Electrochemical and Fluid Properties of Electrolyte Solutions in All-Vanadium Redox Flow Batteries

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All-vanadium redox flow batteries (AVRFB) are a promising approach to compensate for fluctuations of renewable energies in the power grid [1]. An AVRFB comprises two tanks containing aqueous solutions of sulfuric acid and vanadium species in two different oxidation states – V(II) and V(III) in one tank and V(IV) and V(V) in the other. These electrolyte solutions are pumped through an electrochemical cell, where reversible redox reactions occur, reducing vanadium species in one half-cell and oxidizing vanadium species in the other. There is a lack of fluid property data on those multi-component, highly concentrated solutions in the literature, especially with respect to activity coefficients, which have direct implications for key battery properties such as the cell voltage. Hence, they are crucial for optimizing the composition of the electrolyte solution and, thereby, AVRFB in general [2].

In the present work, a laboratory-scale test rig is set up for characterizing key properties of the AVRFB and for producing electrolyte solutions with specified composition. The state of charge (SOC), and, hence, the concentrations of the vanadium species in the solutions, are determined with a novel scheme using UV-VIS spectroscopy. With the test rig, measurements of the open circuit voltage (OCV) are carried out. By virtue of the Nernst equation, the OCV data intrinsically carry information on ratios of activities of the vanadium species. Moreover, independent measurements of the water activities of the studied solutions are carried out with the isopiestic method [3]. Using the OCV and isopiestic data, a thermodynamic model based on the Pitzer equations [4] is currently being developed for describing the activity coefficients in these complex electrolyte solutions. These results will allow for an improved understanding of the behavior of the electrolyte solutions used in AVRFBs, and will eventually contribute to an improved system design.

References

- 1. M. Skyllas-Kazacos et al., ChemSusChem 9 (2016) 1521-1543.
- 2. N. Hayer, M. Kohns, J. Electrochem. Soc. 167 (2020) 110516.
- 3. J.A. Rard, J. Solution Chem. 48 (2019) 271–282.
- 4. K. Pitzer, Activity Coefficients in Electrolyte Solutions, Second Edition, CRC Press, Boca Raton, 1991.