Improved Membranes for Redox Flow Batteries

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Redox Flow Battery (RFB) systems are attractive for stationary electrical-energy-storage (EES) applications due to flexible system architecture due to power-and-energy independence and inherent safety, which is especially important for large-scale EES systems with substantial energy capacities [1]. However, the capital cost of RFB systems has been a major barrier to commercialization of this technology. One attractive path to cost reduction is the development of RFB cells with substantially higher power densities than conventional RFB cells [2]. Ion-exchange membranes (IEM) are commonly employed as a separator in RFB cells to minimize electrolyte crossover, and perfluorosulfonic acid (PFSA) membranes are the most commonly used IEM in RFBs, especially in vanadium redox batteries (VRB), due to excellent resistance to oxidative and corrosive environments [3]. However, commercially available PFSA membranes are relatively expensive, which contributes to high cell stack cost. Therefore, thin membranes are preferred in the RFB system in order to minimize the amount of PFSA material required and to reduce ohmic losses, which can enable high power density RFB cells. However, a thin PFSA membrane will have higher electrolyte crossover rates than thicker membrane of the same material and morphology, which reduces energy efficiency. Therefore, an ideal IEM for RFB applications should have high selectivity for the transport of the charge carrier relative to the transport of the active RFB species ions, as illustrated in Fig. 1 with the VRB system used as an example.
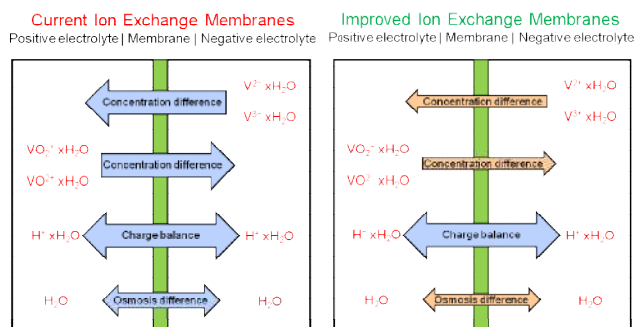

Figure 1. Relative transport rates of charge carriers, active species ions, and water across ion-exchange membrane in VRB system.

The effect of pre-treatments on membrane properties was investigated. It was noted that Nafion® membranes with and without pre-treatments showed significant difference in performance. Membranes boiled in sulfuric acid and then in water had much higher vanadium crossover than those used as-received, while the proton conductivity did not vary significantly. This is presumably due to the strong swelling effect of the boiling process during which the processing temperature is close to the glass transition temperature (T_g) of the wet ionomer and, therefore, the membrane morphology can be altered to a large extent. Membranes soaked in acid or water at room temperature also showed increased vanadium crossover compared to untreated analogs. The water activity of the pre-treatment solution plays a significant role in the swelling effect.

It is well known that membrane-processing history can produce different membrane morphologies [4], which can also significantly influence the results obtained in RFB cells. For example, as-received Nafion® NR212 and N115 membranes have similar proton conductivity values, however, the vanadium permeability of these membranes vary significantly in the as-received state even though they are made from similar materials. As shown in Table I, the Nafion® NR212, which is reportedly produced by a solution-casting method, has much lower vanadium permeability than Nafion® N115, which is reportedly produced by an extrusion method. This discrepancy in vanadium permeability can essentially be eliminated by annealing the extruded Nafion® N115 membranes close to the T_g, as is also shown in Table I.

Table I. Transport properties of Nafion® membranes with various pre-treatments.

Treatment	Proton Conductivity (mS/cm), RH=100%, 25°C	VO²⁺ Permeability x10⁷ (cm²/min), 25°C
NR212, as received	65.6 ± 1.7	1.53 ± 0.10
NR212, annealed at 100°C for 3 days	65.5	1.59
NR212, annealed at 100°C for 10 days	66.4	1.71
NR212, annealed at 150°C for 3 days	61.4	1.69
NR212, soaked in water overnight and annealed at 100°C for 3 days	66.3	1.82
N115, as received	71.0 ± 3.4	4.25 ± 0.17
N115, annealed at 100°C for 3 days	55.5	1.58
N115, annealed at 100°C for 10 days	52.4	1.51
N115, annealed at 150°C for 3 days	45.9	1.41
N115, soaked in water overnight and annealed at 100°C for 3 days	53.9	1.63

As part of an ongoing ARPA-E project, UTRC is collaborating with the 3M Corporation to develop advanced perfluorinated ionomers for RFB applications. Perfluorinated IEMs with improved selectivity relative to commercially-available IEMs are being developed. The proton conductivity and vanadium permeability of some experimental membranes will also be presented, as well as some results obtained in sub-scale VRB cells with different types of membranes.

Acknowledgements

References
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