Breakthrough Electrolytes for Energy Storage (BEES)
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Class: 2018 – 2022

Mission Statement*: To develop fundamental understanding of: (i) solvation and transport properties; (ii) electrode-electrolyte interfaces; and (iii) electron transfer reactions in deep eutectic solvents and soft nanoparticle electrolytes.*

Discovery of new electrolytes is needed for advancing the fundamental science and enabling new opportunities in electrochemical systems including redox flow batteries, supercapacitors, electrocatalysis, electrodeposition, separations and sensors. Specifically, by designing new electrolytes with higher concentrations of electrochemically active species, lack of flammability and ease of control over transport properties, substantial improvements will be realized in energy and power density, safety and reductions in environmental impact, and cost of energy storage systems. The Breakthrough Electrolytes for Energy Storage (BEES) EFRC sets out a comprehensive research program (Figure 1) that leverages expertise in the theory-guided synthesis of novel materials, and the characterization of their properties using simulations and experiments. By understanding the role of chemical structure on physicochemical properties of new electrolytes, efficient electron and charge transfer processes will be enabled.

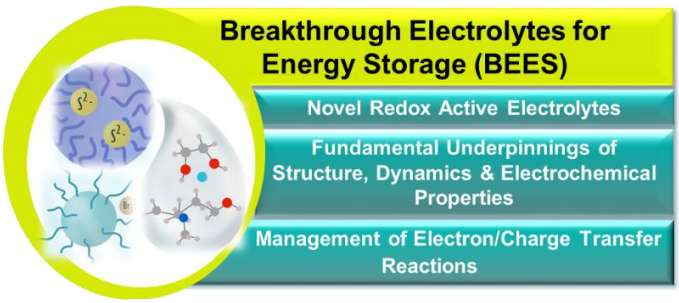

Figure 1. Research overview of BEES

The two research thrusts within BEES are: (1) Deep Eutectic Solvents (DES) and (2) Soft Nanoparticles (SNP):

Thrust 1: **DES** are a class of liquids comprised generally of a hydrogen bond donor, like a halide salt, and a hydrogen bond acceptor. DES are non-toxic, biodegradable, stable, nonvolatile, and nonflammable. They have a high degree of structural flexibility. DES enable electrochemical reactions without the constraints of aqueous solvents. The goal of Thrust 1 is to unravel the fundamental underpinnings of the relationship between the composition and structure that determine the physicochemical and electrochemical properties of DES. With this understanding functionalized DES with redox active groups will be created as new electrolyte systems, improving redox-active material solubility and facilitating fast interfacial electron transfer reaction rates.

The main hypothesis of Thrust 1 is that spatial and dynamic heterogeneity introduced by noncovalent interactions alters the molecular energy landscape and leads to mesoscale organization and dynamics that determine the macroscopic properties of DES. Within the scope of BEES, we will answer the following **scientific questions**:

1. *Is the extent of hydrogen bonding (number, strength, lifetime) in DES a surrogate measure of diffusivity and conductivity of ions?*
2. *Is there a correlation between the melting point, molar free volume and viscosity of DES?*
3. *How are DES structured near the interface? What kind of screening lengths should we expect?*
4. *What are the impacts of surface adsorbed species and metal speciation on the kinetics and reversibility of electron transfer reactions between an electrode and a redox-active DES?*
5. *What are the key structural features of DES that control its reactivity near charged surfaces?*

The answers to these questions will be the basis for (i) tailoring DES structures for specific electrochemical and transport properties, and (ii) extending the electrochemical stability of the DES structures over wide potential windows to enable new electrochemical reactions not feasible in traditional DES systems.

Thrust 2: **SNP** electrolytes are heterogeneous, multiphase systems where liquid droplets are dispersed in a carrier phase. An example of a SNP electrolyte is nano-emulsion in which droplets containing electroactive species are surrounded by a fluid that provides conductivity. Another example is a NOHM (Nanoparticle Organic Hybrid Materials) which are liquids formed from hard nanoparticles with attached, possibly functionalized, polymeric chains. The goal of Thrust 2 is to enable unique paths for decoupling the nature and solubility of electroactive material from the conductivity and transport of ions in the surrounding solution, which may be an aqueous phase or a non-aqueous phase.

The guiding hypotheses for Thrust 2 are (i) that microemulsions and NOHMs can controllably take up and release redox active species and (ii) that SNP-contained redox active species can be converted through direct or mediated electron transfer across the boundaries of the SNP. The following **scientific questions** will be answered:

6. *How does the introduction of an ionic backbone or polar functionalities into polymers or surfactants used in NOHM and microemulsions affect the mobile ion packing and dynamics of these systems?*
7. *How does the introduction of small ions into the NOHM and microemulsions affect the packing and dynamics of polymers or surfactants?*
8. *How does their immersion in electrolyte solutions affect the transport behavior of SNP?*
9. *How do electron and ion transfer rates into microemulsions and the canopy of NOHM depend on the structure and dynamics of polymers or surfactants?*
10. *What interactions drive uptake of solutes into SNP?*

The answers to these questions will be the basis for tailoring new structures for specific electrochemical and transport properties as well as for enabling uptake of electroactive species. The overarching aim will be to develop the electrochemical science underpinnings of SNP electrolytes.

Breakthrough Electrolytes for Energy Storage (BEES)	
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