

In-situ electrode kinetics studies of an all-vanadium redox flow battery

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Redox flow batteries (RFBs) are a promising large-scale energy storage technology. Power and energy capacity are independently scalable, charging and discharging responses are fast, and most components are quite robust. The all-vanadium RFB (VRB) avoids loss of battery capacity due to crossover, a problem in many other RFB chemistries. As a means to drive rational approaches to increased VRB performance, we focus on understanding what loss mechanisms dominate performance loss in VRBs.

The polarization behavior of a battery can be roughly divided into three controlling phenomena which dominate the cell overpotential loss at differing currents¹. At low current, slow reactions result in kinetically-controlled overpotential. By including a dynamic hydrogen electrode (DHE) in the VRB we were able to individually assess each electrode's contribution to the overpotential (Figure 1 shows DHE placement).



We employed three different techniques to study the in-situ kinetic behavior of the VRB. We performed charging and discharging polarization curves in the low current, kinetic region. We also operated the VRB as a symmetric cell in which both sides of the battery had a $V^{3/2+}$ electrolyte or a $V^{5/4+}$ electrolyte. Finally, we performed impedance spectroscopy measurements on each half of the VRB at varying current densities. The three methods yielded the same overall result: the negative side of the battery is kinetically limiting, not the positive. In addition, by

including new, high surface area carbon electrodes, we were able to completely eliminate any kinetic limitation in the battery, resulting in only ohmic and mass transport losses affecting overpotential at any current. These findings indicate that catalysis of either electrode process is unnecessary and that mass transport and conductivity must be improved to develop higher power density VRBs. We are systematically applying these methods to various electrode materials and will report on how aspects of these materials affects observed kinetics.

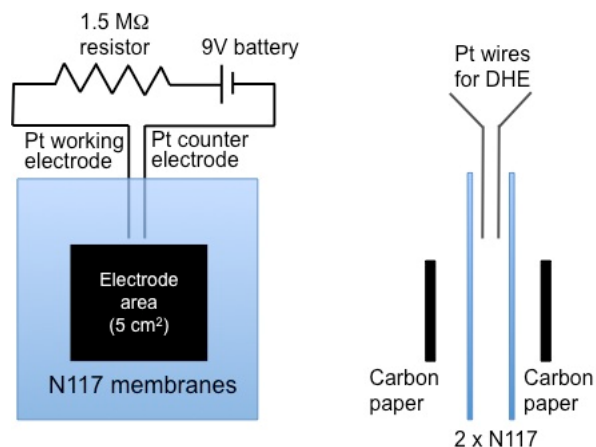


Figure 1. Schematic of the dynamic hydrogen electrode (DHE) used in this study.

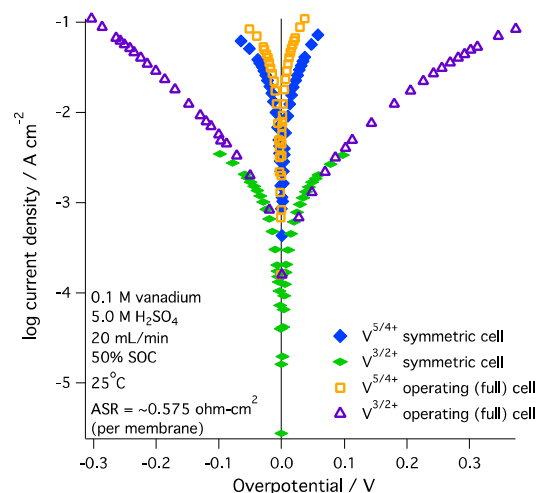


Figure 2. Log current density vs. overpotential in operating (open symbols) and symmetric (closed symbols) cell.

References:

1. D. Aaron, et al. Polarization curve analysis of all-vanadium redox flow batteries. *J. Appl. Electrochem.*, **41**, 1175 (2011).