Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information for

A multiple ion-exchange membrane design for redox flow batteries

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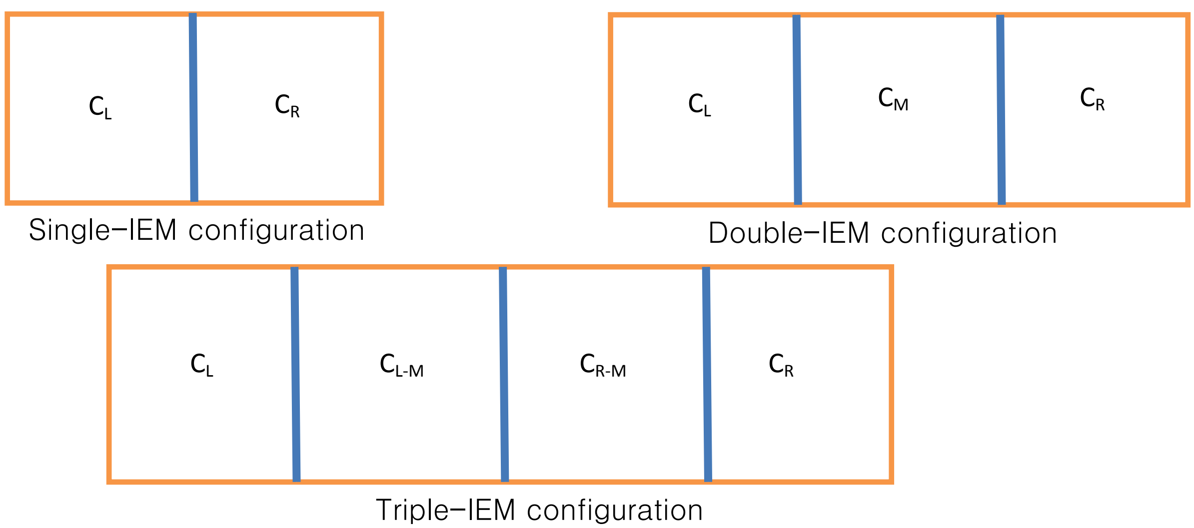
Text S1. Comparison of ion crossover of double-IEM and triple-IEM over single-IEM cell configuration

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).



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**).

<u>(i) Single-IEM configuration:</u>

$$\frac{dC_L}{dt} = -\frac{D_{-+}}{d_1}(C_L - C_R)$$

$$\frac{dC_R}{dt} = \frac{D_{-+}}{d_1}(C_L - C_R)$$

(ii) Double–IEM configuration:

$$\frac{dC_L}{dt} = -\frac{D_{-+}}{d_2}(C_L - C_M)$$

$$\frac{dC_M}{dt} = \frac{D_{-+}}{d_2}(C_L - C_M) - \frac{D_{--}}{d_2}(C_M - C_R)$$

$$\frac{dC_R}{dt} = \frac{D_{--}}{d_2}(C_M - C_R)$$

(iii)Triple–IEM configuration:

$$\frac{dC_L}{dt} = -\frac{D_{-+}}{d_3}(C_L - C_{L-M})$$

$$\frac{dC_{L-M}}{dt} = \frac{D_{-+}}{d_3}(C_L - C_{L-M}) - \frac{D_{--}}{d_3}(C_{L-M} - C_{R-M})$$

$$\frac{dC_{R-M}}{dt} = \frac{D_{--}}{d_3}(C_{L-M} - C_{R-M}) - \frac{D_{-+}}{d_3}(C_{R-M} - C_R)$$

$$\frac{dC_R}{dt} = \frac{D_{-+}}{d_3}(C_{R-M} - C_R)$$

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**.

Table S1. Crossover time ratios of double-IEM and triple-IEM over single-IEM cell configuration to reach a given crossover tolerance (d_1 = d_2 = d_3)

Cell configuration	Crossover time ratio under given crossover tolerance		
	1 ppm	10 ppm	100 ppm
Double-IEM over single-IEM	142	46	15
Triple-IEM over single-IEM	4177	976	150

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 and d_3 = (1/3) d_1]

Cell configuration	Crossover time ratio under given crossover tolerance		
	1 ppm	10 ppm	100 ppm
Double-IEM over single-IEM	71	23	7.5
Triple-IEM over single-IEM	1393	326	82

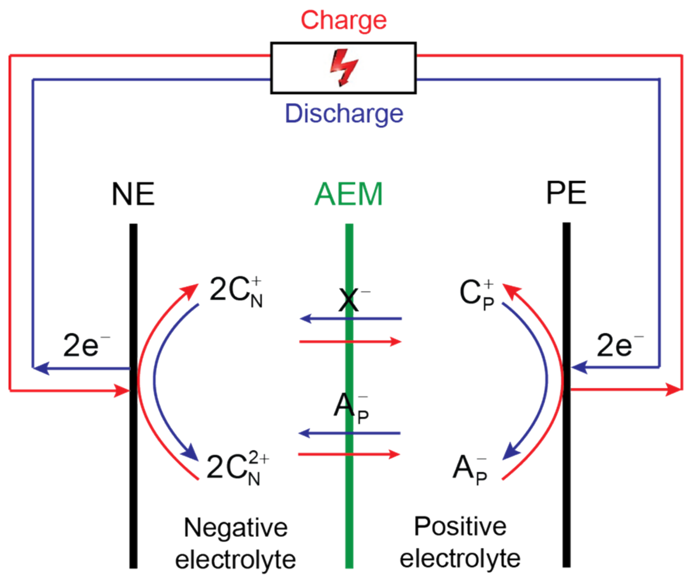


Fig. S1. Schematic of a possible single-IEM RFB that is capable of handling a cation/cation redox pair (or anion/anion pair) vs. an anion-cation hybrid redox pair. A cation/cation redox pair (C_N^{2+}/C_N^+) in negative electrolyte vs. a cation/anion hybrid redox pair (C_P^+/A_P^-) in positive electrolyte. 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.

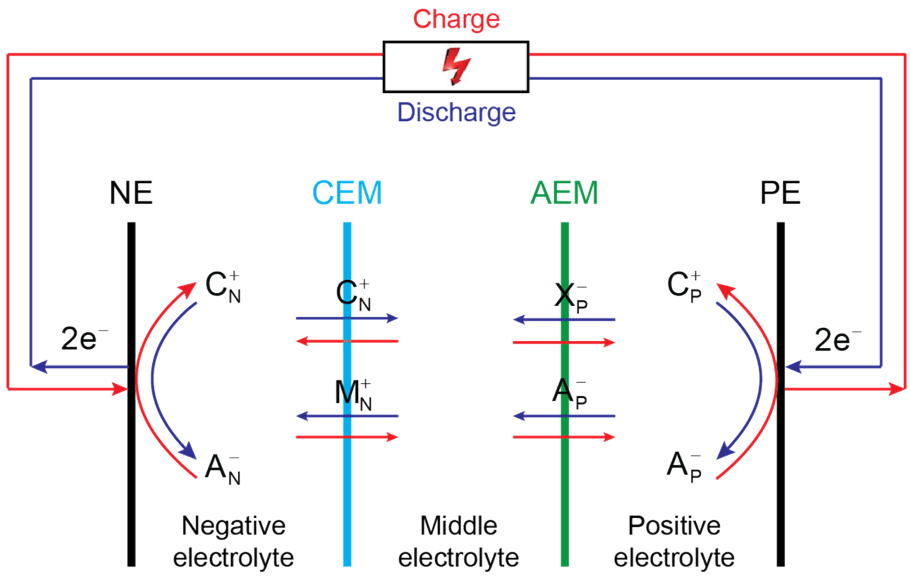


Fig. S2. Schematic of a possible double-IEM RFB that is capable of handling an anion–cation hybrid redox pair vs. an anion–cation hybrid redox pair. An anion/cation hybrid redox pair (A_N^-/C_N^+) in negative electrolyte vs. a cation/anion hybrid redox pair (C_P^+/A_P^-) in positive electrolyte. M_N^+ 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.

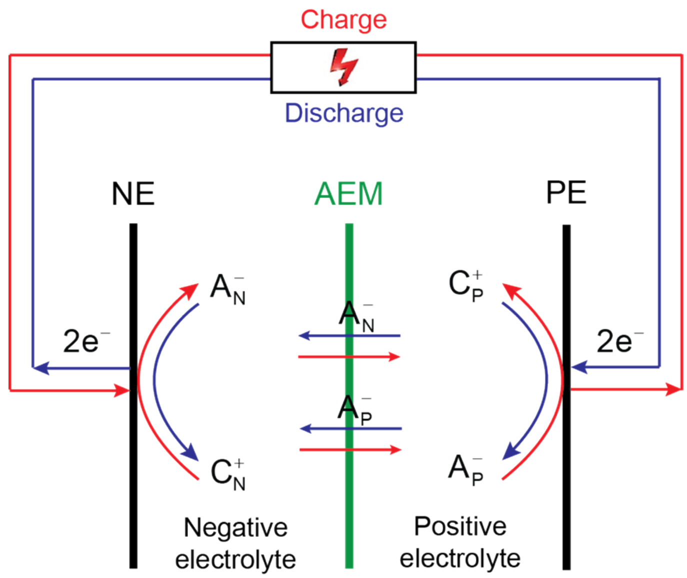
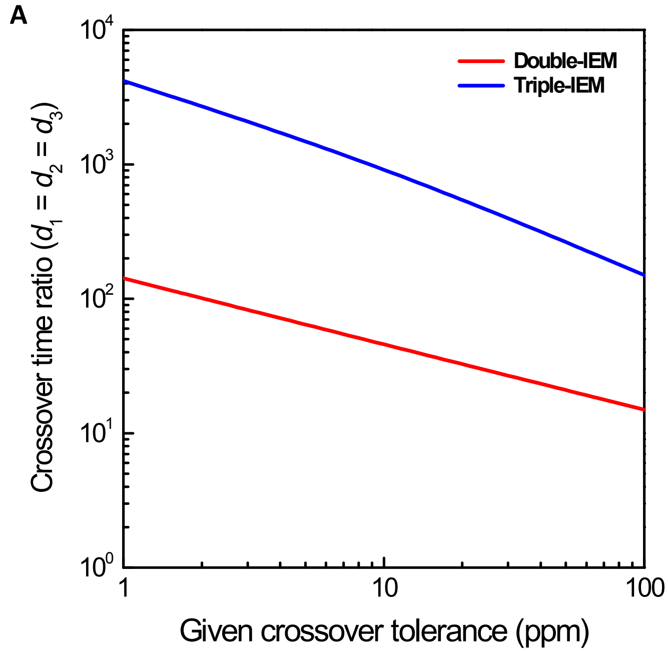


Fig. S3. Schematic of a possible single-IEM RFB that is capable of handling an anion-cation hybrid redox pair vs. an anion-cation hybrid redox pair. A carion/anion hybrid redox pair (C_N^+/A_N^-) in negative electrolyte vs. a cation/anion hybrid redox pair (C_P^+/A_P^-) in positive electrolyte. When (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.



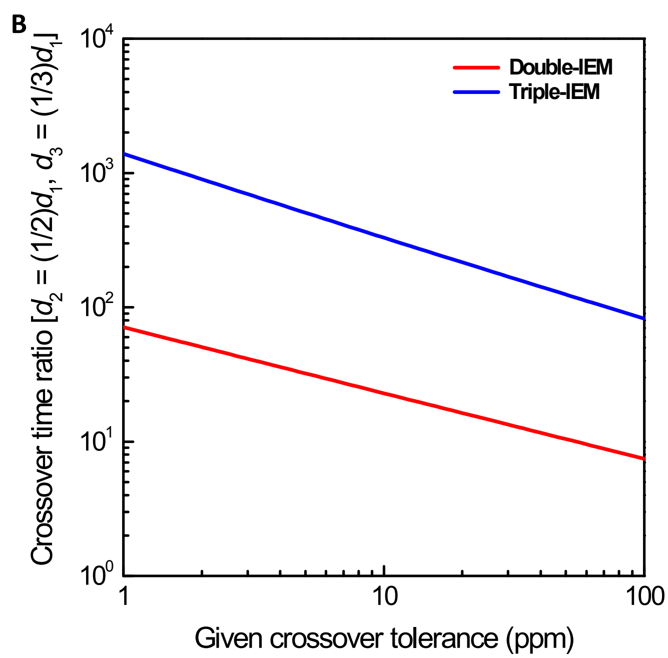


Fig. S4. The crossover time ratio of double-IEM or triple-IEM to single-IEM cell configuration. (a) The crossover time ratio of double-IEM to single-IEM cell configuration to reach a given crossover tolerance. The membranes in the double-IEM configuration have either the same thickness (red line) or 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).

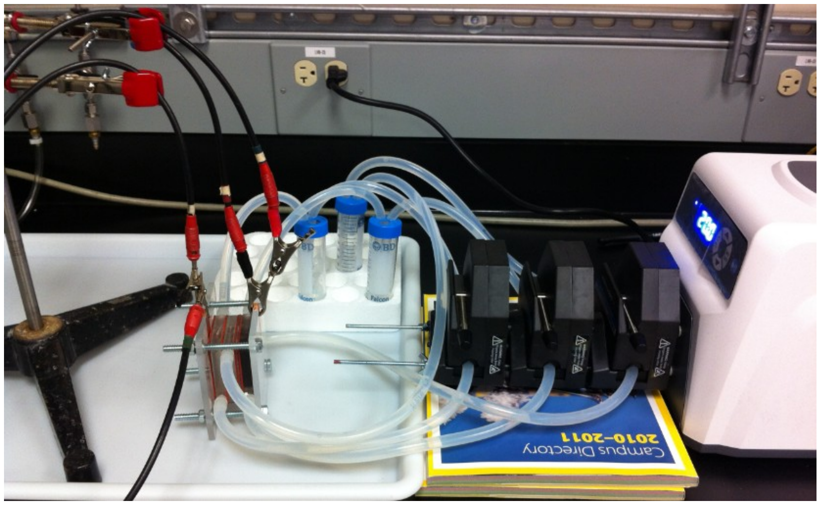


Fig. S5. Experimental setup of double-IEM cell configuration.