

SYMPOSIUM ET10

Redox Active Materials and Flow Cells for Energy Applications
November 26 - November 28, 2018

Symposium Organizers

Xianfeng Li, Dalian Institute of Chemical Physics
Susan Odom, University of Kentucky
Maria Skyllas-Kazacos, The University of New South Wales
Wei Wang, Pacific Northwest National Laboratory

Symposium Support

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* Invited Paper

SESSION ET10.01: Organic Nonaqueous
Session Chairs: Susan Odom and Wei Wang
Monday Morning, November 26, 2018
Hynes, Level 3, Room 309

8:00 AM *ET10.01.01

Complexes with Redox Non-Innocent Ligands for Flow Battery Energy Storage Kathryn Toghil, [Ross Hogue](#) and Craig Armstrong; Lancaster University, Lancaster, United Kingdom.

Redox flow batteries (RFBs) are energy storage devices where solutions of electroactive materials are pumped to/from external tanks to the electrode interface for charging/discharging. As energy is stored externally in solution, capacity can be increased independently of the battery power, thus making RFBs promising candidates for grid-scale energy storage.^{1,2} Established RFBs utilise aqueous electrolyte solutions; however the voltage output is limited by the narrow (~1.5 V) electrochemical window of water. Instead, the development of non-aqueous RFBs, which use organic solvents with wide electrochemical windows, is anticipated to improve the voltage outputs. Indeed non-aqueous RFBs containing metal coordination complexes have recently been reported with voltage outputs in excess of 2 V.³⁻⁶

The work presented here is the incorporation of redox non-innocent ligands in metal coordination complexes for non-aqueous RFBs. The use non-innocent ligands that can undergo reversible redox processes, in addition to redox-active metal ions, is anticipated to give metal complex electrolytes with multiple electron transfer processes, and thus, greater charge capacity. Initially, simple dithiolate ligands, the original non-innocent ligands, in combination with abundant first row transition metals, have been targeted with our aim being low molecular-weight and inexpensive electrolyte materials. The RFB charge/discharge cycling performance of these materials will be presented here.

References:

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8:30 AM *ET10.01.02

Nanoelectrochemical Interrogation of Redox-Active Polymer Electrolytes for Flow Batteries—From New Dynamics in Bulk Fluids to the Behavior of Single Particles Zachary Gossage, Kenneth Hernandez-Burgos, Mark Burgess, Jonathon Schuh, Randy Ewoldt, Jeffrey S. Moore and [Joaquin Rodriguez-Lopez](#); University of Illinois at Urbana Champaign, Urbana, Illinois, United States.

Redox-Active Polymers, RAPs[1], and related colloidal particles, RACs[2], are a new class of materials for a novel concept in size-exclusion nonaqueous redox flow batteries using fluid dispersions.[3] Unlike small organic molecules, RAPs and RACs display complex interactions with the electrolyte environment, conferring them a rich electrochemical behavior. Elucidating new redox properties in ways that are conducive to improved battery performance requires advanced electrochemical tools capable of discerning charge transfer, charge transport, and the projection of nanoscopic reactivity to bulk behavior. This presentation will discuss how integrated electrochemical approaches based on the use of nanoelectrodes, ultramicroelectrodes (UMEs), and the scanning electrochemical microscope (SECM) and its pairing with Raman spectroscopy provide a powerful approach for this purpose.

In a first study,[4] we will discuss recent findings regarding the impact of polyelectrolyte dynamics on the charge percolation and electrolysis efficiency of soluble RAPs. Insightfully using UMEs, we found that charge transport and voltammetric signatures are strongly modulated by specific and non-specific interactions with the electrolyte, by the packing of the polymer chains, and by the structure of the polymeric backbone. These new interactions open new avenues for the control of RAP reactivity as a function of operational conditions.

In a second study,[5] I will discuss new frontiers in the mechanistic characterization of RAPs and RACs using a powerful spectrum of single-particle analysis techniques using nano-SECM and Raman spectroscopy. Using these techniques, we isolated and cycle individual RAC particles, performing experiments over hundreds of cycles. This single-particle approach allowed us to identify the conditions that lead to electrochemical degradation of these particles, and which reflect changes observed previously at the macroscale on bulk fluids. These experiments provide us with unprecedented versatility to identify kinetic bottlenecks, such as charge trapping, and to determine the maximum current densities attainable in flow devices. Altogether, the identification of structure-reactivity relationships, and the use of advanced electrochemical techniques, results in new directions to make better polymers that exploit the versatility of this new type of reacting fluids for energy storage and conversion.

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9:00 AM ET10.01.03

On the Solubility of Charged Organic Species in Non-Aqueous Solvents for Redox Flow Battery Applications Nuwan H. Attanayake¹, Aman P. Kaur¹, Jeffrey Kowalski², Matthew D. Casselman¹, Peter Zhang¹, Sean R. Parkin¹, Fikile Brushett² and Susan Odom¹; ¹University of Kentucky, Lexington, Kentucky, United States; ²Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Redox flow batteries (RFBs) are expected to play a critical role in the grid energy storage by facilitating the widespread adoption of intermittent renewable energy sources like wind and solar.¹ However, the worldwide market penetration of RFB systems is still limited due to technical and economic challenges. The commercially available aqueous vanadium redox flow batteries offer durable performance but suffer from low energy density and high chemical costs. A key advantage of transitioning from aqueous to non-aqueous systems is the possibility of achieving higher energy density through the wider windows of electrochemical stability associated with organic solvents. Despite this promise, non-aqueous flow batteries are a nascent concept and, to date, no redox chemistry has proven competitive due to a combination of low solubility and stability for redox couples and a lack of selective membranes/separators. When building energy dense RFBs, the solubility of redox couples in the neutral and oxidized/reduced form is critical as active species must remain soluble across all states-of-charge. Notably, recent reports have highlighted redox active compounds that are highly soluble in their neutral state but haltingly soluble in their charged form, frustrating practical implementation.²⁻³ To this end, we have been developing a series of phenothiazine derivatives to achieve a high solubility at their neutral as well as charged states (radical cation and dication) through simple and easy molecular engineering strategies. This presentation will focus on the synthesis of highly soluble radical cations/dications with strategic substituents on phenothiazine, their solubility in non-aqueous solvents, spectroscopic, and electrochemical analysis of the radical cation salts.

References

1. Kowalski, J. A.; Casselman, M. D.; Kaur, A. P.; Milshtein, J. D.; Elliott, C. F.; Modekrutti, S.; Attanayake, N. H.; Zhang, N.; Parkin, S. R.; Risko, C.; Brushett, F. R.; Odom, S. A., A stable two-electron-donating phenothiazine for application in nonaqueous redox flow batteries. *J. Mater. Chem. A* **2017**,5(46), 24371-24379.
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9:15 AM ET10.01.04

Design of Organic Molecules for Application in Non-Aqueous Redox Flow Batteries Anuska Shrestha and Melanie S. Sanford; University of Michigan, Ann Arbor, Michigan, United States.

Acylpyridinium and cyclopropenium salts have recently been identified as promising catholyte and anolyte candidates for non-aqueous redox flow batteries (RFBs). Most early work on these systems focused on independently cycling the anolytes and catholytes in static electrochemical cells. In this work, we demonstrate the cycling of these molecules together in a laboratory-scale redox flow battery. Cyclic voltammetry experiments indicate that the two molecules should be compatible in a flow battery. However, initial cycling experiments showed a significant capacity fade resulting from a combination of both (1) crossover of these molecules through the membrane and (2) degradation of the anolyte in presence of the catholyte. This presentation will describe our work on the molecular tailoring of both the anolyte/catholyte structures as well as the membrane in order to address both of these challenges.

9:30 AM ET10.01.05

Recent Progress in Performance Enhancement of High-Stability Mushroom-Derived Non-Aqueous Redox Flow Batteries Tugba Ceren Gokoglan¹, Andrew Hamel¹, Shyam Pahari², Patrick J. Cappillino² and Ertan Agar¹; ¹Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States; ²Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts, United States.

Cost-effective and efficient grid-scale energy storage has the potential to revolutionize electrical distribution. Currently, balancing demand and supply is already a challenging task and the increasing efforts for the integration of renewable sources creates additional complications. Integration of grid-scale energy storage systems could be the solution of this problem enabling utilities to manage fluctuations and provide flexibility, dramatically impacting energy markets.¹ Non-aqueous redox flow batteries (NRFB) have been considered as a promising grid-scale energy storage technology. They can combine high energy density with the advantages of redox flow batteries such as, ability to decouple power and energy ratings, scalability, modularity, and long-life.² Additionally, the low vapor pressure and melting points of non-aqueous solvents offer an improved thermal stability, making operations at extreme environmental conditions possible.³ However, the widespread implementation of NRFBs have been hampered by poor active material stability.⁴

We recently reported a bio-inspired strategy that leverages biological evolution as a toolkit to address the problem of redox-couple instability that impedes commercialization of NRFB.⁵ This approach led us to investigate Amavadin, a redox-active vanadium-containing-biomolecule found in mushrooms, for application as a stable NRFB active-material. An analogue of Amavadin, known as vanadium bis-hydroxyiminodiacetate (VBH) has been selected as a molecular scaffold as a new NRFB active material due to its exceptional stability, redox reversibility and ease of synthesis. We will present the recent progress in performance enhancement of mushroom-derived NRFBs. Fundamental and technical factors underpinning high area-specific resistance and low capacity fade during extended cycling are elucidated using in-situ and ex-situ electrochemical and spectro-electrochemical diagnostic techniques. The results of these analyses will be discussed for various operating conditions and flow cell components.

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9:45 AM ET10.01.06

Towards All-Organic and Non-Aqueous Redox Flow Battery Energy Storage [Craig Armstrong](#) and Kathryn Toghil; Department of Chemistry, Lancaster University, Lancaster, United Kingdom.

Redox flow batteries (RFB) are electrochemical energy storage devices that are uniquely suited to the storage of renewable energy and grid-scale storage due to their decoupled power and capacity [1]. Aqueous flow batteries have achieved commercial success however their energy densities have reached the maximum that can be reasonably achieved due to the narrow 1.23 V electrochemical window of water and maximal solubility of their redox material. In contrast, non-aqueous RFBs can theoretically achieve much higher energy densities by use of solvents which offer larger stability windows and redox materials which undergo multiple electron transitions at high redox potentials [2]. Many non-aqueous systems have been studied thus far, utilising a wide range of chemistries, however significantly higher energy densities than aqueous RFBs have not yet been realised due to low solubilities and cell potentials which do not fully exploit the solvent stability window. The work by our group aims to surpass these limitations by investigating novel materials with desirable electrochemical and physical properties. Most recently, our group has explored the application of a small organic species called 'croconate violet' which undergoes multiple electron transfers and has a desirably low molecular weight. By utilising the reversible reduction and oxidations of croconate violet, a symmetric flow battery may be produced that achieves a ~2 V cell potential and avoids issues with membrane crossover as the same redox material is used in both half-cells. Such a design could surpass the energy density of current aqueous systems and simplify membrane constraints, however, the use of such an electrochemically active molecule raises concerns over stability and long-term viability due to the reactive nature of molecular free-radicals [3]. Work is continuing to assess the long-term stability of such novel organic redox materials as capacity retention is more crucial than energy density for practical application.

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10:00 AM BREAK

SESSION ET10.02: Organic Aqueous I
Session Chairs: Ross Hogue and Susan Odom
Monday Morning, November 26, 2018
Hynes, Level 3, Room 309

10:30 AM *ET10.02.01

New Battery Systems Based on Polymers and Organic Compounds as Active Materials [Ulrich S. Schubert](#); Friedrich-Schiller-University Jena, Jena, Germany.

For renewable energy sources such as solar, wind, and hydroelectric to be effectively used in the grid of the future, flexible and scalable energy-storage solutions are necessary to mitigate output fluctuations. For systems that are intended for both domestic and large-scale use, safety and cost must be taken into account as well as energy density and capacity, particularly regarding long-term access to metal resources, which places limits on the lithium-ion-based and vanadium-based RFB development. Here we describe an affordable, safe, and scalable battery system, which uses organic polymers as the charge-storage material in combination with inexpensive dialysis membranes, which separate the anode and the cathode by the retention of the non-metallic, active (macro-molecular) species, and an aqueous sodium chloride solution as the electrolyte. In parallel, printable solid-state polymer batteries were developed allowing a new generation of metal-free batteries (e.g. with application possibilities for smart labels, internet of things or smart clothes).

11:00 AM *ET10.02.02

Sulfonate Functionalized Viologen Anolyte Materials for Aqueous Organic Redox Flow Batteries Bo Hu, Jian Luo, Camden DeBruler and [Tianbiao L. Liu](#); Utah State University, Logan, Utah, United States.

Aqueous organic redox flow batteries (AORFBs) have emerged as an attractive alternative RFB technology because redox active organic molecule materials are synthetically tunable, sustainable, and potentially low cost. We have previously showed that positively charged viologen molecules are a class of viable anolyte materials for pH neutral anion exchange AORFBs with water soluble ferrocene and TEMPO catholytes. The presentation will cover our recent research efforts in developing sulfonate functionalized viologen molecules as anolyte materials for cation exchange AORFBs with low cost ferrocyanide and halide catholytes. The viologen based cation exchange AORFBs demonstrated outstanding battery performance including capacity retention up to 99.99% per cycle, energy efficiency up to 72% at 60 mA/cm², and a power density up to 120 mW/cm². Particularly, the presentation emphasizes that fundamental understandings of redox active electrolytes at molecular level are crucial to develop new generations of redox flow batteries

for large scale and dispatchable renewable energy storage.

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11:30 AM ET10.02.03

Aqueous Soluble Organic Diquats for Redox Flow Batteries Xiaoliang Wei¹, Jinhua Huang^{2,3}, Zheng Yang^{4,3}, Ilya A. Shkrob^{2,3} and Zhengcheng Zhang^{2,3}; ¹Indiana University-Purdue University, Indianapolis, Indiana, United States; ²Argonne National Laboratory, Argonne, Illinois, United States; ³Joint Center for Energy Storage Research, Argonne, Illinois, United States; ⁴Pacific Northwest National Laboratory, Richland, Washington, United States.

Redox flow battery is considered as a powerful technology for grid-scale energy storage because of the excellent scalability and design flexibility to meet the requirements for diverse grid applications. Inorganic-based flow batteries are the state-of-the-arts, but generally suffer from limited energy density and high chemical costs. Instead, redox-active organic compounds have demonstrated encouraging physico-chemical properties and electrochemical performance as attractive alternative materials for flow batteries, suggesting a promising avenue for developing next-generation flow batteries. Despite the current progress of organic flow battery materials, further improvements in energy density and cycle life are still urgently needed to demonstrate their potential for practical grid applications.

In this contribution, we will introduce the newly developed organic diquat herbicide materials for aqueous organic flow batteries. A series of diquat derivatives were designed and evaluated in flow cells to investigate the structural effects on the flow battery-relevant properties including solubility, redox potential, and chemical stability. A combination of electrochemical analysis, density functional theory (DFT) simulations and electron paramagnetic resonance (EPR) studies were performed to reveal important structure-property-activity insights to the diquat family, which also suggests further developmental needs for performance improvement. The diquat-based flow cell was capable of long cycling with low capacity fading.

11:45 AM ET10.02.04

Elucidating the Molecular Degradation Mechanism in Alkaline Quinone Flow Battery Liuchuan Tong, Marc-Antoni Goulet, Daniel A. Pollack, Daniel Tabor, Alan Aspuru-Guzik, Michael J. Aziz and Roy G. Gordon; Harvard University, Cambridge, Massachusetts, United States.

Among the technologies available for large-scale storage of electrical energy, flow batteries have recently gained considerable interest. They are suitable for longer- duration storage because their energy capacity and power ratings are decoupled. With the aim of minimizing storage costs, researchers have designed electrolytes with synthetic redox-active organic molecules made from inexpensive and earth abundant materials. Quinones in alkaline solution have proved to be promising candidates. Various quinone derivatives have been reported with different substituents. One key criteria of evaluating the performance of a quinone flow battery system is the stability of the quinone molecules, which is an important factor of overall battery calendar life. Therefore, it is essential to understand any mechanisms for molecular degradation in these systems.

Using 2,6-dihydroxyanthraquinone (DHAQ) as the model system, we here present an analysis of the chemical stability and decomposition mechanism of this quinone in alkaline solution during cycling. High resolution LC-MS and advanced NMR techniques were used in elucidating the degradation pathway of DHAQ. This degradation pathway is independent of substituent groups on the anthraquinone, but the rate can depend on the substituent groups. We draw important implications for the rational design of more stable quinone molecules for alkaline flow battery systems.

SESSION ET10.03: Organic Aqueous II

Session Chairs: Tianbiao Liu, Susan Odom, Ulrich Schubert and Shohji Tsushima
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 309

1:30 PM *ET10.03.01

Redox Flow Batteries in ARPA-E Portfolio—Status and Trends Grigori Soloveichik; ARPA-E, Washington, District of Columbia, United States.

Development of redox flow batteries (RFBs) for fast growing grid-scale energy storage is supported in part by the Advanced Research Projects Agency (ARPA-E), which funds high risk, high reward transformational research to reduce energy related emissions, reduce imports of energy from foreign sources, improve energy efficiency across all economic sectors, and ensure US technological lead in advanced energy technologies.

Redox flow batteries are attractive for grid energy storage, because the amount of stored energy can be scaled up or down for rated power depending on the customer's need and also potentially low cost. The cost reduction, which is the major driver in current RFB development, can be achieved by increasing power density (decreasing the stack cost) and using inexpensive active materials and electrolytes (decreasing energy cost). The former approach was funded via GRIDS program and led to development of high power cells based on traditional vanadium chemistry and their transfer to a commercial product. The latter approach was funded via OPEN projects and focused on low cost materials for aqueous RFBs. All-iron RFB uses one of the cheapest and most abundant active materials. However, the cell chemistry includes iron electroplating accompanied by hydrogen evolution side reaction. It required the development of cell rebalancing techniques, which were successfully demonstrated. Iron electroplating was realized on stationary (hybrid RFB) and movable (true RFB) electrodes. Another group of potentially inexpensive active materials is redox active, water soluble organic compounds. Redox potential and solubility of such compounds can be tuned by targeted substitution to increase RFB energy density. Trade-off between these parameters and the active materials cost and membrane crossover will be discussed.

Development of novel ion-selective membranes for RFBs is also being funded via IONICS program. Future ARPA-E program targeting the long duration energy storage will be also discussed.

2:00 PM ET10.03.02

Enhanced Stability of Flow Batteries Using Complexing Agents and Additives Y. Shirley Meng^{1,2}; ¹University of California, San Diego, La Jolla, California, United States; ²Sustainable Power and Energy Center (SPEC), La Jolla, California, United States.

A redox flow battery (RFB) can store large amounts of energy with relatively high efficiency and low cost. We have shown in the past that membrane-less lead flow batteries can operate with ultra long cycle life, enabled by simple additives. Recently, we reported that riboflavin derivatives, such as alloxazine and the sodium salt of flavin mononucleotide (FMN), can be relatively stable active materials for RFBs. Side reactions, such as the base-catalyzed hydrolysis and dimerization of flavins, however, are problematic. I will discuss on a few effective ways to maintain a highly stable FMN-based RFB enabled by the use of complexing agents. While the cycling performance at high efficiency could be further improved, other challenges regarding redox flow batteries will be discussed.

2:15 PM ET10.03.03

Towards Affordable Redox-Targeting Based Flow Battery—From Lithium to Sodium and Beyond Mingyue Zhou¹, Juezhong Yu¹, Yan Chen¹, Yong-Sheng Hu² and Qing Wang¹; ¹Department of Material Science & Engineering, National University of Singapore, Singapore, Singapore; ² Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Considering the great system scalability and operation flexibility, redox flow batteries create their own niche for the large-scale energy storage application. Unlike other rivals like lithium ion and lead-acid batteries, the redox flow battery stores energy in flowable liquid electrolytes other than in immobile solid electrode materials. One of the main obstacles of conventional redox flow batteries is the low energy density (<40 Wh/L) as a result of the limited solubility of redox species in electrolytes, which adds onto system footprint and capital cost.¹ To exploit the high energy density of lithium ion battery in flow systems, various redox-targeting based flow batteries have been developed recently.² The energy density of those systems is no longer associated with the concentration of redox molecules but the amount of solid materials stored in the tanks. Thus, by increasing the loading of solid energy storage materials in the tanks, a markedly increased energy density can be achieved without sacrificing the merits of the flow battery. However, most reported redox-targeting reactions resort to multiple redox mediators and rely on lithium ion as the charge balancing and host ion. The potential mismatch of the multi-mediator system would result in undesirable complexity and low voltage efficiency. In addition, the scarcity of lithium relative to other elements may one day be a barrier for large-scale applications. Here, with the single molecule redox targeting reaction³, a sodium ion-based redox flow battery with high energy density (up to 259 Wh/L) is developed to address the above issues. With a NASICON-type (Na₃V₂(PO₄)₃) both as the anodic and cathodic energy storage materials, an all-organic redox targeting system is demonstrated. In addition, to further reduce the system cost and improve the power capability, aqueous flow systems using open-framework materials are explored for practical applications. In light of operando spectroscopic measurements, the factors dictating the operation of the system at high power are unambiguously disclosed and investigated.

Reference:

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2:30 PM BREAK

3:00 PM *ET10.03.04

Recent Progress in Organic-Based Aqueous Flow Batteries Michael J. Aziz; Harvard School of Engineering and Applied Sciences, Cambridge, Massachusetts, United States.

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. Wide-scale utilization of flow batteries is limited by the cost of redox-active metals such as vanadium or precious metal electrocatalysts. We have developed high performance flow batteries based on the aqueous redox behavior of small organic and organometallic molecules, e.g. [1-8]. These redox active materials can be very inexpensive and exhibit rapid redox kinetics and high solubilities, potentially enabling massive electrical energy storage at greatly reduced cost. We have developed new protocols for measuring capacity fade rates and have discovered that the capacity fade rate is determined by the molecular calendar life, which can depend on state of charge, but is independent of the number of charge-discharge cycles imposed [7]. We will report the performance of the very few chemistries with long enough calendar life for practical application in stationary storage.

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3:30 PM ET10.03.05

Aqueous Redox Flow Battery with Novel Organic Electrolyte Alojika Mukhopadhyay, Jonathan Hamel and Hongli Zhu; Northeastern University, Boston, Massachusetts, United States.

Renewable energy sources such as wind and solar can supply a significant amount of electrical energy in the United States and all over the world. However, only a very efficient and consistent energy storage system can fully utilize the potential of the renewable energy sources because of their sporadic nature. Another critical aspect of electrical power storage is to reduce the power surges and balance overload to improve the robustness and efficacy of the grid. The discharge time at peak power is too short for solid-electrode batteries to regulate the wind or solar power output fully. In contrast, flow batteries permit more economical long-duration discharge than solid-electrode batteries by using liquid electrolytes stored outside of the battery. Currently, commercialized flow batteries use precious transition metal ions in acidic solution, which impose challenges with cost, abundance, and environmental impacts.

Herein, for the first time, we propose Lignin, the second most abundant nature derived biopolymer surpassed only by cellulose, as an anolyte for the aqueous flow battery. Lignosulfonate, a water-soluble derivative of Lignin, is environmentally benign, non-flammable and very inexpensive as it is the main component in the liquid waste of the chemical pulping and biofuel production process. Lignosulfonate utilizes the redox chemistry of quinone moiety to store energy and undergoes a fast two proton two electron reversible redox reaction. In this work, Lignosulfonate was paired with Br^2/Br^- , and the full flowcell runs efficiently with high power density. Also, the large and complex molecular structure of lignin considerably reduces the electrolytic crossover, which ensures very high capacity retention over several cycles. The promising results obtained from this economical organic-inorganic redox combination could be a breakthrough in grid-scale energy storage.

3:45 PM ET10.03.06

Two Electron Transfer TPA-Based Catholyte by Molecular Engineering for a Zinc Redox Flow Battery Xiaowei Wang¹, Wei Tang² and Kian Ping Loh³; ¹NUS Graduate School of Integrative Science and Engineering, National University of Singapore, Singapore, Singapore; ²Electronic Materials (ELE) Department, Institute of Materials Research and Engineering, A-star, Singapore, Singapore; ³Department of Chemistry, National University of Singapore, Singapore, Singapore.

Redox flow battery (RFB) has been increasingly popular for grid-scale energy storage to meet high power demand due to the high capability and designable power. Nowadays, RFB has moved to the milestone of aqueous systems based on organic redox-active materials, in order to achieve sustainability (organic compounds), safety (aqueous electrolyte) and high energy density (redox with more electron transfer). However, mostly organic molecules are insoluble in water and their redox are irreversible in water. Therefore, apart from water solubility, it is important to engineer organic species with stable redox in aqueous ambience by decoding the mechanism that attributes to redox instability. Triphenylamine (TPA) readily undergoes anodic oxidation to form TPA radical cation whose stability depends markedly on para-substitution due to radical transfer from N atom to C atom, leading to a dimerization in non-aqueous phase and radical quenching in aqueous system. Herein, we found that para-substitution by methoxy groups generates 4, 4', 4''-trimethoxytriphenylamine (S3), which exhibits a reversible redox couple of 0.5/0.45 V (vs Ag/AgCl) with one-electron transfer in aqueous system. Moreover, an extremely rapid and reversible two-electron transfer system 4, 4', 4''-trihydroxytriphenylamine (P3) was also prepared with redox potential at 0.46/0.42 V and 0.35/0.31 V (vs Ag/AgCl), boasting a high kinetic rate constant of $1.1 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$. The enol/keto redox couple of P3 exhibits fast and reversible kinetics as catholyte when paired with zinc negative electrode in aqueous RFB, yielding a high working voltage of 1.3 V with good cycling behaviour. This work aims to transform irreversible redox-active organic molecules into reversible ones by molecular engineering to broaden more possibility of redox-active materials for organic aqueous redox flow battery.

4:00 PM ET10.03.07

Benzothiadiazoles—Energy-Rich Anolyte Materials for Non-Aqueous Redox Flow Batteries Jingjing Zhang¹, Jinhua Huang¹, Lily A. Robertson², Rajeev S. Assary¹, Ilya A. Shkrob¹ and Lu Zhang¹; ¹Argonne National Laboratory, Lemont, Illinois, United States; ²University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Redox flow batteries (RFBs) are among the most promising electrochemical storage technologies for grid electricity. Aqueous systems, which are currently making significant inroads into the commercial market, often display compromised cell voltages in typical aqueous solutions. Non-aqueous RFBs (NRFBs) enable a wider electrochemical window than the aqueous counterparts, but require high stability of redox-active organic materials (ROMs) in solution when charged. This is truly a difficult requirement to meet since charged ROMs exist as radical ions in solution. 2,1,3-Benzothiadiazoles (BzNSNs) that combine low redox potentials, high electrochemical stability, and excellent chemical accessibility are an exceptional class of anolyte materials for NRFBs. Systematic investigations were conducted to elucidate the substitution effects on key properties including redox potentials, and stability of corresponding radical anions, and solubility. In terms of cyclability in RFBs, parasitic reactions that involve the sulfur loss and the oligomer formations were shown to restrict the long-term stability of these radical anions, yet the BzNSN molecules are among the leading energy-dense ROMs in performance found to-day.

4:15 PM ET10.03.08

Electrodes Modified with Redox Mediators for Improved Charge Transfer in Redox Flow Batteries Robert K. Emmett; Chemical Engineering, Clemson University, Clemson, South Carolina, United States.

Electrochemical performance of Iron RFBs was improved through incorporating iron redox mediators into the electrodes. Iron nanoparticles in the electrode create "hotspots" for faradaic charge transfer that reduces losses associated with kinetical, ohmic, and mass transfer resistances. Carbon nanotube electrodes are activated using cyclic voltammetry to initiate interactions between redox electrolytes and iron nanoparticles in the electrode. Modified electrodes experienced 152% increase in power density and a 50% increase in energy density in coin cell configurations. Economic value and ready availability of iron paired with enhanced performance makes iron RFBs a viable option for future RFB research. The highest peak power density reported for all-iron RFBs to the author's awareness was accomplished at 178 mW cm^{-2} with iron-modified electrodes.

SESSION ET10.04: Electrode
Session Chairs: Xianfeng Li and Shohji Tsushima
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 309

8:00 AM *ET10.04.01

Designing and Fabricating Engineered Electrodes and Flow Fields in Redox Flow Batteries Shohji Tsushima¹, Takahiro Suzuki¹, Hidetoshi Matsumoto², Kentaro Yaji¹, Shintaro Yamasaki¹ and Kikuo Fujita¹; ¹Osaka University, Suita, Japan; ²Tokyo Institute of Technology, Tokyo, Japan.

For further implementation of redox flow batteries for large scale electrical energy storage, high current density operation with less overpotentials is of

great importance, leading to reduction of the system cost. In this talk, we will discuss minimizing energy loss by designing and fabricating porous electrodes and flow fields. We will present an approach to explore optimal material properties of carbon fiber electrodes, e.g. porosity, fiber diameter, thickness, etc. 2D or 3D cell simulations indicate renewed material properties to be fabricated to achieve high performance redox flow batteries [1,2]. We will show our recent progress on engineered porous electrodes fabricated for reduced fiber diameter and surface modification with emphasis on characterization of electrode, i.e. reaction kinetics and transport properties [3,4]. We also present an optimization of flow fields in redox flow batteries. We will discuss a potential of topology optimization for designing flow fields to achieve better cell performance with less pressure drop [5].

[1] S. Tsushima, F. Kondo, S. Sasaki, S. Hirai, Efficient Utilization of the Electrodes in a Redox Flow Battery by Modifying Flow Field and Electrode Morphology, Proceedings of the 15th International Heat Transfer Conference, IHTC-15

[2] S. Tsushima, T. Suzuki, A Numerical Study on Optimization of Fibrous Carbon Electrodes for Vanadium Redox Flow Batteries with Interdigitated Flow Fields, Proceedings of the 16th International Heat Transfer Conference, IHTC-16

[3] S. Tsushima, K. Yamamoto, T. Suzuki, Investigation of Electrode Losses in All-Vanadium Redox Flow Batteries with an Interdigitated Flow Field, 232th meeting of Electrochemical Society, 2017, abs.6.

[4] Patcharawat Charoen-amornkitt, Takahiro Suzuki, Shohji Tsushima, Ohmic resistance and constant phase element effects on cyclic voltammograms using a combined model of mass transport and equivalent circuits, *Electrochimica Acta*, Vol.258, 2017, 433-441.

[5] K. Yaji, S. Yamasaki, S. Tsushima, T. Suzuki, K. Fujita, Topology optimization for the design of flow fields in a redox flow battery, *Structural and Multidisciplinary Optimization*, 2017, 1-12.

8:30 AM ET10.04.02

Unveiling the Redox Reaction Between Vanadium Electrolyte and Electrode via Electrochemical Analysis and Computational Method Chanyong Choi, Hyungjun Noh, Soohyun Kim, Riyul Kim, Juhuyuk Lee, Jiyun Heo and Hee-Tak Kim; KAIST, Daejeon, Korea (the Republic of).

To enhance the performance of vanadium redox flow batteries (VRFB) and design the durable electrode, it is quite important to understand the redox reaction mechanism of vanadium electrolyte exactly. In spite of its importance, the redox reaction mechanism between vanadium electrolyte and electrode has not fully been unveiled yet.

Here, we report the electrochemical impedance spectroscopy analysis of symmetric positive and negative single cells to understand the mechanism. The symmetric cell analysis allows the individual investigation of the positive and negative redox reaction in a practical single cell structure without any perturbation from crossover and any use of problematic reference electrode. The comparisons of charge transfer resistance (R_{ct}) for heat-treated/untreated carbon felt electrode and positive/negative symmetric cell elucidated the feature of the redox reactions.

In addition, we demonstrated the hydration structure between the vanadium ion and the water molecule by molecular dynamics (MD) simulation, enabling a deeper understanding on the redox mechanism. We believe that the contribution provides an important insight on electrode material design and can motivate further research on study of vanadium electrolyte and redox reaction mechanism.

8:45 AM ET10.04.03

Conductive Polymer Electrodes for Controlled Energy Conversion Processes in Redox Flow Systems Erin L. Ratcliff; University of Arizona, Tucson, Arizona, United States.

Intermittent sunlight necessitates the storage of electricity, ideally in controlled chemical reactions analogous to photosynthesis. Many efforts have focused on the oxidation of water at metal oxide semiconductor surfaces, although light-driven electrochemical reactions at photoelectrodes continue to suffer from sluggish half reactions. Alternatively, redox couples such as ferrocene and quinones used in redox flow systems offer more control over electrochemical kinetics through synthesis, with rates of electron transfer being several orders of magnitude larger than water splitting for improved storage capacity. This talk will focus on alternative electrodes for charge transfer to anolytes and catholytes in redox flow systems. The ideal electrode material should be low cost, compatible with industrial printing methods, and most critically, have predictable kinetics to maximize energy conversion processes in the context of convection and diffusion processes found in redox flow systems. The challenge with inorganic semiconductors continues to be the ability to control interfacial mid-gap states that undergo band bending when interfaced with the electrolyte. Conductive polymer electrodes offer the possibility to control redox properties through synthesis and processing, if critical structure-property relationships are understood. Importantly, these semiconductors demonstrate a hybrid electronic-ionic conduction mechanism, and thus, have unique electrochemical behaviors relative to classical inorganic semiconductor electrodes. This talk will provide new insights into the mechanism of charge transfer at conductive polymer/liquid interfaces. A mathematical framework will be demonstrated using a modified Marcus-Gerischer model that enables prediction of rate constants from simple film properties. Experimental evaluation of potential-dependent rate constants will be demonstrated. Results will be contextualized in electrochemical devices, with consideration to transport and nanoscale phenomena.

9:00 AM ET10.04.04

Biomass-Derived Electrodes for Vanadium Redox Flow Batteries Charles Tai-Chieh Wan¹, Diego López Barreiro², Antoni Forner-Cuenca¹, Jack-William Barotta², Francisco J. Martin-Martinez², Fikile Brushett¹ and Markus Buehler²; ¹Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Redox flow batteries (RFBs) offer a promising pathway towards the goal of widespread, commercially viable energy storage capable of meeting increasing energy demands, seamlessly integrating renewable energy sources into the electric grid, and improving overall grid reliability and resilience. A critical shortcoming of the state-of-the-art all-vanadium redox flow battery (VRFB) that must be addressed is the inherently sluggish kinetics of involved vanadium redox couples, which significantly reduces cell efficiency. This has spurred research and development of novel electrode materials that outperform current materials, achieved by surface treatments or other means^[1]. In addition to superior electrochemical performance, it is desirable that these surface-modified materials can be produced using low-cost methods that are both environmentally-friendly and sustainable.

In this work, we demonstrate that biomass can be used to obtain potentially lower-cost, sustainable electrodes that also enhance vanadium kinetics through the introduction of surface functionalities imparted by the choice of biomass precursor. Unlike fossil-derived carbon precursors (i.e. polyacrylonitrile), the biochemical constituents of biomass (e.g., proteins, carbohydrates, lipids) enable the manufacturing of electrodes with chemical functionalities that are uncommon in current generation carbon electrodes, while using a low-value, renewable carbon source. Activated carbon (AC) with a hierarchical porosity and high surface area is produced by first stabilizing the biomass via hydrothermal processing at 200-300 °C for 6 h to obtain hydrochar, which is subsequently converted into AC by thermal activation at 850 °C in an inert environment. Evaluation of the electrochemical properties via ex-situ cyclic voltammetry and impedance spectroscopy of the biomass-derived activated carbons compared to carbon black (Vulcan XC-72) reveals that the ACs are not only conductive and electrochemically active, but also are, in some cases, more active than carbon black. Furthermore, XPS (and other compositional characterization techniques) suggest that increasing N-containing content reduces charge-transfer resistance and improves activity. The revealed correlation between electrode elemental composition and function will aid in the design of next-generation electrode materials.

[1] Kim, K. J., Park, M. S., Kim, Y. J., Kim, J. H., Dou, S. X., & Skyllas-Kazacos, M. (2015). A technology review of electrodes and reaction mechanisms in vanadium redox flow batteries. *Journal of Materials Chemistry A*, 3(33), 16913-16933.

9:15 AM ET10.04.05

Functional Construction of the Carbon Fiber Electrode Used in the Vanadium Flow Battery Xinzhuan Fan, Haoran Jiang, Jing Sun and Tianshou Zhao; Department of Mechanical and Aerospace Engineering, HKUST Energy Institute, Hong Kong, Hong Kong.

Vanadium flow battery (VFB) is a liquid energy storage battery based on $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ pairs, whose energy is stored in the electrolyte. Compared with other energy storage technologies, VFB has lots of outstanding advantages such as the long cycle life, large scale, high safety and reliability. So VFB has become one of the preferred technologies for scale energy storage.

VFB is composed of the bipolar plate, electrode, separator and electrolyte. As the place where electrode reactions occur in VFB, the electrode is one of the key materials that determines the battery performance and cycle life. In general, The electrode portion near the membrane side often refers to “catalyst layer”, which requires high electrochemical activity and good mass transfer property. While the electrode portion near the bi-polar plate side often names as “conductive layer”, which not only needs good conductivity, but also a large contact area to reduce the contact resistance between the electrode and bipolar plate. The function of the electrodes in different regions is different, so it is unreasonable to use the traditional homogenous electrode directly as the electrode of VFB, which also greatly affects the corresponding battery performance.

In response to this problem, we have constructed a functional carbon fiber electrode for VFB. Firstly, the active layer needs an excellent electrochemical activity and preferable pore structure, so we should produced electrospun fibers with smaller fiber density and fiber diameters between 1 and 4 μm . The smaller density and larger diameter determine that the electrode has a good electrolyte transmission channel; then the electrospun fibers are pre-oxidized and carbonized to ensure that the electrode has rich oxygen-containing groups, and these oxygen-containing groups can not only ensure the hydrophilicity of electrode, but also provide good electrocatalytic activity. Secondly, the conductive layer needs excellent conductivity and large contact area, so we made electrospun fibers with larger densities and smaller diameters between 200-800 nm. The larger density and smaller diameter determine the electrode has a larger contact area; then the electrospun fibers are graphitized to ensure a higher conductivity. Finally, the conductive layer and the catalytic layer are stacked together as a functional composite electrode, and it could be used as a freestanding electrode of VFB.

The functional carbon fiber electrode for VFB constructed by the above method not only solves the contradiction between the electrode activity and conductivity of the conventional electrode, but also effectively improves the mass transfer process of electrode, and greatly reduces the contact resistance between the electrode and bipolar plate.

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. T23-601/17-R).

9:30 AM BREAK

SESSION ET10.05: Materials and System I

Session Chair: Wei Wang

Tuesday Morning, November 27, 2018

Hynes, Level 3, Room 309

10:00 AM *ET10.05.01

Balancing Cost and Value of Energy Storage with New Technology and Novel Applications Imre Gyuk¹ and Vincent L. Sprenkle²; ¹U.S. Department of Energy, Washington, District of Columbia, United States; ²Pacific Northwest National Laboratory, Richland, Washington, United States.

With the increasing penetration of variable renewable generation, energy storage is now becoming one of the hottest topics in the utility industry. The commercial success of energy storage applications will depend on aligning the cost of a project with the benefits of the technology. Research on materials and devices has increased cost effectiveness, cycle life and safety of these systems. Besides Li-ion batteries, flywheels, flow batteries, and advanced lead-carbon batteries are being deployed. The presentation will discuss research on flow batteries as an example of consistent, device driven reduction in cost. Markets are now gradually taking shape as changes in the regulatory framework result in more equitable valuation of storage benefits. The presentation will discuss diverse monetized and unmonetized benefit streams, using multi-megawatt applications of a variety of energy storage technologies and highlight outcomes and objectives of DOE supported energy storage deployments in California, Massachusetts, Washington, Oregon, and Vermont. As major players begin deploying more storage projects, operators are recognizing their value for ancillary services. In particular, smoothing and ramping of wind and solar PV are being addressed. Emergency preparedness through storage microgrids is another important development. There are now over 1700 storage projects close to 20GW capacity listed in the Global Energy Storage Data Base, but with the continuation of the California mandate for 1.3MW of storage and new emphasis in other states, we can expect an exciting upsurge in storage research and many new projects to be realized.

10:30 AM *ET10.05.02

Phenazine-Based Anolyte Materials for Redox Flow Batteries Aaron Hollas, Bin Li, Zimin Nie, Vijayakumar Murugesan, David M. Reed, Wei Wang and Vincent L. Sprenkle; Pacific Northwest National Laboratory, Richland, Washington, United States.

Grid-scale battery storage devices have garnered increased attention for their ability to balance the intermittency of ever-expanding renewable energy deployment and to mediate periods of peak power demand. The redox flow battery has emerged as a viable alternative to traditional solid state batteries. With decoupled electrode and electrolyte storage vessels, the redox flow battery offers design flexibility where capacity and power may be independently tuned. The current state-of-the-art flow battery systems utilize vanadium-based electrolytes, however, the high cost of vanadium has hindered wide-scale deployment.¹ The use of organic molecules as electrolyte materials has emerged as a potentially lower cost alternative.^{2,3} Presented will be our recent efforts in developing aqueous-soluble phenazine derivatives as anolyte materials for redox flow batteries. The phenazine core structure has undergone rational design to affect solubility and redox potential via the introduction of varying substituents on the parent molecule. Promising candidates have been incorporated into a full flow cell and undergone flow cell optimization. An exemplary candidate, when coupled with the benchmark ferri/ferrocyanide catholyte, delivers an OCV of 1.35 V at 50% SOC and achieves stable cycling over extended periods. **References:** 1. Zhang, M.; Moore, M.; Watson, J.S.; Zawodzinski, T.A.; Counce, R.M. *J. Electrochem. Soc.* **2012**, *159*, A1183. 2. Park, M.; Ryu, J.; Wang, W.; Cho, J. *Nat. Rev. Mater.* **2016**, *2*, 16080. 3. Soloveichik, G.L. *Chem. Rev.* **2015**, *115*, 11533.

11:00 AM *ET10.05.03

Slurry Electrodes for Electrochemical Devices Robert F. Savinell, Xinyou Ke, Nathaniel Hoyt, Joseph Murphy, Nicholas F. Sinclair, Mirko Antloga and Jesse Wainright; Case Western Reserve University, Cleveland, Ohio, United States.

Slurry electrodes have many advantages in electrochemical devices and systems. They can be used to de-couple power and energy in energy storage, such as with flow capacitors and with flow batteries involving deposition reactions. Examples are an iron flow battery with a slurry electrode and flow electrochemical capacitors. Slurry electrodes also have high active surface area for enhancing interfacial mass transfer and reaction kinetics making them applicable for recovering metals from dilute streams, for chemical synthesis, and for other electrochemical processes. Slurry electrodes can also be used as sacrificial electrodes and for mechanical regeneration of electrode materials.

In this presentation, we will describe appropriate porous electrode theory and boundary conditions to estimate overpotential and current distribution within the slurry electrode, and describe predictions of electrode materials utilization, and electrode performance. The analysis will demonstrate the importance of physical and electrical properties of a slurry electrode to performance, and will explore effects of cell dimensions and flow operating conditions, such as flow rate. The presentation will address models of the effective electronic conductivity of a slurry electrode, and discuss our perspective about the mechanisms of electronic conductivity. Finally, we will discuss some of the practical problems we have encountered in scaling-up a slurry iron flow battery such as flow blockages caused by slurry solidification, and describe means found to mitigate, or at least reduce the effects of these problems.

Acknowledgments

This work is partial supported by the all iron flow battery project (DE-AR0000352) funded from ARPA-E program of Department of Energy (DOE) of the United States.

Related Publications

T. Petek, et al, *J. Power Sources*, 2015, 294, 620.
T. Petek, et al, *J. Electrochem. Soc.* 2016, 163A5001
N. Hoyt et al., *J. Electrochem. Soc.* 2015, 162, A652.
N. Hoyt et al., *J. Electrochem. Soc.* 2015, 162, A1102.
N. Hoyt et al., *Chemical Engineering Science* 288.

11:30 AM *ET10.05.04

Extracting Ideal Component Properties from Data for Various Flow Battery Types Thomas A. Zawodzinski^{1,2}, Gabriel Goenaga¹, Reed Wittman^{1,2} and Jagjit Nanda²; ¹University of Tennessee, Knoxville, Tennessee, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

A general path to high performance flow batteries can be defined in terms of properties of cell components. Unfortunately, this path requires many trade-offs in the real world. Furthermore, it is likely to be different for different flow battery types. In this contribution, we will provide some comparative discussion of the material properties of electrolytes, electrodes and other components of various types of redox flow batteries including aqueous systems such as all-vanadium RFBs, non-aqueous RFBs and RFBs in which metallic phases are used. Trade-offs in the needed properties will be considered for situations demanding high power density or current density vs. high energy efficiency and high efficiency vs. an operating mode that allows for occasional deviations from high efficiency operation. Our analysis will not take the form of a set of idealized calculations (though some will be included) but will instead consider the actual behavior of operating cells and how various components affect this behavior for the classes of materials mentioned.

Acknowledgements

We would like to gratefully acknowledge the current support of this work by the U.S. Department of Energy, Office of Electricity Delivery and Energy Reliability (Dr. Imre Gyuk).

SESSION ET10.06: Materials and System II
Session Chairs: Aaron Hollas, Vijayakumar Murugesan, Jagjit Nanda and Mike Perry
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 309

1:30 PM *ET10.06.01

New Materials to Accelerate the Commercialization of Redox Flow Batteries Mike L. Perry; UTRC, Glastonbury, Connecticut, United States.

A Redox Flow Battery (RFB) possesses several key advantages that make this technology potentially well suited for large-scale energy-storage applications. This is especially true of applications that require high energy-to-power requirements (*i.e.*, multiple-hour discharge times at rated power) since the energy capacity can be increased by simply adding reactant solution without necessarily requiring (or negatively impacting) the power-delivery components. Despite this inherent scaling-factor advantage relative to conventional battery systems, the initial capital cost of flow batteries has been the major barrier to commercialization of RFB technology. Capital-cost targets for grid-scale energy storage are challenging; battery systems for major grid-scale applications must cost less on a normalized basis (*i.e.*, \$/kWh) than those currently used for portable or transportation applications. One attractive path to cost reduction is the development of RFB cells with substantially higher power densities than conventional RFB cells, which UTRC has developed and demonstrated in complete all-vanadium RFB Systems, including 0.5-MW/3-MWh systems built by Vionx Energy. The focus of this talk will be on new materials that can potentially enable additional RFB-system cost reductions while maintaining the high performance levels required to be commercially-viable. This includes both advanced cell materials (*e.g.*, electrodes, separators/membranes) that can further improve the performance RFB cells, as well advanced RFB active materials. A brief review of the state-of-the-art of each these major RFB components, along with future targets, will be presented. Some of the latest results developed by UTRC and our partners as part of an ongoing ARPA-E *IONICS* Program project will also be included. The major goal of this presentation is to help material developers identify potential opportunities to substantially improve RFB technology.

Acknowledgements

The author would like to thank his many flow-battery development colleagues at both UTRC and Vionx Energy. Portions of the work described here was supported by the U.S. Department of Energy (DOE), which includes these projects: ARPA-E's *GRIDS* Program (DE-AR0000149) and ARPA-E's *IONICS* Program (DE-AR0001478), and the Joint Center for Energy Storage Research (JCESR), Office of Science, Basic Energy Sciences (DE-AC02-

06CH11357).

2:00 PM *ET10.06.02

Flow Batteries—New Designs, Chemistries and Cost Models Yushan Yan; Univ of Delaware, Newark, Delaware, United States.

One of the grand challenges facing humanity today is the development of an alternative energy system that is safe, clean, and sustainable and where combustion of fossil fuels no longer dominates. A distributed renewable electrochemical energy and mobility system (DREEMS) based on cheap renewable electricity could meet this challenge. At the foundation of this new energy system, we have chosen to study a number of electrochemical devices including fuel cells, electrolyzers, and flow batteries. We have been working on the development of hydroxide exchange membrane fuel cells (HEMFCs) and electrolyzers (HEMELs) which can work with nonprecious metal catalysts and inexpensive hydrocarbon polymer membranes. More specifically we have developed roadmaps for HEMFCs and HEMELs, the most chemically stable membranes, and the most active nonprecious metal catalysts. We have also studied why hydrogen oxidation reactions are slower in base than in acid for precious metal catalysts. In this presentation, I will focus on our flow battery work highlighting novel designs, chemistries and cost models e.g., double-membrane aqueous flow batteries with high voltages (i.e., 3 V), single-element-mimic redox pairs, and user-friendly physics-based analytical cost models.

2:30 PM ET10.06.03

Building Electrolyte Design Formulations—From Molecular Asymmetry to Additives Vijayakumar Murugesan, Zimin Nie, Aaron Hollas, Vincent L. Sprenkle and Wei Wang; Pacific Northwest National Laboratory, Richland, Washington, United States.

The performance requirements of redox flow battery (RFB) such as energy density, specific capacity and cycle life, depends on physiochemical properties of the redox active species which are dissolved and externally stored as flowable electrolytes. Designing optimal electrolyte is the critical step in realizing transformational progress in RFB technology. Traditional approach is focused on varying the additives and solvent composition to achieve higher solubility and stability of the specific redox molecule. However, considering the wide range of materials selection associated with this Edisonian process, it is imperative to build a design formulation that will help us bottom up design of RFB electrolytes. In recent years, our team build a framework of electrolyte design formulations based on molecular solvate structure of redox active molecules derived from combined spectroscopic and computational studies. This framework helps us in solvent and additive selection process, and ultimately enhance the solubility and stability of redox molecules through molecular level tuning of their solvate structures. In this presentation, we will discuss the framework of electrolyte design formulations applicable for both transition metal and organic molecule based redox flow battery systems.

2:45 PM ET10.06.04

Non-Covalent Interactions in the Solvation Shell of One-Electron Electron Transfer Reactions Botao Huang¹, Sokseiha Muy¹, Shuting Feng¹, Yu Katayama³, Yi-Chun Lu², Gang Chen¹ and Yang Shao-Horn¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²The Chinese University of Hong Kong, HK, China; ³Yamaguchi University, Yamaguchi, Japan.

Understanding and controlling non-covalent interactions associated with solvent molecules and redox-inactive ions provides new opportunities to enhance the reaction entropy changes and reaction kinetics of metal redox centers, which can increase the thermodynamic efficiency of energy conversion devices such as thermo-electrochemical cells and fuel cells. Here, we report systematic changes in the redox entropy of one-electron transfer reactions including $[\text{Fe}(\text{CN})_6]^{3-/4-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+}$ and $[\text{Ag}(\text{H}_2\text{O})_4]^{+0}$ induced by the addition of redox inactive ions, where approximately twenty different known structure making/breaking ions were employed. The measured reaction entropy changes of these redox couples were found to increase linearly with higher concentration, and greater structural entropy (having greater water breaking tendency) for inactive ions with opposite charge to the redox centers. The trend could be attributed to the altered solvation shells of oxidized and reduced redox active species due to non-covalent interactions among redox centers, inactive ions and water molecules, which was supported by Raman spectroscopy. Not only these non-covalent interactions were shown to increase reaction entropy, which is key to increase the efficiency of thermo-electrochemical cells, but also they were found to systematically alter the redox kinetics, where increasing redox reaction energy changes associated with the presence of water structure breaking cations were correlated linearly with greater exchange current density of $[\text{Fe}(\text{CN})_6]^{3-/4-}$.

3:00 PM BREAK

3:30 PM *ET10.06.05

Electron and Ion Transport in Organic Radical Polymer Batteries Jodie Lutkenhaus; Texas A&M University, College Station, Texas, United States.

Organic radical polymers for batteries represent some of the fastest charging electroactive materials available. Organic radical polymers are electrochemically active owing to the reversible reduction-oxidation (redox) reaction of pendant radical groups and offer a vast synthetic landscape for customization, which can yield theoretical capacities >100 mAh/g. Also, the singly occupied molecular orbitals in the radical groups result in fast electron transfer and consequently rapid charge and discharge (as high as 50 C, where 1 C is the current required to discharge a battery in one hour) and good cycling behavior. Despite these benefits, there remains a poor understanding of the redox mechanism itself, even for the most well-studied organic radical polymer poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl) (PTMA). Here, the nature of electron transport and ion transport is probed to further understand the redox mechanism. Electron transport and charge storage must be accompanied by ion transport and doping for charge neutrality, but the nature of this process in organic radical polymers is not at all understood. This is difficult to intuitively predict because the pendant radical group distinguishes organic radical polymers from conjugated polymers, charged polyelectrolytes or polar polyethylene oxide. Using theory and experiment, it is shown that electrons transport by a hopping mechanism that is facilitated by segmental relaxation of the polymer chain (Sato, K., *et al. Journal of the American Chemical Society* 140 (3), 1049-1056 (2018)). It is also shown for the first time a quantitative view of *in situ* ion transport and doping in organic radical polymers during the redox process (Wang, S., *et al. Submitted*). Two modes of ion transport dominate: ions doping the polymer from internally absorbed electrolyte and ions doping externally from the bulk solution. The nature of doping is controlled by anion type and concentration. These results indicate the importance of electrolyte design specific to organic radical polymers and impact solid state and redox flow battery applications.

4:00 PM *ET10.06.06

Towards Deterministic Electrode Design—Elucidating the Role of Surface Chemistry and Microstructure on Flow Battery Performance Fikile Brushett^{1,2}; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Joint Center for Energy Storage Research, Lemont, Illinois, United States.

Redox flow batteries (RFBs) are promising for energy-intensive grid storage applications, but further improvements are needed for universal adoption [1, 2]. While research efforts have primarily focused on molecular engineering of redox couples as a means of reducing system cost, advances in other critical systems components also hold significant cost reduction potential. Of particular importance are the porous electrodes which are responsible for multiple

critical functions in the flow cell related to thermodynamics, kinetics, and transport including providing surfaces for electrochemical reactions, enabling uniform liquid electrolyte distribution with low hydraulic resistance, as well as conducting electrons and heat. However, there is limited knowledge on how to systematically design and implement these materials in emerging RFB applications, forcing the repurposing of available materials that are not tailored for this electrochemical system. Moreover, current generation materials, which are generally developed via empirical approaches, lack control of surface chemistry (e.g., compositional heterogeneity) and morphology (e.g., broad pore size distribution), which fundamentally limits the performance, durability and consequently the cost of resultant systems. In this talk, I will discuss methods for disambiguating resistive losses in various porous electrodes using model redox couples, diagnostic flow cells, and electrochemical modeling. When applied in combination with spectroscopy and microscopy techniques, structure-performance relations can be elucidated which may eventually lead to design rules that enable the fabrication of chemistry-specific electrodes based solely on the knowledge of the physical and electrochemical properties of the redox active electrolyte.

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4:30 PM ET10.06.07

The Influence of Faradaic Imbalance and Related Cell Corrosion on the Long-Term Performance of All-Vanadium Redox Flow Batteries Mahnaz Nourani¹, Benjamin I. Zackin², Dinesh Sabarirajan², Iryna Zenyuk² and Ertan Agar¹; ¹Department of Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States; ²Department of Mechanical Engineering, Tufts University, Medford, Massachusetts, United States.

Vanadium redox flow batteries (VRFBs) are promising energy storage devices for the integration of renewable energy sources in grid-scale stationary applications, compensating the intermittent nature of renewable energy sources such as, wind and solar. The key advantage of these systems is that power generation and energy storage capacity are decoupled. While the volume of electrolyte and the energy rating can be changed to obtain the required capacity, the size of the cell dictates power rating, providing flexibility and modularity.^{1,2} Despite these benefits, there are problems related to the long-term cycling of these batteries which limit the cycle life and affect the overall performance of the system. One of the main issues associated with the prolonged cycling is faradaic imbalance which is described as the shift of the average oxidation state of the battery from the ideal case of $V^{3.5+}$. Faradaic imbalance happens as a result of irreversible side reactions (e.g., hydrogen evolution). The side reactions seen in VRFB operation often cause a positive shift to the average oxidation state of the electrolyte, which results in the equilibrium potential of the positive half-cell to increase. This potential shift increases the possibility of exceeding the critical polarization potential at the positive half-cell, consequently leading to CO and CO₂ evolution, and related electrode/bipolar plate corrosion.^{3,4} Despite their importance, the issues of faradaic imbalance and corrosion of electrode/bipolar plate have not been widely recognized in the community. These issues not only restrict the performance of the battery; but also can lead to a significant damage to the flow battery system.

This study investigates the effects of faradaic imbalance and related electrode corrosion on the overall performance of a VRFB by conducting two experimental case studies: one with prepared imbalanced electrolytes with different imbalance ratios, and the other one with corroded positive electrode, prepared through an accelerated electrochemical corrosion process. We will separately demonstrate the performance characteristics of the flow battery for both mentioned cases, using various electrochemical characterization techniques such as charge-discharge cycling, polarization curve, and EIS measurements. Additionally, the correlation between the material characteristics of the cell components and the system performance will be discussed.

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4:45 PM ET10.06.08

Study of the Interactions at the Electrode/Electrolyte Interface in Concentrated Solutions Ilona Acznik¹, Katarzyna Lota¹, Agnieszka Sierczynska¹ and Krzysztof Fic²; ¹Institute of Non-Ferrous Metals Division in Poznan, Poznan, Poland; ²Poznan University of Technology, Poznan, Poland.

Development of electrochemical capacitors focuses today on the improvement of their energy density (or specific energy) and cyclability. The energy density might be improved by capacitance enhancement and operating voltage increase. To some extent, the relation between capacitance and voltage and their impact on the energy output reflects an interfacial character of charge storage mechanisms in capacitors; capacitance is intimately linked with the electrode material whereas the operating voltage is governed by the electrolyte applied. Of course, they cannot be considered separately, since the final performance is always a combination of various factors (e.g., electrode porosity – electrolyte viscosity, wettability, etc.). The electrolyte-related issues create an interesting pathway for investigations aiming at maximum voltage increase and energy density enhancement. Undoubtedly, organic media (based on acetonitrile or propylene carbonate) and ionic liquids are the optimal electrolytic solutions in terms of electrochemical stability. However, their impact on the environment and user safety is quite often questioned. Water-based electrolytes seem to be an interesting alternative, but the major objection against their commercialization concerns their low electrochemical stability governed by water decomposition voltage. Although the neutral electrolytes might demonstrate a significant decomposition overpotential once applied to porous carbon electrodes and thus provide the operating voltage up to 1.8 V, the performance of water-based capacitors is still not satisfactory enough for a broad application.

Since the significant disadvantage of water-based solutions is attributed to the solvent decomposition, in our recent study, we decided to decrease the amount of water in aqueous electrolytes to the minimal level. Since the primary study has been done on LiTFSI salt, in our study, we have focused on the conventional inorganic salts, based on the well-known anions like NO₃⁻ or SO₄²⁻.

The paper will discuss the correlation between the pore size distribution of carbon electrodes, electrolyte viscosity, and capacitor performance. Elucidation of the energy/power characteristics as well as cyclability at various temperatures will give a novel insight into 'water'-based electrolytes.

ET10.07.01

Synthesis of Mesoporous β -Ni(OH)₂ Modified CdS Nano-Heterojunction Networks Showing High Visible-Light Photocatalytic H₂ Production Activity Ioannis Vamvasakis and Gerasimos S. Armatas; Materials Science and Technology, University of Crete, Heraklion, Greece.

Over the last years, photocatalytic hydrogen production through water splitting has attracted immense attention as a potential method for low-cost conversion of solar energy into chemical fuels.¹ However, despite tremendous efforts on the development of various semiconductor-type catalysts, key challenges of obtaining catalysts with high activity and long-term stability still remain. Recently, the synthesis of highly crystalline mesoporous semiconductors has been the focus in the field of photo- and electrocatalysis.² These materials combine the high reactivity of semiconductor nanocrystals (NCs) with mesoporous structure, offering new perspectives in designing novel photocatalysts with improved efficiency and reliability. Unlike to bulk-like microstructures and individual nanoparticles, 3D mesoporous networks of connected NCs can benefit from the large and accessible surface area within the assembled structure and enhanced light-harvesting efficiency arising from multiple scattering of light inside the pores.

Herein, we present the synthesis of 3D mesoporous β -Ni(OH)₂-decorated CdS nanocrystal assemblies (NCAs) and demonstrate their excellent performance for the visible-light photocatalytic H₂ production.^{3,4} XRD, high-resolution TEM, XPS, and N₂ porosimetry characterization results corroborate that the resulting materials consist of a porous network of linked β -Ni(OH)₂ and CdS nanoparticles (ca. 4–5 nm in size) and exhibit large internal surface areas (164–207 m² g⁻¹) and narrow distribution of pore sizes (ca. 6 nm). Catalytic studies along with UV-vis/NIR optical absorption, photoluminescence and electrochemical impedance spectroscopy measurements suggest that the p-type β -Ni(OH)₂ behaves as the oxidation active sites (hole collector), promoting efficient charge transfer and separation across the β -Ni(OH)₂/CdS nano-heterojunctions. Consequently, the Ni-modified CdS NCAs catalyst containing 5 wt % Ni reached an outstanding photocatalytic H₂-evolution rate of 1.4 mmol h⁻¹ with an apparent QY of 72% at 420 nm, while demonstrating good stability for at least 20 h in alkaline (5 M NaOH) ethanol solution (10% v/v). This work not only demonstrates the potential of the present p-n β -Ni(OH)₂/CdS photocatalytic system for sustainable hydrogen production, but also opens up new opportunities for the design and in-depth understanding of noble metal-free photocatalysts for efficient solar-to-chemical energy conversion.

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ET10.07.02

Carbon Nanotube/Carbon Nanofiber Hierarchical Composites with Cobalt-Manganese Layered Double Oxide for High-Performance Flexible Membrane Capacitive Deionization Electrodes Meng Ding, Shaozhan Huang and Hui Ying Yang; Singapore University of Technology and Design, Singapore, Singapore.

In this work, our freestanding carbon nanotube/carbon nanofiber (CNT/CNF) composites are prepared from the electrospun nanofibers. After the electrospinning process, the obtained CNFs were coated with Co-Mn layered double hydroxides (LDHs) as the precursors for CNTs. By pyrolysis, hierarchical CNTs are able to grow on the surface of CNFs. And the LDH precursors were converted to Co-Mn layered double oxides (LDOs). The obtained CNT/CNFs are of benefit from the great electrical conductivity of CNTs and high surface area of CNFs. The Co-Mn LDOs provide good chemical reactivity. The prepared composites exhibited excellent desalination performance in long-term operation. The carbon substrates improve the mechanical strength, good conductivity and cycling stability. The combination of CNT/CNF/LDO composites is a promising method for preparing flexible membrane capacitive deionization electrodes with enhanced desalination performance.

ET10.07.03

Thermochemical CO₂-Splitting at High Conversion Efficiency Using Doped-Ferrites Jimmy Rojas, Shang Zhai, Nadia Ahlborg, Kipil Lim, Arunava Majumdar and William Chueh; Stanford University, Stanford, California, United States.

Two-step thermochemical CO₂ splitting (TCDS) cycle has been long pursued for CO₂ mitigation, but the need for high operating temperature (>1400°C) makes it incompatible with the chemical industry infrastructure. Moreover, low CO₂-to-CO conversion makes such cycles far from economical. We designed and synthesized a new class of doped-ferrites and experimentally demonstrated O₂ evolution at 1300°C followed by 7 mL-CO evolution per gram of ferrite at 700°C with CO₂:CO = 100:1 (balance Ar) in purge gas, indicating high conversion efficiency. The mechanism of oxygen exchange is illustrated through various characterizations: Ex situ x-ray diffraction on quenched samples illustrates the phase transition behavior of doped-ferrites while resonant x-ray diffraction sheds light on cation distribution. Furthermore, Fe is shown to be redox active by ex situ x-ray near edge structure. The high CO₂-to-CO conversion efficiency achieved by innovative doped-ferrites opens new opportunities of thermochemical redox chemistry.

ET10.07.04

Polydopamine-Graphene Oxide Derived 3D Nitrogen Doped Graphene@Ni₂P for Efficient Oxygen Evolution Electrocatalysis Huizhu Xu and Dianxue Cao; Harbin Engineering University, Harbin, China.

The composite catalysts which has large specific surface areas, growing uniform particles and high activity are particular important for oxygen evolution reaction. Here we report a three dimensional(3D), nitrogen doped graphene aerogel with abundant Ni₂P nanoparticles in suit. The approach used dopamine undergoes self-polymerization that can functionalize the graphene surface and produce a large volume of graphene hydrogel (PDA/rGO). The PDA/rGO is immersed in an aqueous solution of nickel acetate, which adsorbs nickel ions. The nitrogen doped graphene aerogel with Ni₂P (NGA@Ni₂P) is produced by freeze-drying, 1173K carbonization, 623K phosphatization. The NGA@Ni₂P has a low applied external potential of 1.68 V at 10 mA cm⁻² and the Tafel slope of 78 mV dec⁻¹.

Polydopamine has the properties of reducing, adhesiveness and adsorption of metal ions. Introduce polydopamine in graphene, which not only increased the volume of graphene aerogel, added to the favorable nitrogen species, but the abundant hydroxyl and amino groups in polydopamine, allowing metal ions can be uniformly long on the grapheme. In this case, we use polydopamine to adsorb Ni₂P nanoparticles. Ni₂P nanoparticles have metallic quality, so it

has better oxygen evolution performance. The unique 3D structure, high surface areas, favorable nitrogen species and uniformly grown nanoparticles of NGA-Ni₂P have good performance as electrode material for oxygen evolution reaction.

This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.

ET10.07.05

Natural Selection as a Molecular Design Toolkit—Bio-Inspired Flow Battery Active Materials Shyam Pahari¹, Tugba Ceren Gokoglan², Andrew Hamel², Ertan Agar² and Patrick J. Cappillino¹; ¹Chemistry and Biochemistry, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts, United States; ²Mechanical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States.

Modern electrical grids, especially those comprising energy from intermittent, renewable sources such as wind and solar, *require storage*. Non-aqueous redox flow batteries (NRFB) are a promising technology to meet this growing need. They have the potential to greatly exceed the energy density of their aqueous counterparts while maintaining key advantages over Li-ion systems. These advantages include decoupled power and energy ratings, thermal stability, benign chemical nature and the capability of long-duration storage (months or even years).

Despite the promise of NRFB, *fundamental technical obstacles limit their application*:

- active-material instability (low cyclability)
- active-material insolubility (low energy density)
- poor electrochemical performance (low power, low open-circuit voltage)

We will present a bio-inspired approach that addresses each of these problems using a family of molecules that is naturally occurring and produced biologically. These compounds are analogues of Amavadin, which is found in mushrooms of the *Amanita* genus. Biosynthesis of this molecule evolved over countless generations to bind vanadium selectively and with the highest stability ever reported, using a unique tetradentate, bis-carboxylato-η²-hydroxyimino- binding motif. Ligand-substitution is suppressed, shutting down a major mechanism of decomposition. In this way, natural selection serves as a toolkit for molecular design, elucidating a scaffold for optimized NRFB active materials. We will present a suite of electrochemical and spectroelectrochemical data demonstrating that this Amavadin analogue, which we call VBH, is stable even in the presence of water, is oxygen tolerant and that bulk oxidation and reduction is tightly coupled to formation of the vanadium(v) and vanadium(iv) species, respectively.

Further, we will discuss the key thermodynamic factors used to improve VBH solubility and present recent progress, including stable electrolyte solutions with > 1 M active material and > 2 M supporting electrolyte in organic solvent.

Finally, we will present a detailed computational investigation of the effect of covalent modification of VBH on its open-circuit voltage and its chemical stability in all oxidation states, along with progress on the synthesis of these derivatives.

ET10.07.06

A Stable and Long-Lasting Concentration Cell Based on Reduced Graphene Oxide Membrane and Redox Electrolyte Zhe Wang¹, Yi He^{2,3}, Jing Zhang¹ and Lei Wei¹; ¹School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, Singapore; ²National University of Singapore, Singapore, Singapore; ³School of National Defence Science & Technology, Southwest University of Science and Technology, Mianyang, China.

Concentration cell is a promising solution in developing sustainable energy device. Most of the reported concentration cells employed an ion-selective membrane to separate two half-cells with different solution concentration. Thus, the voltage will be generated because of the concentration gradient which follows Nernst equation. However, the concentration gradient is easily decreased due to continuous diffusion, resulting in short lifetime and low output voltage. Although graphene oxide membrane (GOM) has been developed for providing the two-dimensional confinement of electrolytes to reduce the diffusion, the drawback of the reverse electrodiffusion still exists. Moreover, GOM is unstable in water and can easily disintegrate, which further limit its application area in energy conversion. Therefore, we demonstrate a long-lasting concentration cell based on natural source, humic acid (HA), and water-stable reduced graphene oxide (RGO) membrane. This cell develops a new mechanism based on redox electrolyte and reaches a high voltage of 0.21 V for more than 210 h, provides a new solution for long-lasting concentration cell.

GO dispersion with a concentration of 0.9 mg/mL is prepared by modified Hummer's method. 50 mL GO dispersion is transfer into a glass petri dish and then dried under 323 K for 24 h. After that, GO membrane will be formed at the bottom of the dish. Then 10 mL hydriodic acid (HI) is used to reduce the GO membrane to RGO membrane under 373 K for 1 h. Freestanding RGO membrane is obtained by washed with deionized water and dried under 353 K. SEM images show that the thickness of the RGO membrane is ~ 4 micrometer with a layer distance of 0.36 nm. The FTIR spectroscopy of GO film and RGO film illustrate that the oxygen-containing groups are removed after reduction process. To fabricate concentration cell, the RGO membrane is fixed between two plastic tubes. Thus, one side of RGO membrane is exposed to 20 mL HA solution (1 mg/mL), while the other side is exposed to deionized water, forming a concentration gradient. An open circuit voltage of 0.21 V is measured which last for more than 210 h, indicating its long lifetime. After measuring the cell's performance with different electrolytes, including KCl, Na₂C₂O₄, and HA, we find that good performance can only be achieved using HA as the electrolyte, indicating that this cell is based on redox reaction and the RGO membrane has no ion selectivity. At last, the cyclic voltammogram (CV) curves for HA solution is measured. Experimental result shows that HA is oxidized at the anode side while O₂ is reduced to H₂O at the cathode side. Thus, the redox reactions on both electrodes are clarified. This work reveals its promising application prospect in energy conversion area.

ET10.07.07

The Role of Carbon Surface on the Quinone-Based Molecular Electrochemistry for Energy Applications Graziela C. Sedenho^{1,2}, Diana D. Porcellinis², Yan Jing³, Emily Kerr³, Roy G. Gordon^{3,2}, Frank N. Crespilho^{1,2} and Michael J. Aziz²; ¹São Carlos Institute of Chemistry, University of São Paulo (USP), São Carlos, Brazil; ²School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; ³Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, United States.

Growing global energy demand has motivated interest in new technologies for energy conversion and storage, such as aqueous organic redox flow batteries (AORFB). Quinones are promising as redox-active molecules in AORFB. Many of these molecules are composed entirely by Earth-abundant elements and are nontoxic, nonflammable, and safe for use in energy storage systems. The performance of a quinone-based AORFB depends directly on quinone properties such as redox potential, solubility in water and stability. The number of aromatic rings and the positions and types of side groups affect the redox potential and solubility; this opens a new opportunity in molecular engineering. The electrochemical redox kinetics can also be very important, and the electrode surface can play a decisive role in battery performance. Here, we show that the electrochemical kinetics can be significantly affected by the presence of functional groups on quinone-based molecules. We pay special attention to carbon-based electrodes because they are widely employed in flow batteries due to high electron conductivity and low cost. Based on half-cell experiments, we propose that some candidates for active redox molecules may have their electrochemical kinetics improved or worsened according to the degree of crystallinity of the carbon electrode. This is shown for alizarin red S, which shows two redox couples that are dependent on the structure of the carbon electrode material. We also evaluated some benzoquinones, which are

candidates for the positive electrolyte: commercially available BQDS (1,2-dihydroxybenzene-3,5-disulfonic acid), and several newly-synthesized functionalized benzoquinones. We have observed sluggish kinetics with amorphous carbon and glassy-like carbon electrodes for these molecules. In contrast, graphite electrodes with a high density of plane edges on the surface exhibited a nearly reversible redox response. Based on these results, it is possible to propose new carbon electrode materials based on graphitic structures to be used in AORFB.

ET10.07.08

Quaternized poly(arylene ether benzonitrile) Membranes for Vanadium Redox Flow Batteries [Eun Joo Park](#), Sandip Maurya, Yu Seung Kim and Rangachary Mukundan; MPA-11, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Development of membrane separators is important to enhance efficiency and durability of vanadium redox flow batteries (VRFB). Desired properties of the membranes for the VRFB application include (a) selective ion permeability, (b) high conductivity and (c) good chemical and mechanical stability in acidic-oxidative environment. Our approach to satisfy these criteria is synthesizing cation-functionalized nitrile-containing polyaromatics, poly(arylene ether benzonitrile)s, for membrane separators for VRFB.

A series of high molecular weight poly(arylene ether benzonitrile)s with pendant quaternary ammonium groups were synthesized via aromatic nucleophilic substitution polycondensation. The chemical structures of the polymers were characterized by ¹H NMR and FT-IR spectroscopy. The polymers were cast as transparent and flexible membranes, and the ion exchange capacity was varied from 1.8 to 3.1 meq/g. The presence of highly polar nitrile groups incorporated in the polymer chain enhances the dimensional stability of the membranes. The VRFB single cell performance of the quaternized membranes was measured and compared to standard Nafion membranes. In this presentation, the membrane properties and the electrochemical performance of quaternized poly(arylene ether benzonitrile)s in terms of cycling efficiencies, vanadium permeation and membrane durability will be discussed.

Acknowledgement

This work is fully supported by Laboratory Directed Research & Development, Los Alamos National Laboratory.

ET10.07.09

Electrodeposition of Redox Active Layered Double Hydroxides for Energy Applications [Erika Scavetta](#), Isacco Gualandi and Domenica Tonelli; Univ of Bologna, Bologna, Italy.

At present, there is an increasing demand in the development of new highly efficient and low cost catalytic systems in the field of global energy issues. Layered double hydroxides (LDHs) are lamellar compounds whose structure consists of positively charged brucite-like layers with interlayer anions balancing the positive charge. LDHs containing transition metals are redox active and are very promising materials for several applications due to their versatility, tunable properties, wide range of compositions and low cost.

Recently, these compounds are attracting much interest in the area of electrochemistry for applications such as batteries, supercapacitors, sensors, fuel cells and as efficient electrocatalysts for oxygen evolution reaction (OER). For all these applications, the active material must be well adherent to the conductive support, thus guarantying the formation of a mechanically stable coating.

Our group has proposed and optimized an electrochemical approach to coat any kind of conductive supports, of any shape and dimension, with LDH films. The synthesis is based on the electrochemical generation of hydroxides by cathodic reduction of nitrate ions and its optimization was achieved through a detailed study and understanding of the sequence of reactions involved. The features of the deposited LDH (amount, thickness and composition) depend on the applied potential, the length of cathodic pulse and the composition of the electrolytic solution; the adhesion of the coating to the surface can be enhanced through a proper pretreatment of the electrode support (1).

This contribution is aimed to describe the outstanding results obtained by our research group on the performance of LDH films containing Cobalt or Nickel as bivalent cation and Iron and Aluminium as the trivalent one for two important energy applications, i.e. as supercapacitors and as electrocatalysts for OER. In particular our results show that LDHs containing Co as the bivalent metal can be considered good candidate for supercapacitors development, especially when the trivalent metal is Fe: actually for Co/Fe LDH the redox process significantly involves also the inner surface of the LDH, giving a peculiar electrochemical behaviour, where the capacitance has both Faradaic and charge separation origin. This guarantees a wider voltage window than the one displayed by the Al based LDH, making that material even more suitable for supercapacitor development.

As to OER electrocatalysts are concerned the best performances in terms of onset potential, current density at a fixed potential and turnover frequency (TOF) were obtained for iron-based LDHs both containing Ni or Co as the bivalent metal. Our results shows that the presence of iron is crucial to significantly enhance the OER performances of LDHs.

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ET10.07.10

Investigating the Decomposition of Acylpyridinium Salts as Anolytes in a Redox Flow Battery [Anuska Shrestha](#) and Melanie Sanford; University of Michigan, Ann Arbor, Michigan, United States.

Acylpyridinium (AcPy) salts had been identified as promising anolytes for redox flow battery applications. These materials are extremely stable towards bulk electrolysis cycling as well as to cycling in a symmetrical flow cell (with AcPy on both sides of the cell). However, flow cell cycling of AcPy anolytes in combination with cyclopropenium or ferrocenium catholytes results in >50% fade in capacity over 72 h of cycling. A close examination of the solutions after the battery experiment showed that anolyte decomposition in presence of the catholyte is one of the major causes of the capacity fade. ¹H NMR spectroscopic analysis of the spent solutions revealed that the anolyte is degrading into two products. The structures of these products as well as the degradation pathways leading to their formation will be described in detail.

ET10.07.11

Effect of Non-Uniformity of Functionalized Surface on the Two-Dimensional Transition Metal Carbides for the Hydrogen Evolution Reaction [Eun Seob Sim](#) and Yong-Chae Chung; Division of Materials Science and Engineering, Hanyang University, Seoul, Korea (the Republic of).

The MXenes, which are two-dimensional form of MAX phases, have been introduced as a potential candidate for hydrogen evolution reaction (HER) catalyst due to their high surface area and thermostability. Recent studies of MXenes as an HER catalyst have focused on interaction between hydrogen and the uniformly functionalized surface. However, synthesizing MXenes with uniformly functionalized surface is still remained as a main challenge in this field, which induces gap between experimental and theoretical results. In this study, to evaluate the activity of the HER, the adsorption properties of a hydrogen atom on the non-uniformly functionalized surfaces of Ti₂C-based MXene were investigated using density functional theory (DFT). On the surface where fluorine and oxygen functional groups coexist, a hydrogen atom was turned out to be adsorbed on the top of oxygen functional group with slightly larger adsorption energy than the case on the uniformly oxygen functionalized surface. At the vicinity of oxygen vacancy, compared with adsorption energy of a hydrogen atom on the uniformly oxygen functionalized surface, much larger adsorption energy was obtained when a hydrogen atom interacted with the exposed transition metal while slightly smaller adsorption energy for the on top site of nearest oxygen from vacancy. The change of

adsorption energy of a hydrogen atom affects Gibbs free energy difference of hydrogen, well-established criterion in HER research. The HER activity was evaluated via calculation of Gibbs free energy difference of hydrogen, which was derived from ab-initio thermodynamics. Through these results, it could be inferred that non-uniformly functionalized surface condition influenced the HER activity of Ti₂C-based MXenes. Therefore, this theoretical study will provide further insight into the design of MXenes as a catalyst for HER.

SESSION ET10.08: Membrane
Session Chairs: Xianfeng Li and Yushan Yan
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 309

8:00 AM *ET10.08.01

Membranes for Redox Flow Batteries [Dirk Henkensmeier](#)^{1,2}, Sangwon Kim³, Ruiyong Chen³ and Yongchai Kwon⁴; ¹Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ²Energy & Environment Technology, University of Science and Technology, Seoul, Korea (the Republic of); ³KIST Europe, Saarbruecken, Germany; ⁴Seoultech, Seoul, Korea (the Republic of).

Membranes need to balance a low resistance and a low crossover of redox-active species, and they have to be chemically stable in the electrolyte. For vanadium redox flow batteries, this implies stability against sulfuric acid and stability against VO₂⁺ ions. For many years, the latter criteria strongly limited the choice of membrane materials, and perfluorinated Nafion membranes became the state of the art.[1]

A very recent development is the use of polybenzimidazole membranes, which do not conduct ions in the pure form, but become proton conductive in contact with the sulfuric acid containing electrolyte. The positive charge on the protonated polymer backbone and the narrow size of the electrolyte filled voids between the polymer chains successfully repels vanadium ions in ex-situ permeability measurements. Most interestingly, we observed that *both* voltage efficiency and coulomb efficiency increase when the membrane thickness decreases. This probably is related to the average charging potential, which increases with the membrane thickness and thus a) enhances migration in the electric field, providing some vanadium ions with the energy to pass the energy barrier which hinders them from entering the membrane, and b) possibly enhances side reactions.

This result suggests that cells with thin PBI films would be very efficient in terms of *both* voltage and coulomb efficiency; the thinner, the better.[2]

Building up on this finding, we prepared porous Nafion membranes coated with a thin PBI layer[3] and porous PVDF membranes coated with a thin PBI layer.

Another way to improve the voltage efficiency of PBI membranes is to blend them with anion exchange ionomers.[4, 5]

By alkylating PBI membranes, a permanent charge can be fixed on the PBI backbone, turning the membranes into anion exchange membranes with a high IEC.[6] While the alkyl groups may be a starting point for degradation by VO₂⁺, this type of anion exchange membranes can be used well in other types of flow batteries.[7]

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8:30 AM *ET10.08.02

Diversity-Oriented Approaches for Pairing Redoxmers and Porous Polymer Membranes for Long-Lasting Redox-Flow Cells [Brett A. Helms](#); Lawrence Berkeley National Lab, Berkeley, California, United States.

Here I will discuss emerging strategies for realizing multi-hour energy storage using redox-flow batteries. In particular, I will address design considerations and constraints in active materials, electrolytes, and membranes, which together in the flow cell constitute a highly interactive chemical system. With this new perspective, it becomes possible to design each component to respond to the others when the cell is driven to different states of charge. This collective behavior by the system can be used to prevent active-material degradation, capacity loss due to precipitation, and active-material crossover, all of which compromise the efficiency and integrity of the cell long-term. These insights elevate the prospects for macromolecular design to overcome longstanding challenges to flow-cell development, toward reliable solutions for grid stabilization.

9:00 AM ET10.08.03

Graphene Oxide Frameworks with Size-Modulated Pore Structure as Ion-Selective Layers on Hydrocarbon Membranes for Vanadium Redox Flow Batteries [Soohyun Kim](#), Junghoon Choi and Hee-Tak Kim; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

The laminated structure of graphene oxide (GO) membranes provides exceptional ion separation properties, due to the regular interlayer spacing (*d*) between laminate layers. However, a larger effective pore size of the laminate immersed in water (~11.1 Å) than the hydrated diameter of vanadium ions (> 6.0 Å) prevents its use in vanadium redox flow battery (VRFB). In this work, we report an ion-selective graphene oxide framework (GOF) whose *d* is tuned by cross-linking the GO nanosheets. Its effective pore size (~5.9 Å) excludes vanadium ions by size but allows proton conduction. The GOF membrane is employed as a protective layer to address the poor chemical stability of sulfonated poly(arylene ether sulfone) (SPAES) membranes against VO₂⁺ in VRFB. By effectively blocking vanadium ions, the GOF/SPAES membrane exhibits 4.2 times lower vanadium ion permeability and five times longer durability compared with the pristine SPAES membrane. Moreover, the VRFB with the GOF/SPAES membrane achieves an energy efficiency of 89% at 80 mA cm⁻² and a capacity retention of 88% even after 400 cycles, far exceeding Nafion 115, and demonstrating its practical applicability for VRFB.

9:15 AM ET10.08.04

Flexible Ceramic Membranes for Low-Cost Flow Batteries Gregory Newbloom; Membrion, Inc., Seattle, Washington, United States.

Grid-scale power storage remains one of the largest challenges to wide-spread adoption of clean energy technologies with intermittent energy sources (e.g., solar, wind and tidal). Redox flow batteries (RFB) are an environmentally friendly and scalable technology with the potential to meet this need. However, ion exchange membranes that are crucial to battery performance are expensive, lack chemical stability in a strong oxidizing environment, and/or have poor ion selectivity which leads to electrolyte diffusion across the membrane and performance instability. These issues have limited commercial flow battery manufacturers to two options: 1) perfluorosulfonic acid membranes - which are chemically robust and moderately ion selective but very expensive, or 2) separators - which are cheap but chemically degrade over time and have poor ion selectivity. In this paper, we discuss the design and scale-up of a novel, nanoporous ceramic flow battery membrane that is chemically robust, ion selective and inexpensive enough to reduce the total production cost of commercial flow batteries by > 15%.

In this work, we investigate the use of a primarily inorganic membrane created using sol-gel processing of silicates without calcination or sintering. Silica is an advantageous material for membranes because of its excellent chemical stability and extremely low cost. Furthermore, the gelation process can be utilized to tune the pore size for effective size exclusion of electrolytes (i.e., good ion selectivity). In this study, small angle x-ray scattering (SAXS) was utilized to characterize the membrane pore structure. Model fitting can be utilized to extract the porosity as well as pore shape, size and size distribution. By varying the gelation conditions, average pore radii were found to be in the range of 0.4 – 2 nm. This pore structure is nearly ideal for vanadium-based RFBs given that pores must be able to effectively transport protons (radius of 0.25 nm) but not vanadium ions (radius of 0.5 nm).

Proton conductivity and vanadium permeability were also determined and shown to be identical to an industry standard perfluorosulfonic acid membrane (i.e., Nafion 212). Variation in membrane nanostructure was directly correlated to performance. Furthermore, on-going accelerated chemical oxidative stability testing shows no degradation for silica-based membranes. Long duration RFB cycle testing was found to be identical to Nafion 115 under moderate current densities (80 mA/cm²) when membranes were scaled to a 50 cm² active area. These promising results highlight the commercial potential for a new flow battery membrane that is inexpensive, chemically robust and ion selective.

9:30 AM ET10.08.05

Scaling the Water Cluster Size of Nafion Membrane and Its Application for High Performance Zn/Br Redox Flow Battery Riyul Kim, Seongmin Yuk, Juhyuk Lee, Chanyong Choi, Soohyun Kim, Jiyun Heo and Hee-Tak Kim; KAIST, Daejeon, Korea (the Republic of).

Nafion membranes have been widely used in many electrochemical device as a typical cation exchange membrane. However, it have been considered unsuitable for Zn/Br redox flow batteries (ZBBs) due to its cation selective transport ability. This work shows that pre-hydration treatment can scale the water cluster size of Nafion membrane, which leads to not only high ionic conductivity but also bi-ionic transport property. With increasing the pre-hydration temperature, the water clusters expanded, resulting in the increase of water uptake, ionic conductivity and anion transference number. The bi-ionic transport and low area specific resistance induced by the pre-hydration enable successful operation of ZBB with NRE-212 membrane. As we confirmed that properly pretreated Nafion can be used in ZBB, we present a void-free 16 μm-thick Nafion-filled porous membrane for ZBBs to lessen the cost issue of Nafion. As a result, the ZBB based on the Nafion/PP membrane exhibits a higher energy efficiency, demonstrating that ion exchange membrane can outperform the conventional porous membrane by reducing the membrane thickness with inexpensive porous substrate.

9:45 AM ET10.08.06

Mechanically Robust Poly(Ethylene Oxide) Sodium-Ion Conducting Membranes for Redox Flow Batteries Guang Yang¹, Rose Ruther², Michelle Lehmann³, Ethan C. Self¹, Zhijiang Tang¹, Chelsea Chen¹, Frank Delnick¹, Thomas A. Zawodzinski¹, Tomonori Saito³ and Jagjit Nanda¹; ¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Energy and Transportation Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The advancement of sodium-based energy storage systems relies on the development of high performance sodium ion conducting electrolytes and membranes, which must meet several stringent requirements including high ionic conductivity, chemical and electrochemical stability over a wide voltage window, selectivity to minimize crossover, mechanical robustness, and processability. Poly(ethylene oxide) (PEO) based polymer is one of the most commonly used polymer electrolytes. However, simultaneously improving the mechanical properties and ionic conductivity is the major challenge in PEO based membrane or any polymer electrolytes. We will present two strategies to develop sodium-ion conducting membranes that address this challenge. A crosslinked PEO based electrolyte was developed that demonstrates high ionic conductivity, as well as excellent mechanical and thermal stability. The role of ethylene oxide (EO) complexation with sodium triflate (NaTf) salt and its effect on polymer segmental dynamics and ionic conductivity is elucidated with and without tetraethylene glycol dimethyl ether (TEGDME) as a plasticizer. Ionic conductivities up to 2.0 x 10⁻⁴ S/cm at 20 °C and 7.1 x 10⁻⁴ S/cm at 70 °C were achieved for the plasticized membrane, four orders of magnitude greater than that of the non-plasticized membrane. The storage modulus of the membrane was maintained at ~1 MPa from -20 °C to 180 °C even with the addition of plasticizer. The second method involves the use of TEGDME to plasticize linear high molecular weight PEO based membranes to increase the ionic conductivity. The conductivity of plasticized PEO membranes containing NaTf is about 2 orders of magnitude higher compared to non-plasticized PEO membranes. Vibrational spectroscopy and differential scanning calorimetry (DSC) describe the coordination chemistry in these materials and elucidate the mechanisms behind the increased conductivity. The mechanical properties of the plasticized membranes is significantly improved through the reinforcement with carboxymethyl cellulose (CMC). Importantly, all the materials selected for the membrane (PEO, NaTFS, TEGDME, and CMC) are highly stable at very negative voltages (near Na/Na⁺), and therefore compatible with sodium metal anodes or strongly reducing redox couples. Such a membrane can enable high voltage, high energy density batteries for grid storage applications.

Acknowledgment

This work is supported by Dr. Imre Gyuk, Manager, Energy Storage Program, Office of Electricity Delivery and Reliability, Department of Energy. The spectroscopy effort is supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

10:00 AM BREAK

Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 309

10:30 AM *ET10.09.01

Redox Processes and Design Strategies for High-Energy-Density Redox-Flow Batteries Yi-Chun Lu; Chinese University of Hong Kong, Shatin, China.

Energy storage system is a critical enabling factor for deploying unstable and intermittent renewable power sources such as solar and wind power sources. Redox flow batteries (RFBs) offer unique advantages of high efficiency, low cost, scalability and rapid response for grid energy storage. One of the most critical bottlenecks of RFBs is their low energy density, which is strongly related to the cell voltage and the solubility of the active materials. In this presentation, we will discuss strategies to improve the energy density of aqueous and nonaqueous RFBs and spectroscopic investigation on the redox processes involved in these RFB systems. Design strategies including redox complexing agent (e.g. lithium iodide, lithium bromide), semi-solid approach (e.g. sulfur/C and organic molecules) and highly-concentrated organic molecules (e.g. ferrocene-based) will be discussed. The influence of flow rate and current density on the electrochemical performance under continuous/intermittent flow modes as well as the synergistic interplay between solvent and redox-active materials in solid and liquid phases will be discussed.

11:00 AM *ET10.09.02

Zinc Based Flow Battery for Stationary Energy Storage Hongzhang Zhang and Xianfeng Li; Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian, China.

Zn²⁺/Zn redox couple attracts more and more attention in flow battery due to its characteristics of high solubility, electrochemical reversibility and environmental friendly. Moreover, in aqueous electrolyte, a negative potential together with the abundant reverse in earth crust enable zinc-based flow battery with low cost and high energy density. Until now, many zinc based flow battery systems such as zinc-bromine¹, zinc-nickel and zinc-iron^{2,3} etc. have been investigated, which have very promising prospect to be used in power grid, large energy storage, emergency power supply and other fields. Among them, zinc-bromine is one of the most successfully example of zinc based flow battery system, while zinc nickel and zinc iron systems have obtained tremendous developments recently. Many new zinc based systems such as zinc iodine have been proposed and demonstrated great advantages in some aspects such as energy density. However, secondary batteries that use zinc electrodes typically exhibit short lifetimes, because of problems with undesirable zinc morphology especially zinc dendrites, that form during charge. Hence, the challenge is to deposit a compact, uniform and free of dendrite layer that ensure a long cycle secondary negative electrode. Therefore, in this presentation we will introduce the research and development status of zinc based flow batteries at DICP.

11:30 AM ET10.09.03

Highly Efficient Monolithically Integrated Solar Flow Battery Wenjie Li¹, Hui-Chun Fu², Yuzhou Zhao¹, Jr-Hau He² and Song Jin¹; ¹University of Wisconsin-Madison, Madison, Wisconsin, United States; ²Electrical and Mathematical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

The practical utilization of solar energy demands not only efficient energy conversion but also inexpensive large scale energy storage. Building on mature regenerative solar cells and emerging electrochemical redox flow batteries (RFBs), more efficient, scalable, compact and cost-effective hybrid energy conversion and storage devices could be realized. Here we present an integrated solar energy conversion and electrochemical storage device by integrating regenerative solar cells in aqueous electrolytes with RFBs using the same pair of organic redox couples. In such an integrated solar flow battery (SFB) device, solar energy is absorbed by semiconductor electrodes and photoexcited carriers are collected at the semiconductor-liquid electrolyte interface and used to convert the redox couples in the RFB to fully charge up the battery (i.e. store the solar energy into the redox couples). When electricity is needed, the charged up redox couples will be discharged on the surface of carbon felt electrodes as one would do in the discharge of a RFB to generate the electricity. We demonstrated that such an integrated SFB device can be charged under solar illumination without external electric bias and deliver a high discharge capacity comparable with state of the art RFBs over many cycles. This integrated device can utilize solar energy efficiently -- an overall direct solar-to-output electricity efficiency (SOEE) of 14% has been achieved with advanced performance optimization. With comprehensive mechanism study and deeper understanding of the operation principles of SFBs, we also propose a set of design principles for highly efficient integrated SFB devices.

11:45 AM ET10.09.04

Redox Desalination Using Flow Battery Architectures Eugene Beh, Michael Benedict, Divyaraj Desai, Elif Karatay, David Johnson and Jessy Rivest; Palo Alto Research Center, Palo Alto, California, United States.

The water-energy nexus presents new opportunities for redox flow systems to make a large impact on our energy economy. Current efforts to make redox flow batteries commercially viable have traditionally focused on lowering capital costs; an alternative strategy is to increase the revenues associated with battery operation by creating a valuable product like desalinated water. By placing one or more intervening water chambers, bounded by ion-selective membranes, between the anode and cathode of a traditional flow battery, the system becomes capable of simultaneous water desalination and electrical energy storage. A symmetric flow cell that uses the same redox couple at both electrodes is no longer able to store electrical energy, but enables lowered specific energy consumption for salt removal, as well as greatly lowered reactant capital costs relative to the storage mode. Certain cell designs can additionally be switched reversibly between both operating modes, thereby allowing the stack to be utilized even when a conventional flow battery would normally be idled. We present several examples of devices that use flow battery architectures to perform redox water desalination for energy storage applications as well as nontraditional novel applications with large energy savings.

SESSION ET10.10: New Technologies II
Session Chairs: Xianfeng Li, Yi-Chun Lu and Wei Wang
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 309

1:30 PM *ET10.10.01

Dual Use Hydrogen-Based Flow Battery for Energy Storage and Hydrogen Production Katherine Ayers, Chris Capuano, Luke T. Dalton and Prasanna Mani; Proton OnSite, Wallingford, Connecticut, United States.

Hydrogen generation from water splitting is reaching a tipping point, with large scale electrolyzer systems being deployed for fueling and energy applications, and a growing number of projects under development. Still, the overall lifecycle cost makes wide spread application challenging, due to both capital cost and operating cost of electricity. The oxygen evolution electrode is a significant driver in both capex and opex, since the high voltage and overpotential result in limited material choices for stable performance. Proton OnSite and Pacific Northwest National Laboratory have been developing a versatile electrochemical device capable of serving roles in large scale energy capture and conversion as well as fuel production. The concept involves replacing the high overpotential oxygen evolution electrode in a water electrolyzer cell with a more facile and lower voltage redox couple, enabling the system to operate at significantly higher efficiency. The system can operate in two modes: 1) as a pseudo-electrolyzer, it produces renewable H₂ gas for industrial or energy applications including vehicle fueling and 2) as a hydrogen-redox flow cell, it is capable of high efficiency and low-cost grid scale energy storage. This talk will focus on the progress realized in this project, including materials and electrolyte development, incorporation of 30 bar hydrogen pressure into the system, and synergies and learnings that are applicable to water electrolysis.

2:00 PM ET10.10.02

Photocatalytic Oxidation of Formic Acid Using BiFeO₃—Stability and Reproducibility [Wegdan Ramadan](#)¹, Ralf Dillert² and Detlef Bahnemann^{2,3}; ¹Physics Department-Faculty of Science, Alexandria University, Alexandria, Egypt; ²Institut für Technische Chemie, Leibniz Universität Hannover, Hannover, Germany; ³Laboratory ‘‘Photoactive Nanocomposite Materials’’, Saint Petersburg State University, Saint Petersburg, Russian Federation.

Iron based compounds are tempting; they are cost effective and introduce interesting physical properties like magnetism but could have stability issues as well. In this context, BiFeO₃(BFO) is a multiferroic that has a band gap~2.3eV enabling it to absorb light in the visible region. The conduction and valance band are located at 0.46 eV and 2.68 eV with respect to NHE making it good candidate for water oxidation and oxidation of other organic pollutants like Formic acid (HCOOH). Under solar illumination and in the presence of BFO, as photocatalyst, redox reaction should take place such that holes created in the VB oxidize HCOOH into CO₂ and protons(H⁺)and electrons in the CB should reduce H⁺ into H₂. The CB position is more positive than the value required for H⁺/H₂ reduction. Mass spectrometer showed the formation of CO₂ and less H₂. Hence, what is the fate of the electrons if they are not consumed in protons reduction? To further elucidate this point, XRD and XPS were carried out for the photocatalyst before and after reaction with Formic acid. XRD of BFO after reaction with Formic acid, showed bleaching of most impurity peaks, Fe₂O₃, Bi₂Fe₄O₉ and Bi₂₅FeO₄₀ and relief of the strained crystal lattice. The removal of the impurities under illumination is essentially a photocatalytic process requiring the presence of an electron donor like HCOOH as concluded from results obtained in absence of HCOOH. XPS showed the 4f doublets of Bi³⁺ 4f_{5/2} and 4f_{7/2} with 5.20eV separation, indicating the formation of Bi-O bonds. On the other hand, Fe doublets, 2p_{1/2} and 2p_{3/2}, could not be fitted to a single oxidation state but rather to mixture of Fe²⁺ and Fe³⁺ such that 14% of Fe is Fe²⁺ and 86% is Fe³⁺. These contents change such that Fe²⁺ increases to 36% and Fe³⁺ decreases 64% after reaction. To maintain charge balance in BFO, oxygen vacancies were created and as confirmed from XPS. Stoichiometric ratio of Bi:Fe:O were found to be 1:0.9:2.9 and 1:0.7:2.7 before and after BFO reaction with HCOOH. Optical Emission Spectroscopy of the solution after BFO reaction with CHOOH showed traces of Fe and Bi in the solution indicating small fraction of them were leached into the solution. To assess the effect of the observed changes of the BFO on its photocatalytic performance, BFO powder obtained after a first photocatalytic run was employed in a second run performed under the same experimental conditions. The ratio between CO₂ evolved in the second run to the first experimental run was found to be 0.87. The respective ratio for the amounts of H₂ was calculated to be 0.46. This decrease in the evolved CO₂ by 13% indicates a decrease of the activity of the photocatalyst. These results indicate that under the adopted experimental conditions BFO deviates from the standard definition of a photocatalyst and suffers some changes during the photocatalytic reaction. It is essential to ensure stability of photocatalyst, especially iron-based ones, if we are seeking long term stability and reproducibility.

2:15 PM ET10.10.03

High Power Density Hydrogen-Iron Flow Battery [Litao Yan](#), Wei Wang, Yuyan Shao, Dongping Lu and Qian Huang; Pacific Northwest National Laboratory, Richland, Washington, United States.

Flow battery technologies (e.g all vanadium flow battery, iron chromium and zinc bromide flow batteries) are being commercialized into the application of stationary electrical energy storage. However, the electrolyte materials of vanadium, chromium and bromine are considered costly and more toxic. H₂/Fe (HyFe) flow battery has captured the great attention of the scientific community because it takes the advantages of low cost and environmental-friendly materials, high energy efficiency of > 90%, fast kinetics of hydrogen evolution/oxidation and facile Fe²⁺/Fe³⁺ redox pair. However, the main problem of low power density of HyFe flow battery impedes the implementation of this battery technology. Our study demonstrates that the electronic conductivity of electrolyte solution, complex ligands of iron ions and iron ions diffusion kinetics are the dominant factors to affect the power densities of HyFe flow battery. The temperature effects on electronic conductivities of electrolyte solution, iron ion diffusion kinetics and electrochemical performance of HyFe flow battery are also investigated. The maximum power density of 375 mW/cm² was achieved in our HyFe flow battery.

2:30 PM BREAK

3:00 PM *ET10.10.04

Design and Development of a Vanadium Oxygen Fuel Cell [Chris Menictas](#)^{1,3}, Mandar S. Risbud^{1,3}, Maria Skyllas-Kazacos^{2,3} and Jens Noack^{3,4}; ¹School of Mechanical Engineering, University of New South Wales, Kensington, New South Wales, Australia; ²School of Chemical Engineering, University of New South Wales, Sydney, New South Wales, Australia; ³CENELEST, German-Australian Alliance for Electrochemical Technologies for Storage of Renewable Energy, School of Mechanical Engineering, University of New South Wales, Sydney, New South Wales, Australia; ⁴Fraunhofer-Institute for Chemical Technology, Pfaffzettel, Germany.

Redox flow batteries are one of the most suitable electrochemical systems for large scale energy storage. The All Vanadium Redox Flow Battery (VRFB) technology invented at UNSW is being utilised on a global scale for stationary applications, but its low energy density is currently limiting its use in mobile systems. One promising approach to increasing energy density is the use of the oxygen reduction process for the positive half-cell. This forms the basis for the new Vanadium Oxygen Fuel Cell (VOFC) which eliminates the need for the positive vanadium electrolyte and removes the constraints associated with solubility limits of V(V) at elevated temperatures. Increasing the vanadium concentration from 2M to 4M for the negative electrolyte and the use of the oxygen reduction process for the positive half-cell can theoretically quadruple the specific energy density of the current VRFB from 25 Wh/kg to 100 Wh/kg allowing potential application in new transportation systems.

For long-term operation of the VOFC an important aspect is the regeneration of vanadium (II). The regeneration of V(II) can be performed externally to the cell, for example at a recharging station for electric vehicles. In the present development project of the VOFC at UNSW, a separate regeneration cell has been designed and used to regenerate the vanadium (II) electrolyte. It is critical that the supporting electrolyte for the VOFC be carefully selected so as to avoid the potential generation of hazardous gas at the positive electrode during re-charge. This limits the use of halide-based supporting electrolytes such as HCl that could potentially be used to enhance vanadium ion solubility. The use of electrolyte stabilising agents has therefore been evaluated to allow the use of vanadium electrolytes with concentrations greater than 3 M at elevated temperature. Alternate non-noble metal electrocatalysts have also been studied to improve the performance of the oxygen reduction process without using platinum based catalysts that could potentially catalyse the evolution of

hydrogen in the negative half-cell electrolyte. The design of single and multi-cell VOFC systems will be described together with details on the fabrication of membrane electrode assemblies that are utilised in this hybrid system.

3:30 PM *ET10.10.05

Radical Anion Mediated Phosphorus Anode for Na-Ion Based Nonaqueous Redox Flow Batteries Jagjit Nanda, Ethan C. Self, Rose Ruther, Srikanth Allu and Frank Delnick; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Redox flow batteries (RFBs) are promising energy storage devices for grid-level applications due to their extraordinarily long cycle life (resulting from the use of highly reversible redox couples) and the ability to independently scale their energy and power densities. It may be worthwhile to mention that at present most of the research advances in the area of redox flow batteries has been incremental with the energy density solely determined by the amount of redox species dissolved in the excess solvent or electrolyte that doesn't contribute to the electrochemical capacity. We report a new energy storage mechanism that uses organic radical mediators to chemically mediate the redox process extracting extraordinary capacity from high energy density electrodes. As a proof of principle, we show reversible electrochemical activity using two organic anion radicals (biphenyl and pyrene) that mediate a high capacity anode, red phosphorus (P) yielding about 1500 mAh/g within the state-of-charge window. Such large capacity from redox couples in a flow battery configuration is unprecedented and opens up a new avenue for increasing the energy density of redox flow batteries without any cost penalty. From a cost perspective, both phosphorus and sodium salts are earth abundant and cheap unlike lithium-ion. The new battery architecture has several advantages (I) only the radical anion solution circulate in the cell stack with the active electrode materials stored externally in a plug-flow reactor maximizing capacity utilization, (II) allow adequate space for volume change during redox activity and (III) plug flow reactor design ensures inherently safe battery operation avoiding any accidental short circuit via dendritic growth that could lead to thermal catastrophe. The rate constant and kinetics of mediated reaction between organic radicals and P will be presented.

Acknowledgement

This research is sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. The membrane development work is supported by Energy Storage Program, Office of Electricity Delivery and Reliability, Department of Energy.

4:00 PM ET10.10.06

Redox-Active Electrolytes Modified by Nanoparticles—Towards High-Energy Supercapacitors Krzysztof Fic, Paulina Bujewska and Barbara Gorska; Poznan University of Technology, Poznan, Poland.

Nowadays, eco-friendly water-based electrolytes to ECs are getting more and more popular despite narrow electrochemical window, limited by theoretical voltage of water decomposition (1.23 V). However, it has been proved that operational voltage for devices operating with alkali metal sulfate-based electrolytes could be extended up to 2.2 V and the energy density might be thus significantly improved. Another approach to enhance the energy density of EC is realized by increasing the capacitance of the system. In this aspect, the implementation of redox-active electrolytes or additives, generating faradaic contribution, seems to be a promising strategy.

The processes of changing the oxidation state of a molecule require an alkaline or acidic medium, which unfortunately leads to narrowing of the cell voltage and results in energy density decrease. Therefore, mild, neutral, water-based electrolytes demonstrating redox activity such as alkali metal halides (KI or KBr) have already been proposed. The advantages of these electrolytes include the possibility of using low-cost but corrosion-resistant current collectors.

Recently, alkali metal and ammonium thiocyanates (SCN^-) aqueous solutions have been successfully applied as electrolytes to ECs. The comparative study on the effect of salt concentrations depending on the type of current collectors has been presented. The cell operating with gold current collectors revealed a limited effect on charge propagation resulting from its high conductivity.

In this work, the addition of various nanoparticles (Au, Ag, carbon nanotubes) at extremely low concentrations to potassium thiocyanate solution (KSCN) is presented as an attractive way for electrolyte modification. Our previous work has shown that especially gold has a positive influence on SCN^- based systems performance – better charge propagation, fast redox response and lower resistance has been observed. Furthermore, together with Au nanoparticles, these species could form complexes such as $[\text{Au}(\text{SCN})_2]^-$ and $[\text{Au}(\text{SCN})_4]^-$ and the redox equilibrium Au(I)Au(III) might be established in the solution.

The investigated ECs were manufactured with 7 mol/L KSCN solution with gold nanoparticles and carbon electrodes made of high surface area carbon black, providing a suitable micro-to-meso pore volume ratio. The electrolyte solution displayed very high conductivity (372 mS/cm) and neutral pH (7.5). The systems with potassium thiocyanate and gold nanoparticles were characterized by a high operational voltage (1.6 V) and high capacitance, namely 168 F/g (@1 A/g). Moreover, high energy density has been retained at the whole range of applied current densities: 15 Wh/kg (@1 A/g) and 13.7 Wh/kg (@20 A/g).

The electrochemical characterization will be supported by several operando techniques - Raman spectroscopy, Quartz Crystal Microbalance and Scanning Electrochemical Microscopy, in order to provide a full picture of the interfacial phenomena.

4:15 PM ET10.10.07

Functionalised Graphene as High Surface Area ORR Electrodes in PEM Fuel Cells Theo Suter¹, Noelia Rubio², Mike Whiteley¹, Milo Shaffer² and Daniel J. Brett¹; ¹Department of Chemical Engineering, Electrochemical Innovation Laboratory, University College London, London, United Kingdom; ²Department of Chemistry, Imperial College London, London, United Kingdom.

Fuel cells are one of the keystones of the hydrogen economy but costs remain high, partly due to the high cost of the catalyst system.^{1,2} Typically commercial electrodes are still based on platinum on a carbon black support.^{1,2} Significant research has focused on developing new catalyst systems, with costs and scalability being two of the most important factors for success. Graphene has great potential as a catalyst support material due to its potential to be high surface area and carbon corrosion resistance replacement for carbon black.^{3,4} Functionalising this graphene enables reduced platinum nanoparticle size and increased activity, thus reducing cost without comprising power output. However achieving this without damage and in a scalable manner is an active research area.

In this work we explore a scalable synthesis of functionalised graphenes and their use as high surface area ORR catalyst in fuel cells. The graphene was synthesised by a scalable method utilising layer charging with sodium naphthalene to allow exfoliation, allowing functionalisation of the resultant material. By reacting the charged graphene with particular functional groups/polymers we were able to develop a highly active graphene based electrode. This was

characterised via SEM, TEM and XPS, as well as being tested for ORR activity in RDE and fuel cell systems showing improved performance.

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