## **Pseudo-Steady-State Flow Battery Experiments**

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Redox flow batteries have attributes that make them attractive for grid-scale energy storage [1]. A variety of positive and negative active materials have been tried in flow batteries. The all vanadium system is attractive because mixing of the positive and negative reactants through the separator is benign and can be easily reversed [2]. Nevertheless, movement of the different vanadium ions through the membrane separator complicates the study of these systems, because it causes capacity to decline and performance to decrease with repeated cycling.

The inherent performance of the individual electrodes can be studied more effectively as half cells. The approach taken in this work was to circulate one electrolyte, either  $V^{2+}/V^{3+}$  or  $VO^{2+}/VO_2^{+}$ , contained in a single reservoir through both sides of a cell. Thus, in the first case, V is oxidized to  $V^{3+}$  on one electrode and  $V^{3+}$  is simultaneously reduced to  $V^{2+}$  on the second electrode. In the absence of side reactions like hydrogen evolution, no change in electrolyte composition occurs. This allows one to operate the flow battery at essentially steady-state conditions. The driving force for vanadium ion diffusion through the membrane is minimized by operating at flows that are in large excess of the consumption and production rates given by Faraday's law. This approach is more appropriate than, for example, rotating disk experiments when one would like to study Ohmic and mass-transport limitations in addition to reactant kinetics.

Figure 1 shows the polarization of a  $V^{2+}/V^{3+}$  half cell with identical electrodes. The electrolyte was 1.5 M total vanadium in 2.6 M sulfuric acid. The experiments simulated a high state of charge, with 90%  $V^{2+}$  and 10%  $V^{3+}$ . The polarization curve passes through the origin because the electrolyte is the same at both electrodes. The polarization curve is linear over the wide range of current densities tested. The slope of the polarization curve is the same in the top right and lower left quadrants, indicating that the anodic and cathodic performances of the two electrodes are reproducible. Similar results have been obtained for the  $VO^{2+}/VO_2^+$  electrode.



Figure 1: Polarization curve for 90%  $V^{2+}$ , 10%  $V^{3+}$ .

The experimental approach presented here is particularly well-suited to studying electrode stability, because an electrode can be maintained in a tight voltage window and cycled without having to worry about balancing the electrolyte solutions. The cell can be cycled at a rate that is independent of electrolyte volume.

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## References

- 1. A. Z. Weber, Ma. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, Q. Liu, "Redox flow batteries: a review" *Journal of Applied Electrochemistry*, **41**, *pp*. 1137-1164 (2011).
- M. Kazacos and M. Skyllas-Kazacos, "Performance characteristics of carbon plastic electrodes in the allvanadium redox cell," *Journal of the Electrochemical Society*, **136** pp. 2759-2760 (1989).