Crosslinked Polyethyleneimine Gel Polymer Interface to Improve Cycling Stability of RFBs

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Presentation # 604
Redox flow battery and the membranes

Functionality requirements
- High ionic permselectivity
- Low electric resistance
- High stability
- Low cost
Various RFB membranes

<table>
<thead>
<tr>
<th>Perfluorinated cationic exchange membranes (Nafion™)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Backbone</strong></td>
</tr>
</tbody>
</table>
| tetrafluoroethylene | sulfonate vinyl ether | • Excellent chemical stability  
| | | • High proton conductivity |
| | | **Challenges:** |
| | | • Vanadium crossover  
| | | • Mechanical properties |

<table>
<thead>
<tr>
<th>Non-perfluorinated cationic exchange membranes (CEM)</th>
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<tbody>
<tr>
<td><strong>Typical Non-perfluorinated CEM</strong></td>
</tr>
</tbody>
</table>
| sulfonated poly(aryl ketone ketone) | sulfonated poly(aryl ether sulfone) | • Lower cost  
| sulfonated poly(arylene thioether | sulfonated poly-(fluorenyl ether thioether ketone)  
| sulfonated poly(arylene ether sulfone) | sulfonated poly-(fluorenyl ether thioether ketone)  |
| | **Challenges:** |
| | • Lack of long-term stability  
| | • Mechanical properties |

<table>
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<tr>
<th>Anion exchange membranes (AEM)</th>
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</table>
| polysulfone | pyridinium | • Low V crossover  
| polyphenylene | quaternary ammonium  
| poly(arylene ether ketone) | methylated imidazolium  |
| | | **Challenges:** |
| | | • Lack of long-term stability  
| | | • Low ionic conductivity  
| | | • Mechanical properties |

<table>
<thead>
<tr>
<th>Porous membranes</th>
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</thead>
<tbody>
<tr>
<td><strong>Microporous materials:</strong></td>
</tr>
</tbody>
</table>
| PIM-1 | • Low V crossover  
| zeolites  
| silica modified PAN/PTFE  
| polybenzimidazole (PBI)  
| Chloromethylated PSF  |
| **Challenges:** |
| | • Unproved long-term stability  
| | • Low ionic conductivity |

Membranes for VRB systems

- Chemical stability towards $\text{VO}_2^{+}$ in highly acidic electrolyte

- Limited selectivity

Membranes for aqueous organic systems

- No available IEMs for neutral and alkaline organic electrolyte
- Diverse charge carriers ($\text{Na}^+$, $\text{K}^+$, $\text{OH}^-$)
- Less corrosiveness
- Less active materials cross-over
- Lower conductivity
Transport phenomenon - capacity decay in VRB

Capacity decay of RFB
- Reduce energy output
- Increase possibility of gas evolution and precipitation
- Require routine maintenance

Capacity decay of Nafion-based VRB

Capacity decay of separator-based VRB
Transport phenomenon - Imbalance electrolyte transfer

Nafion based VRB

Separator based VRB

Electrolyte volume

Negative limiting

Positive limiting

Total V concentration
Transport phenomenon - Asymmetrical valence change

Nafion based VRB

Separator based VRB

Concentration of $V^{n+}$

Shifting of SOC
Optimize of Nafion membrane

- Equivalent weight (EW) is the weight of polymer that contains one mole of charge.
- As EW increased, crystallinity increased. Change in the EW value changes the structure of the Nafion membrane.
- Membranes with different EW values are prepared, 1000 and 1500.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>EW</th>
<th>Thickness (µm)</th>
<th>Water uptake (%)</th>
<th>Conductivity (mS cm⁻¹)</th>
<th>Area resistance (mΩ cm²)</th>
<th>Diffusion Coefficient of VO²⁺ (*10⁻⁶ cm² min⁻¹)</th>
<th>VO²⁺ ion flux (*10⁻⁷ mol cm⁻² min⁻¹)</th>
<th>Selectivity Between H⁺ and VO²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDM221-2</td>
<td>1500</td>
<td>31</td>
<td>3.2</td>
<td>16</td>
<td>157</td>
<td>0.17</td>
<td>0.53</td>
<td>98</td>
</tr>
<tr>
<td>N115</td>
<td>1000</td>
<td>135</td>
<td>17.8</td>
<td>77.9</td>
<td>179.1</td>
<td>1.2</td>
<td>0.89</td>
<td>64.9</td>
</tr>
</tbody>
</table>

M. Vijayakumar, etc. ACS Appl. Mater. Interfaces 2016, 8, 34327−34334
Solving capacity decay without membrane modification

Gel Polymer Interface (GPI)
Crosslinked Polyethyleneimine GPI Design and Synthesis

Chemical structures of polyethyleneimine and Glutaraldehyde and their chemical reaction to form crosslinked regions and amino and carboxylic acid groups.

FTIR spectra of (black) pristine GCF and (red) PEIAA-GCF samples.
Characterization of the Crosslinked Polyethyleneimine GPI

SEM images of (a, b) pristine GCF and (c, d) PEIAA-GCF samples with different magnifications (1,000x and 10,000x). SEM-EDX, (e) spectrum and element maps ((f) carbon, (g) oxygen, and (h) nitrogen) of a part of PEIAA-GCF sample. Contact angles of (i) the pristine GCF and (j) the PEIAA-GCF samples.
Flow Battery Test Validation

(a, empty square) Discharge capacity, (a, solid circle) Coulombic efficiency, and (a, empty circle) energy efficiency; (b) voltage time profiles of 1st, 50th, and 100th cycles of cells with (blue) pristine GCF and (pink) PEIAA-GCF electrodes under constant current charge at 50mAcm$^{-2}$. 
Mechanistic study – Reducing V(IV) ion crossover

(a) UV-Vis spectra of the V(IV)OSO₄ solutions ranging from 0.01 M to 0.2 M with a standard calibration curve and (b) UV-Vis spectra of the 3.5M sulfuric acid solutions with (black) pristine GCF or (red) PEIAA-GCF electrode after 5 days with a flow rate of 30 mL min⁻¹ for crossover test.

~25% less V(IV) crossover
Stability of the Crosslinked Polyethyleneimine GPI

Wide scan XPS and inserted N 1 s spectra of PEIAA-GCF electrodes (a) before and (b) after 100 cycles under constant current charge at 50mAcm$^{-2}$. High-resolution XPS C 1 s spectra of (c) pristine GCF and (d) PEIAA-GCF electrodes before and after 100 cycles.
Summary

- We demonstrate a new gel polymer interface (GPI) consisting of crosslinked polyethyleneimine with a large amount of amino and carboxylic acid groups introduced between the positive electrode and the membrane.
- The GPI functions as a key component to prevent vanadium ions from crossing the membrane, thus supporting stable long-term cycling.

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