Energy and sustainability session abstracts IVS 2023:

Electrocatalytic materials, interfaces, and devices for the production of e-fuels and e-chemicals

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The rising share of renewable electricity is testament to the increasing importance of solar/wind-electric routes to harvest sun light in form of potential differences and flowing free electrons. While some electricity is used directly or stored capacitively, an increasing portion calls for direct conversion into valuable molecular e- fuels or e-chemicals. This conversion in the dark is made possible by heterogeneous electrocatalysis on the surface of solid electrodes. More Fundamental understanding of the origin of kinetic barriers is needed for the design of more efficient, tailor-made electrochemical interfaces for the production of fuels and chemicals.

In this presentation, I will report on recent advances in our design and understanding of electrocatalytic materials, interfaces, and devices relevant to the conversion of electricity into value-added molecular compounds.

Surface science for sustainability: Pb leaching from halide perovskites

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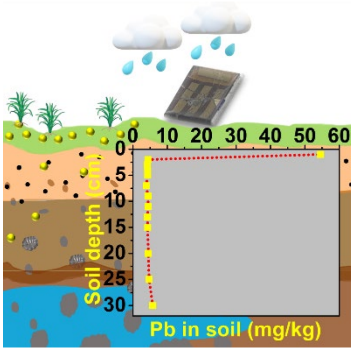
Following the achievement of impressive power conversion efficiencies of perovskite solar cells (PSCs), the current challenges of this technology include long-term stability, upscaling for industrial processing, and its environmental effect. One of the significant concerns of the latter is accidental Pb leaching from PSCs and modules, due to the well-documented Pb toxicity. Such concerns may cause deceleration in PSC commercialization. However, review of the current knowledge shows that this threat is found to be comparable to that posed by currently used Pb-containing products, and a plethora of measures are available to mitigate the environmental impact of Pb.[1]

Pb leaching from damaged PSCs may imply a significant environmental impact on the surrounding soil in the case of module damage. We have examined the penetration profile of Pb from aqueous solutions of dissolved Pb-perovskite into the soil, and the Pb^{2+} adsorption mechanism to soil particles. The penetration profiles in all studied soils showed high affinity for Pb adsorption to soil, hence shallow immobilization of the Pb cations in all studied soils, with negligible odds of reaching and contaminating ground water. We, therefore, suggest that Pb in PSCs and its effect on the environment are not as concerning, as they seem to be.[2]



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[1] A. Mallick, I. Visoly-Fisher, *Pb in halide perovskites for photovoltaics: reasons for optimism*, Mater. Adv. (2021) 2, 6125 - 6135

[2] A. Mallick, R. D. Mendez Lopez, G. Arye, D. Cahen, I. Visoly-Fisher, *submitted*.

Molecular manipulation of heterogeneous electrocatalytic CO_2 reduction using metal-organic frameworks

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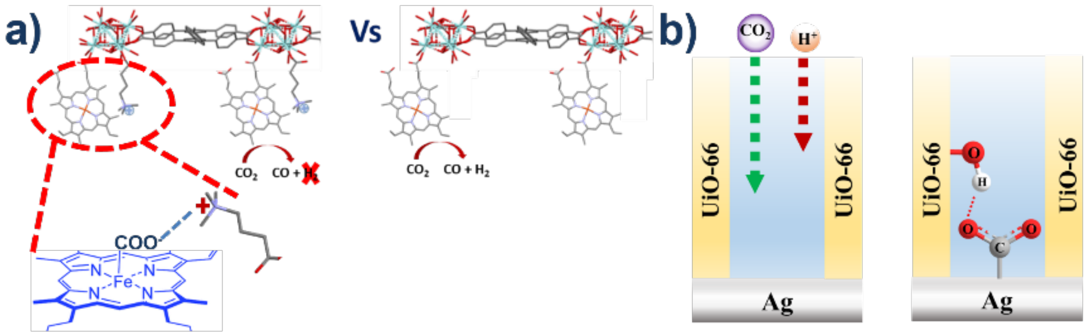
Electrocatalytically driven CO_2 reduction reaction (CO_2RR) to produce alternative fuels and chemicals is a useful means to store renewable energy in the form of chemical bonds. in recent years there has been a significant increase in research efforts aiming to develop highly efficient CO_2RR electrocatalysts. Yet, despite having made significant progress in this field, there is still a need for developing new materials that could function as active and selective CO_2RR electrocatalysts.

In that respect, Metal–Organic Frameworks (MOFs), are an emerging class of hybrid materials with immense potential in electrochemical catalysis. Yet, to reach a further leap in our understanding of electrocatalytic MOF-based systems, one also needs to consider the well-defined structure and chemical modularity of MOFs as another important virtue for efficient electrocatalysis, as it can be used to fine-tune the immediate chemical environment of the active site, and thus affect its overall catalytic performance. Our group utilizes Metal-Organic Frameworks (MOFs) based materials as a platform for imposing molecular approaches to control and manipulate heterogenous electrocatalytic systems. In this talk, I will present our recent study on electrocatalytic CO_2RR schemes involving MOFs, acting as: i) electroactive unit that incorporates molecular CO_2RR electrocatalysts, or ii) non-electroactive MOF-based membranes coated on solid CO_2RR catalysts.



References:

[1] Shimoni, R.; Zhuocheng Shi, Z.; Binyamin, S.; Yang, Y.; Liberman, I.; Ifraemov, R.; Mukhopadhyay, S.; Zhang, L.; Hod, I., Angewandte Chemie Int.Ed., 2022, 10.1002/anie.202206085.
[2] Mukhopadhyay, S.; Shimoni, R.; Liberman, I.; Ifraemov, R.; Rozenberg, I.; Hod, I., Angewandte Chemie Int.Ed., 2021, 60, 13423–13429.
[3] Liberman, I.S; Shimoni, R.S; Singh, C.P.PD; Hod, I., Journal of the American Chemical Society, 2020, 142 (4), 1933-1940.
[4] Shimoni, R.; He, W.; Liberman, I.; Hod, I., Journal of Physical Chemistry C, 2019, 123, 9, 5531-5539.

Elucidating the structure and function of the electrode-electrolyte interface by new solid state NMR approaches

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The development of long-lasting energy storage systems based on rechargeable batteries relies on our ability to control charge storage and degradation processes in the bulk of the electrode materials and at the electrode-electrolyte interface. NMR spectroscopy is exceptionally suited to follow the electrochemical and chemical processes in the bulk of the electrodes and electrolyte, providing atomic scale structural insight into the charge storage mechanisms and ion transport properties. However, interfacial properties, such as the processes governing charge transport between the electrode and the electrolyte, are much harder to study. These processes typically involve thin, heterogeneous and disordered layers that are formed chemically/electrochemically in the battery cell or artificially through coating the electrode material. While NMR is in principle an excellent approach for probing disordered phases, its low sensitivity presents an enormous challenge in the detection of interfacial processes. I will describe recent approaches to overcome this limitation by the use of Dynamic Nuclear Polarization (DNP). In DNP, the large electron spin polarization is used to boost the sensitivity of NMR spectroscopy by orders of magnitude. I will show how we can use this approach, using exogenous and endogenous sources of polarization, to detect the composition and determine the structure of the solid-electrolyte interphase (SEI) formed on sodium anodes, with unprecedented sensitivity. Furthermore, I will present new approaches to probe ion transport properties of various interfaces. These allow us to get insight into the functional role of interfaces, which along with the chemical and structural insight, can provide design rules for beneficial interfaces, an essential aspect for developing long-lasting energy storage systems.

Complex bimetallic and monometallic phosphides as catalysts

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Transition metal phosphides (TMP) are a promising material family that has been studied extensively. Still, synthesizing complex and bimetallic phosphides in a reproducible manner is challenging due to the various available oxidation states and crystallographic phases. The various reactivities of the precursors and phase segregation often produce structures with diverse morphologies and compositions. Such synthetic control is crucial for elucidating these structures' intrinsic properties as catalysts. Here, I will describe a few methods to produce complex bimetallic structures and their electro-catalytic activity towards hydrogen evolution (HER), oxygen evolution (OER) and alcohol oxidation. Specifically, I will present a comparative study that illustrates the catalytic activity of three Ni-P phases towards hydrogen production through electrochemical water reduction as well as hydrogen retrieval by hydrolysis of hydrogen storage materials (ammonia-borane and $NaBH_4$). I will show that $Ni_{12}P_5$ was recognized as a suitable platform for the electrochemical production of γ-NiOOH—a particularly active phase—because of its matching crystallographic structure. An additional incorporation of tungsten by doping produces surface roughness, increases the electrochemical surface area (ESCA), and reduces the energy barrier for electron-coupled water dissociation (the Volmer step for the formation of H_{ads}). We explored the three different phases of nickel phosphide also for the electro-oxidation of methanol, ethanol, isopropanol, ethylene glycol, and glycerol. $Ni_{12}P_5$ exhibits excellent activity (210 mA cm^{-2} at 1.72 V vs RHE), durability, and mass activity (~4.2 A mg^{-1}), outperforming the state-of-the-art catalysts. The high selectivity of the reaction and the large suppression of further oxidation to CO_2 are a marker of a preferred bidentate adsorption configuration that conveys a specific O–H activation reaction path. The catalysts show excellent activity towards alcohol oxidation and durability, likely thanks to the mild conditions required for the process, which allow the formation of a regenerating thin active layer of oxidized nickel.[1-3]

1. Ghosh, S.; Kadam, S. R.; Houben, L.; Bar-Ziv, R.; Bar-Sadan, M., Nickel Phosphide Catalysts for Hydrogen Generation through Water Reduction, Ammonia-Borane and Borohydride Hydrolysis. Appl. Mater. Today 2020,20, 100693.
2. Ghosh, S.; Kadam, S. R.; Kolatkar, S.; Neyman, A.; Singh, C.; Enyashin, A. N.; Bar-Ziv, R.; Bar-Sadan, M., W Doping in Ni12p5 as a Platform to Enhance Overall Electrochemical Water Splitting. ACS Appl. Mater. Interfaces 2022,14(1), 581-589.
3. Ghosh, S.; Mondal, B.; Roy, S.; Shalom, M.; Sadan, M. B., Alcohol Oxidation with High Efficiency and Selectivity by Nickel Phosphide Phases. J. Mater. Chem. A 2022,10 (15), 8238-8244.

Operando characterization of charge extraction and recombination profiles in solar cells with nanoscale resolution

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The next generation of solar energy conversion systems requires design and integration of new semiconductor materials. Detailed understanding of the opto-electronic properties of these materials, their driving forces and the loss mechanisms that limit device performance is essential to the development of high efficiency systems. However, these materials and systems are difficult to model and only few experimental methods are available for direct characterization of dominant loss processes under relevant operating conditions. To this end, empirical extraction of the spatial collection efficiency (SCE) and the spatial external luminescence efficiency (SELE) are operando, analytical tools that provide functional depth profiles of the active regions in the device. By coupling external quantum efficiency (EQE) measurements and optical modeling, SCE extraction allows quantifying charge transport properties and loss mechanisms across the device depth profile under real operating conditions with very few assumptions. Similar to SCE, combining optical modeling with wavelength dependent photoluminescence quantum yield (PLQY) measurements enables extracting the SELE - the probability that an electron hole pair photogenerated at a specific point will contribute to photoluminescence from the device. In this contribution we will introduce the SELE concept and will show a first demonstration of the SELE extraction method applied to GaAs samples. Extracting the SELE enables simple distinction between different losses such as surface recombination and self-absorption. The quantification of surface recombination losses makes this an excellent tool for characterizing the effect of surface passivation layers. Furthermore, since the PLQY is directly related to the obtainable photovoltage from the device, the SELE also maps the contribution of different regions in the device to the photovoltage. As a result, combining the SELE and SCE profiles at specific operating points provides detailed spatial information on charge extraction, contribution to the photovoltage, and discrimination between radiative and non-radiative recombination processes at the surface and in the bulk of the device.

Molecular layer deposition of alucone thin film on $LiCoO_2$ to enable high voltage operation

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Extracting the theoretically high capacity of $LiCoO_2$ (LCO) is desirable for enhancing the energy density of currently used lithium-ion batteries (LIBs) for portable devices. The bottleneck for exhibiting the high capacity is associated with the limited cut-off positive voltages beyond which degradation of electrode/electrolyte takes place. In this work, we demonstrated a facile molecular layer deposition (MLD) of hybrid organic/inorganic alucones thin films and tested their efficacy as cathode layer interface for improving electrochemical performances of LCO cathode, specifically for high voltages operations (above 4.5 V vs Li/Li^+). The alucone coated LCO samples have shown significant improvements in the electrochemical performances of the LCO, revealing superlative cycling stability, higher specific capacity, and greater capacity retention. The ethylene glycol/Al (EG/Al) coated LCO has exhibited the superlative electrochemical performances, demonstrating capacity retention of 94 % at C/3 rate and 92% at 1C after 100 cycles, at a cut off voltage of 4.45 V. In order to enhance the power density and to gain superior capacity with a stable cycling performance, we have pushed the cut off potential up to 4.55 V. The strategy for the preparation of alucones coated LCO for improved electrochemistry shown in Fig. 1.

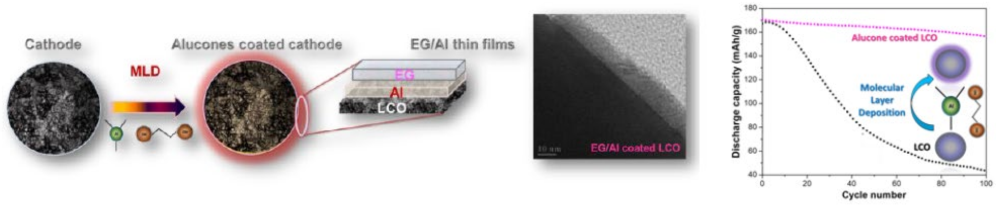

Fig. 1. The MLD of alucones-based thin films prepared as coating over LCO cathode for improved electrochemical performance.

[1] O. Lidor-Shalev, N. Leifer, M. Ejgenberg, H. Aviv, I. Perelshtein, G. Goobes*, Rosy*, and M. Noked,* Batteries & Supercaps (2021), 4, 1 –11