Advanced Membranes for VRFB. A Collaboration with SNL, PNNL and ORNL

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Project

• VRFB Proven technology; 6MWh VRB on a 32 MW wind farm in Japan.

• Near Commercialization; Prudent Energy and UniEnergy Technologies

• Separation of energy and power

• At the electrodes only electron transport is occurs. Allows for deep discharge, long life cycles and little capacity fade

The problem is cost, DOE capital cost target $100/kWh\(^1\)
According to a recent study,\(^1\) current capital costs is $380/kwh

Cost of VRFB

Base capital cost of VRFB, largest cost stems from vanadium. The stack costs is the second largest expense.

The membrane separator accounts for 40% of the cost of the stack.

Nafion™ $250-500/m²
Perfluorinated polymer (primarily C-F)

Developing hydrocarbon polymer (C-H) with equal or better performances to Nafion at a price target of $40/m²
Membrane Considerations

**Performance**
- High current efficiency
- High voltage efficiency
- High energy efficiency \( CE \times VE = EE \)

**Durability**
- Charge-Discharge cycles: >4,000 cycles
- Accelerated Durability: Vanadium +5 soaking studies

**Cost** [Membrane impacts more than material costs]
- More durable = Less maintenance
- More efficient = smaller stack
Collaboration Structure:
To more effectively utilize our R&D resources by tasking each lab on their respective strengths and to prevent work duplication (leverage – no duplication)

Membrane Synthesis

Transport Studies

Flow Battery Testing
State of Hydrocarbon polymers in VRFB

One of the more common type of polymer backbone being explored for alternative VRFB membranes

S-Radel (SPAE) $^3$

SRadel ($R = H$ or $\text{-SO}_3\text{H}$)

Nafion 117

Failure after 40 cycles

Energy efficiency (%)

Cycle number

SFP A E $^4$

Energy efficiency (%)

Cycle number

Failure after 77 cycles

Film damage


Sulfonated arylene ether type polymers good EE, but there are durability problems; under 100 cycles
• All poly(phenylene) backbone high chemical-thermal stability

• Membranes are flexible; poly(phenylene)s [PPP] are known for being brittle

• Ease of tailoring polymer backbone [cation exchange membrane]

• Donnan Exclusion: Fixed negative charges allow positive charge to pass

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Thickness $^\circ$ (mil)</th>
<th>IEC (meq/g)</th>
<th>Water uptake</th>
<th>$D$ of $V^{4+}$ [cm$^2$/min]</th>
<th>HFR$^2$ (Ωcm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDAPP 1.4</td>
<td>4.2</td>
<td>1.4</td>
<td>36%</td>
<td>$4.4\times10^{-7}$</td>
<td>0.96</td>
</tr>
<tr>
<td>SDAPP 1.6</td>
<td>3.4</td>
<td>1.6</td>
<td>43%</td>
<td>$8.1\times10^{-7}$</td>
<td>0.70</td>
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<tr>
<td>SDAPP 2.0</td>
<td>3.6</td>
<td>2.0</td>
<td>85%</td>
<td>$4.3\times10^{-6}$</td>
<td>0.35</td>
</tr>
<tr>
<td>Nafion 117</td>
<td>7.0</td>
<td>0.99</td>
<td>35%</td>
<td>$4.7\times10^{-6}$</td>
<td>0.84</td>
</tr>
</tbody>
</table>

SDAPPs show slightly better EE

SDAPP1.4 shows stable EE even after +400hrs

After +600 hrs SDAPP1.4 shows drop in performance

SDAPP slightly better EE than Nafion, longer cycle life than poly(arylene ether) however, +4,000 cycle lifetimes are required for VRFB

Durability Investigations

Skyllas-Kazacos used ex-situ V\(^+5\) soaking [0.1M] to gauge membrane lifetime.

**Solution:** 0.1M V\(^{5+}\) + 5 M S, 40°C

Linear relationship between ex-situ in-situ data suggest that 300 days in V\(^+5\) may simulate 4,000 cycles; more concentrated solutions should provide shorter time windows.

**Correlations between in situ and ex situ durability studies – able to approximate soaking times that would correspond to 4,000 cycles**
Conclusions:

• Collaboration between the labs has been beneficial and has helped speed up R&D
• Hydrocarbon SDAPP have shown better performances than Nafion
• Typical hydrocarbon materials have show very low cyclic lifetimes (>100 cycles), however the SDAPP have shown +400 cycles
• Improvements still need to be made to reach +4,000 cycles

Future:

• Understanding V+5 degradation mechanisms
  • Mechanical
  • Viscosity
  • SEM

Also looking at IR and NMR, for mechanistic details

• Improving DAPP oxidative resistance for longer lasting membranes
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