Mitigating capacity fade in vanadium redox flow batteries using asymmetric currents during cycling

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Vanadium redox flow batteries (VRFBs), unlike other conventional energy-storage devices, have great potential in solving problems related to grid-scale energy storage and demand. This can be attributed to the unique architecture of VRFBs which allows for the decoupling of energy storage and power output; the former being dictated by the size of the electrolyte storage tanks and the latter being governed by the size of the cell stack [1].

In these systems, proton exchange membranes (PEM) have been successfully employed as the separators which transport charge carrier ions while blocking the crossover of the active species. Despite being designed to permit the passage of protons, these membranes permit the unwanted transport of vanadium as well (crossover). The crossover of active species facilitates side reactions which in turn, diminish the system's capacity and operating voltage; conversely, it increases the associated operating costs [2-3]. Studies that have been conducted so far have largely focused on tailoring the properties of the membrane to minimize the crossover of vanadium ions [4].

In addition to tailoring membrane properties, our recent studies [3,5,6] indicate that one potential approach to reduce the crossover during VRFB operation is altering the operating conditions (e.g., flow type, flow rate) based on the membrane properties. The idea behind this approach is that by adjusting the operating conditions, it is possible to minimize the driving forces that are responsible for species crossover in the membrane. To this end, the goal of this study is to investigate the possibility of using asymmetric current conditions (i.e., different currents during charging and discharging) to mitigate the capacity loss of VRFBs. The operation of a VRFB was simulated for both a convection-dominated and a diffusion-dominated membrane using an in-house experimentally validated VRFB model. During the simulations, the charging current was varied while the discharging current was held constant.

As can be seen in Fig. 1, increasing the charging current from 400 A m^{-2} to 1000 A m^{-2} increased the capacity retention by ~ 7.1%. This can be attributed to the fact that increasing the charging current density increases the magnitude of the electro-osmotic crossover during charging which compensates for the osmotic crossover and reduces the net convective crossover. Conversely, increasing the charging current density decreased the voltage efficiency of the convection-dominated membrane by ~ 6% (Fig. 2). This can be attributed to the

increased ohmic losses that result from an increase in the charging current density. Furthermore, when both membranes are compared, a more significant improvement in capacity retention was observed for the diffusion-dominated membrane because of the fact that diffusion has less time to affect the capacity during a single cycle as a result of increased charging current.

The findings of this study highlight the importance of intelligently selecting operating conditions to reduce the capacity fade of VRFBs. Along with other simulation results for both membranes, a detailed discussion with regards to the physical reasons for these observed trends will be presented in the talk.
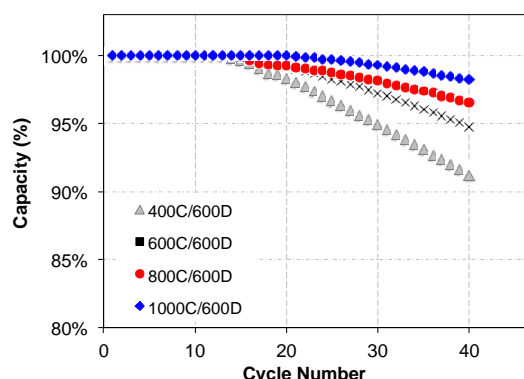

Figure 1. Capacity loss over 40 cycles when operated at 400C/600D (i.e., charging at 400 A m^{-2} and discharging at 600 A m^{-2}), 600C/600D, 800C/600D, and 1000C/600D for the convection-dominated membrane.
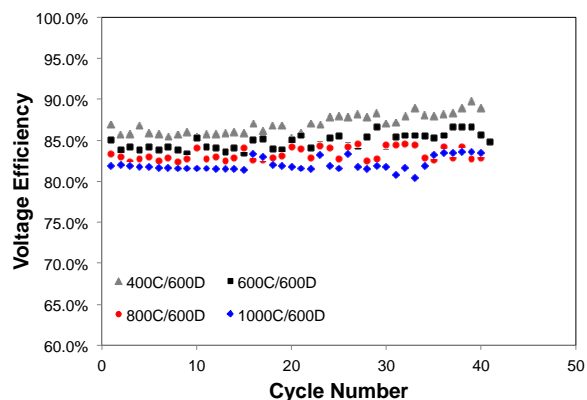

Figure 2. Voltage efficiency over 40 cycles when operated at 400C/600D (charging at 400 A m^{-2} and discharging at 600 A m^{-2}), 600C/600D, 800C/600D, and 1000C/600D for the convection-dominated membrane.

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