Importance of ion-ion interactions in membranes for all-vanadium redox flow batteries

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Redox Flow Batteries (RFBs) have the high capacity energy storage necessary for improving power grid efficiency through peak shaving, as well as aiding in the integration of intermittent power sources, such as wind energy and solar energy. Recent efforts to make RFBs more economical have focused on creating cheaper battery membranes that still have good ionic selectivity and conductivity[1]. These quantities can be evaluated through accurate characterization of the multi-component mass transfer processes occurring in RFBs.

Studies of binary diffusion in membranes for RFBs are ubiquitous in the literature[2], however there are surprisingly few publications on the effects of multicomponent diffusion in RFBs. Especially in ion-selective membranes, the effects of ion-ion interactions may be important. For example in Heintz *et al.'s* study on interdiffusion of sodium chloride and hydrochloric acid in neosepta cation exchange membranes[3] found that ion-ion interactions were comparable in magnitude to ion-membrane interactions. This shows that the importance of ion-ion interactions in membranes for RFBs should be tested, so we have measured ion-ion interactions for $VOSO_4$ and H_2SO_4 in cation-exchange, porous, and anion-exchange membranes.

This talk will briefly discuss how analysis of Barnes' transient diffusion model can be used to quickly measure binary diffusion coefficients and sorption equilibria with a single batch dialysis measurement. These results can be used to measure ion-ion interactions using the Steffan-Maxwell formalism given in equation 1.

$$-c_i \nabla \mu_i = \sum_{j \neq i} \frac{RT c_i c_j}{c_T D_{ij}} \left(\vec{v}_i - \vec{v}_j \right) \qquad (1)$$

For n diffusing species, this system of n force explicit equations can be reduced to a system of n-1 flux explicit equations by taking the membrane velocity as the reference and applying the Gibbs-Duhem equation[5].

Taylor and Krishna[6] show that at long times, the concentration in a batch dialysis cell will decay exponentially toward equilibrium, with decay constants that are the eigenvalues of the transport matrix. Using this simplification at long times, and the binary diffusion coefficients, the ion-ion interactions can be measured by performing an interdiffusion experiment. The values of the binary diffusion coefficients and the ion-ion interactions will be given for $VOSO_4$ and H_2SO_4 diffusing through cation-exchange, porous, and anion-exchange membranes. The importance of the ion-ion interactions relative to the ion-membrane interactions will be discussed.

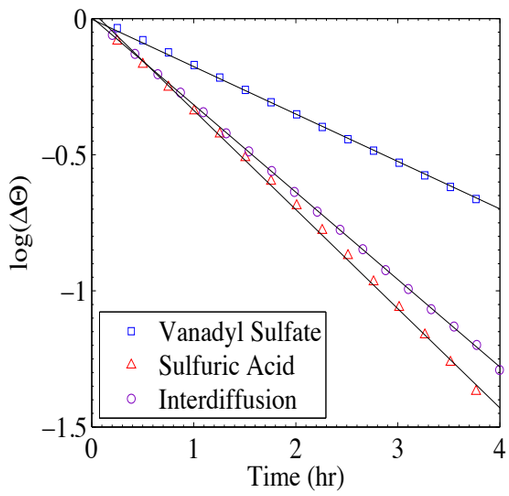

Figure 1: Long time exponential decay towards equilibrium for $VOSO_4$, H_2SO_4, and Interdiffusion in Celgard.

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