

Solvation of Vanadium Cations in Aqueous and Perfluorosulfonic Acid Membranes

Fatemeh Sepehr and Stephen J. Paddison

Department of Chemical and Biomolecular Engineering,
University of Tennessee, Knoxville, TN 37996

In recent decades the demand for replacing the fossil fuel with renewable green energy sources such as solar and wind was significantly increasing as a result of environmental issues. One of the limiting factors for the utilization of the renewables in electrical supply grid is the intermittent nature of these sources which requires the employment of megawatt scale electrical energy storage devices. The Redox Flow Battery (RFB) is among the promising large-scale electrical energy storage systems that have been received huge attraction due to its superior properties. The RFBs provide long life-span, simple installation, low cost of maintenance, the possibility of instant charging by replacing electrolytes and the ability to repeatedly store and convert electrical energy to chemical energy and vice versa. In addition, RFBs have the unique advantage of having power and energy decoupled due to the separation of the electrolyte reservoirs and the battery stacks.^{1,2}

Of the many reported RFBs, the Vanadium Redox Flow Battery (VRFB) demonstrates excellent electrochemical activity and reversibility. The VRFB consists of a V^{2+}/V^{3+} sulfate solution at the negative electrolyte and a VO^{2+}/VO_2^+ sulfate solution at the positive electrolyte separated by a Proton Exchange Membrane (PEM). The wide span between the standard reduction potentials of the two half-cells in these batteries produces a standard voltage of 1.25 V, which is comparable to the other types of RFBs.³ Also, having all the active species from one element at different oxidation states, makes the regeneration of electrolytes easier.

Despite the numerous advantages of VRFBs, there still exist a number of issues that hinder the commercialization of these storage devices. For example, the poor stability of VO_2^+ solution at high temperatures and high concentrations, results in precipitation of hydrated V_2O_5 and energy loss.⁴ Although, the stability of VO_2^+ ion may be increased by addition of hydrochloric acid, eventually it will form a gel type precipitate involving the V^{3+} cation.⁵ It is therefore important to understand the chemistry and thermodynamics of solvation of vanadium cations in the electrolyte for optimal design.

The other challenging area arises from the membranes used in these devices. The most widely used PEM in VRFBs is Nafion which becomes degraded as a result of exposure to highly acidic environment at electrolytes. It has also been found that the low ion selectivity of PEMs allows permeation of vanadium cations and cross contamination of the electrolytes. Hence, the nature of the diffused cations within perfluorosulfonic acid (PFSA) membranes is of great importance, as the hydration behavior of cations is crucial to their interaction with the sulfonic acid groups. However, the structure of the hydrated vanadium ion, the oxidation state of the ion, and its interaction with sulfonic acid groups inside hydrated PFSA membranes are not understood.⁶

In this work the hydration structure of all four vanadium cations in bulk water is examined with ab initio electronic structure calculations. The thermodynamics of

solvation is considered within the context of a quasi-chemical theory of solution.⁷ The quasi-chemical theory, divides the region around a solute into inner- and outer-shell domains. The inner-shell, where the strong ion-water interactions exist, is treated quantum mechanically, and the outer-shell contributions to the solvation of ion are assessed using a dielectric continuum model. By coupling the inner- and outer-shell results, the free energies of solvation for the four vanadium ions are calculated and compared with the experimental values.

To study the solvation in PFSA membranes, quantum chemical calculations were performed of hydrated vanadium cations in proximity to trifluoromethanesulfonic (triflic) acid. The introduction of triflic acid to each of the four Vanadium hydrated ions was done from different initial positions for the acid molecule(s) with respect to the aqueous complex, and global minimum energy conformations for each system determined. It has been found that for V^{2+} and V^{3+} ions the triflic acid molecule tends to coordinate directly with the central cation, while with using the triflate anion instead of triflic acid, the structure becomes more stable for anion not entering the first hydration shell of vanadium cations. Figure 1 shows the results for V^{2+} ion.

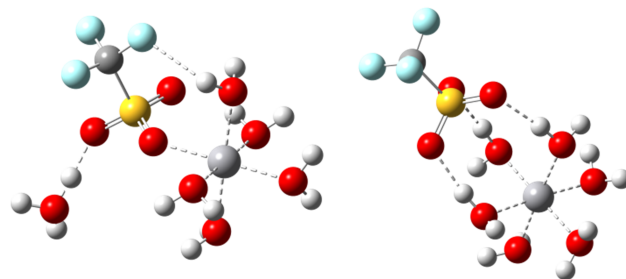


Figure 1. Introduction of triflic acid (left) and triflate anion (right) to hydrated V^{2+} complex.

Our results indicate the presence of weak interaction between the diffused vanadium cations and sulfonic acid groups. However, it is also important to investigate how the morphology of the membrane is affected by the presence of vanadium cations. Previously, our study of hydrated PEMs using coarse grain simulations have led to valuable information on the effect of equivalent weight, molecular weight and hydration on the morphology.⁸ A similar methodology is implemented in the present work to understand the hydrated morphology of PFSA membranes with absorbed vanadium cations and sulfuric acid.

References

1. M. Skyllas-Kazacos, D. Kasherman, D. R. Hong and M. Kazacos, *J. Power Sources*, **35**, 399 (1991).
2. X. Li, H. Zhang, Z. Mai, H. Zhang and I. Vankelecom, *Energy Environ. Sci.*, **4**, 1147 (2011).
3. L. Li, S. Kim, W. Wang, M. Vijayakumar, Z. Nie, B. Chen, J. Zhang, G. Xia, J. Hu, G. Graff, J. Liu and Z. Yang, *Adv. Energy Mater.*, **1**, 394 (2011).
4. F. Rahman, M. Skyllas-Kazacos, *J. Power Sources*, **189**, 1212 (2009).
5. M. Vijayakumar, L. Li, Z. Nie, Z. Yang and J. Hu, *Phys. Chem. Chem. Phys.*, **14**, 10233 (2012).
6. M. Vijayakumar, M.S. Bhuvaneshwari, P. Nachimuthu, B. Schwenzer, S. Kim, Z. Yang, J. Liu, G. L. Graff, S. Thevuthasan, J. Hu, *J. Membr. Sci.*, **366**, 325 (2011).
7. L. R. Pratt, R. A. LaViolette, *Mol. Phys.*, **94**, 909 (1998).
8. D. Wu, S. J. Paddison, J. A. Elliott and S. J. Hamrock, *Langmuir*, **26**, 14308 (2010).