

Ex situ measurements of transport properties of vanadium ions for vanadium redox flow batteries

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The Vanadium redox flow battery (VRFB) is a low cost and high efficiency device designed for energy storage and grid storage applications. The battery consists of positive and negative cells operating with $\text{VO}^{2+}/\text{VO}_2^+$ and V(II)/V(III) redox couples, respectively. The cells are separated by an ion exchange membrane, which allows proton conduction to maintain electrical balance during the charge/discharge cycles.¹

Nafion, a membrane commonly used to study VRFB application, has been observed to allow vanadium ion crossover.² This causes self-discharge of the battery and affects battery lifetime.³ By gaining a better understanding of the effects of the vanadium ions in the membranes and moving through the membrane, this knowledge can be extended to comparison of other membranes for uses in VRFBs. It also serves as a steppingstone for the development of improved membranes for application in VRFBs.

Here we report fundamental studies of vanadium ion transport properties in Nafion membranes. Previous studies have shown the VO^{2+} ion permeability to have a dependence on acid concentration in solution.^{4,5} This study is extended to observe the effects of additional vanadium ions diffusing with and against each other. The transport of one species is assumed to be intrinsically linked to the transport of the other vanadium species. These crossover measurements were monitored with a variety of tools including ESR, pH measurements, ICP, and UV/vis to catalogue the full range of ion mobility in the presence of other ions and sulfuric acid.

For example, a comparison of 0.1M VO^{2+} permeability measured in $0.5\text{M H}_2\text{SO}_4$ diffusing against protons, VO_2^+ , and V^{3+} resulted in values of $1.48 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $1.17 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $0.92 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. The moles of VO^{2+} observed to collect over time in the counter solution as the VO^{2+} ion diffused across the membrane and into the counter solution, is shown in Figure 1.

While these fundamental studies are carried out ex situ, they are meant to build a greater understanding of transport in Nafion in order to characterize alternative membranes and assemble a library of knowledge to build on future modeling projects. The ultimate goal is to work towards a fuller understanding of transport properties of the operating system.

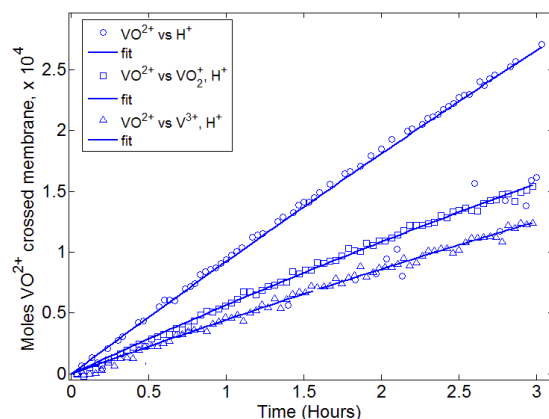


Figure 1. Cross over measurements of 0.1M VO^{2+} in $0.5\text{M H}_2\text{SO}_4$ diffusing opposite $0.7\text{M H}_2\text{SO}_4$ (circles), 0.1M VO_2^+ in $0.5\text{M H}_2\text{SO}_4$ (squares) and 0.1M V^{3+} in $0.5\text{M H}_2\text{SO}_4$ (triangles) Permeability values determined from the fits are reported in the text.

References

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