Highly Selective Proton-Conducting Composite Membranes for Redox Flow Batteries

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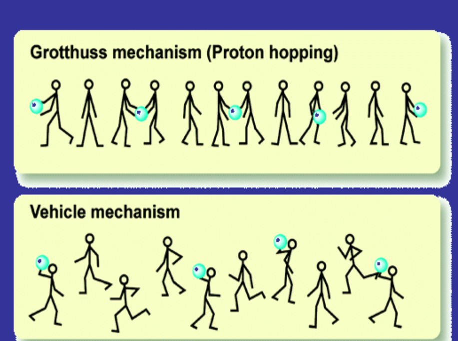
Introduction

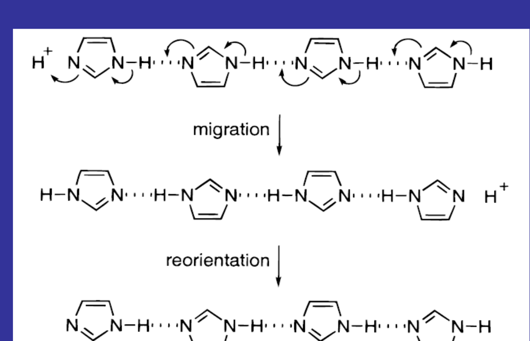
- Redox flow batteries (RFBs) have been considered as a promising technology to store intermittent renewable energies such as solar and wind power due to their advantages over conventional batteries. The advantages of RFBs include modularity, transportability and flexible operation, making them well suited for transmission and distribution deferral applications. Despite the advantages, RFBs with reduced cost and improved performance (e.g., efficiency and durability) need to be developed for broad market penetration.
- Ion exchange membranes in RFBs that separate two soluble redox couples as electroactive species should allow rapid proton transport, but suppress the transport of reactive species between anode and cathode compartments. Nafion membrane is widely used in RFBs due to its high proton conductivity and excellent chemical stability in strong acid and oxidation conditions. However it's expensive and has high permeability of reactive species, e.g., vanadium ions.
- Development of low-cost, highly selective proton-conducting membrane has the potential to produce cost effective and high performance RFBs for grid energy storage.

Objective/Approach

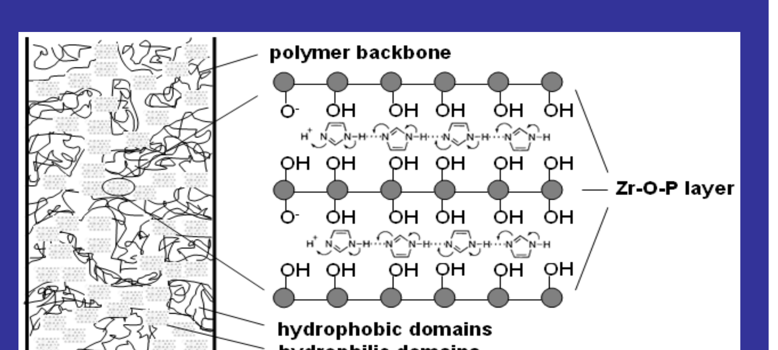
- The objective of this Phase I SBIR project is to develop a low-cost, robust, and highly selective proton-conducting composite membrane for RFBs for stationary electrical energy storage. The goal of the Phase I project is to develop a membrane with low cost (target cost < $100/m^2), high proton conductivity (≥ 0.08 S/cm), and low permeability of reactive species.
- Utilize zirconium phosphates (ZrPs) as inorganic proton conductors, modify ZrPs (mZrPs) with *N*-heterocycles which can promote proton transport and reduce crossover of reactive species through the membrane
- Incorporate mZrPs into the hydrophilic domains formed by acidic groups (i.e., sulfonic acid) of an acidic polymer membrane (e.g., sulfonated polysulfone (SPSf) or poly(ether ether ketone) (SPEEK)), prepare mZrP-SPSf or mZrP-SPEEK composite membranes
- Optimize the composition of composite membranes to maximize proton conductivity and minimize water uptake, dimensional change, and permeability of reactive species; correlate the relationship of composition-property-performance



Grotthuss mechanism



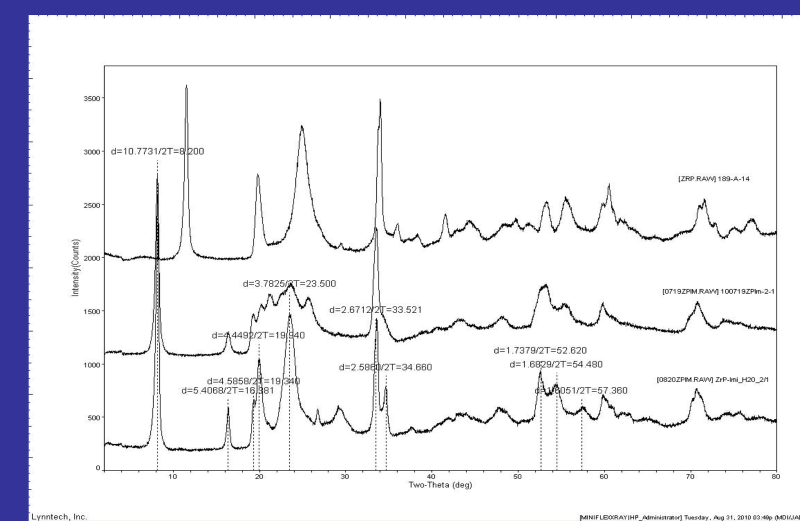
Proton transfer via imidazole



Composite membrane

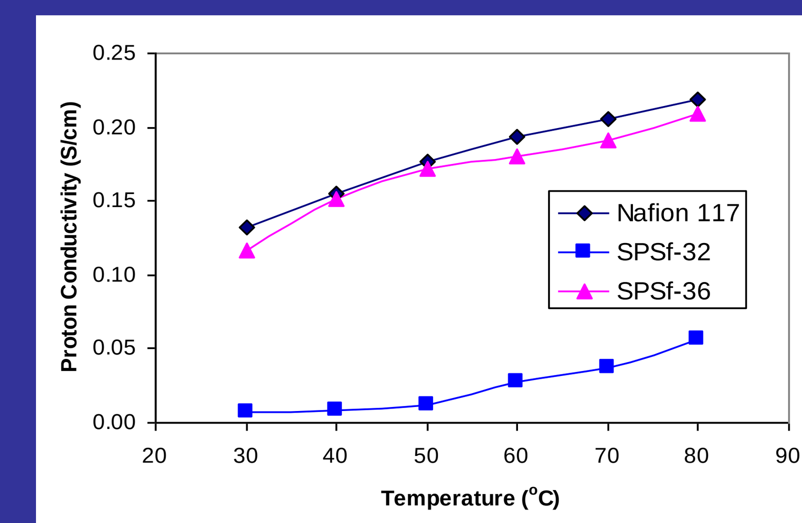
Experimental Results

XRD Patterns of ZrP and Modified ZrP



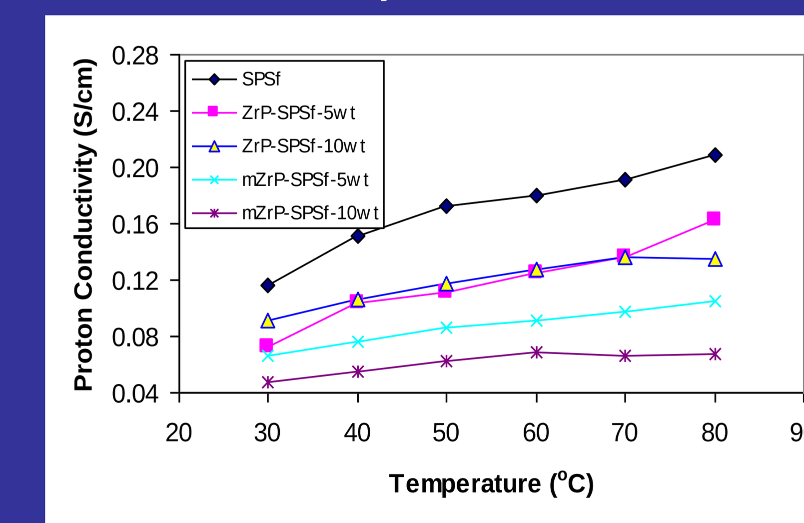
- Imidazole can be intercalated into ZrPs, the exfoliated ZrPs could have a good distribution in composite membranes, imidazole can promote proton conduction within ZrPs by Grotthuss mechanism
- Maximum molar ratio of ZrP:Im is ~2:1

Proton Conductivity of Nafion 117 and SPSf



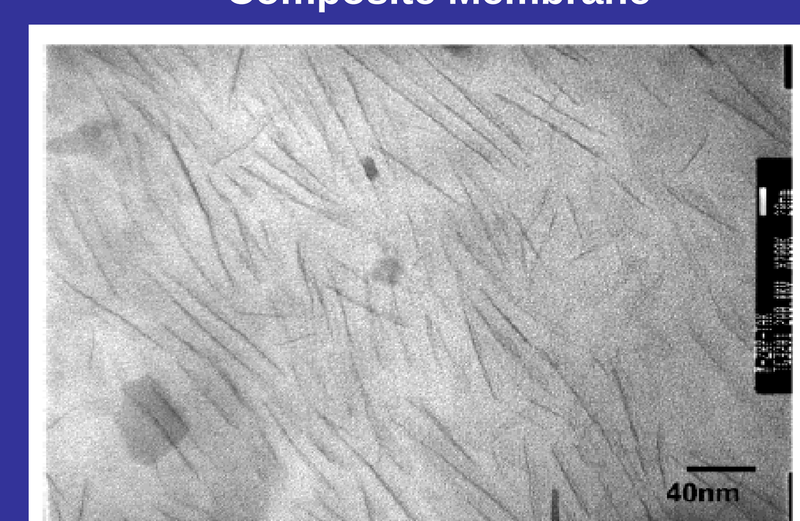
- SPSf-36 exhibits a proton conductivity of >0.1 S/cm at RT, and comparable conductivities to those of Nafion 117 over temperature range of 30-80 °C
- Proton conductivity and dimensional stability have to be balanced to obtain good performance in RFBs

Proton Conductivity of SPSf-32 and Its Composites Membranes



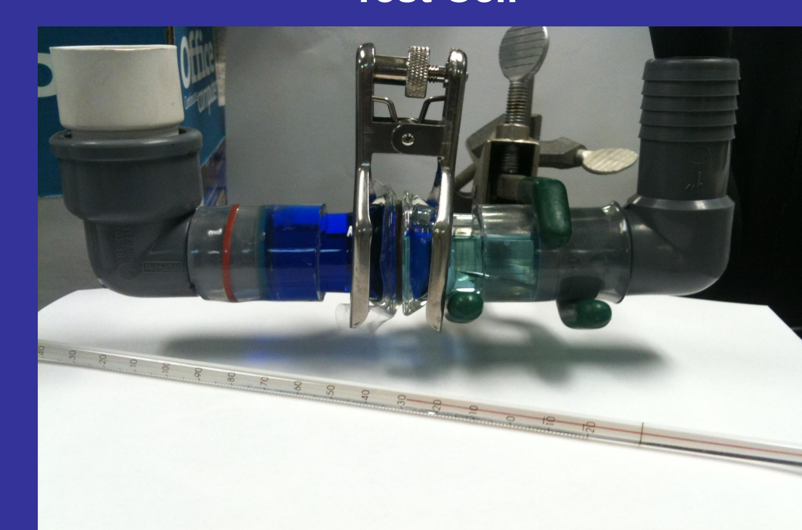
- Composite membranes show lower proton conductivities than plain SPSf membrane, but much lower activation energy for proton transport
- E_a (plain SPSf) = ~17 kJ/mol
  E_a (composite) = ~3-4 kJ/mol

TEM Image of ZrP-Based Composite Membrane



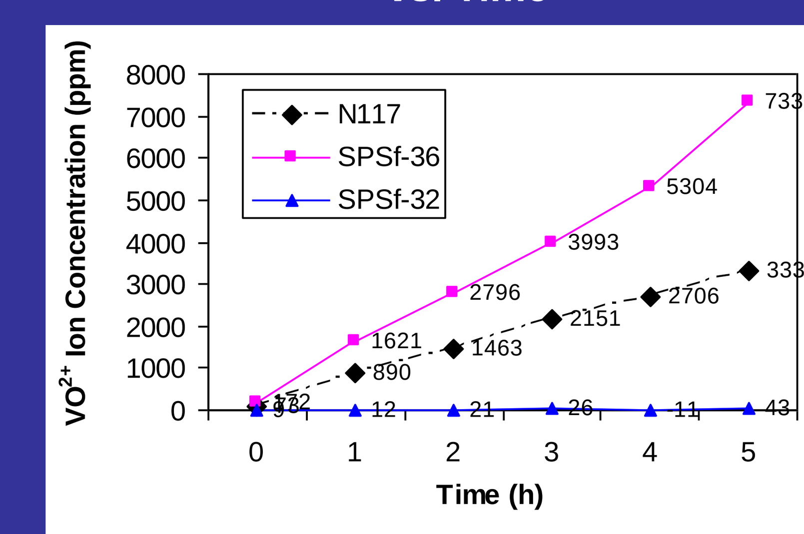
- ZrP can be evenly distributed in polymers
- ZrP can occupy the hydrophilic domains in sulfonated polymers, resulting in narrow water/proton pathways which can lower permeability of reactive species

VO^{2+} Ion Permeability Test Cell



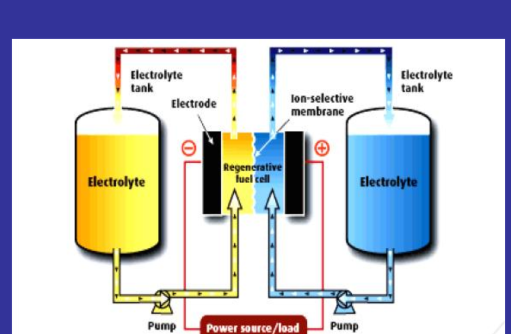
- Left: 2 M $VOSO_4$ + 2 M H_2SO_4
  Right: 2 M H_2SO_4
- UV/vis absorbance at 765.5 nm (VO^{2+})
- Record data hourly for 5 hours

VO^{2+} Ion Concentration vs. Time



- Permeability decrease in the order of SPSf-36 > Nafion 117 > SPSf-32
- Composite membranes are expected to have lower permeability than those membranes

Applications



Single Cell

DICP's 10 kW System

DICP's 100 kW System

Back-up Power

Renewable Energy Storage

Smart Grid System

Technology Advantages

- **Low cost**. The composite membranes are based on industrial polymers (polysulfone or poly(ether ether ketone) and low-cost zirconium phosphates.
- **Tunable proton conductivity and physical properties**. The polymers can be sulfonated to desirable degree, proton conductivity, dimensional and mechanical stability can be tuned by controlling degree of sulfonation and compositions.
- **High proton conductivity and Ultralow permeability of reactive species**. The composite membrane consists of components that conduct protons heavily depending on Grotthuss mechanism, which requires low activation energy without water and leads to high proton conductivity and low permeability of reactive species.
- **Improved performance of RFBs**. The composite membrane can improve columbic/voltage/energy efficiencies and durability of RFBs.

Conclusions

Lynntech has developed a new series of low-cost composite membranes with high proton conductivity and ultralow permeability of vanadium ions that have the potential to be used in all vanadium RFBs. The proton conductivity and physical properties (dimensional and mechanical properties) of these membranes are tunable by adjusting the degree of sulfonation, composition, and filler distribution. Preliminary results have shown SPSf membranes exhibits comparable proton conductivity to that of Nafion 117 and much lower permeability of VO^{2+} ion. Composite membranes show proton conductivity in the range of 0.05-0.1 S/cm at room temperature and much low activation energy for proton transport. Future work will be focusing on the optimization of the membrane compositions and application of these membranes in all vanadium RFBs.

Lynntech's composite membrane has the potential for the mass production of cost-effective RFBs for large scale electrical energy storage. RFBs are promising for grid energy storage and the market of all vanadium RFBs is forecast to grow to a value of more than $1.5bn/year by 2025.