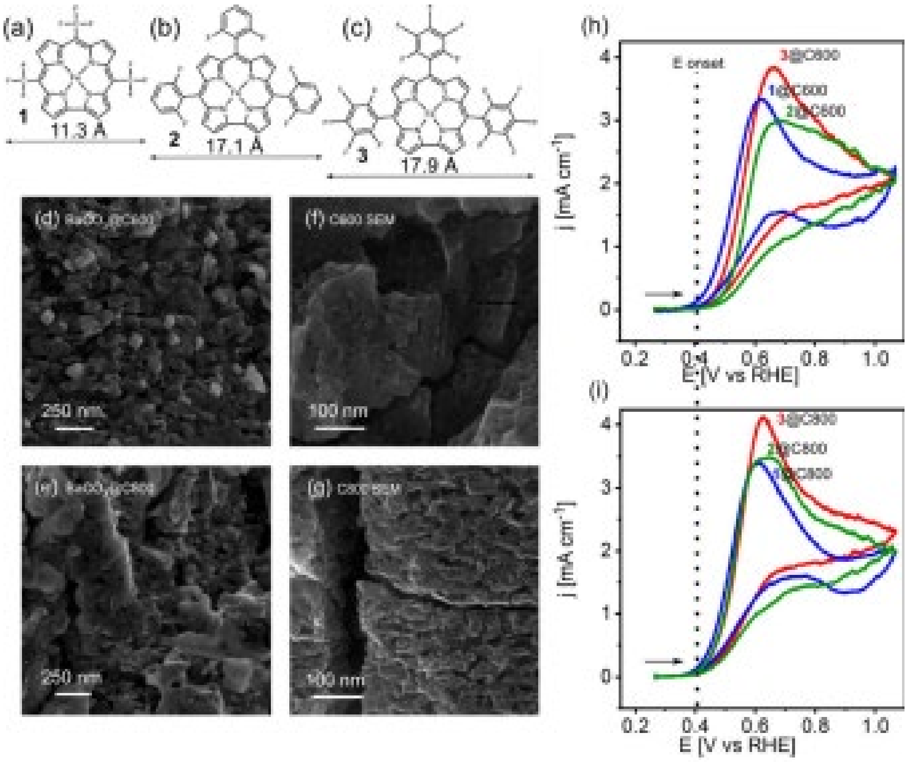

Figure 1: (a)-(c) Molecular structure of the three pre-designed catalytic sites. (d)-(g) Scanning electron micrographs of the $BaCO_3$@carbon composites, pyrolyzed at 600,800 °C, prior and after template removal. (h)-(i) Cyclic voltammograms of hydrazine oxidation of corroles 1–3 adsorbed on C600,C800.

PC31

Amorphous Ni-B-based Materials for Electrochemical – Thermally-Activated Chemical (E-TAC) Water Splitting

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Electrochemical–thermally-activated chemical (E-TAC) water splitting, invented in the Technion and further developed by H_2Pro (Caesarea, Israel), is a membraneless technology for the “green” H_2 stationary production based on abundant materials. Conventional E-TAC anodes are based on the reversible β-$Ni(OH)_2$↔β-NiOOH transition between the crystalline hydroxide/oxyhydroxide phases. High crystallinity and, consequently, slow phase transition could be one of the main reasons of the kinetic hindrances and decrease in active mass utilizations in the E-TAC process.

This study aims to develop amorphous Ni-based materials capable to perform in the E-TAC cycles and to investigate their properties. Towards this end, a facile one-step chemical reduction method was applied to deposit NiB (oxy)hydroxide using $NaBH_4$ as the reducing agent and $Ni(ac)_2$ as the precursor, to synthesize nickel-boron-based agglomerates directly on the surface of the Ni/Ti/carbon substrates or to obtain powder of the particles in the solution. As expected, the X-ray diffractograms in θ/2θ scan mode confirmed that the applied synthetic technique results in amorphous material. TEM imaging of the as-synthesized powders showed that the powder consists of core-shell-like near-spherical nanoparticles (ca. 10-20 nm) interconnected in chains. HR-EDX mapping of the intact powder revealed that the shell is enriched by oxygen, whereas the core mainly consists of Ni and B. Galvanostatic charge/discharge measurements were used to study the rate capability of the material. The rate capability tests showed that the electrode capacity of the final slow cycle is significantly higher than that of the first slow cycle, suggesting that the slow charging and discharging results in the increase of the oxide shell thickness followed by the shrinking of the particle core. To provide an experimental prove, the as-synthesized material was exposed to slow potential cycling within the range of 1.13-1.48 V vs. RHE (to assure the occurrence of the reversible $Ni(OH)_2$↔NiOOH reaction). HR-EDS mapping of the oxidized material clearly illustrated the growth of spongy, crystalline, layered structures around the cores which are fully or partially depleted, dependent of the particle sizes.

Series of electrochemical galvanostatic charges followed by thermally activated chemical (5M KOH, 95C) discharge tests have proven the feasibility of the developed amorphous Ni-B-based material for the anodes of the E-TAC process. The capacity values of the electrodes currently reach ca. 600 C g^{-1} (vs. theoretical capacity of 1400 C g^{-1}). The further investigation is needed to elucidate the effect the initial crystallinity degree of the material, as well as light needs to be shed on the crystallinity evolution of the material during the E-TAC process itself.

Poster Presentations- Devices and Fabrication

PD1

Multiple Cation and Anion High Entropy Cathode for Na ion batteries

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Li ion based batteries are the widely used energy storage device, although scarcity of lithium resources with their mounting prices has pushed the researchers to search for another alternative [1]. Here, replacement of Li with more terrestrially abundant metal ion could be a solution to combat the surge demand of energy storage devices. Currently, there is a noticeable interest towards the Na ion battery technology because of the abundant sodium resources. Further, similarity in manufacturing process (both Na and Li extraction occurs through brine deposit) and electrochemistry to Li ion systems ensures large scale application of Na ion batteries. Attention has also drawn to reduce the utilization of cobalt based battery electrode materials because cobalt which is an important element for Li battery construction is mined mostly in Democratic Republic of Chicago (DRC), where child labor, dangerous working conditions are practiced due to which serious health issues (lung diseases) and birth defects has been observed among miners [2]. To compete with the Li ion batteries, it is needed to develop efficient cathode material that are able to accumulate larger sodium ions without structure degradation for Na ion battery application and that too without cobalt in view of above concern. Recent theoretical studies have found that the entropy stabilized oxides have the ability to accommodate larger sodium ions with high structural stability and mobility

[3, 4]. Basically, high entropy contributes towards the uniform distribution of elements and hence, is able to tolerate the mechanical stress during conversion reaction.

Keeping in view the above mentioned concerns and studies, here we report a multiple cation and anion high entropy cathode for Na ion battery application. In this work, Na_x and Li_y stoichiometry is varied from (x: 1 to 0.8; y: 0 to 0.2) in the O3 phase high entropy cathode (NaLiNiMnFeTiMgOF) to optimize the capacity and electrochemical stability. O3 phase is able to accommodate large concentration of Na ions; the problem associated with this phase is there irreversible capacity and electrochemical stability. With stoichiometric Na0.9Li0.1, a reversible capacity of 109.26mAh g^{-1}@C/15 is achieved with excellent electrochemical stability of more than 90% after 200 cycles. Whereas, Owing to the combination of high potential redox active Fe^{3+}, the high entropy cathode is able to achieve 4.3V with appreciable electrochemical stability. This study paves a way to design the efficient stable cathode for Na ion batteries.

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PD2

Ratchet based Ion Pumps for selective ion separations

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In recent years there has been a growing demand for membranes capable of extracting a single solute from water. The introduction of an ion selective separation technology can drive a dramatic progress in a range of applications such as water treatment, resource extraction from sea water, bio memetic systems, chemical sensors, and more. For example, to decontaminate drinking water from lead pollution, a system needs to be at least six orders of magnitudes more permeable to lead than towards sodium ions. However, membrane-based separation technologies have so far achieved selectivity values, which are several orders of magnitude lower than that. To promote the passage of a specific solute over others with such a high selectivity, the flux of the undesired solutes should be completely inhibited or preferably be driven in an opposite direction. In this talk we will show that an ion pump based on a flashing ratchet[1] mechanism, can drive same-charge ions in opposite directions, according to their diffusion coefficients.

Electronic flashing ratchets are non-equilibrium devices that utilize modulation of a spatially asymmetric electric field to drive a steady state particle flux. An important hallmark of ratchets is the ability to invert the direction of particle flow with a change in the input signal frequency. The stopping frequency, which is the frequency at which the particle flux changes its direction, is determined by the potential distribution and particles transport properties. As a result, for a given ratchet, there can be a frequency at which particles with the same charge but different diffusion coefficients are transported in opposite directions. This concept, that was never applied to ion separations, can enable the extraction of ions with extremely low relative concentrations if their diffusion coefficient is even slightly different from the main ions in the solution. We show by simulation, that for the prevalent ions in water, ions with a relative diffusion coefficient difference as small as 1% can be driven to opposite directions with a velocity difference as high as 1.2 mm/s.[2] Since the direction of ion transport is determined by the input signal frequency, the sorting properties can be tuned in real time providing a simple fit-to-purpose solution for a variety of ion separations applications.

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PD3

AZ31 Magnesium Alloy Foils as Thin Anodes for Rechargeable Magnesium Batteries

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In recent decades rechargeable Mg batteries (RMB) technologies have attracted much attention from researchers and manufacturers, because the use of thin Mg foils anodes may enable to develop high energy density batteries based on abundant elements. One of the most critical challenges for devolving RMB is finding suitable electrolyte solutions that enable efficient and reversible Mg cells operation. For this reason, most RMB studies concentrate on the development of novel electrolyte systems, while only few studies have focused on the practical feasibility of using pure metallic Mg as the anode material. Pure Mg metal anodes have been demonstrated to be useful in studying the fundamentals of nonaqueous Mg electrochemistry. However, pure Mg metal may not be suitable for mass production of ultrathin foils (< 100 microns) due to its limited ductility. The metals industry overcomes this problem by using ductile Mg alloys. We demonstrate herein the feasibility of processing ultrathin Mg anodes in electrochemical cells by using AZ31 Mg alloys (3% Al; 1% Zn). Thin film Mg AZ31 anodes present reversible Mg dissolution and deposition behavior in complex ethereal Mg electrolytes solutions that is comparable to that of pure Mg foils. Moreover, we demonstrated that secondary Mg battery prototypes comprising ultrathin AZ31 Mg alloy anodes (≈ 25 µm thick) and $Mg_xMo_6S_8$ Chevrel phase cathodes exhibit cycling performance that is equal to that of similar cells containing thicker pure Mg foil anodes. The possibility of using of ultrathin processable Mg metal anodes is an important step in the realization of rechargeable Mg batteries.

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PD4

Anthraquinone-doped layered double hydroxide for battery supercapacitor

hybrid

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The rapid degradation of coals, petroleum, gasoline etc., and the associated environmental pollution with them has forced us to find alternative energy solutions. Researchers are working tirelessly to generate energy from different sources such as solar radiation, wind, tide, etc. The main problem with these sources is that they are not constantly available for use as fossil fuels. Thus, it is essential to store the energies generated from the above-mentioned sources and utilize them when needed. In the last two decades, batteries and supercapacitors have emerged as the most useful energy storage, which can resolve the problem. Yet, batteries and supercapacitors have their pros and cons, and in most cases, are complementary to each other. Thus, combining the pros of both battery and supercapacitor may be a suitable solution. Transition metal oxides/hydroxides are well-known battery-type materials and carbonaceous materials are known for their capacitive type storage as well. A combination of both these types of materials can enhance the overall performance of the device. The energy density of such devices can further be extended by adding the redox-active element to the electrode.

In this contribution, we have electrochemically deposited NiMn-layered double hydroxide (NM-LDH) on the electrochemically exfoliated 3D graphite foam. To enhance the storage capacity, we have further doped the electrode with redox-active anthraquinone-2-sulfonic acid (AQS). SEM and EDS study confirms the uniform deposition of NM-LDHs and doping of the AQS. The electrochemical performances of the composite were studied using cyclic voltammetry and galvanostatic charge-discharge measurements. The composite electrode exhibits a specific capacity of 1225 mAh/g. These studies confirm that AQS-doped NM-LDH on exfoliated graphite is an excellent hybrid material for energy storage and may be used for future applications.

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PD5

Single Cell Behavior Monitoring Using Electrochemical Mediators

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Bioelectrochemical devices enables molecular communication between biological and electronic systems. However, ‘bioactuators’ (devices that convert electronic signals to biological ques) are not commonly available as they require electronic contact with the biological system to allow selective electronic communication transfer [1]. Here, we present a novel bioelectronic device that is comprised a bi-modal electrochemical-optical lab-on-a-chip (EO-LOC) platform to study the behavioral response of single genetically modified *E. coli* bacterial cells. For that purpose, we used electrochemical mediator molecules in proximity to genetically engineered *E. coli* cells. Pyocyanin is the actuator for fluorescent protein (*phiLOV)* expression by reduction on the promotor gene. Electrochemically controlled redox cycle of Ferro/Ferricyanide is playing a role of electron acceptor in proximity of the cell and amplifying/suppressing the fluorescent signal. This electrochemical-biological system allows electric control of biological behavior. We integrate the EO-LOC with a microfluidic platform to enable controlled and automated analysis of cells cellular response to different chemical and electrical ques. We performed electrochemical and flow validation of the EO-LOC. The behavioral fluorescent responses from the cells to the electrical stimulation was demonstrated successfully. Furthermore, by analyzing the fluorescent responses, we characterized the behavioral distribution among the cells (Figure 1). While we were expecting similar behavior in the chemical and electrochemical group, a different single-cell fluorescent response distribution with respect to chemical and electrical stimulations was observed. The results show a controlled physiological turn-on mechanism using electric signals on a single cell level.

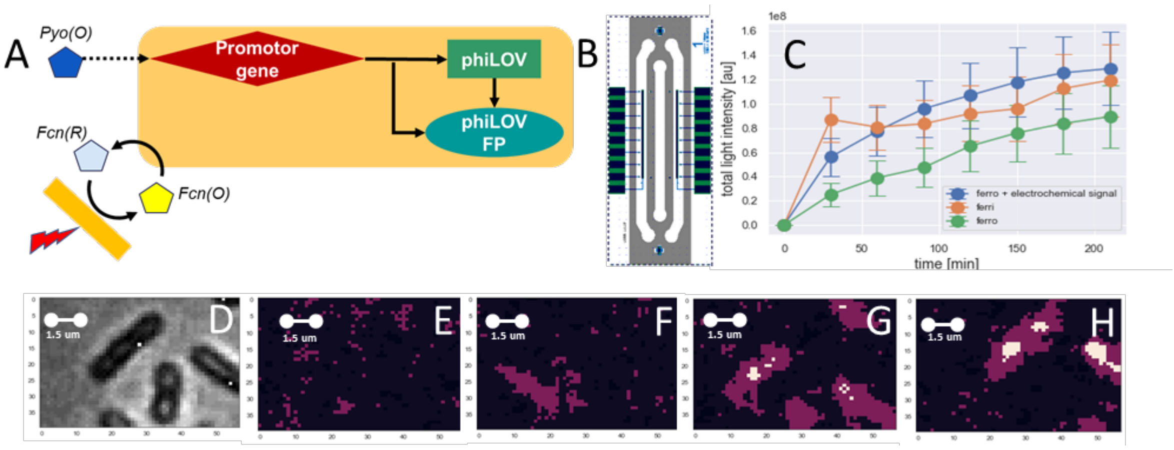

Figure 1. Population of bacterial cells fluorescent response to electrochemical stimulation (A) Suggested redox reaction-based model of biological cell manipulation using external electric ques (B) Top view of the lab-on-a-chip design (C) Total fluorescent intensity measured from the fluorescent microscope images of bacteria for different time durations. (D) Brightfield image of single bacterial cells. Fluorescent images of the single cells following electrochemical stimulation for (E) 0, (F) 1, (G) 2, and (H) 3 hours. The experiment featured 3 independent groups of E. coli cells in different microchannels. Group 1 was electrochemically stimulated. Group 2was chemically stimulated. Group 3 was the control group.

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PD6

Shell-Matrix Interaction in Nanoparticle-Imprinted Matrices: Implications for Selective Nanoparticle Detection

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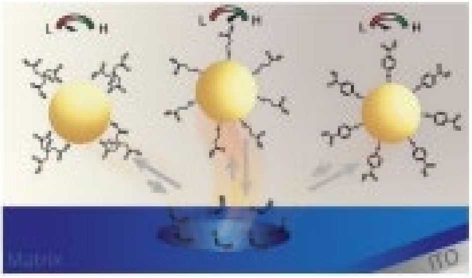
In the last years, nontoxicity has become at the forefront of research due to its relevance and importance to the environment and human health. In spite of the fact that the exposure risk to engineered nanomaterials depends on their physicochemical properties including their surface chemistry, the regulations are based mainly on the particle size. Since the use of NPs is unavoidable, there is an urgent need for small, easy-to-use, and field-available sensors for the detection of NPs. There is a wide range of laboratory techniques to characterize NPs spanning from electron microscopy to light scattering; however, most if not all of these are complex, cost-effective, and require skilled operators. Electrochemical detection methods would provide a cheap and easy tool to help characterize NPs based on their surface chemistry. The selective recognition of nanoparticles (NPs) can be achieved by nanoparticle imprinted matrices (NAIMs), where NPs are imprinted in a matrix followed by their removal to form voids that can reuptake the original NPs. The recognition depends on supramolecular interactions between the matrix and the shell of the NPs. Speciation of nanoparticles, that is, their differentiation based on size, shape and stabilizing shell, is becoming important because properties such as toxicity are strongly depended on these parameters.

In this study[1], we use the NAIM approach for carefully studying the NP-matrix interaction through the recognition effect. Specifically, gold NPs (AuNPs) are capped with three carboxylic-based shells: citrate (AuNPs-cit), 3-mercaptopropionic acid (AuNPs-MPA) and 4-mercaptobenzoic acid (AuNPs-MBA) were adsorbed onto a solid electrode, i.e., indium tin oxide (ITO). The adsorption of the NPs was followed by depositing a controllable thin film via electrografting of (4-carboxyphenyl) diazonium (CBD). The AuNPs were removed by electrochemical dissolution and the recognition of the various AuNPs was studied by electrochemistry, spectroscopy, and other techniques. We found that the NAIM system is highly selective and differentiates between the originally imprinted AuNPs and the other particles having the same Au core, but different carboxylic acid capping agents. The recognition is due to the supramolecular interaction between the surface functionality of the AuNPs and the matrix investigated by FTIR and other approaches. The effect of film thickness on the reuptaking of the AuNPs was also examined.



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PD7

Stabilizing lithium-sulfur cells with practical loading using Li_2S_8-containing ethereal electrolyte solution.

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Stabilization of Li-S cells cycled with an areal charge/discharge capacity of 2 mAh cm^{-2} at current densities of 1-2 mA cm^{-2} was achieved using ethereal LiTFSI/$LiNO_3$/DOL/DME electrolyte solution containing 0.1M Li_2S_8. This electrolyte solution enables stable lithium metal stripping-plating both in symmetric Li|Li (Fig.1) and full Li-S cells (Fig.2) with composite binder free sulfur impregnated activated carbon fibers cathodes. The addition of Li_2S_8 substantially extends cycling life of these cells due to the formation of smooth non-dendritic Li metal surface protected with an effective SEI enriched with Li sulfides, sulfites and sulfates species. Symmetric Li|Li could be cycled stably for more than 1000 hours at 1-2 mA cm^{-2} with Li_2S_8-containing electrolyte solutions. Full Li-S cells demonstrate more than 500 stable cycles (at least 3 times more than with Li_2S_8 free electrolyte solution) at a current density of 1 mA cm^{-2} and an areal capacity of 2 mAh cm^{-2}. The most stable cycling results were achieved for the cells cycled with discharge cut off voltage of 1.9 V preventing the depletion of $LiNO_3$. The use of electrolyte solutions containing liquid lithium poly-sulfides makes possible considerable decrease in the amount of the electrolyte solution and increases the energy density of the cells.

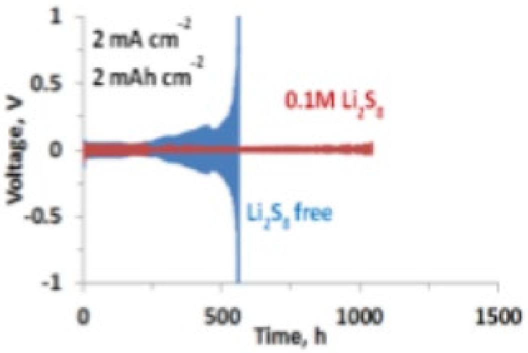

Fig. 1. Cycling performance of Li|Li metal symmetric cells in Li_2S_8 free LiTFSI/$LiNO_3$/DOL/DME electrolyte solution and with the addition of 0.1 M Li_2S_8 (as indicated). 30 ° C, amount of the electrolyte solution 100 µl per cell.

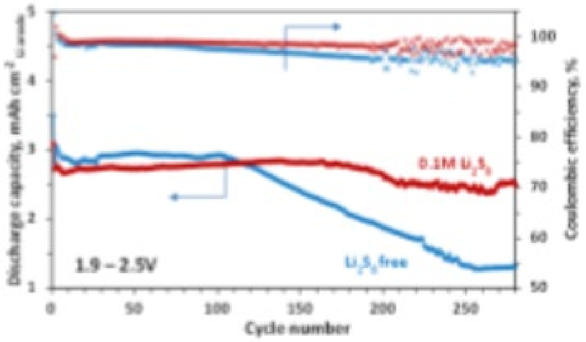

Fig. 2. Cycling performance of Li-S cells cycled between 1.9 and 2.5 V. (a) Blue curves: S loading 6 mg/per electrode (4.5 mg cm^{-2}); red curves: S loading 4 mg/per electrode (3 mg cm^{-2}). Current density 1 mA cm$^{-2}_{Li\ anode}$. 30 °C, amount of the electrolyte solution 80 µl per cell.

PD8

Electrospun nanofiber mesh cathodes for ultrathin flexible batteries

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Nanofiber meshes are a promising platform for constructing light, flexible, and mechanically robust batteries for a range of application including wearable electronics, healthcare services, and energy devices. This is due to their large surface-to-volume ratio, highly porous structure, light weight, and the ability to perform even under significant mechanical deformation.

In this work, meshes of Polyethylene glycol (PEO) polymeric nanofibers loaded with lithium iron phosphate (LFP) ($LiFePO_4$) nanoparticles and C65 nano carbon black were formed via electrospinning. The LFP containing meshes were tested as a cathode to evaluate the ion transport properties of ultrafine electrospun meshes and assess the potential of this fabrication technology for ultra-thin flexible lithium-ion batteries. In particular, we examined the effect of dispersion and grain size of the LFP particles on the cathode performance. When cycling the cells at a c/20 rate, fiber that were loaded with ball-milled nanosized LFP demonstrated an improved initial discharge capacity compared to non-milled micron-sized LFP (133 vs. 115 mAh/grLFP). Both cathodes demonstrated high reversible capacity retention and stable performance during the first 10 cycles. These preliminary results indicate that the spun meshes hold a great potential for the formation of flexible batteries, towards the goal for fully electrospun flexible batteries in the future.

PD9

Development of Advanced Composite Pressure Vessels for Hydrogen Storage

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Energy production from renewable sources instead of fossil fuel-based energy sources is crucial to combat climate changes and significantly decrease greenhouse gas emissions. However, renewable sources such as solar, wind, and hydro energy are extremely weather dependent, and hence, require a bulk system to store the excess energy to fulfill the energy needs constantly. During the last decades, hydrogen became a promising green and clean alternative to classical batteries as effective energy storage. Hydrogen has the highest energy content by weight unit and can be stored in different quantities by several techniques. Moreover, hydrogen can be produced from different sources, and hence, can be effectively integrated with renewable energy storage.

While hydrogen demand and production are growing, the increasing need for effective hydrogen storage is still one of the significant and critical issues in the development of the so-called "hydrogen economy". The state-of-the-art techniques for hydrogen storage are based on fully metallic pressure vessels, while the weight parameter is a significant limitation of this storage, especially for automotive applications. Alternatively, composite storage vessels offer high strength and low weight but frequently suffer from limited gas locking properties.

Herein, we suggest improving the hydrogen barrier of the vessel's polymer shell by integrating of metallic inner liner in the cylinder. Our strategy includes the selection of the appropriate polymer for the vessel's shell, the development of electrochemical-derived metal coating, and hydrogen permeation analysis. The metal coating of the polymer shell involves the development of electroless deposition of Ni layer and further electroplating of Cu layer. The metallic coating aimed significantly decrease the hydrogen permeability through the polymer but is also based on the prevention of the well-known hydrogen embrittlement. In this way, we suggest a novel multilayer polymer-metallic vessel for effective hydrogen storage.

PD10

Enhanced stability of 4.6V $LiCoO_2$ cathode by an Integrative combination of surface coating and electrolyte solution

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Increasing the operation voltage of $LiCoO_2$ (LCO) cathodes beyond the conventionally used potential range (usually up to 4.45V) is a major target for the Li-ion battery researchers and developers. Charging the LCO cathodes to 4.6V results in significant enhancement of the specific capacity of LCO electrodes and the possible energy density of rechargeable Li batteries up to around 900 Wh/kg. However, operating Li cells comprising LCO cathodes at such high charging potentials facilitates the occurrence of side reactions and early failure of the cathode. Herein we demonstrated a highly effective approach that combines an application of Li-Al-F based surface coatings and a wise selection of electrolyte solutions containing fluorinated co-solvents. In contrast to other studies which usually focus on modification of one parameter (i.e coating, electrolyte solution, binder, etc.) here we demonstrated a holistic approach that takes into account the influence of both coating and electrolyte solutions compositions. Using 1M LiPF6 FEC:DFEC: DMC as the electrolyte solution for coated LCO cathodes, we were able to obtain a superior behavior of 4.6V LCO electrodes showing a high initial capacity > 220 mAh/g and excellent long-term performance during hundreds of cycles (78% capacity retention at 0.5C after 500 cycles at 100% DOD). Moreover, impressive stability was found at elevated temperatures as well (e.g., at 45ºC) with an initial capacity of 220 mAh/g and 84% capacity retention after 100 cycles. The stabilization mechanism enabled by the Li-Al-F coating and the use of electrolyte solutions that contain fluorinated co-solvents was further revealed by a systematic post-mortem analysis (including XRD, XPS, NMR HR-TEM, and ICP measurements) of both LCO cathodes and Li anodes after prolonged cycling. The conducted measurements provided deep insights into the effect of the surface chemistry on the cathode performance and not less important shed light on the influence of the negative electrodes on the cells' stability.

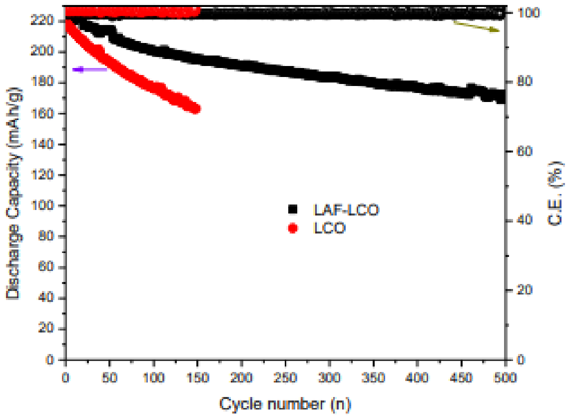

Fig. 1. Long term cycling performance obtained at 0.5C for bare LCO in LP57 and fluorinated electrolyte solutions

PD11

Effect of Nanostructed Additives Shape on the performances of the Solid Electrolyte in All Solid-State Sodium Batteries

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Abstract:

Solid electrolytes based on Polyethylene oxide (PEO) have been studied for decades, owing to their facile and low-cost processing, good electrochemical stability, and excellent complexation with alkali metal salts. It is well known that nano structures materials improve the electrochemical performance of polymer electrolyte. Here we study the effect of Inactive ceramic TiO_2 nanoparticles *shapes* at all solid-state sodium batteries by electrochemical characterizations which includes ionic conductivity, time resolved impedance spectroscopy, transference number and batteries performances.

The electrolytes with nanotubes additives show better performances at symmetric cells where conductivity as well as stability were measured. The batteries performances show also better results while using nanotubes as additives to the electrolyte in comparisons than those with nanowires.

PD12

Double Gas Treatment: A Successful Approach for Stabilizing the Li and Mn-rich NCM Cathode Materials' Electrochemical Behavior[1]

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Herein, a systematic surface modification approach via double gas (SO_2 and NH_3) treatment at elevated temperatures is taken to achieve a stable electrochemical performance for Li and Mn-rich NCM cathode materials $0.33Li_2MnO_3•0.67LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ (HE-NCM). Partial surface reduction of Mn^{+4} and the formation of a modified interface comprising Li-ions conductive nano-sized Li_2SO_4/Li_2SO_3 phases are established. Prolonged cycling performance in Li coin-cells demonstrates significantly improved capacity retention (~2.2 times higher than the untreated sample) for the double-gas-treated cathodes after 400 cycles at a 1.0 C rate. Stable discharge potential and lower voltage hysteresis during cycling were also achieved. The comparative electrochemical studies in full-pouch cells [*vs*. Graphite anode] also demonstrates considerably stabilized electrochemical behavior for the double-gas-treated HE-NCM than the untreated sample. Lower gases (O_2, CO_2, and H_2) evolution in the first charge-discharge cycle and better thermal stability are indeed two crucial achievements of this treatment. The electrodes' post-cycling investigation established integral morphological integrity of the gas-treated cathode materials and lower transition metals (TMs) dissolution from the active cathode. The positive effects of double-gas treatment are related to the modified surface, lessening the undesirable side reactions at the electro-electrolyte interphase with the battery solutions.

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PD13

Hydrogen Permeation through Ti-6Al-4V

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Ti-6Al-4V isthe workhorse among titanium-based alloys. Its applications include, among others, aircraft, marine, chemical industry, power generation, and implants. Although renowned for its corrosion resistance, a sufficiently high concentration of hydrogen in Ti-6Al-4V can cause severe damage to the material. Hydrogen may be introduced into the metal during various manufacturing processes or from the service environment. Being a small atom, hydrogen can easily diffuse into the material and interact
with its lattice. The incorporation of hydrogen in titanium results in the formation of brittle phases of titanium hydride, which decrease the toughness and ductility of the metal, leading to cracks and finally to a catastrophic failure. This phenomenon is popularly known as hydrogen embrittlement (HE). Over the decades, HE has been the subject of extensive research and was found to be significantly affected by the initial microstructure of the material. Ti-6Al-4V is an α+β alloy. Hydrogen interacts differently with the α (hexagonal close-packed, HCP) and the β (body-centered cubic, BCC) phases, resulting in dissimilarity in the hydrogen solubility and diffusivity. The diffusion coefficient of hydrogen in the β phase is orders of magnitudes larger than in the α-phase. In the case of a continuous network of β-phase in the alloy, hydrogen will preferentially diffuse through the β-phase lattice and react with the α-phase
along the α/β interphase boundaries. Thus, the phase ratio and the microstructure in Ti-6Al-4V have a critical effect on the material's susceptibility to HE. Understanding the diverse possibilities of hydrogen interaction with the phases may be useful to explain the wide range of hydrogen diffusion coefficients in Ti-6Al-4V.
In this study, the hydrogen diffusivity, permeability, sub-surface concentration, and hydride formation in wrought Ti-6Al-4V samples are investigated. The electrochemical permeation test is run using the classical Devanathan & Stachursky cell. Scanning electron microscopy (SEM) is used to observe the microstructure whereas X-ray diffraction (XRD) is used to identify phase transformations and hydride formation. Hydrogen distribution is analyzed by time-of-flight secondary ion mass spectrometry (ToF
SIMS) imaging. X-ray photoelectron spectroscopy (XPS) and reflection electron energy loss spectroscopy (REELS) are also used to inspect and map the chemical composition. In the near future, additional experiments

will be conducted with additively manufactured Ti-6Al-4V. By comparing those results to those for the wrought alloy, we hope to be able to evaluate the effect of the manufacturing process on the hydrogen permeation through Ti-6Al-4V.

PD14

Aqueous & Non- Aqueous Ion Batteries

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The alarming global warming trends and their negative consequences on the world economy and population health require a drastic reduction in CO_2 emissions. Being one of the major sources of greenhouses gas pollution, fossil fuel-based electricity generation technologies must be replaced with environmentally friendly energy sources like sun or wind. Despite the significant improvement in the electricity production efficiency of these systems during the last decade, their intermittent nature, resulting in a fluctuating power supply, poses numerous challenges related to their integration into the existing grids designed to comply with less or non-variable energy sources. In the search for viable and cost-effective solutions for largescale energy storage, effective rechargeable batteries are a natural solution. Extensive efforts are currently underway to develop safe and cost-effective electrolytes for large-scale energy storage. Here, we demonstrate a cost-effective aqueous electrolyte solution combining 14M LiCl and 4M CsCl that allows stable operation of a 2.15-V battery comprising a TiO_2 anode and $LiMn_2O_4$ cathode. Addition of CsCl to the electrolyte plays a double role in system stabilization: the added chloride anions interact with the free water molecules, whereas the chaotropic cesium cations adsorb at the electrified interface, preventing hydrogen formation.

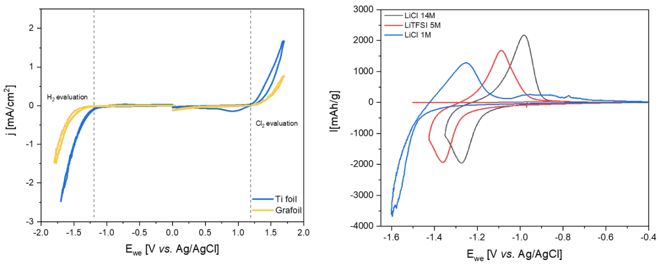

Figure: (a) Electrochemical stability window of neat titanium and grafoil current collectors tested by CV at 10 mV/s in saturated LiCl solution. (b) Cyclic voltammograms of TiO_2 anodes coated on grafoil collected at a scan rate of 1 mV/s.

Ref. Suo, L., Oh, D., Lin, Y., Zhuo, Z., Borodin, O., Gao, T., Wang, F., Kushima, A., Wang, Z., Kim, H.C., et al. (2017). How Solid-Electrolyte Interphase Forms in Aqueous Electrolytes. J. Am. Chem. Soc.

At the second article we show development of effective ALD - based surface coatings for stabilization of high energy Na-NCM cathodes. As this work is aimed to concentrate on the surface modifications and the mechanism beyond the cathode stabilization enabled by this coating, the cathodes were prepared by ion-exchange rout (electrochemical insertion of Na to the charged cathode). To evaluate the effect of the artificial interfaces, on the performance of the Na-NCM cathode of 3 different ALD surface coatings, namely, sodium aluminate ($Na_xAl_yO_z$), lithium aluminate ($Li_xAl_yO_z$), and alumina (Al_2O_3) was applied on the cathode particles. While the use Al_2O_3 as a coating layer is well known, the implementation of the other ALD treatments is not yet reported for this cathode. Our finding reveals an improved behavior of the cathode for all the selected coatings, compare to the uncoated compound, however, the better performance was obtained for the $Na_xAl_yO_z$. Based on our observation we have concluded that the improved performance of the $Na_xAl_yO_z$ coated cathode is attributed to a reduction in O_2 release and manganeseigration out of the active mass.

Figure: (a) Plots of differential capacity (dQ/dE) *vs.* voltage for the second cycle in galvanostatic cycling experiments and (b) voltage profiles during the first cycle of uncoated and ALD-coated electrodes in standard coin-type sodium cells with 1M $NaPF_6$ in PC (2% FEC) electrolyte solution at C/10.

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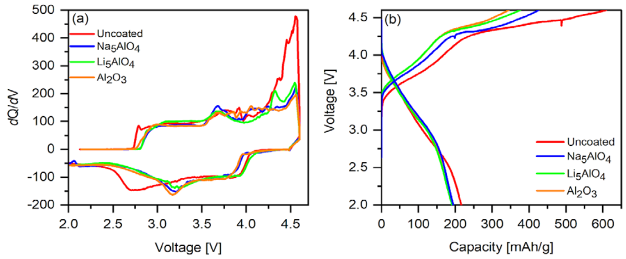

PD15
Protection of NMC cathodes by electrophoretically deposited composite ceramic layers

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School of Chemistry, Tel Aviv University

Surface coating is crucial in mitigating the aging problem of high-voltage $LiNi_xMn_yCo_{1-x-y}O$ (NMC) cathodes for Li-ion batteries. By avoiding the direct contact of the active cathode material and the electrolyte, side reactions can be hindered. Electrophoretic deposition (EPD) method offers easy control of the thickness and morphology of a deposited film through simple adjustment of the deposition time and applied potential. Since we deal with lyophobic particles dispersed in suspension, the particles are stable only kinetically (not thermodynamically). As a result, the repulsion energy between particles is a very important factor in maintaining a stable suspension.

We studied the effect of the solvent type, concentration of the charging agents, EPD voltage, the time and the size of lithium aluminate particles and lithium germanium phosphate on the thickness and morphology of the electrophoretically deposited on $LiNi_{0.6}Mn_{0.2}Co_{0.2}O$ cathodes ceramic and composite films. Electrochemical performance of Li/NMC cells with pristine and coated cathodes has been investigated. In addition, mechanochemical treatment of lithium aluminate particles was undertaken and tested to clarify the influence of modification process on the impedance of protective coating and stability of the cells. EPD procedures of lithium aluminate, alumina and their composites with LiF on Ni and NMC cathode surfaces have been developed.

It was found that the deposition rate is directly proportional to the applied voltage, deposition time and the content of charging agents - acetyl acetone and PEI. The type of solvent (ethanol or acetonitrile) has little effect on the deposition rate and the morphology of the coatings. The total impedance of NMC/Li cells with composite nanoparticles protecting coatings is close to that of the cells with pristine cathodes. The R_{SEI} on Li is lower in the cells with coated cathodes. Cycling at c/3 rate of the cells comprising NMC622 with dry-ball-milled nanosize LAO protecting layer reveals lower degradation rate upon charge to 4.8V, as compared to the pristine NMC622 cathode (9.6% vs. 16.6% loss over 20 cycles, respectively).

The capacity of LAGP-coated cathodes was by about 10% higher than of pristine NMC upon cycling at different voltage cut-offs.

PD16
Electrochemical Coatings of Titanium Implants by Hydroxyapatite Nanoparticles

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Medical implants are a common treatment in reconstructive medicine. Many implants are currently manufactured from titanium alloys, that are biocompatible and have mechanical strength suitable for orthopedic and dental implants. Coatings allow adding modifications to the implant surface and the addition of bioactive functionalities while maintaining the mechanical properties of the bulk.[1]

Hydroxyapatite (HAp) is a calcium phosphate (CaP) mineral, it is the main inorganic component of bones and promotes osteogenesis.[2] Hence, it is commonly used in coatings on metal implants. Currently, HAp coatings can be formed by several methods including electrochemical deposition. The latter can be carried out in two different approaches starting with either ions or nanoparticles (NPs). Electrochemical deposition using ions, i.e., phosphate and calcium as building blocks is based on the application of a negative potential, which elevates the pH on the electrode surface and causes the deprotonation of HPO_4−
to form HAp.[3] Deposition of NPs as building blocks is driven also by a change of pH electrochemically, which causes the destabilization of the NPs.[1] This approach prevents the formation of undesired CaP phases and allows the functionalization of the coatings. Electrochemical deposition is a low-cost, simple, and flexible technique for coating conductive substrates, which allows the coating of complex geometries.

In this project, we aim to embed biological macromolecules such as proteins into the coating and develop a novel method of electrochemical deposition for NPs with biological substances. We have already shown that HAp NPs can be easily deposited using sol-gel electrodeposition. The different parameters that affect the deposition have been studied. This approach embeds the HAp inside a ceramic material, whereby its properties can be tuned using different sol-gel precursors.

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PD17

Enhancing Performance of Anode-Free Li-metal Batteries by Addition of Ceramic Nanoparticles

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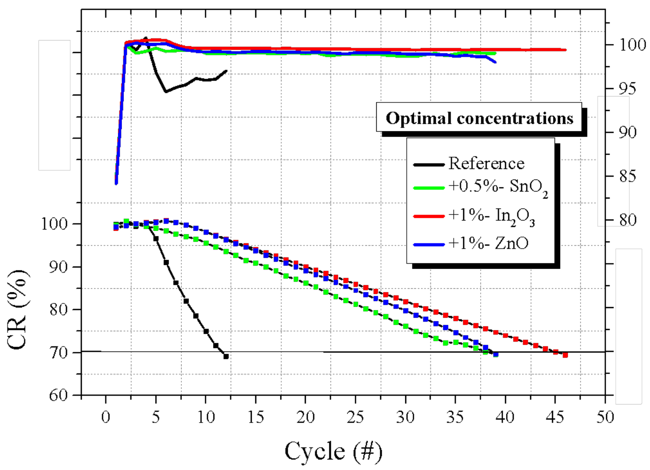
Abstract

Because of their higher energy density, compared to lithium-ion batteries, rechargeable lithium-metal batteries (LMB) have been considered one of the most attractive next-generation energy-storage systems (ESS). A promising approach to improving LMB performance, that has gained interest in recent years, is the use of anode-free lithium-metal batteries (AFLMB). Such battery configuration enables elimination of the problem of using excessive amounts of lithium in LMBs, hence increasing the specific energy of the battery.

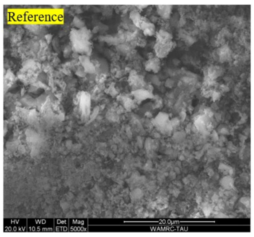
This work explores the beneficial effects of integrating metal-oxide nanoparticles (MONPs) into the liquid electrolyte of AFLMB. It was found that the addition of low concentrations of MONPs significantly improves coulombic efficiency (CE), capacity retention (CR) and the Solid-Electrolyte-Interphase (SEI) properties. SEM

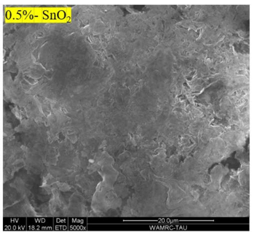
images revealed a smoother lithium morphology for MONPs cells and XPS analysis showed great differences in the SEI composition. The resistance of the cell components has been significantly lowered due to the addition of MONPs.

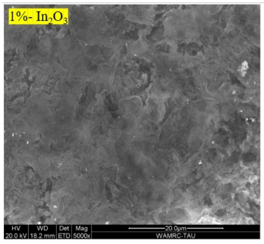
The performance of the AFLMB, without MONPs, was 97.1% CE and CR of 70% within 12 cycles, while cells with 1% In2O3 or 1% ZnO addition resulted in 99.6% and 99.2% CE, and CR of 70% within 46 and 39 cycles, respectively. Combination of these MONPs resulted in 99.9% CE, which is among the highest found in the literature for AFLMB.

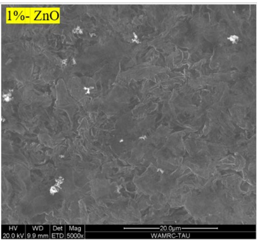


Resistance table (ohm)	**End of third discharge**			**Cycle 70%CR**		
Additive type	Rb	R-SEI	R-CT	Rb	R-SEI	R-CT
Reference	3.5	5.5	17.4	14.8	49.4	214.4
+1%- In_2O_3	8.0	1.2	9.0	12.3	4.9	238.2
+1%- ZnO	5.0	3.4	13.5	10.6	8.7	202.5
+0.5%- SnO_2	6.8	1.6	11.7	9.4	6.4	179









PD18

Stabilizing High-Voltage Lithium-Ion Battery Cathodes Using Functional Coatings of 2D Tungsten Diselenide

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Functional surface coatings were applied on high voltage spinel ($LiNi_{0.5}Mn_{1.5}O_4$; LNMO) and Ni-rich ($LiNi_{0.85}Co_{0.1}Mn_{0.05}O_2$; NCM851005) NCM cathode materials using few-layered 2H tungsten diselenide (WSe_2). Simple liquid-phase mixing with WSe_2 in 2-propanol and low-temperature (130°C) heat treatment in nitrogen flow dramatically improved electrochemical performance, including stable cycling, high-rate performance, and lower voltage hysteresis in Li-coin cells at 30 and 55°C. Significantly improved capacity retention at 30°C [Q_{401}/Q_9 of 99% *vs.* 38% for LNMO and Q_{322}/Q_{23} of 64% *vs.* 46% for NCM851005] indicated efficient functionality. TEM and XPS clarified the coating distribution and coordination with the cathode surface, while postcycling studies revealed its sustainability, enabling lower transition metal dissolution and minor morphological deformation/microcrack formation. A modified and stable SEI was apparently formed owing to W and Se deposition on the Li anode during cycling. The synergistic functionalization provided a significant dual benefit of cathodic and anodic stability.[1]

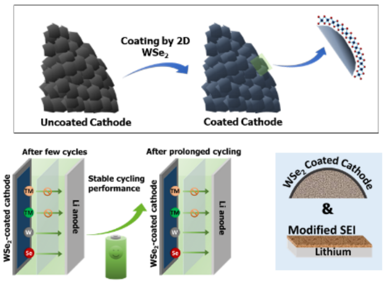

Figure 1: Schematic illustrations demonstrating the surface coating of cathode materials and their positive impacts on cathodes' electrochemical behavior.

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[1] S. Maiti, R. Konar, H. Sclar, J. Grinblat, M. Talianker, M. Tkachev, X. Wu, A. Kondrakov, G. D. Nessim, and D. Aurbach, ACS Energy Lett. 7 (2022) 1383-1391.

PD19

Differential Charge-based Electrodeposition of Chitosan

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Stimuli-responsive polymers, such as chitosan, gelatin and alginate are commonly used as smart materials with various physicochemical properties. Here we present a novel use of the positively charged chitosan—a pH response biopolymer that can be electrodeposited onto electrodes during hydrolysis, and affect the electrochemical current generated by electro-active species. Our approach based on tuning the current density used for the chitosan electrodeposition that can affect the thickness of the electrodeposited film and the underlying electrochemical signal recorded from charged electro-active species. We characterized the thickness of the chitosan film electrodeposited at either -50.9 A/m^2 ('Low Current'; Fig. 1A) or -127.3 A/m^2 (High Current) current density for 1 to 5 minutes. We recorded cyclic voltammograms (CV) with the differently modified electrodes in the presence of the charged electro-active couples $[Fe(CN)_6]^{3-}$/($[Fe(CN)_6]^{4-}$and $Ru(NH_3)_6Cl_2/Ru(NH_3)_6Cl_3$ (Ru^{2+}/Ru^{3+}). The peak currents measured for the negatively charged $[Fe(CN)_6]^{3-}$/($[Fe(CN)_6]^{4-}$ by either the low current (anodic, I_{pa}: 188 ± 7 nA; cathodic, I_{pc}: -189 ± 12 nA) or the high current (I_{pa}: 152 ± 9 nA; I_{pc}:-153 ± 9 nA) chitosan-modified electrodes and for a bare electrode (I_{pa}: 166 ± 5 nA; I_{pc}:-161 ± 5 nA) (Fig. 1B). Furthermore, the positively charged Ru^{2+}/Ru^{3+} measured by the modified electrodes resulted cathodic current peaks at -0.2V (low current: -2.9 ± 0.51 nA; high current: -3.06 ± 0.07 nA) is lower than the those measured with the bare electrode (-4.08 ± 0.15 nA) (Fig. 1C). The obtained results suggest the increased electrostatic force of the charged chitosan on the positively and the negatively charged electro-active species.

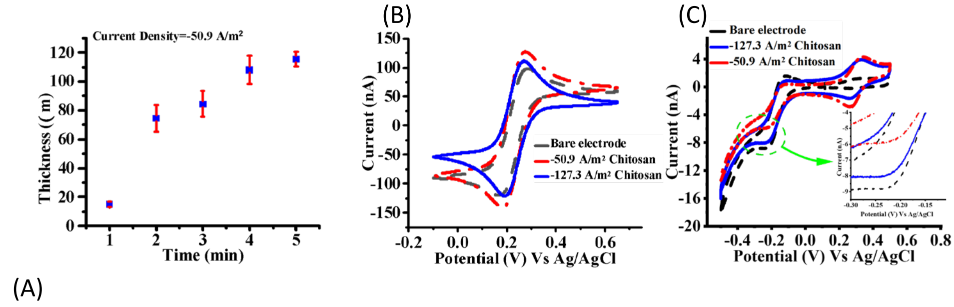

Figure 1. (A) Chitosan thickness. (B) CV of 5mM $[Fe(CN)_6]^{3-}$/($[Fe(CN)_6]^{4-}$ recorded by bare electrode (dashed, black) or the chitosan-modified electrode electrodeposited for 1 minute at either -50.9 A/m^2 (dashed-dot, red) or -127.3 A/m^2 (solid, blue). (C) CV of 400 µM $Ru(NH_3)_6Cl_2$/$Ru(NH_3)_6Cl_3$ recorded by the bare electrode (dashed, black) or the chitosan-modified electrode electrodeposited for 1 minute at either -50.9 A/m^2 (dashed-dot, red) or -127.3 A/m^2 (solid, blue).

PD20

Rhenium Sulfide Incorporated in Molybdenum Sulfide Nanosheets for High-Performance Symmetric Supercapacitors with Enhanced Capacitance

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Supercapacitors (SCs) are considered potential energy storage devices and have drawn significant attention because of their superior intrinsic advantages. Herein, we report the synthesis of ReS_2 embedded in MoS_2 nanosheets (RMS-31) by hydrothermal technique. The prepared RMS-31 electrode material demonstrated superior pseudocapacitive behavior in 1M KOH electrolyte solution, provided by the heterostructure of RMS-31 nanosheet architectures. RMS-31 has a specific capacitance of 244 F g^{-1} at a current density of 1A g^{-1} and a greater areal capacitance of 540 mF cm^{-2} at a current density of 5 mA cm^{-2}. The symmetric supercapacitor device with RMS-31 electrode delivers an energy density of 28 Wh cm^{-2} with a power density of 1 W cm^{-2} and reveals long-term stability at a constant current density of 5mA cm^{-2} 10000 cycles while accomplishing retention of 66.5%. The high performance of this symmetric device is attributed to the synergistic effect of ReS_2 and MoS_2 and the presence of metallic 1T-MoS_2 phase in the RMS-31. To the best of our knowledge, this is the first report of increasing the interlayer spacing of 2H-MoS_2 by incorporating ReS_2 for symmetric supercapacitor applications.

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PD21

Addressing the Debye length challenge for specific and label-free biological sensing using a novel Meta-Nano Channel Biosensor

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The biologically-modified field-effect transistor (BioFET) is a attractive platform for specific and label-free biosensing due to its numerous advatnages. Debye screening is a well-recognized challenge for any BioFET-based technology. Moreover, the screening length is the smallest at the double layer, since the solution ion population at the interface is higher than the bulk population. To address the small Debye screening length, the potential drop across the solution is electrostatically modified such as to minimize the potential drop over the double layer. This increases the screening length by decreasing the population of the double layer ions. However, this is not possible with BioFET as the reference electrode biasing simultaneously affects both the double layer and the BioFET conducting channel.

The current study addresses the Debye screening challenge with the novel Meta-Nano-Channel (MNC) BioFET[1]. The MNC BioFET, which is fabricated in a complementary-metal-oxide-silicon (CMOS) process, allows to decouple the electrostatics of the double layer from the electrodynamics of the conducting channel. It is demonstrated how the double layer can be electrostatically tuned in order to optimize the screening length without affecting the conducting channel using the MNC BioFET. Finally, we demonstrate specific and label-free sensing of 10 ng/ml prostate specific antigen (PSA) and by electrostatically increasing the double layer screening length, the sensing signal increases from 70 mV to 133 mV.

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PD22

Increasing the Cycle Life of Silicon-Anode Lithium Ion Battery

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Because of their higher energy density, compared to common graphite-anode lithium-ion batteries (GLIB), rechargeable silicon-anode lithium ion battery (SLIB) have been considered as one of the most attractive next-generation energy-storage systems (ESS). Silicon is a low-cost and environmentally friendly material, and is the second most abundant element in the Earth's crust. Its theoretical capacity of 4200mAh g-1, is an order of magnitude greater than that of graphite. Nevertheless, the main and most important challenge with this anode is the short cycle life due to very large expansion and contracting during cycling. This work explores the beneficial effects of integrating metal-oxide nanoparticles (MONPs) into the liquid electrolyte of these system. It was found that the addition, to the electrolyte, of low concentrations (0.1 to 5%) of MONPs significantly improves coulombic efficiency (CE), capacity retention (CR) and the SEI properties. We were able to double its cycle life relative to MONPs free electrolyte.

PD23

Is Pre-Carbonization Necessary for Effective Laser Graphitization?

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Abstract: Laser-graphitization offers a new approach to obtaining high-quality 3D graphene films simply and efficiently. Over the years this method was developed to include different carbonaceous precursors and irradiation parameters. Precarbonization is a step in the synthesis where the precursors are annealed at high temperatures under an inert atmosphere to increase the carbon content in the samples prior to the laser reaction. Some studies report this step while others do not, thus its necessity and beneficially have to be evaluated. In this study, we compare the laser products of as-prepared and precarbonized carbon nanodots (CNDs). The study investigates the samples from the initial synthesis step of microwave-assisted formation of CNDs, through separation of the CNDs by particle size, the precarbonization step conducted at different temperatures, to the final 3D graphene films products. By analyzing the chemical structure and graphitization level of the intermediates, we could realize the chemical characteristics responsible for successful laser-graphitization. We have found that precarbonization indeed leads to improved graphitic products, only to a certain extent. The best graphitization level is achieved when the CNDs were precarbonized to 300°C obtaining I_D/I_G ratio= 0.44 as compared to 1.08 when as-prepared CNDs are used. On the other hand, when annealed to 400°C the laser produces more defected graphene films (I_D/I_G ratio= 0.83). Moreover, both the surface chemistry and the core structure of the CNDs affect the final results.

A careful examination of the surface chemistry reveals the coverage of oxygen- and nitrogen-containing functional groups required for the optimal thermochemical reaction.

PD24

Protection of NMC cathodes by electrophoretically deposited composite ceramic layers

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School of Chemistry, Tel Aviv University

Surface coating is crucial in mitigating the aging problem of high-voltage $LiNi_xMn_yCo_{1-x-y}O$ (NMC) cathodes for Li-ion batteries. By avoiding the direct contact of the active cathode material and the electrolyte, side reactions can be hindered. Electrophoretic deposition (EPD) method offers easy control of the thickness and morphology of a deposited film through simple adjustment of the deposition time and applied potential. Since we deal with lyophobic particles dispersed in suspension, the particles are stable only kinetically (not thermodynamically). As a result, the repulsion energy between particles is a very important factor in maintaining a stable suspension.

We studied the effect of the solvent type, concentration of the charging agents, EPD voltage, the time and the size of lithium aluminate particles and lithium germanium phosphate on the thickness and morphology of the electrophoretically deposited on $LiNi_{0.6}Mn_{0.2}Co_{0.2}O$ cathodes ceramic and composite films. Electrochemical performance of Li/NMC cells with pristine and coated cathodes has been investigated. In addition, mechanochemical treatment of lithium aluminate particles was undertaken and tested to clarify the influence of modification process on the impedance of protective coating and stability of the cells. EPD procedures of lithium aluminate, alumina and their composites with LiF on Ni and NMC cathode surfaces have been developed.

It was found that the deposition rate is directly proportional to the applied voltage, deposition time and the content of charging agents - acetyl acetone and PEI. The type of solvent (ethanol or acetonitrile) has little effect on the deposition rate and the morphology of the coatings. The total impedance of NMC/Li cells with composite nanoparticles protecting coatings is close to that of the cells with pristine cathodes. The R_{SEI} on Li is lower in the cells with coated cathodes. Cycling at c/3 rate of the cells comprising NMC622 with dry-ball-milled nanosize LAO protecting layer reveals lower degradation rate upon charge to 4.8V, as compared to the pristine NMC622 cathode (9.6% vs. 16.6% loss over 20 cycles, respectively).

The capacity of LAGP-coated cathodes was by about 10% higher than of pristine NMC upon cycling at different voltage cut-offs.

PD25

Conversion of Cellulose Biomass into electrical power using Cellulase enzymes in a photo-electrochemical cell

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Exploiting biomass and other cellulose-based material as fuel attracts increasing attention in the last few decades. Crops are composed of ca 70% of Cellulosic materials which are not exploited as food and ends up as waste. Methodologies to expand its uses and especially methodologies to convert it into green energy are required.

Photo-electrochemical cells are attractive configurations to utilize light and chemical energy into electrical power. These cells use a light-induced reaction to enable the oxidation of fuels such as biomass waste products, which subsequently generate electrical power. While the strong oxidation abilities of a semiconductor can enable the oxidation of small sugar molecules, it can’t reach non-soluble long-chain molecules such as cellulose.

The degradation of cellulose by cellulases enzymatic complex can lead to glucose which in turn can be consumed by bismuth vanadate-cobalt phosphate ($BiVO_4$-CoP) generated holes (Fig.1). The generated electrons can be further used in a photobioelectrochemical cell configuration to reduce water into oxygen using an enzymatic biocathode. Here we present the integration of $BiVO_4$/CoP with cellulase complex for one-pot conversion of cellulose to electricity. The usage of PEC cells promotes great opportunities for an efficient conversion of chemical energy to electrical power.

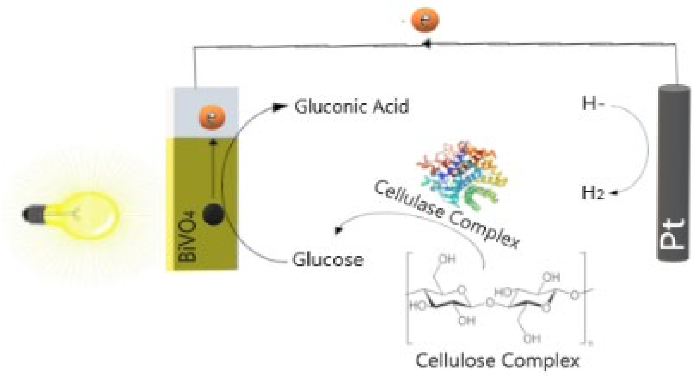

Figure SEQ Figure * ARABIC 1: *Schematic diagram of photobiofuel cell consisting of BiVO4 based photoanode and the cellulase complex*

PD26

Cellulose to Electricity Conversion by Bias-Free Biofuel Cell

Nidaa Shrara Herzallh, Yifat Cohen, Roy Cohen, and Omer Yehezkeli

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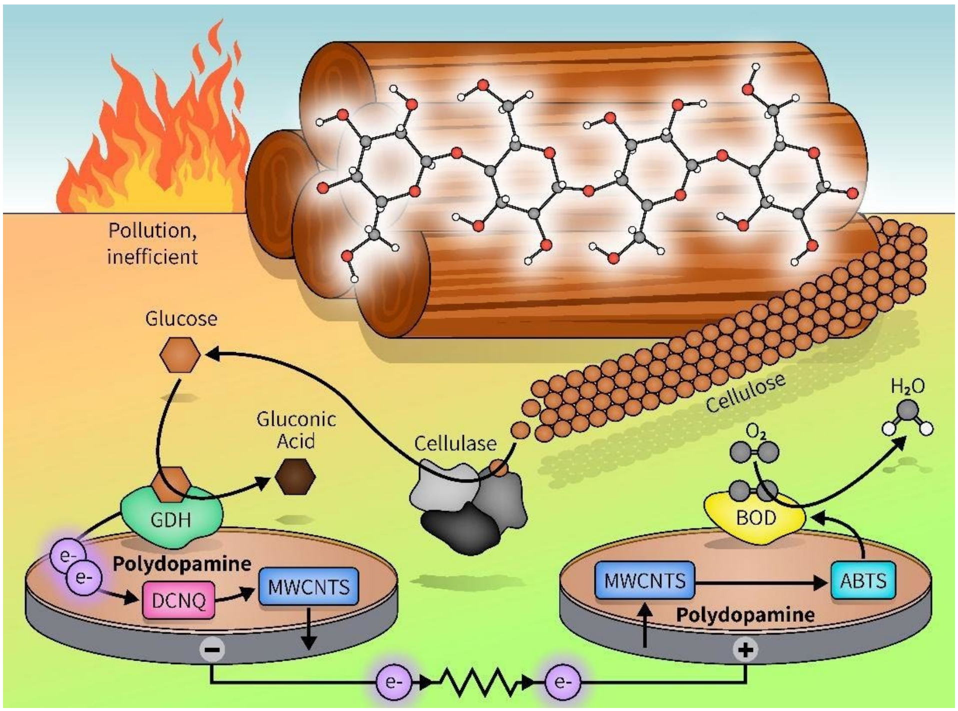
The conversion of biomass and other cellulose-based materials to clean energy has high promise for a sustainable world. Herein we present a green methodology to convert cellulose directly into electrical power output by utilizing cellulase complex and enzymatic biofuel cell. FAD-dependent glucose dehydrogenase (FAD-GDH) based anode and Bilirubin oxidase-based cathode were used for cell construction. Commercial cellulase complex was utilized for cellulose degradation into glucose monomers which were then oxidized by the FAD-GDH based anode to yield gluconic acid and high bioelectrocatalytic currents. The electrons are subsequently transferred to the bilirubin oxidase based cathode and allow the oxygen reduction reaction. The designed biofuel cell allows direct biomass to electricity conversion while operating under neutral pH and standard conditions. The constructed biofuel cell was characterized at different cell conditions and further optimized under air and under oxygen saturated atmosphere and a maximal operational lifetime of 32 hours was achieved. The cell has produced electrical power of 300µW/cm^2 and 600µW/cm^2 under air or oxygen, respectively. Therefor the constracted biofuel cell allows the generation of bias-free electrical power while only cellulose and O_2 are required for its operation.



N.S. Herzallh, Y. Cohen, R. Cohen, O. Chmelnik, Y. Shoham and O. Yehezkeli, Cellulose to Electricity Conversion by Bias-Free Biofuel Cell, Sustainable energy & fuels, 2021.

PD27

Multi-Spray Pyrolysis for Combinatorial Synthesis of Materials Libraries and their High-Throughput Screening: Application to Li-Ion Conducting Electrolytes

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We present a multi-head spray pyrolysis system and its application in high-throughput combinatorial synthesis for research of solid Li-ion conductors. Each spraying nozzle is fed with a separate precursor solution. The overlap of areas that are sprayed leads to unprecedented composition flexibility of the films obtained after pyrolysis. Thus, a library with a continuous composition spread of a Li-La-P-O model system is formed. The Li-ion conduction was determined on 169 cells of the library, using high throughput impedance measurements in a controlled environment. While the activation energies that were found were relatively small, Li-ion conduction was still low. This low mobility is hypothesized to originate from the sub-optimal occupation of Li sites in the non-stoichiometric materials' lattices, and/or porosity and tortuosity issues.

PD28

Electrochemical Sensing Using Mediator-Modifier Interactions in Solution

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State-of-the-art electrochemical sensors rely on detecting the electrons transferring between electrodes modified with selective probes and the molecules of interest[1,2]. While these sensors are based on heterogenous recognition reaction at the surface of the electrode, the detection performance is limited by the exposed area of the probe. Here, we propose a new approach for electrochemical sensing that is based on homogenous recognition reaction between the analyte and the probe. Our method is based on combining electro-active species with a family of structural modifiers; a unique combination that offers an adjustable component for identifying and quantifying different analytes. As a proof-of-concept study of our approach, we used cysteine as the analyte, catechol as the electro-active species and boronic acids (phenyl m-OMe and p-CF_3) as the structural modifiers (Fig.1A). First, we validated the effect of the boronic acids on the electrochemical signal generated from catechol (Fig.1B) by using differential pulse voltammetry technique. The catechol and boronic acid mixture generated an oxidation peak at 0.6V vs Ag/AgCl that was not visible with either catechol or boronic acid alone. Fig. 1C shows the electrochemical signal recorded in the presence of 100µM catechol, 200µM m-OMe phenyl boronic acid and increasing concentrations of cysteine (0-100µM). We observed an increasing current characteristic at 0.6V vs Ag/AgCl (1-2.5µA) for the increasing cysteine concentrations that resulted a linear relationship (Fig.1D) with a slope of 0.015±0.001, a dynamic range between 10-100µM and limit-of-detection of 9.7µM. Moreover, substituting m-OMe phenyl boronic acid with p-CF_3 phenyl boronic acid resulted a cysteine-dose response characteristics with a slope of 0.013±0.001, a dynamic range between 10-100µM, and a limit-of-detection of 9.4µM (Fig.1E). To identify the analyte in the presence of interfering electro-active species, our future work will focus on utilizing chemometrics to integrate the signals in the presence of different boronic acid modifiers. This method may enable to identify analytes in complex matrices such as body fluids or differentiate between structurally similar molecules.

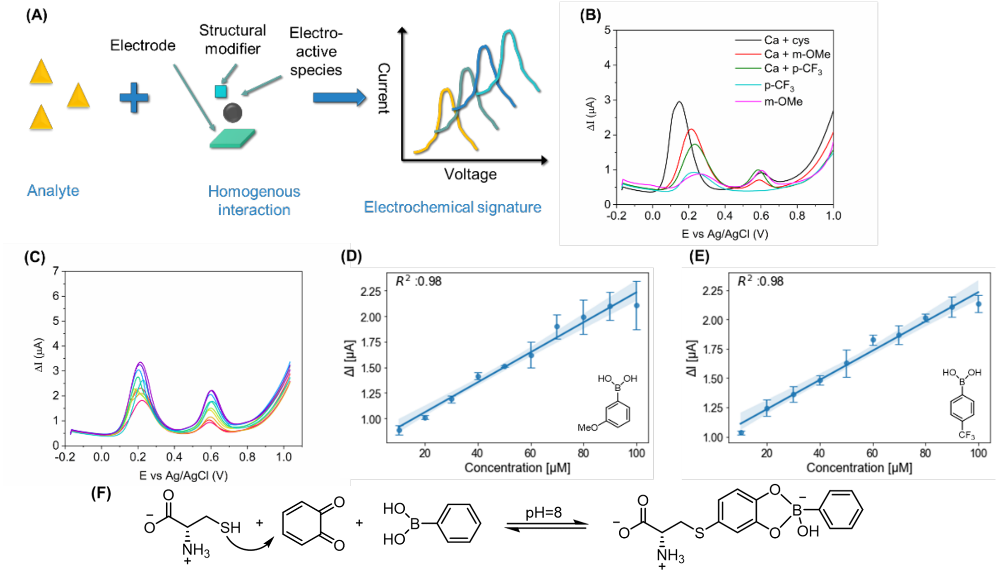

Figure 1. *(A) Homogenous recognition-based electrochemical sensing. (B) Differential pulse voltammograms of either catechol alone, m-OMe phenyl boronic acid alone, p-CF_3 phenyl boronic acid alone, catechol with m-OMe phenyl boronic acid, and catechol with p-CF_3 phenyl boronic acid. (C) Differential pulse voltammograms of a mixture containing catechol, m-OMe phenyl boronic acid and increasing concentrations of cysteine (10-100µM). Linear regression analysis of a mixture containing catechol, increasing concentrations of cysteine (10-100µM), and either (D) m-OMe phenyl boronic acid or (E) p-CF_3 phenyl boronic acid. Measurements were performed in a 150 mM phosphate buffer saline solution (pH=8), 3mm glassy carbon disk working electrode, commercial Ag/AgCl reference electrode (3M NaCl), and a platinum wire as the counter electrode (F) proposed reaction mechanism.*

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PD29

Amperometric dual sensing of glucose and L-lactate based on O_2-insensitive flavoenzymes

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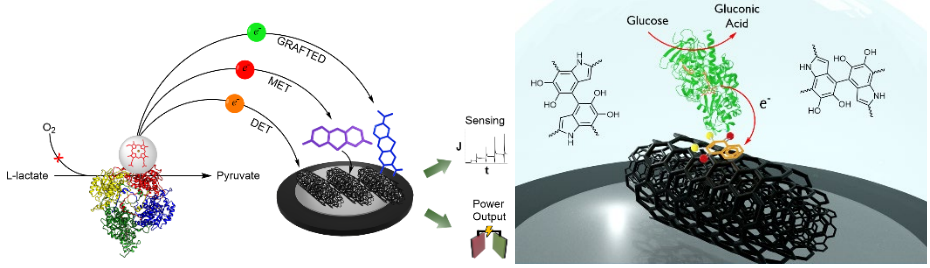
Glucose and L-lactate sensing have great importance for medicine, energy production, food and health. The most common biosensors are O_2-dependent, which limits their accuracy. While O2-independent biosensors for glucose have been developed in the last decade, lactate O_2-independent biosensing has yet to show its promise. These known lactate biosensors have a wide detection range, yet their developed bioelectrocatalytic currents are low and unattractive for biofuel-cell applications. Since lactate can be found in great quantities on our skin, it could be utilized for both sensing and energy production. I hereby present a simple, low-cost amperometric biosensor for glucose or lactate, as well as a combination of the two. I will elaborate on the properties of each and present a biofuel-cell application using glucose or lactate as fuel.



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PD30

Impact on stability at three-Na ion activity of $Na_3V_2(PO_4)_2F_{(3-x)}Br_x$ structure for Na-ion battery

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The leading energy storage technology in portable and automotive application recognized the lithium-ion batteries (LIBs) as excellent viable energy storage devices. However limited abundancy of lithium drives to go for alternatives to LIB technology, [1,2] and in this aspect, sodium (Na)-ion technology appears as promising alternative in terms of availability, cheaper cost and similar electrochemical intercalation/deintercalation activity. Recent studies have shown that polyanionic compound, $Na_3V_2(PO_4)_3$, having Na super ionic conductor (NASICON) structure possesses stable 3D open framework for rapid Na-ion diffusion with high reversible capacity. Furthermore when one $(PO_4)^{-3}$ ion is replaced by three F- ion, the new fluorophosphate, $Na_3V_2(PO_4)_2F$ (NVPF) structure is obtained which can deliver higher energy density and theoretical capacity (128 $mA.h.g^{-1}$) for the extraction of two Na^+ ion through two redox plateaus at 3.7 and 4.1V vs Na/Na^+[3]. Moreover, to boost up the capacity, extraction of third Na^+ ion has been approached by recent group of studies, and interestingly, the improvement of capacity by ~65 $mA.h.g^{-1}$ is observed by their outstanding approach. Despite this tremendous success, one major issue that decline the practical application is the structural and electrochemical stability upon prolonged cycling[4,5].

In this context, here we report the controlled facile synthesis of micro hollow-spheres of $NVPF_{(3-x)}Br_x$,[x=0.1,0.2,0.3,0.4] with high crystalline orthorhombic structure. The electrochemical measurement is conducted through assembled coin cell in the potential window of 1.2 V to 4.3 V vs Na/Na+. During first cycle activation at low rate of current density (8.5 mA.g^{-1}), the highest irreversible capacity is observed for NVPF$_{(3-x)}$Br$_x$,[x=0.4] (72.4 mA.h.g^{-1}); limiting the cycling durability whereas, for NVPF$_{(3-x)}$Br$_x$ [x=0.2] it is only 21.2 mA.h.g^{-1} indicates promising stability features. Further study reveals the excellent cycling stability of NVPF$_{(3-x)}$Br$_x$ [x=0.2] compared to the other as synthesized materials and pristine NVPF as well at moderate (25.6 mA.g^{-1}) and high (64 mA.g^{-1}) current density rate with highest discharge capacity of 170 mA.h.g^{-1}. This study emphasizes the possibility of improving stability without compromising the capacity for NVPF cathode towards Na battery and the fact is explained based on details XRD, XPS and electron microscope studies.

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PD31

Determination of Sodium Ion Transference Numbers in Polymers Electrolytes Based on Electrochemicals Methods

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Over the past few years, the field of solid batteries has gained a lot of popularity. Due to significant limitations found in liquid lithium batteries over the last few years, polymers and other non-liquid materials have attracted attention as candidates for electrolytes in lithium batteries. The assembly of lithium batteries with solid electrolytes was first discovered in the 1970s, however, the research has been abandoned in favor of batteries containing aprotic solvents. There is significant research being conducted in this field today, expecting this work will lead to applicative innovations in the near future.

One of the key parameters for solid-polymer-electrolyte characterization is the transfer number of the cation. This number defines the cations' contribution to the positive charge mobility in the electrolytic medium. As the transfer number nears 1, the current mobility in the electrolyte medium will be increasingly carried by the cations. In a deeper perspective, this number determines the extent of polarization caused by negative charge carriers in the cell. Therefore, it will predict the degree of efficiency of the battery, especially in high currents.

Currently, there are two experimental techniques used in the literature for calculating the transference number: one is electrochemical, and one is NMR spectroscopy. This study focuses on electrochemical methods.

In this study we examine the different electrochemical ways proposed in the literature and try to examine the advantages and disadvantages of each way and way.

PD32

Advanced atomic layer deposition (ALD) protective coatings produced on Li-ion battery powdered anode materials

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Ever-growing concerns of limited energy resources and environmental pollution cause an urgent need in the development of renewable energy technologies. Lithium-ion batteries (LIBs) have become the major alternative energy storage devices due to high energy density, safety and ecological performance. The most commonly used anode material for LIB is graphite benefiting from its low cost, high abundance, superior conductivity, good capacity retention, and long cycle-life. Yet, the performance of graphite anode in LIB challenged by the need to produce and grow a solid-electrolyte interphase (SEI), which is a result of electrolyte components decomposing. Various ex-situ and in-situ strategies have been suggested to overcome this problem. Among them applying the protective coatings is one of the most effective measure. Such coatings serve as a barrier preventing electron-transfer through the SEI and therefore eliminating the undesirable redox processes at the electrode surface. At the same time, the protective coatings are permitting/regulating the Li-ion transport in both directions. The most effective fabrication method allowing maximum possible (atomic) resolution and control over the composition of the growing protective coating is the atomic layer deposition (ALD). Moreover, ALD enables conformal coating of complex-profile active electrode materials, like porous materials and powders. The latter is a unique capability of the ALD technique. In this work, hybrid (metal-organic) ALD-coating on graphite powdered anode material (MesoCarbon MicroBeads, MCMB) was studied in terms of its electrochemical performance. Specifically, spectroscopic (FTIR, Raman) and electrochemical (galvanostatic charge/discharge profiles) analyses were used for characterization and evaluation of the MCMB/ALD active anode material, respectively. Standard slurry-coating method was used to fabricate the composite anodes from MCMB/ALD and polyvinylidene fluoride (PVDF) binder. The electrochemical evaluation was performed in half-cell configuration. The effects of slurry drying temperature and electrode loading on the capacity, coulombic efficiency, and cyclability of LIB were systematically studied. The results obtained in this work contribute to the basic knowledge of the composite anode formulation and fabrication particularly in terms of functioning of the protective metal-organic thin-coatings.

PD33

Electrochemical Corrosion Studies of Electrophoretically Deposited $Ti_3C_2T_x$-TiO_2

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In recent years, two-dimensional (2D) transition-metal carbide, nitride, and carbonitride, known as MXenes, have received significant attention due to their high conductivity, high surface area, and electrochemical activity.[1] These unique properties make MXenes suitable for various clean energy technologies such as batteries, and fuel cell. MXenes can be obtained by selective etching of a MAX phase, Mn 1AXn, where M represents an early transition metal, A is a group IIIA or IVA element, and X represents carbon or nitrogen. MXene's general formula is Mn-1XnTx, where Tx stands for–O, –OH, or –F surface terminations. Major drawback of MXenes is their poor chemical stability. It undergoes severe degradation in aqueous medium. Low pH and oxidative environment further accelerate the degradation mechanism. Thus, it is imperative to improve the corrosion stability of MXenes for long-term energy applications. Coating of corrosion resistant ceramic material, such as TiO2, is known to enhance the corrosion stability.[2]In this regard, a suitable coating technology plays a crucial role.

Here, corrosion studies of the electrophoretically deposited Ti3C2Tx MXene and Ti3C2Tx-TiO2 are investigated. The deposits were characterized by scanning electron microscopy (SEM), and X-ray diffraction (XRD). Applied voltage and duty cycle during deposition controls the deposit thickness and surface roughness. The effects of TiO2 incorporation on Ti3C2Tx stability is studied by cyclic potentiodynamic polarization (CPP) corrosion tests. Positive shift in corrosion potential and reduction in corrosion current is observed, implying electrochemical oxidation resistance of Ti3C2Tx-TiO2.

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PD34

Recent Studies of Nickel-Rich Positive Electrodes for Lithium-Ion Batteries

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The most promising cathode materials for lithium ion batteries (LIBs) are the lithium intercalation transition metal oxides of layered structure (space group *R-3m*), $Li[Ni_xCo_yMn_z]O_2$ (x+y+z=1) (NCM). NCM materials can exhibit specific capacity > 200 $mAhg^{-1}$ and high rate capability at Ni-content of ≥80 %. However, they have disadvantages: low electronic and ionic conductivities, structural instability, and fast capacity fading upon cycling. In this presentation, we focus on a family of Ni-rich (x=0.8 and 0.85) materials with various content of Co and Mn. The main questions studied were lattice doping with low charged B^{3+} and highly charged Mo^{6+} cations of NCM in relation to the electrode behavior, structural stability, electronic properties, and thermal reactions with battery solutions. The data demonstrate the substantial improvement of the doped electrodes in terms of cycling performance, lower voltage hysteresis, and reduced self-discharge upon high temperature storage. The electronic structure of the undoped and B-doped materials was modelled using density functional theory, which identified interstitial positions as the preferential location of the dopant. We have established that the boron segregates at the surface, effectively reducing the surface energy and increasing the oxygen binding energy, and possibly, as a result, inhibiting oxygen release. Additionally, the presence of borate species near the surface can reduce the nucleophilicity of surface oxygen. Cycling of the Li-cells did not cause noticeable changes in the microstructure of the B- and Mo-doped materials, whereas a propagating network of cracks was observed across all grains in the cycled undoped NCM85 cathodes. Analysis by HR-TEM and ^6Li and ^{11}B ss-NMR allowed for the correlation of capacity fade and degradation of NCM materials with their structural characteristics. We conclude that doping of these cathodes with B^{3+} or Mo^{6+} (even at a minute level) is a promising path towards enhanced electrochemical activity in advanced LIBs.

PD35

Li/Graphene Oxide Primary Battery System and Mechanism

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A novel Li/graphene oxide (Li/GO) battery is introduced as an alternative viable primary battery system based on a spontaneous redox reaction between Li metal and GO cathode.[1] Here, we present an efficient synthesis of GO by the modified Hummers method and focus on a comprehensive study of the reduction mechanism. Various physical and electrochemical methods thoroughly analyzed the Li/GO battery. GO rich in oxygen-bearing functional groups on graphene layers provided lithium storage sites and delivered a high discharge capacity of around 720 mAh/g at 12 mA/g. Products formed on the surface during reduction were analyzed, and a mechanism was proposed. The results uncovered the reasons underlying the improved electrochemical properties and the contribution of the irreversible capacity of reduced GO in graphene-based composite electrode materials for metal-ion batteries. The Li/GO concept is expected to shed light on the design of similar Metal/GO batteries based on other active metal anodes (e.g., M=Na, Mg, Al, Zn). The results will be discussed elaborately at the time of the presentation.

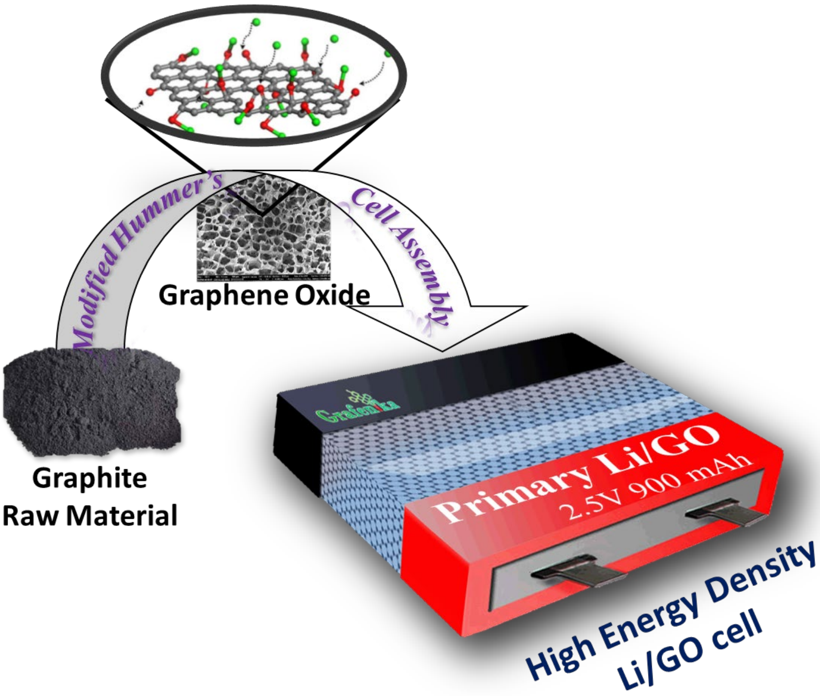

Figure: Synthesis of graphene oxide (GO) and Li/GO cell production.

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PD36

Different Molecular Arrangements: *On Surface* versus *In Solution*

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Coordination chemistry has been used to control the shape, size, and topology of supramolecular structures and to limit the possibilities to produce mixtures of multiple sets of structures.[1] In general, the development of defined supramolecular structures with desirable properties occurs with retention of the structural integrity of the molecular starting materials, but the assemblies can have different molecular arrangements and appearances.[2,3] The formation of both metallo-organic crystals and nanoscale films that have entirely different compositions and structures despite using the same set of starting materials was demonstrated (Figure 1).[4] The reaction of an iron polypyridyl complex with a copper salt by diffusion of one solution into another resulted in iron-to-copper exchange, concurrent ligand rearrangement, and the formation of metal–organic frameworks (MOFs). This observation shows that polypyridyl complexes can be used as expendable precursors for the growth of MOFs. In contrast, alternative depositions of the iron polypyridyl complex with a copper salt by automated spin coating on conductive metal oxides resulted in the formation of electrochromic coatings, and the structure and redox properties of the iron complex were retained. The possibility to form such different networks from the same set of molecular building blocks by "in solution" *versus* "on surface" coordination chemistry broadens the synthetic space to design functional materials. Electrochromic coatings are considered materials that have great potential for smart window technology that can reduce the carbon-footprint of buildings.

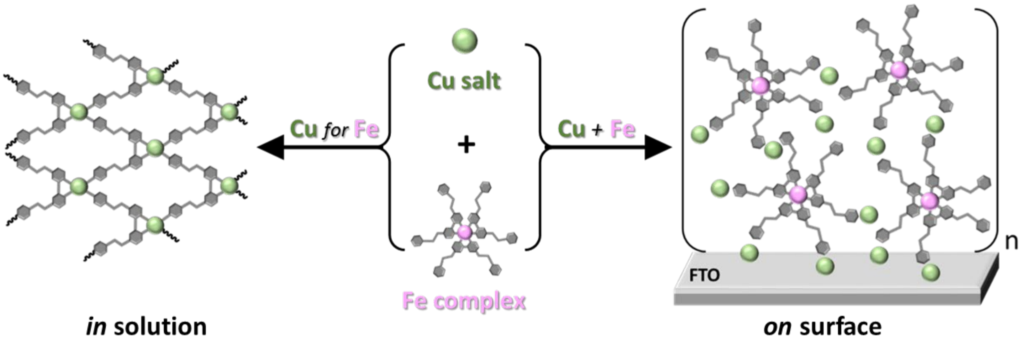

Figure 1. Coordination Networks in Solution versus on Surface.

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