Renewable energy, such as wind and solar, can help mitigate the issues of air pollution, climate change, and fossil-fuel shortage. However, renewable energy sources are intermittent, so their integration to the grid must be managed. Therefore, the key to the development of large-scale renewable energy is the energy storage system. Currently, redox flow battery (RFB) is considered as one of the best energy storage systems for intermittent renewable energy sources like wind and solar. The advantages of RFBs include flexible designs, excellent scalability, and long cycle life. Aqueous RFBs are also safer and more reliable compared to flammable lithium-ion batteries as the redox pairs are separated in different tanks during non-operation.

A key component for RFBs is the ion-exchange membrane (IEM), which is electronically insulating while preventing the cross-mixing of reactive species and allowing the passage of supporting ions to balance the charge on both sides. Different IEMs are required for different RFB systems due to the different reactive species and balancing ions.

For the zinc-cerium double membrane RFB which has the highest cell voltage in reported aqueous RFBs, the vital issue is the insufficient chemical stability of commercial anion-exchange membranes in the oxidative cerium electrolyte. An oxidatively stable anion-exchange membrane was developed for the zinc-cerium double membrane RFB system. Four different aromatic polymer backbones were examined and hexafluoroisopropylidene polybenzimidazole (F₆PBI) showed the best stability in the cerium electrolyte. To achieve the ClO₄⁻ exchange functionality for zinc-cerium double membrane RFB, tris(2,4,6-trimethylphenyl)phosphonium (TTMePP⁺) and tris(2,4,6-trimethoxylphenyl)phosphonium (TTMPP⁺) functionalized F₆PBI polymers were synthesized and casted into membranes. The prepared TTMPP-PBI membrane exhibited good balance of anion conductivity and oxidative resistance.
Besides the outstanding stability in the cerium electrolyte, the prepared TTMPP-PBI membrane exhibited excellent acid doping level in 3 M sulfuric acid solution due to its ability to form acid-base acid doping at the lone-pair nitrogen and oxygen sites, and cation-anion acid doping at the positive cations. The high acid doping level led to low area specific resistance in the RFB cell. This membrane was also tested in vanadium redox flow battery (VRFB) and showed the better voltage efficiency and energy efficiency compared with Nafion 115 and F6PBI membranes.

In the next section, we explored an alternative pathway to functionalize the F6PBI by using methyl iodide to produce methylated hexafluoroisopropylidene polybenzimidazolium (DMF6PBI) membrane with higher acid doping level and improved conductivity in sulfuric acid electrolytes. We used DMF6PBI for all vanadium redox flow battery. Although higher voltage efficiency and energy efficiency were achieved, DMF6PBI is chemically unstable in the vanadium electrolyte. A detailed investigation of the degradation mechanism was taken to provide guidance for the future vanadium resistant membrane design.

Overall, multiple polymer membranes were synthesized in this work. TTMPP-PBI membranes achieved improved stability in the cerium electrolyte and better performance in VRFBs. DMF6PBI membranes showed better VRFB performance but limited chemical stability. Future research can focus on developing materials with improved RFB performance and limiting the degradation on these types of membranes in order to make RFBs an economically viable option for grid-sized energy storage.