# Testing and Qualification of New Membranes for Flow Batteries


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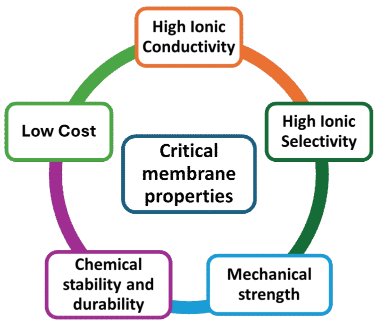
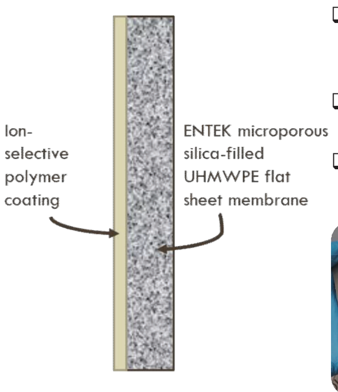
Membranes in Redox Flow Batteries (RFBs) are a critical system component that serves the important function of separating the anolyte and catholyte while selectively allowing protons or hydroxyl ions to pass through the membrane. Currently, perfluorinated sulfonic acid (PFSA) polymer membranes (e.g. Nafion®) dominate the RFB space due to their high ionic conductivity and superior chemical durability in the highly oxidative electrolytes used in many RFBs. However, high cost, relatively poor selectivity (to prevent crossover) and increasing concerns about adverse environmental and regulatory issues surrounding perfluoroalkyl substances (PFAs) have created an opportunity for new membrane technologies. This poster highlights the approach and methods that ENTEK employs in the development of new membranes for RFBs using sulfonated hydrocarbon ionomers.


## Key Features of Membranes in Flow Batteries:

- ❑ High ionic conductivity for protons and/or hydroxyl ions – improves voltaic efficiency and power
- ❑ High ionic selectivity to prevent crossover of electroactive species (e.g. Br, V, Fe ions.) – increases coulombic efficiency
- ❑ Good mechanical stability and durability – no major changes in dimensions due to swelling and high mechanical strength for easy handling and durability
- ❑ Chemical stability and durability – stable in highly acidic and oxidative conditions, especially at high SOC and elevated T
- ❑ Low cost and manufacturing available at scale - system level goal of $0.05/kWh for levelized cost of service (LCOS)
- ❑ Other goals: rapid wetting/hydration for deployment and sealable to flow frame and channels

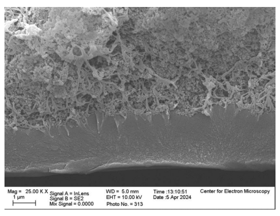



## New Membranes for Flow Batteries:

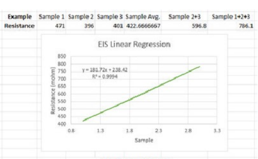



*ENTEK Composite membrane separator Pat. Pend. WO 2022/133394 A1

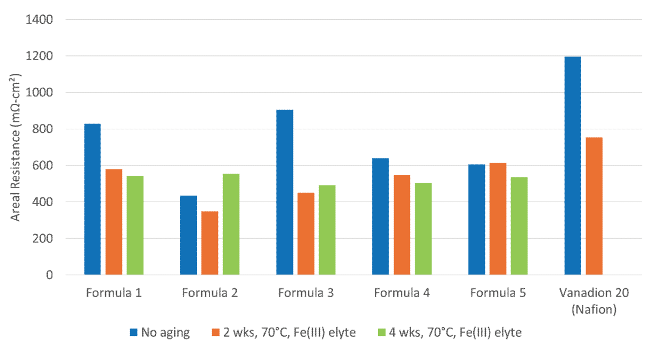
- ❑ ENTEK has been developing new composite membranes* for flow batteries leveraging our Pb acid and Li ion separator manufacturing.
- ❑ 200 µm thick microporous UHMW polyethylene/ $SiO_2$ base sheet coated with a layer of non-porous hydrocarbon ionomer.
- ❑ Coating formulation, coat weight/thickness and processing conditions can be optimized for different RFB chemistries.



## Testing: Ionic Resistance

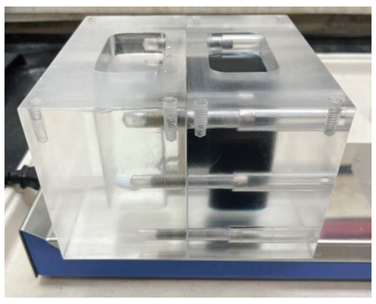


- ❑ Ex-situ testing of ionic resistance allows for rapid screening of candidate coating formulations.
- ❑ Membranes can be wetted in the electrolyte of choice.
- ❑ Through-membrane impedance is measured using a test cell connected to a potentiostat/impedance analyzer.
- ❑ The real component of the impedance at 100 kHz is measured for 1, 2, and 3 layers of separator.
- ❑ Membrane resistance is calculated by plotting number of layers against the impedance and fitting a line.
  - ❑ The line's slope is the impedance added per layer of separator. This process allows removal of the background impedance of the test fixture.
- ❑ Membranes can be aged in electrolyte at elevated temperature to monitor changes in resistance as a function of aging time.

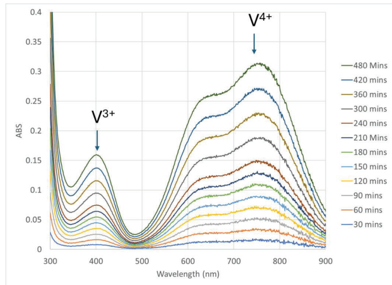



Areal ionic resistance measurements for different coating formulations taken before and after aging in electrolyte to determine stability of the membrane over time. Nafion is included for comparison. Target areal resistance is <600mΩ-cm²

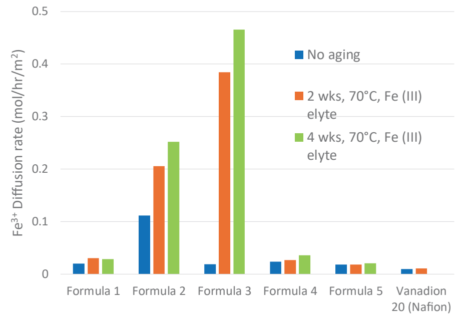
## Testing: Diffusional Crossover



The image above shows the diffusion cell with vanadium electrolyte on the rich side and $H_2SO_4$ w/$MgSO_4$ on the left. The graph below shows the UV-Vis spectra of the lean side vs. time. The ideal membrane would show no crossover.



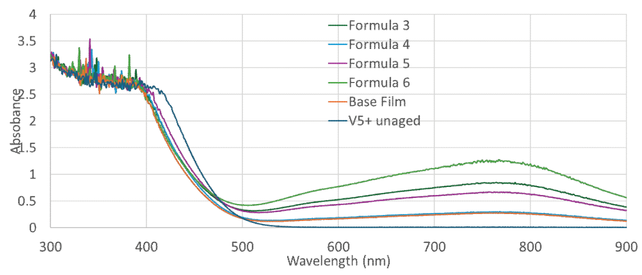

- ❑ Diffusion of electroactive species across the membrane can lead to coulombic inefficiency in the cell.
- ❑ Diffusional crossover can be measured in a two-chamber diffusion cell separated by the membrane. On the right side, there is an electrolyte-rich solution while on the left, there is a lean solution (no electroactive species).
- ❑ Aliquots are removed from the lean side at periodic intervals to determine diffusional crossover rate using UV-Vis spectroscopy.
- ❑ Diffusion rate can be calculated using the concentration change over time.




Diffusion of Fe(III) through different coating formulations as a function of weeks aged.

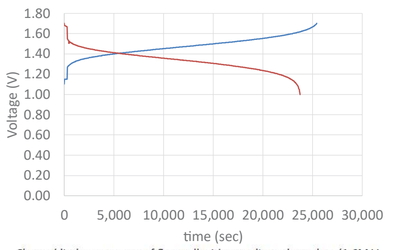
## Testing: Chemical Stability and Durability

- ❑ The unique spectroscopic properties of vanadium ions provide an opportunity to assess the chemical stability of candidate ionomers by monitoring changes in oxidation state of the electrolyte as a function of membrane aging time in solution at elevated temperatures.
- ❑ Unsupported and supported ionomer coatings can be soaked in $V^{5+}$ solutions (yellow) for various periods of time. This represents high SOC in the VRFB battery. Aliquots can be removed from the aged electrolyte to determine the amount of the $V^{5+}$ that has converted to $V^{4+}$ by UV/Vis.
- ❑ The graph shown below is the UV/Vis absorption of the $V^{5+}$ electrolyte after soaking with membrane samples for 3 weeks at 50°C. Formula 6 shows the least stability (greatest [$V^{4+}$]) of the membranes evaluated.

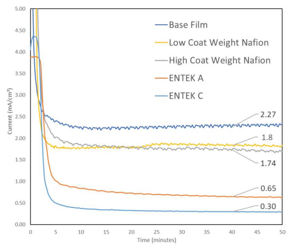



## Testing: Flow Battery Single Cell Testing

- ❑ The characterization of membranes outside the cell is a good predictor of behavior in the cell, but actual cell data is required to assess ion migration across the membrane in an applied field.
- ❑ In addition, cell testing allows us to evaluate coulombic efficiency, voltage efficiency, and energy efficiency at various loads.
- ❑ Composite membranes can be tested before aging and after aging to assess the performance differences and durability.




Charge/discharge curves of flow cell with vanadium electrolyte (1.6M V, 4M H2SO4 – U.S Vanadium). Cell is cycled at 25 mA/cm2 in a 25 cm² cell at RT. 100 ml electrolyte for both analyte and catholyte.




Chronoamperometry of membranes in 25 cm² cell in all-iron electrolyte. A 0.7V bias was applied to the cell which is below the charging potential of 1.45 V. The resulting steady-state current is due to the cross-over of Fe³⁺. ENTEK C is significantly improved relative to Nafion.

## Summary

As RFBs enter the market in a meaningful way, the commercial availability of membranes that meet the unique requirements of each application and cell chemistry is critical to their success. ENTEK has been working with customers, researchers and collaborators to help define standardized testing and qualification protocols. In addition, ENTEK is working to develop new approaches to membrane technology.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