Interconnected Ionic Domains Enhance Conductivity in Microphase Separated Block Copolymer Electrolytes

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Electronic Supporting Information
Supplemental Data

Figure S1. RSoXS patterns near the carbon edge for a.) PS-b-P2VP (diblock 25-b-25 kg/mol, before CVIR) and b.) PS-b-P2VP/NMP+ \Gamma (after the CVIR reaction). Panels c.) and d.) are the respective RSoXS patterns near the nitrogen edge.
Figure S2. RSoXS patterns near the carbon edge for a.) P2VP-b-PS-b-P2VP (12k-23k-12k) (before CVIR) and b.) P2VP/NMP⁺-b-PS-b-P2VP/NMP⁺ (post CVIR). Panels c.) and d.) are the respective RSoXS patterns near the nitrogen edge.
Figure S3. Processed SEM image (taken from collected 8 µm x 8 µm images) of self-assembled PS-b-P2VP/NMP with a targeted P2VP volume fraction of 45%.
Figure S4. Processed SEM image (taken from collected 8 µm x 8 µm images) of self-assembled PS-b-P2VP/NMP with a targeted P2VP volume fraction of 47.5%.
Figure S5. Processed SEM image (taken from collected 8 µm x 8 µm images) of self-assembled PS-\(b\)-P2VP/NMP + I with a targeted P2VP volume fraction of 50%.
**Figure S6.** Processed SEM image (taken from collected 8 µm x 8 µm images) of self-assembled PS-b-P2VP/NMP + I with a targeted P2VP volume fraction of 52.5%.
Figure S7. Processed SEM image (taken from collected 8 µm x 8 µm images) of self-assembled PS-\(b\)-P2VP/NMP \(\Gamma\) with a targeted P2VP volume fraction of 55%.
Table S1. Normalized capacitance values for self-assembled PS-b-P2VP/NMP+I BCEs on IDEs.

<table>
<thead>
<tr>
<th>Targeted P2VP volume fraction</th>
<th>Time for CVIR (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>45% P2VP</td>
<td>13.0 ± 0.3 pF nm⁻¹</td>
</tr>
<tr>
<td>47.5% P2VP</td>
<td>13.2 ± 0.3 pF nm⁻¹</td>
</tr>
<tr>
<td>50% P2VP</td>
<td>14.3 ± 0.4 pF nm⁻¹</td>
</tr>
<tr>
<td>52.5% P2VP</td>
<td>15.8 ± 0.2 pF nm⁻¹</td>
</tr>
<tr>
<td>55% P2VP</td>
<td>13.4 ± 0.9 pF nm⁻¹</td>
</tr>
</tbody>
</table>

Note: Average values for 3 samples. Standard error values reported.

Figure S8. Processed SEM images of self-assembled BCEs with varying molecular weight. The red color indicates the largest connected P2VP/NMP⁺ I domain within the image. The molecular weight of the triblock or diblock copolymers in each of the images (in g/mol of each block) is shown under each image.
Table S2. In-plane conductivity, conversion of P2VP to P2VP/NMP+ I, and IEC data for BCE thin film samples with varying $M_n$ and morphological period.

<table>
<thead>
<tr>
<th>$M_n$ values</th>
<th>Period (nm)</th>
<th>Conversion</th>
<th>IEC (mmol g$^{-1}$)</th>
<th>In-plane ionic conductivity $\sigma$ (mS cm$^{-1}$)</th>
<th>In-plane ionic conductivity normalized to IEC $\sigma^*_N$ (mS cm$^{-1}$/mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12k-23k-12k</td>
<td>21</td>
<td>0.45 ± 0.00</td>
<td>1.66</td>
<td>15.2 ± 0.5</td>
<td>9.2</td>
</tr>
<tr>
<td>25k-25k</td>
<td>30</td>
<td>0.41 ± 0.00</td>
<td>1.52</td>
<td>14.2 ± 0.4</td>
<td>9.3</td>
</tr>
<tr>
<td>25k-56k-25k</td>
<td>34</td>
<td>0.43 ± 0.01</td>
<td>1.51</td>
<td>17.3 ± 0.5</td>
<td>11.5</td>
</tr>
<tr>
<td>40k-44k</td>
<td>43</td>
<td>0.42 ± 0.01</td>
<td>1.60</td>
<td>20.7 ± 0.6</td>
<td>12.9</td>
</tr>
<tr>
<td>57k-57k</td>
<td>55</td>
<td>0.41 ± 0.04</td>
<td>1.52</td>
<td>11.9 ± 0.3</td>
<td>7.8</td>
</tr>
<tr>
<td>102k-97k</td>
<td>65</td>
<td>0.41 ± 0.00</td>
<td>1.49</td>
<td>14.4 ± 0.6</td>
<td>9.7</td>
</tr>
<tr>
<td>133k-132k</td>
<td>77</td>
<td>0.41 ± 0.01</td>
<td>1.52</td>
<td>19.1 ± 0.1</td>
<td>12.6</td>
</tr>
</tbody>
</table>

Note: Average values for 3 samples. Standard error values reported.

To illustrate the importance of connectivity and to understand how the size of the morphological period $d$ size influenced ionic conduction, we compared the ionic conductivity of diblock and triblock copolymer electrolytes with varying $M_n$ values. Figure S8 depicts the processed SEM images for diblock PS-$b$-P2VP/NMP+ I and symmetrical triblock P2VP/NMP+ I-$b$-PS-$b$-P2VP/NMP+ I samples of varying $M_n$ values. The values of $d$ for the different samples are provided in the SEM images and Table S2. All the different BCP variants were naturally PS rich without addition of homopolymer, and thus the degrees of ion domain connectivity in the samples were poor. Table S2 reports the P2VP to P2VP/NMP+ I conversion, IEC, in-plane iodide anion conductivity, and IEC normalized in-plane conductivity of the samples exposed to methyl iodide vapor for 24 h. No ionic conductivity trend with respect to $d$ was observed. The lack of a trend between ionic conductivity and $d$ for diblock and triblock PS-$b$-P2VP/NMP+ I samples was probably attributed to each sample displaying different degrees of ion domain connectivity, as seen in Figure S8. Our future work will look to
investigate the influence of BCE period size and anion conductivity for P2VP rich systems.

Methods

Random copolymer synthesis

(PS-r-2VP)-OH random copolymers were synthesized by varying compositions of styrene (S) and 2-vinyl pyridine (2VP) via nitroxide-mediated controlled radical polymerization. A representative polymerization procedure is described for the synthesis of copolymer as follows: a mixture of OH-modified initiator, S, and 2VP was degassed by three freeze-thaw cycles. The mixture was heated at 160 °C for 72 h under a nitrogen atmosphere. Conversion of both S and 2VP in the random copolymerization was determined to be greater than 95% in all cases. The resulting copolymers were dissolved in THF and then precipitated in hexanes. $M_n$ was in the range of 2000-7500 g/mol, with PDI values of 1.2-1.6, and the fraction of S was determined by $^1$H NMR spectroscopy.
Equations used to determine the amount of homopolymer to add to attain a targeted volume fraction

\[
\bar{v}_i = \frac{(w_{i\text{BCP}}f_i + w_{i\text{hp}})\rho_{i\text{hp}}^{-1}}{\sum_{i=1}^{2}(w_{i\text{BCP}}f_i + w_{i\text{hp}})\rho_{i\text{hp}}^{-1}} \quad <S1>
\]

\[
f_i = \frac{Mn_{i\text{block}}}{\sum_{i=1}^{2}(Mn_{i\text{block}})} \quad <S2>
\]

\(i\) = a particular block or homopolymer (hp) chemistry (e.g., PS or P2VP)

\(w_i\) = weight of BCP or hp added to the solvent mixture

\(\rho_i\) = density of the hp and the block material in the BCP (\(\rho = 1.05 \text{ g cm}^{-3}\) for PS and \(\rho = 1.114 \text{ g cm}^{-3}\) for P4VP) – values taken from Polymer Data Handbook\cite{2}

\(\bar{v}_i\) = targeted volume fraction in the BCP and hp mixture

\(f_i\) = mass fraction of a particular block in the BCP

Fabrication of substrates with SiN\(_x\) windows for STEM and RSoXS

Silicon wafers coated with SiN\(_x\) on both sides were patterned with a 10 x 10 array of rectangles on the SiN\(_x\) on the backside of the wafer. The patterned SiN\(_x\) would later serve as mask during KOH etching. Self-assembly of PS-\(b\)-P2VP diblock or triblock copolymers was then carried out on the front side of the wafer. Following the DSA process, the wafer was back etched using KOH wet etch procedure. With the front side of the wafer sealed and protected by a holder, the exposed silicon rectangles on the back side of the wafer was removed by KOH solution until the etching reached the silicon
nitride on the front side, creating the imaging windows. The wafer was then cut up into individual windows for STEM imaging and RSoXS experiments.

**Procedure to make IDEs**

**Figure S9.** a.) Process flow diagram to make interdigitated electrodes (IDEs) using conventional photolithography. b) A picture of IDEs patterned on a two inch diameter silicon wafer with 100 µm thermally grown SiOx layer.
EIS measurements and ECE modeling

**Figure S10.** Photos of electrochemical testing of IDEs with Gamry Reference 600 Potentiostat/Galvanostat with Frequency Response Analyzer. A few drops of fresh deionized water (18.2 MΩ) is placed over the IDE being tested.
Figure S11. a.) Diagram of the integrated ECE model into IDE with BCE. b.) ECE model used to fit data in the Nyquist plot collected from EIS. c.) Model fit to EIS data in the Nyquist plot using Simplex Algorithm. The red underline in Panel C represents the BCE (i.e., film) and brush resistance and the calculated chloride ion conductivity of the sample is reported. Equation <S1> below was used to determine the chloride ion conductivity from the BCE (i.e., film) and brush resistance.
\[ \sigma_{\text{FILM BR}} = \frac{1}{R_{\text{FILM BR}}} \cdot \frac{d}{l(n-1)t} \]  \hspace{1cm} <S3>

\( R_{\text{FILM BR}} \): the in-plane resistance of the BCE and brush layer
\( l \): length of the teeth (0.45 cm)
\( t \): thickness of the BCE film and brush layer (ranged from: nm to nm)
\( N \): number of electrodes (\( N = 22 \))
\( d \): interdigitated electrode teeth (100 µm)

\[ C_{\text{FILM BR}} = \frac{1}{(Z_{\text{CPE}}(\omega=\omega_{\text{max}}))^n \cdot \omega_{\text{max}}} \cdot \frac{1}{t} \]  \hspace{1cm} <S4>

\( C_{\text{FILM BR}} \): the BCE and brush layer capacitance
\( n \): ideality of the capacitor (set equal to one for all model fits – assume ideal capacitor)
\( t \): thickness of the BCE film and brush layer (ranged from: nm to nm)
\( \omega \): angular frequency
\( \omega_{\text{max}} \): angular frequency at the semicircle maximum

Equation <S3> was used to calculate the ionic conductivity of the thin film BCE film on an IDE, while equation <S4> was used to calculate the normalized capacitance of the thin film BCE.\[3\]

References