ORGANIC BATTERY DAYS

University of Houston | October 13–14, 2022

ABSTRACTS OF PLENARY LECTURES

PL1: Polymers for High Power Density Organic Batteries

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Redox-active polymers are useful as electrode-active materials in organic secondary batteries and organic redox flow batteries, based on the efficient diffusion of redox reaction throughout the polymer layer due to the fast electron self-exchange reaction of adjacent redox-active groups. We report here that the polymers enhance the power density by using them as electron-transfer mediators of lithium metal oxides. Rate constants for the charging, or the oxidation, of various lithium metal oxides with polynorbornene bearing dimethylfluoflavine with a highly positive potential of 4.1 V vs. Li^+/Li were evaluated (Figure 1). The order of the kinetic parameters was consistent with the rate performance of the composite electrodes of the lithium metal oxides and a small amount of the polymer in ~0.5 wt%, supporting a catalytic mechanism based on interfacial electron transfer process.

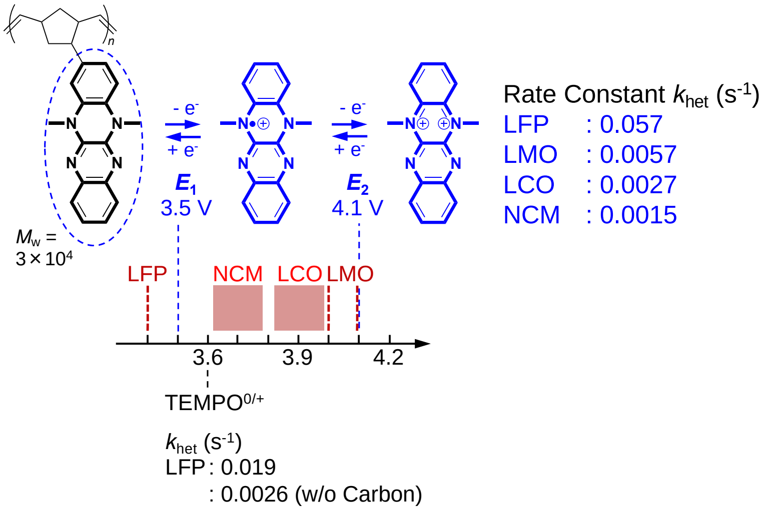

Figure 1. Potential diagram and rate constants for the catalytic charging of lithium metal oxides with polynorbornene bearing dimethylfluoflavine as the redox-active site.

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PL2: Novel Architectures and Experimental Strategies for Organic Electrical Energy Storage

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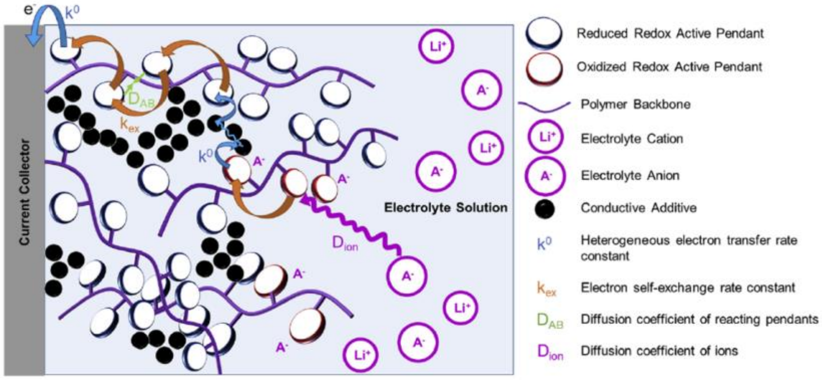
This presentation will deal with the development of new architectures and experimental strategies for organic-based electrical energy storage applications. The presentation will begin with a brief overview of the methods and materials employed with emphasis on organic-based polymeric systems. Studies on electrolyte screening for Li metal deposition and dendritic growth will also be discussed. The presentation will conclude with an assessment of future directions. [1]



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PL3: Recent Progress in Aqueous Organic Flow Batteries

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The ability to store large amounts of electrical energy is of increasing importance with the growing fraction of electricity generation from intermittent renewable sources such as wind and solar. We have developed an approach to electricity storage in flow batteries using the aqueous redox chemistry of small, potentially inexpensive organic and metalorganic molecules. The primary challenges of making such chemistries suitable for practical deployment are cell-level performance, molecular lifetime and mass-production cost. I will report our recent progress in these directions.

ABSTRACTS OF INVITED TALKS

IT1: Discovering New Organic Electrodes

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In the first section of the talk, we introduce two examples showcasing the development of organic materials as high-capacity high-energy cathodes or binders for both lithium and beyond Li ion batteries. [1-4] Particularly, a series of new anodically stable electrolytes enables us to develop Mg ion batteries using these polymers as electrode and binder materials. The first example is the development of high voltage polyanthraquinones (14PAQ and PAQS) for Mg ion batteries,[1] and the second example is that one polymer (PAQS) is tested as binder for Li-S batteries and can provide catalytic advantages to mediate the redox potentials of the sulfur and reduce the shuttling effects. [5]

The second section is the discovery of new organic electrodes with high voltages/energy densities. Firstly, the high-throughput first principles simulations (density functional theory (DFT) calculations), [6] are used to evaluate important properties (such as redox potential), and the most promising material candidates will be suggested for synthesis. Secondly, standardized data generated from experimental characterizations will be utilized to develop machine learning (ML) models to accelerate the prediction of materials performance metrics. Finally, an artificial intelligence (AI) based on Bayesian optimization/Optimal experimental design [7] for extremely efficient organic cathode materials discovery. The AI will guide the computational and experimental feedback loop to identify the desired material candidates while requiring a minimal number of experiments. We will use a series of π-conjugated quinoxaline-based heteroaromatic molecules (3Q) as examples.

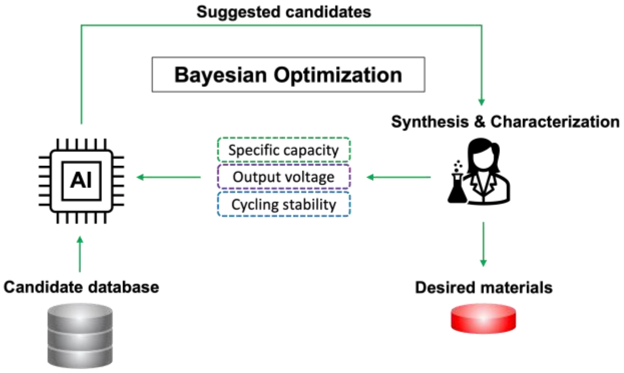

Figure 1. Feedback loop for organic cathodes discovery.

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IT2: Design Organic Small Molecules for High-Performance Electrode Materials

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Redox-active organic materials (ROMs) are of significant interest for next-generation electrode materials in secondary batteries due to their advantages over conventional transition metal oxides, such as abundance, sustainability, low cost, easy tunability, and large specific capacity. [1] Most importantly, flexible intermolecular stacking structures of ROMs consisting of secondary bondings allow fast diffusion for charge-carrying ions, facilitating high-rate charge/discharge of the cells. However, in practice, most electrodes based on ROMs still suffer from slow rate performance and low capacity utilization due to their electrically insulating nature. Furthermore, continuous dissolution of ROMs into organic electrolytes due to high solubility often leads to rapid capacity decay.

To circumvent those issues, polymerization of redox centers has been most popularly introduced, so far; however, polymeric materials often have difficulties in large-scale synthesis, controlling molecular weight and polydispersity, and fabricating uniform electrodes with reproducibility. In contrast, small molecules have many advantages, including easy synthesis with scalability, well-defined chemical structures, and free from batch-to-batch variation and formation of large agglomerates, providing excellent reproducibility in the cell performance and allowing straightforward analysis of the electrochemical properties.

In this talk, we present novel molecular designs to tune redox voltages of small-molecule ROMs without deterioration of their specific capacity. [2-6] Then, we introduce strategies to achieve high cycle stability, such as composite fabrication with nanocarbons, including CMK-3 and CNTs. Finally, we demonstrate several small molecules with simple molecular structures but considerably low solubility in organic electrolytes due to strong intra-/inter-molecular secondary interactions, providing high cycle stability and superior rate capability. [7-8]

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IT3: Chemical and Structural Analysis Principles for High-Voltage Organic Li-ion Cathodes – the case of conjugated sulfonamides and their derivatives

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The redox chemistry of organic molecules is increasingly attracting interest as it has the potential to provide battery electrode material candidates combining high capacities, practical redox potentials and allow for transition metal-free chemistries. While many redox chemistries have been extensively explored, achieving high redox potentials has long remained a challenge. What is more important, lithiated organic redox chemistries (akin Li-ion inorganic cathodes) have been lacking over the past years making difficult thus far practical implementation of an all-organic Li-ion battery technology.

In this talk I will discuss our recent advances for the development of organic Li-ion cathode materials based on aromatic conjugated sulfonamides. This family of redox compounds benefits from strong electron delocalization of sulfonyl groups, resulting in organic *n*-type redox materials with intrinsic oxidation and hydrolysis resistance when handled in ambient air, and yet display reversible electrochemistry for charge storage. [1] I will also discuss how these chemistries can be easily adapted for other alkali (Na^+ or K^+) cation storage, and present a comparative analysis of Li-, Na-, and K-ion phases disclosing the impact of the alkali cation on the physicochemical properties of these materials. [2] Finally, I will disclose how coordination chemistry can further boost the performance of the conjugated sulfonamides by bringing also the advantage of intrinsic electrical conductivity and ability for high efficiency monovalent but also multivalent cation storage. [3]

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IT4: Polymorphism and Electrochemical Behavior of Organic Electrodes Materials

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Over the last decade, tremendous progress has been made to develop rechargeable organic batteries through the use of molecular engineering by playing with substitutions and other (intramolecular) electronic effects; in other words, thanks to the traditional “through bond” rationalization without any three-dimensional geometrical consideration concerning these bonds. However, the electrochemical performance of organic host structures relies also on the crystal packing like the inorganic counterparts, which calls for further efforts in terms of crystal chemistry to make a robust redox-active organic center electrochemically efficient in the solid state. For instance, the relation between polymorphism and electrochemical insertion properties is well-documented in the literature for inorganic electrode materials [1]. The key component is the crystal arrangement that differs from one form to another inducing variation in terms of ion diffusivity inside the crystal packing and/or electronic structure. Tarascon and co-workers [2] have demonstrated that $LiFeSO_4F$ (tavorite-type structure) displays an average operating potential of 3.6 V vs. Li^+/Li, whereas the triplite-type polymorph reacts at 3.9 V vs. Li^+/Li (i.e., +300 mV as potential gain). However, similar studies on organic electrode materials are scarce.

Following our ongoing research aiming at elaborating lithiated organic cathode materials, we will report on the impact of polymorphism on the electrochemical behavior of dilithium (2,3-dilithium-oxy)terephthalate vs. Li. Having isolated dilithium (3-hydroxy-2-lithium-oxy)-terephthalate through an incomplete acid-base neutralization reaction, its subsequent thermally induced decarboxylation mechanism led to the formation a new polymorph of dilithium (2,3-dilithium-oxy-)terephthalate referred to as Li_4-*o*-DHT (β-phase) [3]. This new phase is able to operate at 3.1-V vs. Li^+/Li, which corresponds to a positive potential shift of +250 mV compared to a polymorph formerly reported and referred now to as Li_4-*o*-DHT (α-phase) [4].

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IT5: Towards the Applicability of Density Functional Tight Binding to Charge Transport in Quinones in Solution and in the Solid State

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Organic electrode materials in batteries have been receiving steadily increasing attention due to the low cost, low carbon footprint and inherent safety associated with them. Quinones, which exhibit wide voltage tunability, have shown particular promise in this regard, having found application in redox flow batteries as well as water splitting devices. Crystalline quinones have also been investigated as electrode material in a variety of batteries, including lead-acid and lithium ion batteries. However, the mechanism of charge transport in these materials is not fully understood. With the goal of developing a computationally efficient method to study charge transport in crystalline quinones, we have benchmarked the performance of the semi-empirical density functional tight-binding (DFTB) method for the description of proton/electron transfer involving quinones in solution, band structure and band gap of crystalline quinones [1]. We have also investigated the ability of DFTB in combination with the Crystal Structure Analysis by Particle Swarm Optimization (CALYPSO) method to predict the crystal structure of quinones. Our results reveal strengths and areas for improvement of the DFTB method which should facilitate long timescale and large length-scale simulations for the study of charge transport in crystalline quinones and other crystalline organic systems.

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IT6: Polymer Particles Containing Redox-Active Organo-Disulfides and Their Potential Application in Organic Batteries

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Organo-disulfides are potential two-electron electroactive compounds for cathode electrodes. This talk will focus on the design of redox active microparticles crosslinked with organic disulfide redox centers with an eye towards cathode active materials. Specifically, crosslinking poly(glycidyl methacrylate) microparticles with redox-responsive bis(5-amino-l,3,4-thiadiazol-2-yl) disulfide moieties (DS) yield redox active particles (RAPs) capable of electrochemical energy storage via a reversible 2-electron reduction of the disulfide bond. [1] The resulting DS-RAPs show improved electrochemical reversibility compared to a small molecule disulfide analogue in solution, attributed to spatial confinement of the polymer-grafted disulfides in the particle. Moreover, DS-RAPs resulted in the synthesis of an insoluble material capable of facile blending with necessary additives and casting from suspension onto electrode substrates in approaches similar to conventional inorganic cathode materials. Fixation of the disulfide onto a polymer scaffold prevents diffusion of the reduced species after charging, resulting in improved electrochemical kinetics at the electrode surface. This phenomenon is important in the context that "shuttling", or diffusion of reduced species across the battery separator, is a critical challenge in the design of Li-S batteries. Initial galvanostatic cycling of these materials yielded good stability over multiple cycles, showing promise for the concept as an energy storage material.

References

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IT7: Organic Electrode Materials for Divalent Metal-ion Batteries

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Growing demand for high-energy and low-cost energy storage systems has driven intensive research into sustainable battery technologies. Rechargeable magnesium (Mg) and calcium (Ca) based batteries are receiving increasing attention because of their inherent advantages in terms of the potential feasibility of employing metal anodes, high theoretical energy densities and abundant raw material resources. [1,2] One of the key challenges in the development of Mg and Ca batteries is to identify suitable cathode materials with reliable electrochemical properties. [1,2] Due to the strong electrostatic interaction of the divalent metal ions with oxide cathode materials, the intercalation of Mg- and Ca-ions into classical inorganic host structures suffer from sluggish kinetics and severe polarization, leading to low electrochemical reversibility. In contrast, organic materials with flexible structures could allow fast ionic diffusion, offering energetically favorable migration pathways for divalent metal ions during the electrochemical processes. [3,4] Herein, we demonstrate that the quinone-based polymer cathode materials could enable highly reversible Mg and Ca-ion batteries. In addition, organic materials with anion storage properties have been investigated for high-performance Mg and Ca battery systems with high energy density and high power density.

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IT8: Mechanics of Organic Mixed Ionic-Electronic Conductors

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Organic mixed ionic-electronic conductors (OMIECs) are the core functional component of organic electrochemical devices such as organic electrochemical transistors, electrochromic devices, energy harvesters/storage, and light-emitting devices. The redox reactions in OMIECs involving the ionic/electronic transport are usually accompanied by a microstructural evolution of the polymeric material and a macroscopic volumetric change. Furthermore, the strong coupling between carrier transport in OMIECs and mechanical deformation presents a limit to the reliability of OMIEC based devices. In this talk, I will focus on understanding the mechanics of OMIECs using continuum theories, nanoindentation experiments, and multiphysics modelling. We formulate a continuum theoretical framework that describes the underlying physics of mass transport, electron/hole conduction, mechanical deformation, and stress evolution. The theory is implemented into finite element modelling that is capable of simulating the electrochemical performance and mechanical behaviours of OMIECs-based devices. Lastly, we quantitatively measure the breathing strain, the evolving mechanical properties upon doping/dedoping, and mechanical damage of organic conductive polymers using nanoindentation experiments.

IT9: Organic/Aqueous Hybrid Electrolytes for Reversible Zn and Al Deposition of Zn Metal and Zn-Al Alloy Anodes

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Rechargeable metal batteries employing reactive metal anodes have long been the pursuit of researchers working in the field of electrochemical energy storage for large energy densities. Although lithium metal anodes are appealing owing to their low redox potential and high theoretical capacity, their applications are limited by safety concerns, short cycling life, and low Li abundance. Therefore, multivalent-metal anodes, such as aluminum, zinc, magnesium, and calcium, are considered promising candidates for resolving the technical issues while using Li metal anodes. However, electrochemical performance and stability of multivalent-metal anodes are also deteriorated due to Zn dendrite formation and corrosion, and hydrogen evolution reaction in aqueous electrolytes.

In this talk, I will introduce two kinds of organic/aqueous hybrid electrolytes for reversible Zn and Al deposition of Zn metal and Zn-Al alloy anodes. Computational and experimental results correlate the solvated structure and interfacial chemistry of two hybrid electrolytes with facile and stable Zn- and Al-ion plating/stripping behaviour occurring on the surface of Zn metal and Zn-Al alloy anodes. This study is expected to provide new insights into the molecular-level design of Zn^{2+} and Al^{3+} solvation structures for hybrid electrolytes and potentially facilitates future electrolyte exploration for multivalent metal-based energy storage technologies.

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IT10: Atomistic Modelling and Data-driven Approaches for Molecular Discovery

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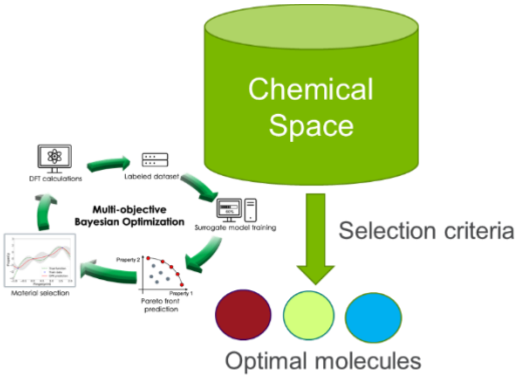
Discovery of optimal materials essential are essential for redox flow battery research, where *a priori* computations for predicting optimal properties are essential to accelerate redoxmer discovery. Optimal properties include redox windows, [1] toxicity, [2] synthesizability, [3] solubility, [4] reactivity and stability. [5] Additionally, further co-design of new functionality could be introduced in to the molecule by careful molecular engineering to include new attributes such as self-repairing or self-reporting. Understanding various properties require significant a priori computations for materials discovery, property prediction, and optimization using atom-atom and molecule by molecule approaches. Atomistic modelling can provide a priori data to accelerate discovery of electrolytes, electrodes, and membranes to reduce the cost and time of discovery. Coupled with data science and multi-scale techniques, atomistic modelling can address prediction of molecular level properties of materials (redox potentials, solvation, spectroscopic, and reactivity) to down-select optimal materials or material combinations. In this presentation, I will describe some of our recent efforts [1-5] in active learning coupled with large scale first principles simulations to down select/optimize desired molecules for non-aqueous redox flow battery molecules.



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IT11: Reversible Ketone Hydrogenation and Dehydrogenation for Aqueous Organic Redox Flow Batteries

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Redox flow battery is one of the prominent technologies for solving the intermittency during grid modernization with renewable energy. [1] Aqueous organic redox flow batteries employing organic redox-active materials as electrolytes offer an environmentally benign, low cost, and versatile tunability towards better battery performance. Development of the electrolyte material has been focusing on a small palette of organic molecules that are known for their redox activity. [2] Tremendous efforts are paid into the molecular design for material solubility, stability, redox potential, etc. We show how the molecular engineering of fluorenone activates redox activity in a molecule that is conventionally considered redox-inactive. [3] By starting with demonstrated thermally stable fluorenone core, the demonstrated ketone-based flow battery exhibited long term stable operation for more than 4-month. During the study, unconventional coupled chemical reaction electrochemical process was revealed.

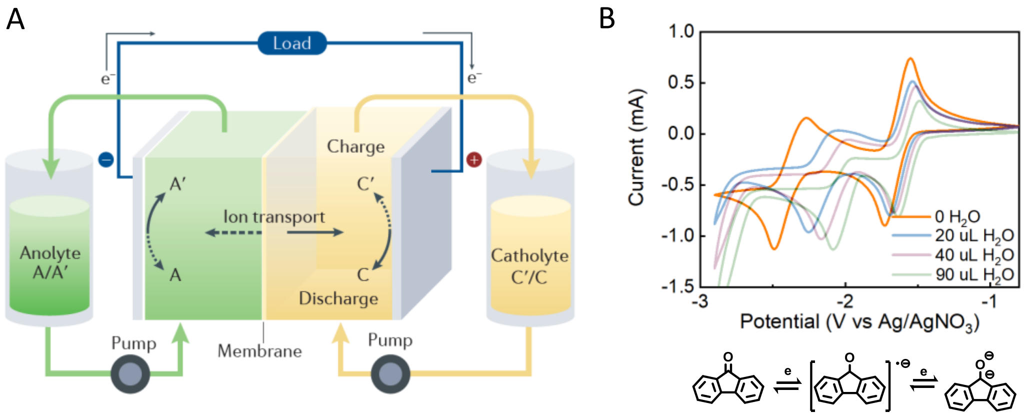

Figure 1 (A) Flow battery design. (B) Ketone hydrogenation.

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IT12: Predicting the Solubility of Organic Energy Storage Materials Based on Functional Group Identity and Substitution Pattern

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Organic electrode materials (OEMs) based on abundant elements, e.g., C, N, O, and S, provide sustainable alternatives to conventional electrode materials that rely heavily on finite and unsustainably sourced transition metals. The application of OEMs in lithium-ion batteries (LIBs) and redox flow batteries (RFB) requires organic molecules with either low or high solubility in battery electrolytes. Currently, the identification of new OEM candidates with desirable solubilities relies on chemical intuition and trial-and-error experimental testing, which is costly and time intensive. Herein, we develop a simple empirical model that predicts the solubility of anthraquinones in battery electrolytes based on functional group identity and substitution pattern. Within this statistical scaffold, a training set of 38 anthraquinone derivatives allows us to predict the solubility of more than 800 quinones with high confidence. Internal and external validations show that our model can predict the solubility of anthraquinones in battery electrolytes at a much higher accuracy than conventional solubility models reported in the literature. As a demonstration of the utility of our approach, we identified several new anthraquinones with low solubilities and successfully deployed them in Li-organic batteries

IT13: Industrial Perspectives on Organic Batteries for Energy Storage

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The energy sector is currently undergoing transition, driven by population growth, demand for more and cleaner energy, and increasing customer choice. To facilitate the growth and uptake of renewable energy in a more electrified energy system, developing efficient and economical means of storing and distributing electricity is vital. Next-generation battery technologies and other electrochemical energy storage and conversion technologies have great promise to enable energy transition.

As the need for longer duration storage increases, many new organic redox chemistries have been proposed to facilitate lower cost flow batteries. While flow batteries based on organic molecules have promise, there are many problems that must be overcome to commercialize them. This talk will describe some of Shell's ongoing research and development activities in organic batteries, the partnerships and collaborative innovation mechanisms used to advance these concepts, and some technoeconomic considerations that are relevant in technology maturation.

IT14: Redox Gating Achieves New Electrostatic and Ionic Doping Limits

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Redox gating, intrinsically distinct from conventional electrolyte gating, combines reversible redox functionalities with common ionic electrolyte moieties to engineer charge transport for power-efficient electronic phase control. A colossal sheet carrier density modulation beyond 10^{16} cm^{-2} for up to thousands of cycles of durable switching can be achieved in the sub-volt regime for archetypical functional oxide thin films. In this approach, charge carriers are injected into the channel material without the unbridled perturbations that arise from ionic defects—cation/anion vacancies or ionic intercalated species such as protons—normally associated with traditional electrolyte gating processes. Moreover, the redox gating represents a simple and practical way to decouple the electrical and structural phase transitions, thereby improving the device longevity and operation response time. The redox gating works for a wide variety of both n- and p-type materials regardless of their crystallinity or crystallographic orientation, including all other functional heterostructures and low-dimensional quantum materials composed of sustainable elements.

IT15: Bioorganic Films for Cleaner Energy Production

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Under the arena of recent cleaner and sustainable energy demands, biological fuel cells have gained a stimulated research focus. A typical biofuel cell is constructed with enzymes or microorganisms to produce energy using a natural fuel like glucose. They can be utilized as alternative energy sources for various implantable and disposable energy applications. Such systems are often challenged by unstable biofilm designs, slower interfacial electron transfer rates, and lower energy densities. [1] These challenges can be overcome by utilizing successful strategies for biomolecular immobilization and by tuning their electron transfer properties. [2] We have recently shown that freestanding carbon nanotube papers (or bucky papers) with optimum thickness are capable of holding a blue copper cathodic enzyme, bilirubin oxidase (BOD) to demonstrate direct electron transfer features via its multiple Cu sites. [3] Moreover, this biocathode exhibited relatively high current densities for the reaction of four-electron reduction of molecular oxygen to water in the absence of a mediator or a chemical modification to the electrode. We believe proper understanding of biocatalytic properties of BOD enzyme is beneficial for designing cathodic compartments for biological fuel cells and metal‒air batteries.

This presentation will also include an introduction to the Organic and Biological Electrochemistry Division of the Electrochemical Society (ECS) and some exclusive benefits for its membership.

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IT16: Improved Rate Performance and Energy Density in Conjugated Polymers with Mixed Ionic-Electronic Conduction

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Conjugated polymers offer a number of unique properties as battery electrodes, including intrinsic conductivity when doped, rapid and reversible charge and discharge, and excellent stability in the presence of electrolytes. While a number of strategies have focused on increasing the energy density of conjugated polymer electrodes, strategies to improve the rate performance of these materials are limited. In this work, we report on the use of conjugated polymers with mixed ionic and electronic (MIEC) conduction for improved rate performance. By modifying the side-chains of conjugated polymers with ionically-conductive functional groups, we demonstrate we can increase both rate performance and energy density while maintaining excellent stability. Specifically, we focus on naphthalene dicarboximide (NDI)-based conjugated polymers with ion-conducting ethylene glycol (EG) side chains. First, we compare the performance of NDI-based polymers containing EG side-chains (PNDI-T2EG) to that of NDI-based polymers with aliphatic 2-octyldodecyl side chains (PNDI-T2). For thick (20 µm, 1.28 mg cm^{-2}) electrodes with a 60 wt% polymer, the PNDI-T2EG electrodes exhibit 66% of the theoretical capacity at an ultrafast charge–discharge rate of 100C (72 s per cycle), while the PNDI-T2 electrodes exhibit only 23% of the theoretical capacity. Electrochemical impedance spectroscopy measurements on thin (5 µm, 0.32 mg cm−2), high-polymer-content (80 wt%) electrodes reveal that PNDI-T2EG exhibits much higher lithium-ion diffusivity than PNDI-T2. Next, we analyzed the performance of a systematic series of NDI-based polymers with EG side-chains, varying in side-chain content from 0 to 100 wt %. We found that the storage capacity, rate performance, and ion diffusivity improved with increased content of EG side-chains. These results demonstrate that the rate performance and capacity are significantly improved through the incorporation of EG side chains, and this work demonstrates a route for increasing the rate of ion transport in conjugated polymers and improving the performance and capacity of conjugated-polymer-based electrodes.

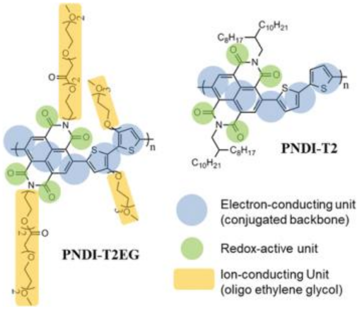

Figure 1. Chemical structures of **PNDI-T2** and **PNDI-T2EG**.

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IT17: An Ultrafast, Durable, and High-Loading Polymer Anode for Aqueous Zinc-Ion Batteries and Supercapacitors

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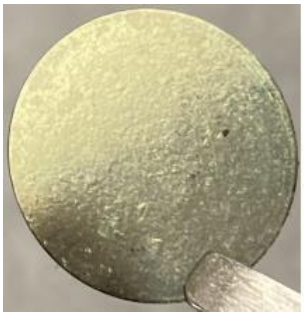
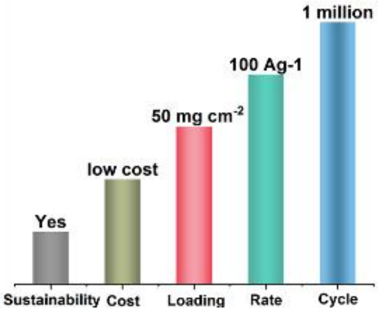
With high theoretical capacities (820 mAh g^{-1} and 5855 mAh cm^{-3}), suitable electrochemical potential (−0.763 V vs standard hydrogen electrode), low cost, and rich abundance of component materials, aqueous zinc-ion batteries (ZIBs) and capacitors (ZICs) have exhibited great promise for grid-level energy storage and other stationary applications. Zn metal as excessive Zn are often used to compensate for the uncontrollable dendritic growth, corrosion behaviour, and low Coulombic efficiency (CE) of the Zn metal. As such, most of the ZIBs and ZICs developed using these electrode materials exhibited actual device energy and power densities that were significantly lower than the corresponding theoretical values. Another key performance metric that needs to be improved in ZIBs is their high-rate charge and discharge. In addition to the dendrite-derived problems commonly experienced in batteries based on other metal anodes, ZIBs are disadvantaged by hydrogen gas evolution from water decomposition especially under high-rate charge/discharge, leading to poor cycle life.

Herein, an ultrafast, stable, and high-loading polymer anode for aqueous Zn-ion batteries and capacitors (ZIBs and ZICs) is developed by engineering both the electrode and electrolyte. The anode polymer is rationally prepared to have a suitable electronic structure and a large π-conjugated structure, whereas the electrolyte is manufactured based on the superiority of triflate anions over sulfate anions, as analyzed and confirmed via experiments and simulations. This dual engineering results in an optimal polymer anode with a low discharge potential, near-theoretical capacity, ultrahigh-loading capability (≈50 mg cm^{-2}), ultrafast rate (100 A g^{-1}), and ultra-long lifespan (one million cycles). Its mechanism involves reversible Zn^{2+}/proton co-storage at the carbonyl site. When the polymer anode is coupled with cathodes for both ZIB and ZIC applications, the devices demonstrate ultrahigh power densities and ultra-long lifespans, far surpassing those of corresponding Zn-metal-based devices.





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ABSTRACTS OF CONTRIBUTED TALKS

CT1: Four Electron Exchange on Benzene Ring

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Batteries with cathodes based on organic materials are gaining attention due to several advantages. They offer more sustainable, cheaper and safer energy storage compared to current Li-ion technology. Their drawback is low volumetric energy density which can be partially compensated with high capacity organic materials. Multihydroxybenzenes seem perspective as they can exchange several electrons per small benzene ring. We have chosen 1,2,3,4-tetrahydroxy- benzene as the best candidate to make a stable and high capacity redox polymer. A model compound soluble in different electrolytes was prepared and electrochemically characterised. Best electrochemical results were obtained in acidic aqueous electrolyte, but organic electrolytes showed poor reversibility. This behaviour resembles to catechols. Four electron reaction was confirmed by using reduced and oxidized model compounds which showed almost identical CV curves. In the last step we prepared insoluble polymer poly(2,3,4,5-tetrahydroxystyrene) (Figure 1) which was used as positive organic material inside Li-organic battery. Electroactivity in Li battery was very low as we are limited to organic electrolytes, but it worked well in a three-electrode experiment with acidic aqueous electrolyte. The results suggest that this polymer is promising in proton type batteries.

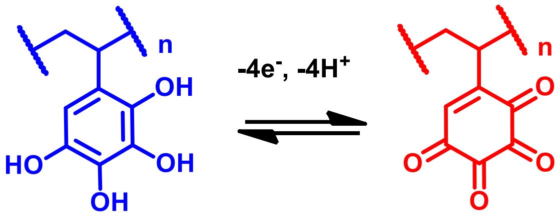

Figure 1. Proposed four electron redox reaction of poly(2,3,4,5-tetrahydroxystyrene).

CT2: Halogenated Carboxylates as Organic Anodes for Stable and Sustainable Sodium-Ion Batteries

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Organic materials are competitive as anodes for Na-ion batteries (NIBs) due to the low cost, abundance, environmental benignity, and high sustainability. Herein, we synthesized three halogenated carboxylate-based organic anode materials to exploit the impact of halogen atoms (F, Cl, and Br) to the electrochemical performance of carboxylate anodes in NIBs. The fluorinated carboxylate anode, disodium 2, 5-difluoroterephthalate (DFTP-Na), outperforms the other carboxylate anodes with H, Cl, and Br, in terms of high specific capacity (212 mAh g^{-1}), long cycle life (300 cycles), and high rate capability (up to 5 A g^{-1}). As evidenced by the experimental and computational results, the two F atoms in DFTP reduce the solubility, enhance the cyclic stability, and interact with Na^+ during the redox reaction, resulting in a high-capacity and stable organic anode material in NIBs. Therefore, this work proves that fluorinating carboxylate compounds is an effective approach to developing high-performance organic anodes for stable and sustainable NIBs.

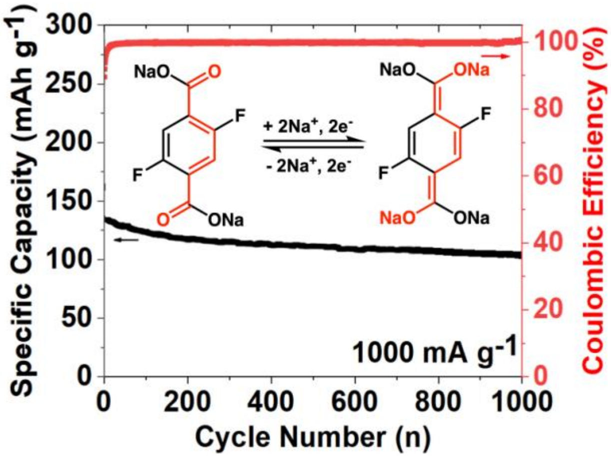

Figure 1. Scheme of redox reaction mechanism of DFTP-Na and its cycle life at 1A g^{-1}.

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CT3: Tuning and Improving Active Electrode Materials Thanks to Organic Chemistry Toolbox

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Lithium-ion batteries are currently considered as the most promising energy storage technology. However, although the requirements for increased battery energy and power stay challenging, main issues we face today are the high global cost, the environmental impact and severe safety concerns. For example, cobalt is a critical metal widely used in batteries which is rapidly approaching a near-critical supply level and lithium resource leads to geopolitical issues. [1] An interesting and encouraging alternative is the use of organic-based electrode active materials such as carbonyl-containing molecules or polymers. Unlike their inorganic counterparts, a single organic active material can store various cations from lithium to potassium, and even magnesium without any modification. [2]

Lithium π-conjugated carboxylates were discovered by Armand *et al.* and are promising negative electrode material. [3] Compared with other organic negative materials, they show a relatively low working potential (0.8-1.4 V *vs.* Li^+/Li), and display interesting capacities (for instance 120 $mAh.g^{-1}$ for lithium perylene-3,4,9,10-tetracarboxylate). Another part of our investigation focus on aromatic polyimides which could be considered as good candidates for positive electrode materials. They also exhibit an attractive working potential of 2.1 and 2.5 V *vs.* Li^+/Li respectively for pyromellitic dianhydride (PMDA) and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) based polyimide. [4]

Herein we report our latest results on the synthesis of a new type of carbonyl-based negative electrode material, as an unprecedented alternative to lithium π-conjugated carboxylates-based negative electrodes. In particular, new synthetic strategies allow us an easy tailoring of the chemical structures for a fine-tuning of redox properties. Also, aiming at increasing the working potential of imide moieties, we study the synthesis of various substituted electron-poor imide-based materials. An optimized three-step synthesis was designed from the PMDA platform. Significant improvements were obtained with the new material, such as a higher working potential as compared to the reported analogues (+400 mV) and a theoretical capacity 1.5 times higher than the PTCDA based imide (190 $mAh.g^{-1}$). Our work opens up exciting possibilities for the future of this domain.

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CT4: Organic Magnesium Batteries: The Way to Commercialization?

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Magnesium batteries are potentially safer and cheaper alternatives to lithium batteries for high-density energy storage. However, prototypes of magnesium batteries reported during the past two decades have shown low energy density and sluggish kinetics. The technology has never been able to come out of laboratories as a result. Recent development of organic electrode materials and their application in magnesium storage have achieved results apparently far exceed those by traditional intercalation materials, suggesting for the first time a possible pathway into the market. In this presentation, we will critically analyze organic magnesium batteries and propose research directions towards commercialization.

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CT5: Polymers Derived from Aromatic Dianhydrides as Promising Cathodes for Rechargeable Ca-Metal Batteries

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Finding efficient, sustainable, and cost-effective battery technology is one of the main challenges in the transition to a renewable energy economy. Rechargeable batteries with anodes made of energy-dense multivalent metals represent a major opportunity in this regard. For this reason, they have been the subject of intense research in recent years. Calcium has emerged as one of the front runners in the multivalent race due to its abundance and low redox potential. Recent reports of room temperature calcium plating and stripping in calcium tetrakis(hexafluoroisopropyl)borate - $Ca[B(hfip)_4]_2$ - in ether-based solvents have opened the doors for extensive exploration of calcium metal-based batteries. [1]

However, strong interactions of the divalent calcium ion with solvents, salts, and cathodes severely limit the performance of the technology in question. Cathodes based on organic polymers, which at least theoretically have a more open structure and allow easier ion diffusion compared to their traditional inorganic counterparts, could be the solution. Polyimides derived from aromatic dianhydrides with robust, electrochemically inactive backbones in combination with highly reactive functional groups are a good candidate and have already been explored in other non-aqueous multivalent metal systems. [2] Herein, we have investigated the electrochemical performance of three selected anhydrides and the corresponding polyimides in a non-nucleophilic electrolyte based on weakly coordinating anions and a calcium metal anode. The reversibility of the electrochemical mechanism was confirmed by ex situ infrared spectroscopy. The electrochemical tests were carried out in two- and three-electrode setups in order to overcome problems related to the strong passivation of the calcium metal anode during cycling. The feasibility of high energy density was investigated by studying the species coordinating reduced carbonyl groups, using SEM / EDS.

Although still far from commercial application, organic calcium metal batteries represent a promising next-generation battery technology if electrolytes that enable reversible plating and stripping and sustainable organic cathodes are developed simultaneously.

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CT6: Investigation of Bipolar Isoindoline Nitroxide Materials for Nonaqueous Redox Flow Batteries

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Redox flow batteries (RFBs) are an up-and-coming energy storage technology which decouple power from capacity. Aqueous RFBs such as those based on vanadium or zinc/bromine chemistries have thus far enjoyed commercialisation, but nonaqueous chemistries promise higher voltages and greater solubilities, boosting energy density. [1] To date however, nonaqueous designs based on small redox-active molecules often suffer from crossover of the electroactive species, leading to an irreversible loss of capacity. [2] Here we synthetically hybridise isoindoline nitroxide (TMIO) [3] with reductive moieties via aromatic ring substitution to produce bipolar molecules which can act as both cathode and anode, thereby mitigating the issue of crossover. We will demonstrate the facile derivitisation of known isoindoline structures to yield these bipolar intermediates, as well as through electrochemical characterisation. Finally, preliminary proof-of-concept flow devices based on a single hybrid will be discussed.

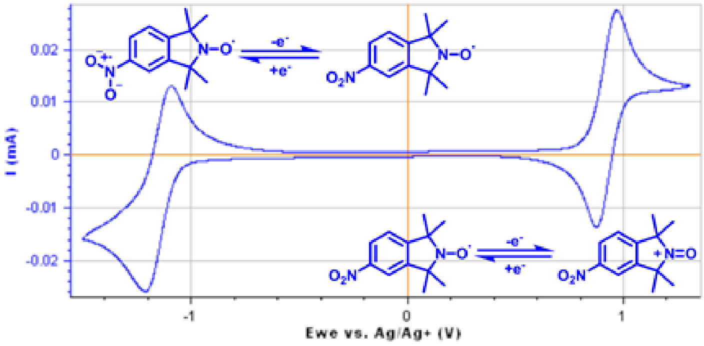

Figure 1. Cyclic voltammogram of 5-nitro-1,1,3,3-tetramethyl-isoindolin-2-yloxyl (NTMIO) demonstrating the ability to act as both catholyte and anolyte

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CT7: Towards an organic electrode without conductive carbon for lithium-ion battery

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Lithium-ion batteries using organic electrodes are the subject of much research in order to reduce the performance gap with inorganic electrodes and specially to improve the environmental footprint of the batteries. However, to overcome the low conductivity of organic materials, it is necessary to add a large amount of conductive additive, which does not contribute to energy storage, and therefore leads to a reduction in energy density. Recent work on lithiated perylene-3,4,9,10-tetracarboxylate as a negative electrode has shown that it is possible to reduce this amount of conductive carbon considerably probably owing to the hyper-conjugated perylene center. [1]

Perylene is a discotic polyaromatic molecule with a high intermolecular π-staking. This type of molecules can form a self-assembled columnar material favoring charge mobility. [2] This property is already well studied in OFETs, [3] photovoltaic cells, [4] and liquid crystals, [5] but it almost has never been studied in Li-ion batteries. This conductive property could allow to considerably reduce the amount of conductive additive and thus to realize commercially viable organic electrodes. In order to confirm this hypothesis, our research first focused on the mechanistic understanding of the insertion/deinsertion of lithium ions into a series of substituted perylene diimide based columnar materials upon cycling. Different techniques like Fourier-Transformed Infra-Red spectroscopy, X-rays diffraction and Transmission Electron Microscopy allowed us to give first trends for the design of conductive additive free electrode.

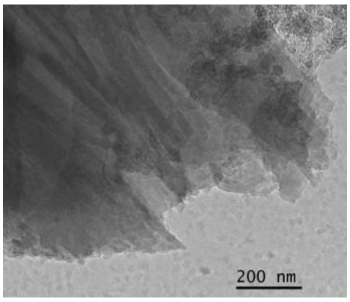

Figure 1. TEM image of N,N′-Dipropyl-3,4,9,10-perylenedicarboximide.

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CT8: Soluble Organic Catalysts for Non-Aqueous Lithium-Air Batteries

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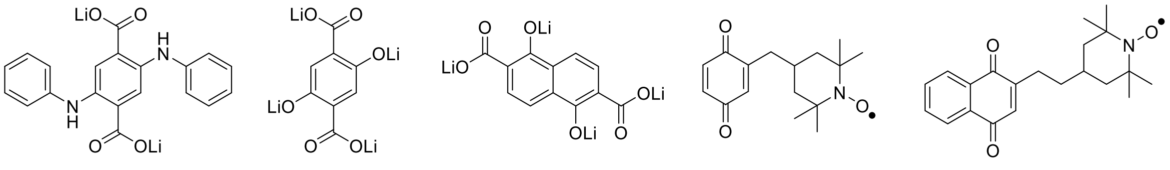
The chemistries based on the O_2/Li_2O_2 couple in aprotic electrolyte seem promising to provide ultrahigh-energy density values and outperform the current LIB technology. The main targeted application is to power electrified vehicles, with the hope of achieving high driving range. Unfortunately, serious side-reactions have plagued their development for practical applications so far. For example, during the discharge process, undesired insulating products are formed instead of lithium peroxide. Moreover, the blocking/clogging effect on the air electrode due to a deposition process leads to an overpotential during both the discharge (Oxygen Reduction Reaction: ORR) and charge processes (Oxygen Evolution Reaction: OER), which results in electrode degradation, electrolyte decomposition and precocious cell failure.

A promising approach to reduce these overpotentials is to use organic redox mediators by taking advantage of their tunability. For several years, our group has been developing organic redox mediators for Li-O_2 applications using two different strategies: insoluble or soluble organic catalysts.

Insoluble organic catalysts such as Li_2DAnT (alone or in combination with Li_4-*p*-DHT [1]) or Li_4-DHNDC [2] are included in the formulation of the air electrode but, unfortunately, they cannot prevent the clogging effect to occur after a few cycles. A better approach is to use soluble catalyst such as *p*-BQ-CH_2-TEMPO and NQ-$(CH_2)_2$-TEMPO [3] as electrolyte additives. Their structures include a quinone moiety, known for its activity for ORR and a TEMPO moiety, suitable for OER. We here report their effect on the cycling behavior of Li-O_2 batteries and their influence on ORR and OER processes.



Li_2DAnT Li_4-*p*-DHT Li_4-DHNDC *p*-BQ-CH_2-TEMPO NQ-$(CH_2)_2$-TEMPO

Figure 1. Structures of Li_2DAnT, Li_4-*p*-DHT, Li_4-DHNDC, *p*-BQ-CH_2-TEMPO and NQ-$(CH_2)_2$-TEMPO.

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CT9: Structural Lithium-ion Battery Cathodes based on Organic Redox Active Polymers and Kevlar Aramid Nanofibers

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Structural energy storage requires batteries with good energy storage as well as mechanical properties. This technology may lead to substantial mass and volume savings in electric automobiles, cube satellites, and aerospace applications by storing energy within the vehicle's body panels. However, until now, most studies on structural energy storage focus on conventional cathode materials such as lithium iron phosphate (LFP), lithium cobalt oxide (LCO) or nickel manganese cobalt oxide (NMC). Not just potential environmental hazards, but these materials also exhibit poor rate capabilities at higher C-rates and low-capacity retention during long-term cycling of batteries. These also suffer with poor adhesion to current collectors that leads to delamination of the electrode layer. Organic radical polymers are a promising alternative because they are environmentally benign, they exhibit rapid charge transfer ability, and good cycling stability. In this work, we report for the first time, structural lithium-ion battery cathodes using organic redox active polymers such as PTMA (poly (2,2,6,6-tetramethyl-piperidenyloxyl-4-yl methacrylate)) as the electrochemically active material. A one-step, polymer-compatible thermal cross-linking method is carried out to significantly inhibit PTMA's dissolution in the electrolyte. PTMA slurries are casted on mechanically strong reduced graphene oxide (rGO)/branched aramid nanofiber (BANF) films. The rGO/BANFs composites provide structural support and improved adhesion with the active material while also acting as the current collector. The effects of cross-linking agent and active material contents on the electrochemical and mechanical performance are investigated. This work provides a pathway for utilising environmentally benign, redox active radical polymers as active materials in structural lithium-ion batteries.

CT10: Engaging Electrochemists: An Introduction to the Electrochemical Society

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Electrochemistry and solid state science and technology are the keys to solving many global challenges. Shannon Reed, Director of Community Engagement, highlights engagement opportunities with The Electrochemical Society (ECS).

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ABSTRACTS OF POSTER PRESENTATIONS

P1: Bioinspired and Biodegradable Redox-active Polypeptides: From Ring-opening Polymerization of N-Carboxyanhydrides for Sustainable Energy Storage

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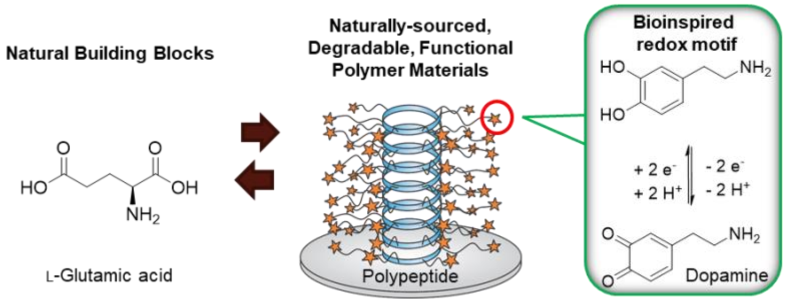
Energy storage systems developed with a combination of sustainable materials and redox-active molecules are attractive solutions to ethical and environmental issues associated with current metal-based platforms. Although not perfected, organic-based redox-active polymers have been employed in battery designs advancing efforts in sustainability while competing with metal-based redox-active systems. Polypeptide-based materials have previously been investigated and utilized in solid-state and redox flow battery applications showcasing the versatility of these materials while demonstrating their innate degradability. [1-2] However, there is still room for improving the biocompatibility of these materials. In this work, we aim to design and synthesize electroactive polypeptides by ring-opening polymerization (ROP) of *N*-carboxyanhydrides (NCAs), in which biologically inspired redox-active moieties, such as dopamine and flavin, will be installed at the side chains. This bioinspired strategy could pave a way toward the development of renewable energy storage systems with low toxicity to enhance their biocompatibility.



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P2: Engineered Slide-Ring Materials for Energy Storage Applications

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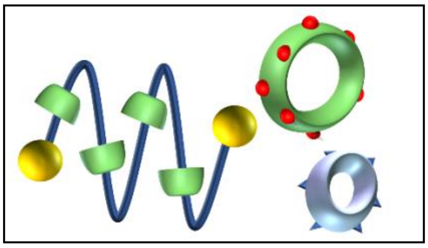

Fig. 1: Schematic of a simple PR and modified slide rings

Slide-ring materials, also known as polyrotaxanes (PRs), possess unusual properties owing to the unique mobility of slide rings across a mechanically interlocked molecular axle. A PR can be modified through reactions that target specific sites on rings while leaving the underlying structures intact. Careful selection of reactants can result in new configurations that may alter bonding environments or lead to novel interactions between components. In the context of energy storage applications, engineered PRs have already been shown to enable high-capacity materials in Li-ion batteries. [1] In this early work, PRs consisting of α-cyclodextrin (CD) rings threaded on a polyethylene glycol (PEG) backbone and stoppered with bulky cage molecules [2] were modified to impart new functionalities to the slide rings. Modifications made to a given PR are repeated for free, un-attached CD rings.

Our present work investigates the structure-property relationship of modified PRs and the corresponding free-CD rings (Figure 1) for their electrochemical stability and ability to serve directly as lithium hosts. Preliminary data shows that the stoppering of PEG works to improve the electrochemical stability of the polymer by impeding decomposition reactions at the terminal hydroxyl groups, in line with other recent reports. [3, 4] Modified CD rings have been observed to be stable above 2.5 V when cycled against Li metal. A subset of the PRs of interest has also displayed a reversible capacity of over 600 mAh/g when cycling between 0 – 2.5 V against Li-metal. However, achieving such a capacity requires substantial additions of conductive carbon black. This suggests that the poor electronic conductivity of these materials may be a critical hurdle for their direct implementation as electrodes. The corresponding free-CD ring to this same PR has also been observed to rapidly absorb lithium salts at room temperature and in large molar ratios. Early DFT simulations show that the uptake is driven primarily by interactions with the salt's anion. The poster presentation will discuss structural modification in PRs and the resulting properties with ions via electrochemical analysis.

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P3: Bio-based High-Voltage Polyhydroxyanthraquinones as Organic Cathode Material for Batteries

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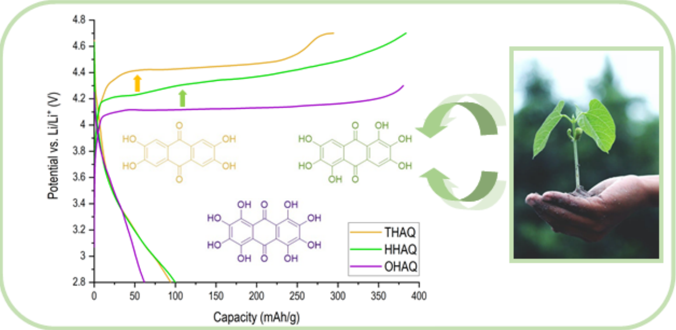
Despite still being the state-of-the-art battery chemistry for many applications, the predicted high deployment numbers of Lithium-Ion Batteries raises various environmental concerns related to the scarcity, topographical limited harvesting and energy-intensive mining and processing of crucial inorganic electrode materials such as nickel, cobalt and manganese. As a sustainable alternative, Organic Electrode Materials (OEMs) have been proposed as promising alternative due to their modifiable organic structures, abundancy and energy-efficient processing. [1-3] Although multiple materials show impressive capacities, OEMs exhibiting high redox potentials (>3.5 V vs. Li^+/Li) remain scarce and many starting materials are still derived from the fossil fuel feedstock. [4,5] In this work, we present a set of high-voltage, bio-based polyhydroxyanthraquinones and their polymer counterparts as cathode materials for LIBs with high initial capacities. Dependent on the molecular structure, the high-voltage discharge potentials are typically between 3.6-4.2 V with initial specific capacities of up to 383 mAh g^{-1}. Furthermore, we show that a facile polymerization process, utilizing formaldehyde as linker and MWCNTs as scaffolds, improved the cyclability of the materials, retaining capacities as high as 94 mAh g^{-1} after 100 cycles when utilizing both the catechol-like moieties and the anthraquinone functionality.



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P4: Cyclotetrabenzil Macrocycle Based Lithium-Ion Chemistry

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Organic electrode materials with high theoretical capacity, structural variety, and minimal environmental impact are potential candidates for electrochemical energy storage. In this work, we investigate the redox chemistries of supramolecular molecules based on the naphthalene cyclotetrabenzil macrocycle. This material could reversibly accept and release 8 Li^+ in two-step reactions with a specific capacity of 274.5 mAh g^{-1}. In contrast to the acyclic form, the macrocycle exhibits stable cycling with 80% of its initial capacity remained after 200 cycles. The shape-persistent macrocyclic structure of the macrocycle reduces solubility owing to increased molecular weight and forces the carbonyl (C=O) groups to be blocked in s-cis conformation, resulting in two one-electron reactions. Additionally, the increased strain in the ring structure lowers the reducing ability of the macrocycle, thus making the reduction of the first four C=O easier while the other four C=O more difficult. This research provides better understanding of the redox properties of macrocycle-based organic active materials.

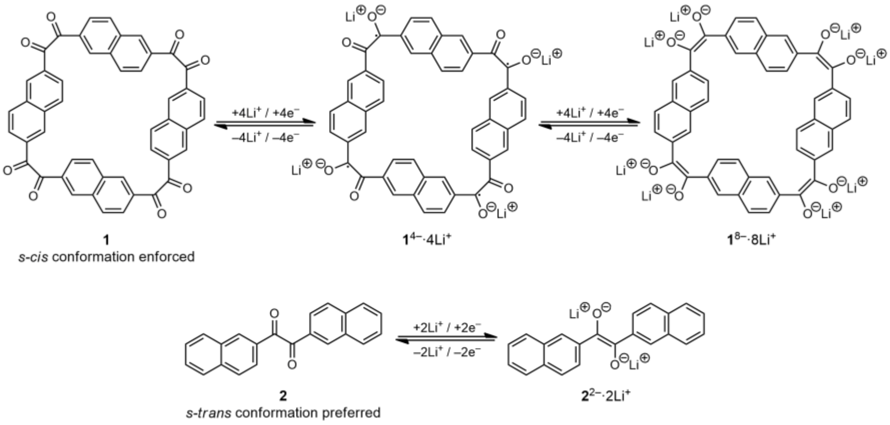

Figure 2. Illustration of electrochemical redox mechanisms of naphthalene cyclotetrabenzil macrocycle and monomeric acyclic counterpart.

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P5: High Spatial Resolution Quantitative Chemo-Mechanical Mapping of Organic Composite Cathode for Sulfide-Based Solid-State Batteries

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Understanding the chemo-mechanical behaviors of electrodes, particularly at the electrode/electrolyte interfaces, is critical for improving the performance of all-solid-state batteries. However, due to the instability of electrolyte materials under ambient conditions, such characterizations are challenging, particularly for sulfide-based all-solid-state batteries. Herein, by combining time-of-flight secondary-ion mass spectroscopy and in-SEM nanoindentation measurements, a systematic quantitative investigation of the chemo-mechanical behaviors of pyrene-4,5,9,10-tetraone (PTO) /Li_6PS_5Cl composite cathodes is carried out. Chemical and quantitative mechanical information of the composite cathode were collected with high spatial resolution after developing and implementing an air-free characterization protocol. By directly connecting the Young's modulus and hardness with the Li distribution in the composite cathode, a comprehensive chemo-mechanical mapping of the PTO/Li_6PS_5Cl composite cathode has been established. This work improves our knowledge of the critical chemo-mechanical phenomena that occur at the cathode/electrolyte interfaces in all-solid-state batteries, which can provide critical insights into further improvements of battery performances through rational structure design, material selection and material modification.

P6: Studying Superlithiation with proton free terephthalates

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Organic electrode materials (OEMs) are split into several classes, but one class in particular – superlithiation materials – are of a particular interest due to their fascinating mechanism. Superlithiation materials are even able to reach extremely high capacities, one example of which is Dilithium BenzeneDiPropiolate [1] at 1363 mAh.g^{-1} or the "3D periodic polyimide nano-networks" [2] which were found to reach 1260 mAh.g^{-1}. This is chiefly due to superlithiation materials being able to store up to an effective 1:1 C:Li ratio, much higher than the 6:1 ratio of lithiated graphite. Lithium terephthalate (**1**), is able to reach an excessive carbon to lithium ratio of 3:4. [3]

The mechanisms behind superlithiation however, remain poorly understood. A more fundamental approach to understanding the superlithiation mechanism is instead taken. Henceforth, an investigation into the effect of substituting the hydrogens of lithium terephthalate with halogens is performed. With the overall aim of showing that proton free OEMs are also able to undergo superlithiation, and to study the aforementioned proton free materials with neutron scattering, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy etc. allowing for a deeper understanding of the superlithiation mechanism.

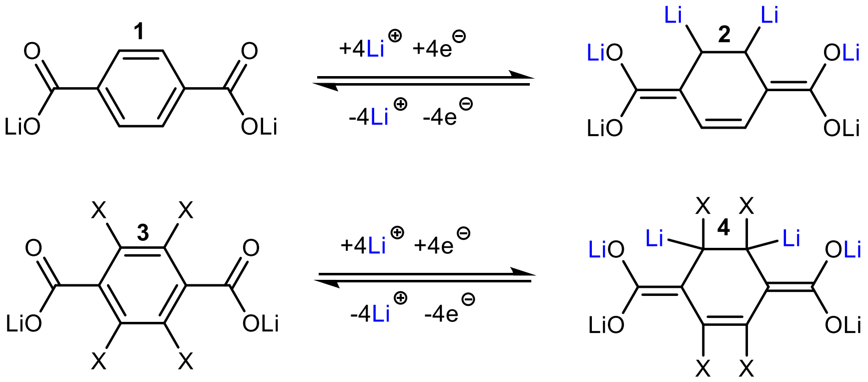

Figure 1: Terephthalate (**1**) and halogenated analogues (**3**) where X=F, Cl or Br And the proposed superlithiation products (**2**) and (**4**).

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P7: Building a full Li-ion prototype using a lithiated organic active material for the positive electrode

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The development of efficient and lithiated *n*-type organic electrode materials is essential to promote a new generation of Li-ion battery. Although such materials should be less expensive and more environmental friendly than the inorganic counterparts [1], functional limitations have to be overcome to implement them in viable prototypes. For instance, it is required to decrease the amount of conducting carbon in the electrode formulations.

The lithiated air-stable $Mg(Li_2)$-*p*-DHT compound (for magnesium (2,5-dilithium-oxy)-terephthalate) offers a theoretical capacity of 230 mAh/g (corresponding to the exchange of two electrons/two lithium ions per ring [2]), which is in the range of inorganic materials currently commercialized [3]. Although for now, only half of this capacity value is experimentally reached, we succeeded in fabricating robust electrode films with high content of active material (80 wt%) together with a decent areal capacity (1 mAh/cm^2). Here, we report the electrochemical performance of those electrodes in Li-ion configuration (using graphite as the negative electrode) measured in coin cells but also in multi-layer pouch cells. Preliminary tests in coin cells (CR2032) allowed us to optimize the electrode formulation and the balancing of the system giving rise to good capacity retentions (91% after 80 cycles). The second step was to build a first Li-ion multilayer pouch cell prototype based on $Mg(Li_2)$-*p*-DHT with 200 mAh of capacity (Figure 1). The first electrochemical data upon cycling will be presented too.

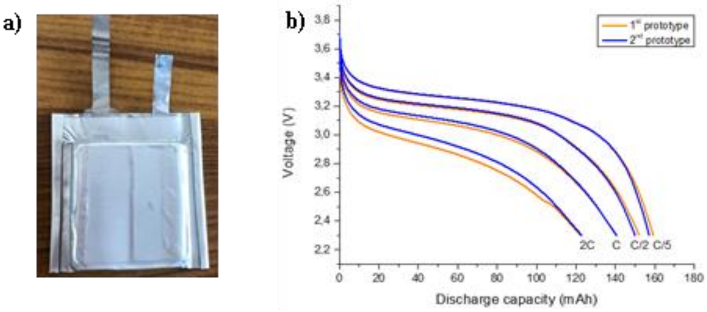

Figure 1. a) Picture of a multilayer pouch cell prototype (5/34/37 design). b) Typical discharge capacity values obtained at various C-rates for two prototypes

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P8: Building a full Li-ion prototype using a lithiated organic active material for the positive electrode

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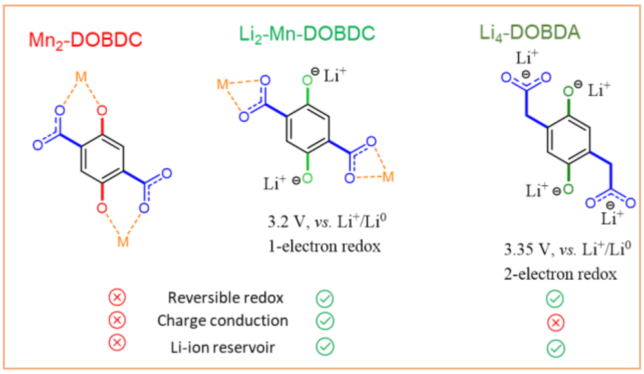
Organic materials/Metal–organic frameworks (OMs/MOFs) have emerged as an important, yet highly challenging class of electrochemical energy storage materials. The chemical principles for electroactive OMs/MOFs remain, however, poorly explored because precise chemical and structural control is mandatory. Herein, two different Li-phenolate OMs/MOFs were disclosed with aim of raising the operating potential and enable the charge conduction. First one is electrically conducting Li-ion MOF cathodes with the generic formula Li_2-M-DOBDC (wherein M = Mg^{2+} or Mn^{2+}; $DOBDC^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate), by rational control of the ligand to transition metal stoichiometry and secondary building unit (SBU) topology in the archetypal CPO-27 (Mn_2-DOBDC). These Li_2-M-DOBDC material validates the concept of reversible redox activity and electronic conductivity in MOFs by accommodating the ligand's noncoordinating redox center through composition and SBU design. [1] Secondly, although many efforts have been directed on tuning through substituent electronic effect, the chemistries than can operate above 3 V vs Li^+/Li^0, and thus be air stable in the Li-reservoir form remain finger-counted. We revealed an innovative organic Li-ion cathode material the tetralithium 2,5-dihydroxy-1,4-benzenediacetate (Li_4-DOBDA) with a remarkably high redox potential of 3.35 V vs Li^+/Li^0 attained notably in the solid phase. [2]



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P9: Size-Selective Covalent Organic Framework (COF) Composite Membrane to Overcome the Shuttle Effect in Organic Batteries

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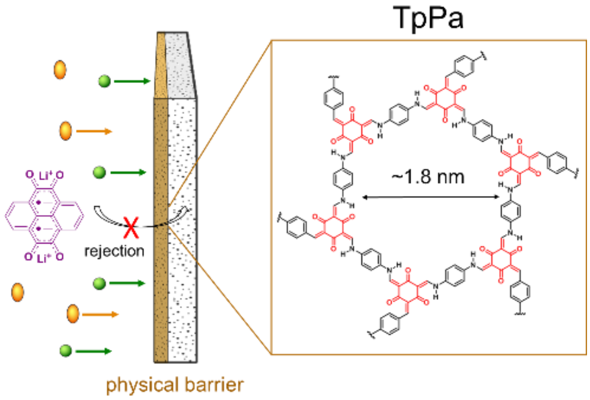
The essential elements of currently available lithium-ion battery technologies, such as Li, Ni, and Co, could soon be pressured by the EV and electronics market. Organic batteries are a promising alternative battery chemistry to alleviate the pressure on Li-ion batteries because of their high capacity, the abundance of component elements, and low environmental impact. However, the realization of organic batteries is still plagued by rapid capacity fade during battery operation which is often attributed to the shuttle effect of dissolved redox organic intermediates. [1] To overcome this issue, we applied a COF-based membrane as a battery separator to block the crossover of dissolved organic species and improve the cyclability. [2] Herein, we describe the design and fabrication of a composite membrane consisting of a thin COF layer supported by a conventional Celgard membrane (denoted as TpPa@Celgard). The effectiveness of TpPa@Celgard was evaluated in conjunction with pyrene-4,5,9,10-tetraketone (PTO), a high-capacity organic cathode which suffers from significant dissolution and crossover of its redox intermediates. [3] The TpPa@Calgard was shown to be efficient in blocking the bulky PTO anion intermediates from diffusional crossover in an H-cell with no negative impact on the Li ion flux. In the battery coin cell, a significantly enhanced first cycle coulombic efficiency was recorded with relatively low cycling stability, which may be due to other factors related to electrode and membrane engineering. This work sheds light on important parameters to be considered for designing efficient membrane separators.



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P10: Redox active disulfide crosslinked polymeric particles for energy storage application

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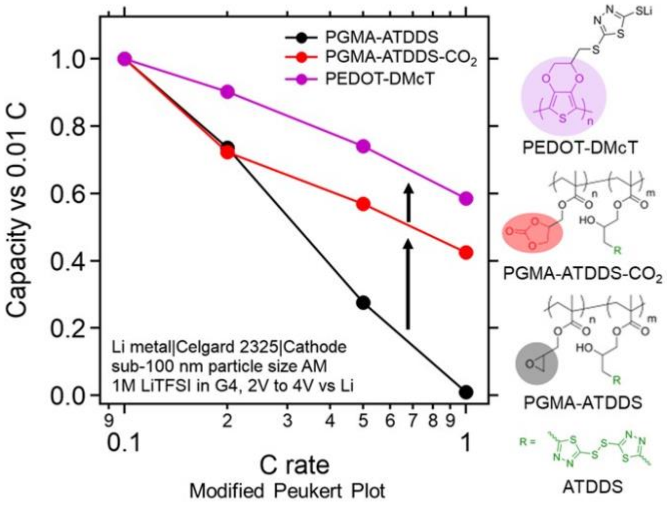
Disulfide redox active particles (RAP) were synthesized with different polymeric backbones, side chain functionalizations and redox centers with reversible 2 electron redox behaviors. Previously reported poly(glycidyl methacrylate) (PGMA) polymer particles functionalized with bis(5-amino-l,3,4-thiadiazol-2-yl) disulfide were further improved with various side chain to improve charge transport and local polarity to improve the discharge capacity, exceeding 80% of the theoretical capacity. Furthermore, a poly-3,4-ethylenedioxythiophene (PEDOT) semiconducting nanoparticles were synthesized to replace the inert PGMA polymer backbone, and then covalently attached with 2,5-Dimercapto-1,3,4-thiadiazole (DMcT) as redox center. Cycling over multiple charging rates reveals PEDOT-DMcT can retain more capacity at higher rates as a result of the electrocatalytic effect and electronic conduction of the PEDOT backbone.

These results highlight a class of disulfide RAP for energy storage applications and promising way to fabricate polymeric cathode materials.



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P11: Using Dynamic Crosslinks in Redox Active Colloids to Enable Electrode Cleaning

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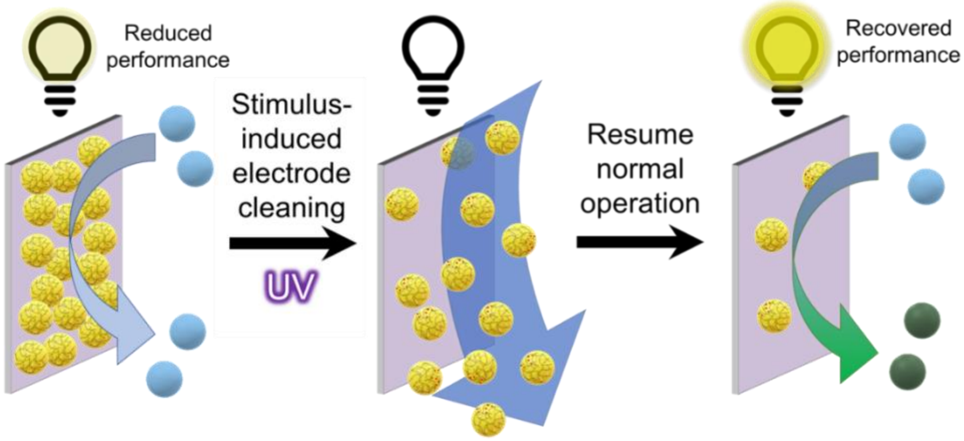
Redox active colloids are a promising approach to enabling organic redox flow batteries because of their ability to use cheap, porous membranes and circumvent solubility limits of compounds. [1, 2] Yet, there are concerns about their tendency to foul electrode surfaces. This can lead to surface passivation and ultimately, reduced electrochemical performance. [1] To counteract this issue, we have designed a redox active colloid (PGMA-ATTDS) that integrates a redox active, dynamic crosslink into the polymer structure that can assist in removal of the particle from the electrode before permanent degradation occurs. This crosslink works by cleaving under exposure to either ultraviolet or electrochemical stimuli that changes the local particle swelling. We show that under the same conditions, PGMA-ATTDS particles can be removed from an artificially fouled surface at over 80% compared to PGMA particles that are permanently crosslinked being removed at 10%. Further, electrochemical activity of an electrode is probed in the pristine, artificially fouled, and recovered conditions to show reduced performance with the presence of an artificially fouled electrode that can be recovered by the prescribed cleaning procedure.



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P12: Machine Learning-Accelerated Multiscale Modeling of Radical-Containing Polymers for All-Organic Batteries

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Non-conjugated radical-containing polymers are a class of charge-carrying polymers that rely on pendant stable radical sites to transport charges successfully. They constitute promising materials for applications in all-organic energy storage or memory devices. The properties of these soft electronic materials depend on the coupling of electronic and conformational degrees of freedom over a wide range of spatiotemporal scales. Bottom-up, predictive modeling of such properties requires multiscale approaches that efficiently connect quantum-chemical calculations to mesoscale coarse-grained (CG) methodologies.

We present an efficient computational scheme that uses supervised machine learning (ML) to predict electronic-structure information pertaining to charge transport at CG resolutions. ML models are trained on data coming from quantum-chemical calculations on all-atom conformations sampled from condensed-phase simulations. Predictions of electronic couplings, spin densities, and energy levels are studied as a function of CG mapping and resolution. Trained ML models subsequently enable electronic property predictions directly from CG polymer condensed-phase simulations. We validate the approach by comparing to the standard methodology that requires backmapping to atomistic resolution and subsequent quantum-chemical calculations. The proposed ML-assisted scheme drastically accelerates multiscale computational workflows that connect electronic properties to mesoscale morphological features, thereby enabling high-throughput modeling aimed at the understanding and rational design of radical-containing polymers for all-organic batteries.

P13: Effect of Stereoregularity On the Electrochemical Properties of Poly(vinylcarbazole)

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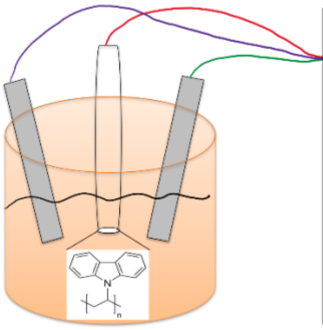
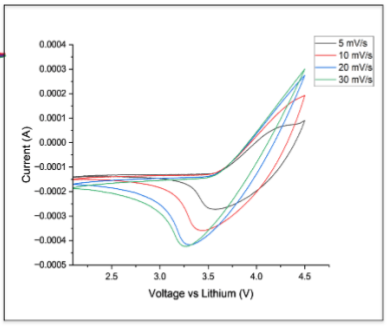
Redox active polymers have gained popularity as electroactive materials for energy storage. According to the nature of their backbone, redox active polymers can be classified as conjugated or non-conjugated polymers. Conjugated redox active polymers have alternate single and double bonds that offer conductivity through dopants. Poly(vinylcarbazole) (PVK) is one type of pendant conjugated polymer that has has carbazole side groups that helps in hole transport. It been studied as a positive electrode in lithium-ion batteries.

In this work, the effect of isotacticity on electrochemical properties in four different isotactic samples of polyvinyl carbazole has been reported. Previously, effect of stereoregularity on the electrochemical properties has been studied in conjugated as well as non-conjugated polymers. Authors have reported a comparative study of hole mobility with change in the stereoregularities in these polymers. This work, however, focusses on the variation in the electron kinetic parameters, namely, homogenous ($k_{ex,app}$), and heterogenous rate constants (k^0) and also the electron diffusion coefficients (D_{et}) in each of the different isotactic polymers. Two very fundamental electrochemical tests, cyclic voltammetry and chronoamperometry on a three-electrode beaker cell have been carried out to calculate the rate constants and diffusion coefficients.

A fixed trend of variation of the above-mentioned properties has been described in the results. Further possible investigation of factors affecting such trend has been proposed in the future work.





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