Materials and transport properties for membranes in new energy storage devices

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Motivation


Microphase segregation: To circumvent the brittleness of ionic polymers, distinct phases can be combined to decouple desirable properties:
- Mechanical stability (e.g. as a discrete structure)
- Ionic conduction (e.g. as matrix)

Purpose of study: 1) Explore ion selectivity for polycyclopropenium (PCPCy) polymers using a novel flow cell characterisation technique 2) Optimize sample preparation by methodical study of thermal properties.

Membrane processing

Sample preparation methods: 1) PCPCy was drop casted onto a porous substrate prior to characterization, to provide mechanical stability.
2) To optimize processing conditions and investigate the feasibility of a free standing film, the glass transition temperature \( T_g \) of PCPCy was recorded using Differential Scanning Calorimetry. BMimTFSI (ionic liquid) and DMSO (solvent) were used as dopants to reduce the \( T_g \) and thus the polymer's brittleness.

Results: Two distinct regimes (\( T_g \) reduction effects with increasing wt%) are observed separated by a cross-over region. They are associated to:
1. screening of electrostatic interactions
2. polymer chain solvation

Materials & microstructure

Materials characterized:
- Nafion®117 (commercial)
- Snowpure®-200 (commercial)
- PCPCy homopolymer (synthesized)
- PS-b-PCPCy diblock copolymer (synthesized)

Relevant PCPCy material length scales:
1) Ion vicinity: Delocalized nature of cyclopropenium ionic charge
2) Microstructure: Polystyrene (PS) block introduced for mechanical stability (i.e. microphase segregation)

PCPCy structure upon BMimTFSI doping:
- No difference observed with Wide Angle X-ray Scattering up to 10 wt%
- Ionic aggregate structure is not modified
- Ionic liquid is believed to intercalate into PCPCy

Transport properties – Ion selectivity

I. Novel technique: faster & more accurate

Method: Selectivity of ionic polymer membranes is assessed by measuring the transference number \( t_z \). A method relying on two flowing electrolytes on either side of a membrane was implemented, where the flux of a particular ion is monitored with applied current.

The transference number can in this case be expressed as follows with \( z \) the valency, c the concentration and D the diffusivity of ions:

\[ t_z = \frac{z^2 D c}{z D c + z^2 D c} \]

II. Calibration

- Nafion®117 was used to prove the validity of the novel characterization method
- Snowpure®-200 served as a reference for the synthesized membranes

<table>
<thead>
<tr>
<th>Membrane Selectivity Result</th>
<th>PCPCy Cation</th>
<th>PCPCy Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®117</td>
<td>( t_z = 0.94 )</td>
<td></td>
</tr>
<tr>
<td>Snowpure®-200</td>
<td>( t_z = 0.01 )</td>
<td>( t_z = 0.10 )</td>
</tr>
<tr>
<td>PCPCy</td>
<td>( t_z = 0.38 )</td>
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</tbody>
</table>

III. Novel materials

- PCPCy was tested to evaluate the selectivity of a polymer bearing a delocalized charge
- PS-b-PCPCy was characterized to investigate the effect of microphase segregation on the selectivity of the system

Conclusions

- A novel method for transference number measurement was demonstrated on Nafion®117
- PCPCy displays lower selectivity compared to commercial products, possibly due to sample preparation and insufficient functionalization
- The reduced fraction of charged phase in PS-b-PCPCy leads to decreased selectivity despite improved mechanical properties
- Brittleness of PCPCy was successfully reduced upon doping