

## Double-Membrane Design for High-Voltage and Low-Crossover Redox Flow Batteries

Shuang Gu\*, Ke Gong, Emily Z Yan, and Yushan Yan\*

Department of Chemical & Biomolecular Engineering,  
University of Delaware  
5 Innovation Way, Newark, DE 19716, USA

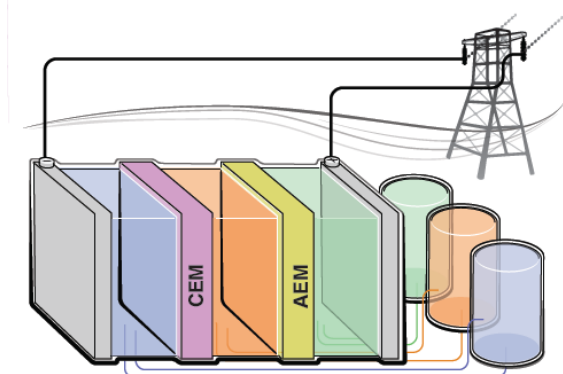
\*[shgu@udel.edu](mailto:shgu@udel.edu) and \*[yanys@udel.edu](mailto:yanys@udel.edu)

Decoupling energy capacity and power delivery, redox flow batteries (RFBs) have great design flexibility and scalability, particularly suitable for the applications of renewable (e.g., wind and solar) electricity storage<sup>[1, 2]</sup>. As electrochemical devices, RFBs are also free from geographical or geologic limitations that are faced by the pumped hydro and the compressed air electricity-storage technologies. However, the generally low energy and power density of RFBs have been identified to be main drawbacks especially when compared with other battery systems, reducing the cost-effectiveness of RFBs. Increasing the solubility of electroactive species by choosing alternative redox pairs or using different electrolytes can theoretically increase the energy density, but leaving the power density unchanged. Improving electrode performance by using better electrode design or utilizing more active catalysts can increase the power density, but not the energy density. The ideal and straightforward solution would be the increase of cell voltage for RFBs, which increase the energy density and power density simultaneously.

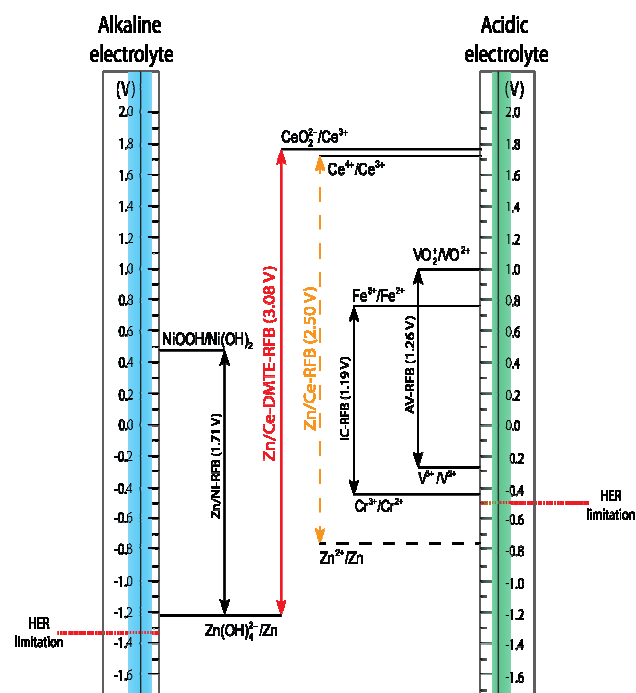
The cell voltage is simply determined by the two redox pairs used, and in general the cation-based redox pairs have more positive redox potentials (favorable for the positive electrode of RFBs) and anion-based redox pairs have more negative redox potentials (favorable for the negative electrode of RFBs). In principle, the use of single ion-exchange membrane (IEM) in current RFBs requires the same ionic type of redox pairs in both positive and negative electrodes: either all cation-based redox pairs (when anion-exchange membrane, AEM, used) or all anion-based redox pairs (when cation-exchange membrane, CEM, used), fundamentally limiting their cell voltages. For example, the earliest RFB, i.e., the iron-chromium RFB (IC-RFB, [(Fe<sup>3+</sup>/Fe<sup>2+</sup>)/(Cr<sup>3+</sup>/Cr<sup>2+</sup>)] with +1.18 V standard cell voltage) and the currently most popular RFB, i.e., the AV-RFB [(VO<sub>2</sub><sup>+</sup>/VO<sub>2</sub><sup>2+</sup>)/(V<sup>3+</sup>/V<sup>2+</sup>)] with +1.26 V both belong to the all-cation-based RFBs. The polysulphide-bromine RFB (SB-RFB, [(S<sub>4</sub><sup>2-</sup>/S<sub>2</sub><sup>2-</sup>)/(Br<sub>3</sub><sup>-</sup>/Br<sup>-</sup>)] with +1.36 V) is a typical all-anion-based RFB. Besides, the single IEM cell structure also requires the same or similar supporting electrolyte in positive electrolyte and negative one, which sometimes limits the choices of redox pairs and further narrows the available range of cell voltages.

Here we present the double-IEM design (one AEM, one CEM, and a middle electrolyte, **Scheme 1**) in one cell that can use cation-based redox pairs and anion-based redox pairs at the same time. As a result, ultra-high cell voltage can be achieved in aqueous RFBs, e.g., 3.08 V (standard voltage) of a zinc-cerium RFB [denoted as Zn(OH)<sub>4</sub><sup>2-</sup>/Zn||Ce<sub>2</sub>O<sup>6+</sup>/Ce<sup>3+</sup>, where Zn(OH)<sub>4</sub><sup>2-</sup>/Zn and Ce<sub>2</sub>O<sup>6+</sup>/Ce<sup>3+</sup> are negative and positive pairs, respectively, and the double vertical lines are for the CEM and AEM couple]. To the best of our knowledge, this more-than-3 V cell voltage is the highest among all known aqueous

RFBs (**Figure 1**). Enabled by the effective redox pair isolation and the ion buffer function provided by the middle electrolyte, the double-IEM RFBs have significantly lowered counter-ion-crossover rate between positive electrolyte and negative electrolyte, compared with the single-IEM RFBs. The multi-IEM approach may also have implications in primary and other secondary battery designs.



**Scheme 1** Schematic of double-membrane RFB cell configuration.



**Figure 1** Standard voltage and preferred cell configuration of aqueous RFBs. Single-CEM cell is preferred for an anion/anion redox pair vs. an anion/anion redox pair (left region); single-AEM cell is preferred for a cation/cation redox pair vs. a cation/cation redox pair (right region); and double-IEM cell is preferred for an anion/anion redox pair vs. a cation/cation redox pair (middle region).

### References

- [1] Z. G. Yang, J. L. Zhang, M. C. W. Kintner-Meyer, X. C. Lu, D. W. Choi, J. P. Lemmon, J. Liu, *Chem Rev* **2011**, *111*, 3577-3613.
- [2] B. Dunn, H. Kamath, J. M. Tarascon, *Science* **2011**, *334*, 928-935.

**Key words:** Cell voltage, Crossover, Ion exchange membranes, Redox flow batteries, Energy storage.