ND Energy

6th Annual

RESEARCH SYMPOSIUM

POSTER SESSION

Friday, May 5, 2023

Dahnke Ballroom

UNIVERSITY OF NOTRE DAME | RESEARCH

ND Energy

Sixth Annual Research Symposium
Poster Session Schedule
May 5, 2023 | 3:15-4:30 p.m. | Dahnke Ballroom

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AME	Aerospace and Mechanical Engineering
CBE	Chemical and Biomolecular Engineering
CEEES	Civil and Environmental Engineering and Earth Sciences
CHEM	Chemistry and Biochemistry
RAD LAB	Notre Dame Radiation Laboratory

High Pressure Studies of Boltwoodite and Implications for Used Nuclear Fuel Disposal

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Abstract

Nuclear energy is the most reliable and low-carbon energy source available, but managing nuclear waste is complicated by its radioactivity and complex interactions with the environment. U.S. policy is to dispose of used fuel from commercial reactors in a geologic repository in Yucca Mountain, Nevada. When used fuel pellets were exposed to water from Yucca Mountain, uranium (VI) minerals formed including boltwoodite, $(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$.[1] A more robust fundamental understanding of the structural stability of these sparingly soluble alteration products of uranium dioxide would advance uranium chemistry and provide information about the potential mobility of uranium, fission products, and higher actinides incorporated into these mineral phases.[2,3] The goal of this project is to characterize pressure-induced structural changes of uranyl minerals relevant to nuclear waste to further the fundamental understanding of uranium chemistry for safe storage and treatment of used nuclear fuel.

High (gigapascal range) pressure studies are often used to elicit phase transitions in crystalline material such as uranium dioxide.[4,5] While these transitions typically occur at pressures greater than 20 gigapascals (GPa),[4,5] more subtle structural changes such as an induced agostic interaction in a uranium (III) organic structure occur at pressures below 4 GPa.[6] Low GPa-range pressures are geologically relevant, and can be achieved experimentally using diamond anvil cells. This work uses single crystal X-ray diffraction to determine atomic positions and Raman spectroscopic measurements to characterize short-range order and changes in symmetry within these minerals. Preliminary results indicate a significant decrease in the space between uranyl silicate sheets in boltwoodite resulting in increased interlayer cation coordination number as pressure increases from 0 to 14.81 GPa. This observation has implications for the mobility of radionuclides associated with alteration phases of uranium dioxide in the context of used nuclear fuel disposal.

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Hybrid Molybdenum Bronzes as a Tunable Material Platform

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Abstract

Metal oxide bronzes of the form AxMO3 (A = cation, M = metal) display favorable electronic properties for applications ranging from energy storage to catalysis. These inorganic solid-state materials, however, can require high-temperature syntheses and are difficult to tune post-synthetically. To address these challenges and introduce additional chemical functionality, here, we show initial steps toward the development of a class of materials we call “hybrid bronzes” that combine the favorable structural, redox, and electronic properties of extended inorganic bronzes and the tunable functional groups and synthetic control of organic molecules. In particular, we have focused on incorporating molecular species into two-dimensional layered molybdenum bronzes to modulate their electronic properties. We have generated a library of air- and water-stable hybrids under mild, solution-state reaction conditions. We have then begun examining their structure-property relationships utilizing powder X-ray diffraction, vibrational and electronic spectroscopies, and electrochemical methods. Critically, despite their dimensional reduction, these hybrids maintain high electronic conductivity and we are in the process of elucidating how molecular incorporation tunes their band gaps and mixed ionic/electronic transport. Additionally, we have begun utilizing the unique tool of high-pressure experimentation to understand stimulus-induced changes and how structure dictates the electronic behavior of these materials. Ultimately, we seek to develop a new tunable material platform for energy-related applications.

Characterizing Sulfur Copolymer Composite Cathodes for All-Solid Batteries

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Advisor:
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Abstract

High energy density and high-performance metal-sulfur batteries are sought after as a potential improvement on the current Li-ion battery technology. The high energy density that would be achieved from metal-sulfur batteries can be used to power large vehicles, such as semi-trucks and airplanes, aiding in the global movement towards more sustainable energy. The use of sulfur as a cathode material in these devised batteries is beneficial due to the abundance of sulfur as well as its low cost. A solid polymer electrolyte will be used for the battery in this study as opposed to the standard liquid electrolyte. This is a safety benefit since the volatile, flammable liquid components would be eliminated from the batteries. Liquid electrolyte batteries are also more susceptible to the polysulfide shuttle effect where reaction intermediate metal sulfides (MxSy) dissolve into the electrolyte, “shuttle” to the anode, and then react with it, thus diminishing the electrochemical capacity of the cell. In this work, we investigate lithium-sulfur batteries based on solid polymer electrolytes and sulfur copolymer cathodes with built-in ion transport channels. We report on the synthesis of the crosslinked sulfur copolymer as well as the characterization of the bulk material properties of the copolymer and the overall composite cathode. These characterizations include differential scanning calorimetry for determining the glass transition temperature to examine the existence of unincorporated elemental sulfur in the synthesized copolymer, dielectric / impedance spectroscopy for characterizing ionic conductivity and Li+ transference in this copolymer system, absorption spectroscopy for evaluating the absorption of the lithium polysulfides into the polar region of the polymers, and Raman spectroscopy during cycling of the battery for gaining information on the charge / discharge reaction pathways with sulfur and polysulfide speciation along with the ionic interactions that impact cation transport in the solid state.

Additive Manufacturing and Scalable Nanomanufacturing of Sustainable Energy and Sensor Systems

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Advisor:
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Abstract

Nanoscale materials are attractive building blocks for a broad range of emerging technologies due to their unique and often superior properties. However, transforming nanoscale materials into macroscale devices and systems while translating their unique properties from nanoscale to macroscale remains a major challenge due to many scientific and technological obstacles.

Here we present our research on developing versatile and synergistic additive manufacturing and scalable nanomanufacturing methods to manufacture and transform a broad range of emerging nanoscale materials into advanced energy and electronic systems in a highly scalable and intelligent manner. We present our recent research progress on several closely related topics. First, we present our research on scalable nanomanufacturing to create nanoscale building blocks and printable inks with desired physical property, colloidal stability and printability. Second, we present our work on developing novel additive, hybrid and autonomous manufacturing methods to fabricate multifunctional and flexible/wearable devices for energy conversion, sensing and health monitoring. Finally, we present innovative thermal processing and sintering methods that enable high-throughput and ultrafast processing of printed semiconducting and metallic nanoparticles on delicate and temperature sensitive materials.

Nonthermal Plasma Chemical Models for Atom- and Energy-Efficient Ethane Conversion

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Advisor:
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Abstract

The context of this project is captured in the mission of its funding resource, the "Center for Innovative and Strategic Transformation of Alkane Resources" (CISTAR): to expand the economic benefits of using natural gas while assuring those uses' environmental sustainability. Conversion of ethane to ethylene has obvious economic incentive, given that over 150 million tons of ethylene are produced each year. However, this process requires significant improvement in its environmental impact. This project investigates a novel approach to ethane dehydrogenation through plasma and plasma catalysis. Plasmas allow for low temperature chemistry beyond thermal equilibrium, and therefore present an electrified, potentially energy efficient process for chemical conversions. Modeling techniques require non-equilibrium thermodynamic considerations, and any kinetic analysis must include electron impact driven rate parameters. Due to the novelty of these modeling approaches, their inputs and outputs require careful attention and are the focus of this poster.

Effect of Zirconium(IV) Oxide Surface Modification with Polyphenols in Water Radiolysis

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Advisor:
Jay LaVerne, Professional Specialist, Notre Dame Radiation Laboratory; Concurrent Professional Specialist, Department of Physics and Astronomy

Abstract

It was previously demonstrated that surfaces of some oxides enhance molecular hydrogen generation in water radiolysis compared to that observed with bulk water. In particular, it was shown, that surface hydroxyl groups and surface water play important roles in hydrogen generation. This work focuses on the chemical modification of hydroxyl groups on the surface of zirconium(IV) oxide with catechol and its derivatives to further explore the mechanism of hydrogen generation. Catechol is a polyphenol, containing two vicinal hydroxyl groups in the benzene ring. It is known for its antioxidant properties and for its ability to form strong complexes with metal ions. Surface modification was performed at neutral pH in de-aerated deionized water. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) confirmed the presence of the complexes on the surface of the oxide. Surface hydroxyl groups were fully substituted by catechol and its derivatives, while para-hydroquinone, phenol, and an aliphatic analog of catechol failed to bond to the surface. Complexes of ZrO2 with catechol demonstrated a significant decrease in hydrogen production in radiolysis. The impact of the substituents in the polyphenol ring on the complex performance under irradiation will be discussed.

Exploring the Change in Uptake and Interatomic Distances of Ion Mixing of Uranyl Oxalate Hydroxide Hydrate with Rubidium and Cesium Counter Cations

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Abstract

Uranyl Oxalate Hydroxide Hydrate [M(UO2)2(C2O4)2(OH)·2H2O (M=Na, K, Cs, Rb, NH4)] is a uranium-containing compound that is of interest due to its potential application in the nuclear fuel cycle and relevance to environmental systems. Oxalates are present in nature and are used as precipitating agents in the nuclear fuel cycle. Uranyl Oxalate Hydroxide Hydrate is known to be stable under ambient conditions, and it can contain several different monovalent counter cations. Several isostructural compounds of Uranyl Oxalate Hydroxide Hydrate have been studied with different countercations, including K and NH4. These isostructural compounds contain the same 2-D anionic framework, and the structure of the layer is built by condensing the structural units through sharing oxalates to chains and connecting parallel chains by sharing OH to create the 2-D six-membered anionic framework.

Rubidium and cesium counter cations have been of particular interest due to their larger ionic radii, leading to potential substitution in the crystal lattice, and this study aims to explore the change in structure and uptake when uranyl oxalate hydroxide hydrate is mixed with different molar ratios of rubidium and cesium counter cations. The resulting compounds from the mixing are characterized using a variety of characterization methods, including single crystal X-ray diffraction (XRD), powder XRD, and inductively coupled plasma optical emission spectroscopy(ICP-OES), which will aid in determining elemental composition and crystal structure, as well as characterizing the mother liquor to determine change in cation uptake. We can hypothesize that there would be significant differences in interatomic distances and ion uptake of the newly synthesized compound when contrasted with their isostructural counterparts. The results will examine the changes in structure due to the incorporation of varying ratios of rubidium and cesium ions, specifically interatomic distances, percent occupancy of the rubidium and cesium ions, and mother liquor composition. These findings have significant implications for the understanding of materials for nuclear waste management, where the incorporation of counter cations can improve the efficiency of environmentally-friendly processes within the nuclear fuel cycle, and for environmental processes involving uranyl oxalates in the presence of these cations.

Reactions of Metal Ions with Water Radiolysis Products in Nuclear Reactor Coolant Water

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Advisor:
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Abstract

Radiation-induced corrosion is still a major problem that the nuclear industry is facing. Corrosion of the reactor's structural alloys releases different metal ions in the coolant water. To minimize the corrosion and activity transport in the piping of nuclear reactor, Zn is injected into coolant water of boiling water reactors (BWRs). All these metal ions circulating in the coolant loop will participate in complex reactor chemistry, can substantially alter the chemistry of coolant water, and also can affect activity transport patterns through cooling piping and ultimately exposure of workers. Therefore, it is important to study the redox chemistry of these transition metal ions present in the coolant water of nuclear reactors

This work reports new experimental and kinetic data of the redox reactions occurring in coolant water of a nuclear reactor when metal ions (M=Zn, Ni) are present. All the conditions of nuclear reactors' coolant water like temperature and pressure are simulated in the lab and studied with the help of a Linear Accelerator. The pulse radiolysis experiments were performed using an 8 MeV Linear Accelerator. A multichannel detection system equipped with a monochromator and photomultiplier tube is used for the UV-visible transient absorption measurements. A custom-built high-temperature high-pressure titanium sample cell with sapphire windows has been used for the entire temperature range of 25-300ºC experiment.

In this study, we have investigated the reaction rates of hydrated metal ions M2+/+ with water radiolysis products (e-aq, •OH, H, and H2O2) for a 25-300ºC temperature range and 200 Bar pressure using a time-resolved pulse radiolysis technique. For the first time, we have reported molar extinction coefficients for the whole temperature range. The reaction kinetics was studied by analyzing the absorption signals of transient monovalent aqueous metal ions M+ (M = Zn, Ni). By fitting the short time scale kinetic curves, extinction coefficients and formation rates of monovalent metal ions were extracted. Monovalent metal ions undergo back-oxidation reactions with •OH, H, and H2O2. To obtain the reaction rate constants for the decay of M+ at various temperatures, we fitted the curves using a kinetic model. We have demonstrated how an injection of Zn reduces corrosion and restricts activity transport. The measured rate constants for temperatures up to 300ºC make it possible to evaluate the contribution of the reactions of metal ions to the complex reactor radiation chemistry.

Isolation of Catalytically Relevant Sites in 2D Extended Solids through Atom-transfer/exchange Reactions

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Abstract

Atom transfer or exchange chemistry is well-developed for providing fine synthetic control over molecular species under mild conditions. However, it is solid-state materials that offer the favorable chemical stability, electronic properties, and reactivity desired for energy-related applications and catalysis. Indeed, heterogeneous catalysts are used in over 70% of industrial chemical processes, yet tuning solid-state compounds is often energy-intensive. Utilizing atom transfer/exchange chemistry to synthesize or modify solid-state materials remains virtually unexplored. Two-dimensional bimetallic cyanides called Hofmann clathrates have been studied as model compounds for fundamental coordination chemistry and for applications as spin-crossover materials, porous adsorbents for chemical separations, and heterogeneous catalysts. We seek to use these 2D cyanide systems to intercalate and/or template atom transfer or exchange reactants, which can then be stimulated to yield materials that cannot be accessed through normal means or to stabilize and study active sites relevant to catalysis, such as FeIV=O species.

Optimizing Additive Manufacturing of Thermoelectric Materials using Bayesian Optimization-Enhanced Active Machine Learning

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Advisor:
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Abstract

This project developed a Bayesian optimization-enhanced active learning algorithm to optimize the processes of additive manufacturing and sintering of high performance and low-cost thermoelectric (TE) films for energy conversion. This machine learning framework synergistically integrates high-throughput materials synthesis and characterization, Bayesian optimization (BO), and expert physical insights into a self-improving algorithm to rapidly engineer and optimize the manufacturing processes for TE materials. With the help of BO, such an approach can self-learn on-the-fly by actively generating data necessary to improve the model accuracy until reaching the target material performance. Using this method, we have demonstrated record high performance metrics for several n-type and p-type TE materials by optimizing both material compositions and manufacturing processes. We have also shown that our method can work with relatively small data sets, which reflects the situation for most engineering problems. Our demonstrated material optimization speed is significantly faster than traditional trial-and-error methods.

Probing Radiation Stability of Nuclear Separation Ligands: Pulse Radiolysis and EPR Approaches

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Abstract

Nuclear energy is considered the most environmentally friendly among conventional energy sources. Nevertheless, it generates highly radioactive waste that should be handled with care. Spent nuclear fuel mainly contains uranium, plutonium, and the bulk of minor actinides. When separated, all these components can be reused, which reduces the amount of material disposed of as high-level waste.

Solvent extraction is the prominent technique for the separations implemented in the nuclear fuel cycle. These processes are based on the use of special ligands dissolved in organic solvents, which are mixed with aqueous solutions of spent fuel. During the separation processes these compounds will be exposed to ionizing radiation and will react with radiolysis products of water or/and solvent. Evaluation of the radiation stability of ligands and their degradation pathways is crucial for the safe application and development of new separation approaches.

In this work, we aim to implement a combined technique to probe the radiation stability of currently used and proposed nuclear separation ligands. The reactions between the primary products of water radiolysis and ligands are investigated by pulse radiolysis using an 8 MeV linear accelerator with a multichannel transient optical absorption system. This approach allows us to estimate rate constants for the reactions of hydrated electrons with Bis(2-ethylhexyl) phosphate (DOP) and tributyl phosphate (TBP).

Another group of methods is based on the use of EPR to study secondary paramagnetic species originating from ligands subjected to X-ray irradiation. In the case of solid compounds, such as n-octyl(phenyl)-N,N-diisobutyl carbamoyl methyl phosphinoxide (CMPO), the radicals formed upon irradiation are stable at room temperature for several days and can be detected directly. The analysis of the EPR spectra made it possible to obtain information about their structure and composition. The energetic efficiency of radiolysis, determined by radiation chemical yield (G-value) of radical formation, was also calculated. This approach does not work for liquid ligands, but in this case, we were able to detect transition radicals using spin traps. The N-(4-Pyridylmethylene)-tert-butylamine N,N′-dioxide (POBN) spin-trap was dissolved in TBP, thus the radicals originated from the irradiated substance were converted to more stable spin adducts and measured by EPR at room temperature. With the spin trap method, the structural information on paramagnetic species is limited, but it allows one to estimate the number of radicals and the G-value of their formation. The last of the approaches used is associated with the chemical generation of OH radicals in an aqueous solution and direct observation of the resulting radicals using a continuous flow mixing EPR. In this approach, quantitative measurements are hardly possible due to the low solubility of the ligand in water, which is compensated by the presence of rich structural information, as shown in the example of a TBP solution.

The proposed combined technique makes it possible to elucidate various aspects of the radiation stability of ligands, including primary and secondary processes occurring in different media. The application of this technique to other groups of substances of particular interest is discussed.

Microporous Iptycene-based Polybenzoxazole Membranes for H2/Alkane Separations

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Advisor: Ruilan Guo, Frank M. Freimann Associate Professor of Engineering, Department of Chemical and Biomolecular Engineering

Abstract

Energy is fundamental to the growth of the global economy; the need to develop cheaper and more efficient separation processes that are environmentally sustainable cannot be overstated. Membrane-based gas separation has received enormous interest in energy applications because of its smaller carbon footprint, reduced spatial requirements, and far less thermal requirement than mature gas separation processes such as cryogenic distillation and pressure swing absorption. [1] Membranes from polymers are promising for the industrial separation of gases because they are cheaper, more robust, easier to fabricate, and scalable; they have been chiefly deployed to separate and purify hydrogen but usually operate at room temperature. Some processes, such as dehydrogenation-oligomerization in the refining & petrochemical industry, require hydrogen separations at elevated temperatures. Current polymer membranes can't meet this industrial need due to poor thermal stability or low performance at elevated temperatures. This is because many polymers either have low glass transition temperatures (T_g) or those with high T_g, such as polybenzimidazole, often have low permeabilities because of their strong hydrogen bonding and pi - pi electron stacking. [2] [3] Additionally, glassy polymers usually lose their selectivity with increasing temperature because the gas permeation process is activated with its temperature dependence increasing exponentially. This study looks at the high-temperature performance of Iptycene-based Polybenzoxazole, a polymer with exceptional separation performance at ambient temperature, [4] for hydrogen separation.

This was done by firstly tuning thermal protocols to obtain a desirable microstructure with optimum performance at ambient conditions. Then, the best protocol was used to convert the precursor polymers to iptycene-based polybenzoxazoles that were tested at high temperatures under pure and mixed-gas conditions. It was observed that the less temperature-sensitive configurational free volumes due to the iptycene macromolecules made the microstructure of the polymers non-collapsible at high temperatures and resulted in good separation performance at temperatures up to 200℃. The promising findings from this study are envisaged to contribute to better alignment of the process and separation conditions industries by eliminating or reducing the need for interstage cooling and trimming down the capital and operating costs incurred on heat exchangers.

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Hybrid Tungsten Bronzes: A Tunable Organic-inorganic Platform

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Abstract

Tungsten oxide has been investigated for applications including electrochromic devices, catalysis, and energy storages as well as for intriguing solid-state physical phenomena such as metal-insulator transitions and superconductivity. A primary reason for its detailed study and implementation is that WO3 can be reduced to form a non-stoichiometric compound known as a bronze that features the formula AxWO3 (A+ = charge-balancing cation). Reduction populates the conduction band, yielding free electrons with high carrier mobilities that, dramatically alter the chemical and electronic properties of the system and lead to a transition from insulative to conductive behavior. However, the synthesis of some tungsten bronzes requires high temperatures, and controlling their properties is difficult after the synthesis. To incorporate molecular-level tunability, we are developing hybrid organic-inorganic tungsten bronzes. This new hybrid bronze platform consists of two-dimensional tungsten oxide layers similar to the tungsten bronzes, in proximity to organic molecules that can incorporate added functionality, such as catalytic, redox-, or photo-activity. Our work (1) explores the synthetic control of layered hybrid tungsten bronzes, and (2) studies the structure-property relationships within this new material system. We have developed improved synthetic techniques and added to our growing set of previously unreported hybrid bronze materials. We have then applied a diverse range of diffractive, spectroscopic, and electrochemical characterization techniques to gain fundamental understanding of their optical and electronic behavior that will be relevant for energy-related applications.

High-Performance Polymeric Gas Separation Membrane Designed by Explainable Graph Augmented and Imbalanced Machine Learning

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Advisor:
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Abstract

Gas separation using polymer membranes promises to dramatically drive down the energy, carbon, and water intensity of traditional thermally driven separation, but developing the membrane materials is challenging. Machine learning (ML) can speed up this process, but the small and imbalanced data hinders its effectiveness. Here, to overcome these limitations, we leverage a novel graph augmented and imbalanced ML method to guide the design of polymer membranes with performances simultaneously exceeding the upper bounds in multiple industrially important gas separation tasks. This ML technique is interpretable with explainable polymer substructures, adopts augmentation to enrich labels, and applies semi-supervised learning to balance the training data. Two predicted candidates are synthesized and experimentally validated to perform beyond the upper bounds for multiple gas pairs (oxygen/nitrogen, hydrogen/methane, and hydrogen/nitrogen). The molecular origin is revealed by combining the inherent interpretability of our ML model, experimental characterization, and molecular simulation. Our study presents a unique explainable graph ML technique to tackle small and imbalanced data problems in general, and the developed polymers may be used for industrial gas separation.

Water-Assisted Ion Conduction in Solid-State Charge-Transfer Complex Electrolytes for Lithium Batteries

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Abstract

Currently, research on solid-state organic electrolytes mainly focuses on polymer electrolytes where ion transport is facilitated by chain segmental motion. A limited number of prior reports suggest that solid-state electrolytes based on organic charge-transfer (CT) complexes can have surprisingly high ionic conductivity. Here, we report that processing and environmental conditions drastically impact charge transport properties of CT complex electrolytes based on tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) mixed with lithium bis(trifluoromethylsulfonylimide) (LiTFSI). Thermal annealing and water vapor treatment decreases electronic conductivity and increases ionic conductivity. The electrolyte with 1-1-2-0.45 molar ratio of TTF-TCNQ-LiTFSI-H_2O has an ionic conductivity of 2×10^{-3} S/cm at 25 °C with order 10^4 times lower electronic conductivity. In this system where ion conduction is decoupled from the mobility of the organic phase, thermal annealing helps reduce CT connectivity and expose more surfaces to interact with LiTFSI, and water promotes the dissociation of LiTFSI.

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