“Passive mitigation of ionic crossover in all-vanadium redox flow batteries via novel asymmetric cell topologies”

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Abstract

Scalable architecture of redox flow batteries (RFBs) is a promising solution for large-scale energy storage. The capability of decoupling energy storage capacity from power generation provides RFBs with flexibility for delivering desired storage capacity or output power for a given application. Among many chemistries developed for RFBs, all-vanadium redox flow batteries (VRFBs) currently show great potential for widespread commercialization. VRFBs utilize vanadium ions (in four different oxidation states) in the negative and positive electrolytes; this characteristic frees them from irreversible capacity decay as a function of electroactive species transport through the membrane (i.e. crossover). However, crossover of vanadium ions and water is inevitable during the charge/discharge cycling. This undesired ionic and water crossover not only results in a lost discharge capacity during cycling, but also has real-time influence on the cell performance

Several parameters affect solute (vanadium ions) and solvent (water) crossover during cycling; these include: membrane characteristics, cell architecture, electrolyte composition, and electrochemical operating conditions (load profile). Therefore, it is necessary to understand these coincident contributors affecting the transport of vanadium ions and water through the membrane.

In this talk, we will present experimental data tailored to quantify the contributions to capacity decay stemming from ion-exchange membrane properties (e.g. equivalent weight and degree of reinforcement), flow field design, electrode configuration and electrolyte properties. A major focus has been to understand the effect of the electrode/membrane interface on the overall capacity decay and contact resistance. Novel ex-situ conductivity cells have been devised to assess ionic conductivity of the ion-exchange membranes along with electrolytes leading to details on the impact of interfacial phenomena on ionic conductivity and crossover.

To quantify the long-term influence of crossover, a unique set-up has been designed and built that enables real-time measurement of ionic transport across the polymeric membrane using ultraviolet-visible (UV/Vis) spectroscopy. The test system enables separation of contributions to crossover emerging from concentration and electrostatic potential gradients. Also, to investigate the instantaneous impact of crossover on the VRFB performance, a real-time current density distribution diagnostic has been implemented for measuring the in-plane current density distribution. The insights gained from this suite of experimental diagnostics have enabled identification and quantification of major contributors to capacity decay originating from the membrane, cell configuration, electrolyte composition, and operating conditions. These findings have inspired design of systems with enhanced performance and greatly decreased crossover loses. Through asymmetric design, crossover is significantly mitigated during long-term cycling, improving the energy storage efficiency of VRFBs. The novel cell configurations designed and engineered for this work provide an inexpensive and passive solution for further adopting the VRFBs as a safe and robust technology for grid-scale storage.