Electronic Supplementary Information for

A multiple ion-exchange membrane design for redox flow batteries

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Text S1. Comparison of ion crossover of double-IEM and triple-IEM over single-IEM cell configuration

Assumptions are as follows: (1) The concentration of all ions in their electrolytes is uniform; (2) The volume of all electrolytes is the same; (3) The diffusion coefficient of all anions in the AEM is the same and also equals to the diffusion coefficient of all cations in the CEM; and (4) The ion selectivity of AEM for the anion and CEM for the cation is 99% (i.e., the diffusion coefficient of any anion is 99 times that of any cation in AEM, and the diffusion coefficient of any cation is 99 times that any anion in CEM).

![Diagram of single-IEM, double-IEM, and triple-IEM configurations](image)

Scheme S1. Configuration of single-IEM, double-IEM, and triple-IEM RFBs.

With the aforementioned assumptions, the crossover behavior of electro-active ions in each side of the RFB becomes symmetric. We consider the following crossover as an example for analysis: Electro-active anion crossovers from left side to the right side of a RFB cell. The following differential equations can be established for each case (Scheme S1).

(i) Single-IEM configuration:
\[ \frac{dC_L}{dt} = -\frac{D^+}{d_1} (C_L - C_R) \]
\[ \frac{dC_R}{dt} = \frac{D^+}{d_1} (C_L - C_R) \]

(ii) Double-IEM configuration:
\[ \frac{dC_L}{dt} = -\frac{D^+}{d_2} (C_L - C_M) \]
\[ \frac{dC_M}{dt} = \frac{D^+}{d_2} (C_L - C_M) - \frac{D^-}{d_1} (C_M - C_R) \]
\[ \frac{dC_R}{dt} = \frac{D^-}{d_2} (C_M - C_R) \]

(iii) Triple-IEM configuration:
\[ \frac{dC_L}{dt} = -\frac{D^+}{d_3} (C_L - C_{L-M}) \]
\[ \frac{dC_{L-M}}{dt} = \frac{D^+}{d_3} (C_L - C_{L-M}) - \frac{D^-}{d_2} (C_{L-M} - C_{R-M}) \]
\[ \frac{dC_{R-M}}{dt} = \frac{D^-}{d_3} (C_{L-M} - C_{R-M}) - \frac{D^-}{d_1} (C_{R-M} - C_R) \]
\[ \frac{dC_R}{dt} = \frac{D^-}{d_3} (C_{R-M} - C_R) \]

Where, \( D^+ \) and \( D^- \) are diffusion coefficients of the electro-active anion in CEM and AEM, respectively; \( C_L, C_R, C_M, C_{L-M}, C_{R-M} \) are the concentrations of the anion in left electrolyte, right electrolyte, middle electrolyte, left-middle electrolyte, and right-middle electrolyte, respectively; \( d_1, d_2, \) and \( d_3 \) are IEM thickness in single-IEM, double-IEM, and triple-IEM, respectively; and \( t \) is time.

The concentration of the electro-active anion in left electrolyte is one unit and zero in all other electrolytes at time zero. For the double-IEM configuration, two IEM thicknesses are considered: 1) the same and 2) a half of the single-IEM thickness. For triple-IEM configuration two IEM thicknesses are also considered: 1) the same and 2) a third of the single-IEM thickness. With these assumptions above conditions, the differential equations listed above were solved by Matlab®, and the results are shown in Figure S4 and Table S1 and S2.
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<tr>
<th>Cell configuration</th>
<th>Crossover time ratio under given crossover tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 ppm</td>
</tr>
<tr>
<td>Double-IEM over single-IEM</td>
<td>142</td>
</tr>
<tr>
<td>Triple-IEM over single-IEM</td>
<td>4177</td>
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</tbody>
</table>

Table S2. Crossover time ratios of double-IEM and triple-IEM over single-IEM cell configuration to reach a given crossover tolerance \([d_2 = (1/2) d_1 \text{ and } d_3 = (1/3) d_1]\)

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Crossover time ratio under given crossover tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 ppm</td>
</tr>
<tr>
<td>Double-IEM over single-IEM</td>
<td>71</td>
</tr>
<tr>
<td>Triple-IEM over single-IEM</td>
<td>1393</td>
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Fig. S1. Schematic of a possible single-IEM RFB that is capable of handling a cation/cation redox pair (or anion/anion pair) vs. an anion–cation hybrid redox pair. A cation/cation redox pair (C$_N^{2+}$/C$_N^{0+}$) in negative electrolyte vs. a cation/anion hybrid redox pair (C$_P^{0+}$/A$_P^-$) in positive electrolyte. $X^-$ is the balancing anion. When A$_P^-$ does not react with either C$_N^+$ or C$_N^{2+}$ (no electrochemical reaction or other chemical reactions), a single AEM can be sufficient for this RFB, although a double–IEM configuration is preferred. For an anion/anion negative pair vs. an anion/cation hybrid positive pair, a CEM can be sufficient.
Fig. S2. Schematic of a possible double-IEM RFB that is capable of handling an anion–cation hybrid redox pair vs. an anion–cation hybrid redox pair. An anion/cation hybrid redox pair ($A_N^-/C_N^+$) in negative electrolyte vs. a cation/anion hybrid redox pair ($C_P^+/A_P^-$) in positive electrolyte. $M_N^+$ and $X_P^-$ are the balancing ions. When $C_N^+$ and $A_P^-$ do not react with each other, a double-IEM (CEM/AEM combination) is sufficient for this RFB, although a triple-IEM configuration is preferred.
Fig. S3. Schematic of a possible single-IEM RFB that is capable of handling an anion–cation hybrid redox pair vs. an anion–cation hybrid redox pair. A carion/anion hybrid redox pair ($C_N^+/A_N^-$) in negative electrolyte vs. a cation/anion hybrid redox pair ($C_P^+/A_P^-$) in positive electrolyte. When (1) $A_N^-$ does not react with $C_P^+$; (2) $A_P^-$ does not react with $C_N^+$; and (3) $A_N^-$ does not react with $A_P^-$, a single AEM is sufficient for this RFB, although a triple-IEM configuration is preferred.
Fig. S4. The crossover time ratio of double-IEM or triple-IEM to single-IEM cell configuration. (a) The crossover time ratio of double-IEM to single-IEM cell configuration to reach a given crossover tolerance. The membranes in the double-IEM configuration have either the same thickness (red line) or a half of the single-IEM membrane thickness (blue line). (b) The crossover time ratio of triple-IEM to single-IEM cell configuration to reach a given crossover tolerance. The membranes in triple-IEM configuration have either the same thickness (red line) or a third of the single-IEM membrane thickness (blue line).
Fig. S5. Experimental setup of double-IEM cell configuration.