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Electrolyte Solution and Polymer Equilibrium in PFSA Ion Exchange Membrane

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The electrolyte separator is a significant component in redox flow battery cell. The function of this membrane is to separate positive and negative electrolyte solutions or other energy carrying species while allowing ionic connection between two half-cells. Ideally, the separator should have high conductivity to minimize ohmic loss, especially at high current density level. Low active species crossover is also desired to inhibit self-discharge and capacity loss. In addition, the separator's stability is emphasized in the potentially extreme working environment of RFBs. Currently, a proton exchange membrane is one type of electrolyte separator used in RFB research. Nafion made by DuPont is widely regarded, as a standard membrane because its properties have been well investigated and understood in the PEM fuel cell application.

In a vanadium redox flow battery, the working environment for ion exchange membrane is very challenging because of its high acidity, low water activity and high vanadium ion concentration. The membrane performance is strongly related to the presence of electrolyte species in the membrane. It has been proven that the PFSA membrane conductivity is highly dependent on its water uptake[1,2]. The low water activity in electrolyte environment can cause a reduced water content thus lowering proton transport rates. Like other metal ions, vanadium can also be exchanged into the membrane and decrease the proton concentration, especially in the case of anion absence in membrane[3]. Because metal ions generally move much slower than protons in the membrane, lowered proton concentration can definitely cause reduced membrane conductivity by eliminating the most effective charge transporter. In addition, some metal ions can also reduce proton mobility by cation-proton interaction.

The impact of exposure to concentrated vanadium/sulfuric acid solutions on membrane performance, especially conductivity, has not been thoroughly revealed yet. Upon equilibration with practical electrolyte solutions, the proton exchange membrane can absorb or exchange considerable amounts of electrolyte species, including water, sulfuric acid and vanadium ion. To understand the membrane properties under operational conditions, it is important to build relate the equilibrated membrane performance to its composition. The presence of electrolyte species in the membrane has a strong reducing impact on membrane's conductivity (Figure 1). Vanadium ions present in membrane can decelerate charge transport across membrane, but the conductivity loss is not necessarily related to ionic valence state. This somewhat surprising lack of dependence on ion charge suggests that details of vanadium coordination and solvation in the membrane have a strong role on the conduction mechanisms in the membrane. Complicating factors include the lower water content of the membrane in concentrated electrolytes, the effects of multiple anions in the membrane i.e. sulfonic acid group and sulfuric acid exist simultaneously in membrane. The availability of anions for interaction with vanadium species is mainly determined by dissociation balance between these two acids.

In this talk, we will fully describe the composition of membranes exposed to concentrated electrolytes, some transport properties of these membranes and indications of the interactions between the ions and water molecules to reveal the origin of these effects on transport.

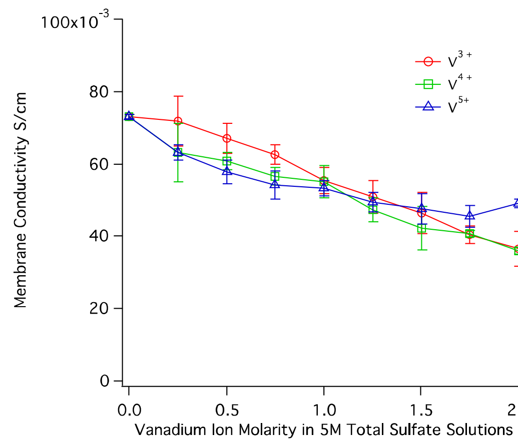

Figure 1. Nafion 117's conductivity after being equilibrated in electrolyte solution with 5M total sulfate and 0-2M vanadium ion at different valence states.

Reference:

1. T. A. Zawodzinski et al., *Journal of The Electrochemical Society*, **140**, 1041 (1993).
2. T. Zhijiang et al., *ECS Transactions*, **41**, 25–34 (2012).
3. T. Okada, Y. Ayato, M. Yuasa, and I. Sekine, *Journal of Physical Chemistry B*, **103**, 3315–3322 (1999).