Journal of The Electrochemical Society, **160** (9) F1040-F1047 (2013)
0013-4651/2013/160(9)/F1040/8/$31.00 © The Electrochemical Society

Composition and Conductivity of Membranes Equilibrated with Solutions of Sulfuric Acid and Vanadyl Sulfate

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The sulfuric acid, vanadyl (VO^{2+}) and water equilibrium in Nafion membranes contacted by solutions containing these species is described. Of particular interest is the influence of composition on ionic transport behavior in membrane separators for an all-vanadium redox flow battery (VRFB). Ex-situ membrane conductivity measurements were conducted on Nafion 117 membranes equilibrated in electrolyte solutions of varying sulfuric acid and vanadyl ion concentrations. Electrolyte species imbibed in the membrane were analyzed by an experimental protocol including titration, ICP-OES and weight analysis. Sulfuric acid in the membrane can increase proton concentration but reduce proton mobility by reducing water content. In a mixed vanadyl/proton form Nafion, vanadyl has a mobility of $6.28 \times 10^{-5}\ cm^2 \cdot V^{-1} \cdot s^{-1}$, much lower than proton mobility of $8.79 \times 10^{-4}\ cm^2 \cdot V^{-1} \cdot s^{-1}$ in H^+-form Nafion. The presence of vanadyl in Nafion can also decrease the proton mobility: $u_{H^+} = (8.79 - 8.04 \times x_{VO^{2+}}) \times 10^{-4} cm^2 V^{-1} s^{-1}$. With equilibration in a practical electrolyte containing 5 $mol \cdot dm^{-3}$ total sulfate, Nafion's conductivity is decreased due to uptake of vanadyl ions.

[DOI: 10.1149/2.083309jes]

Manuscript submitted May 3, 2013; revised manuscript received June 25, 2013. Published July 10, 2013. This was Paper 684 presented at the Boston, Massachusetts, Meeting of the Society, October 9–14, 2011.

The vanadium redox flow battery (VRFB) is an electrochemical energy storage system of great potential for various applications due to several distinctive properties.[1–4] A VRFB system generally consists of an energy converting subsystem and electrolyte solution storage and transfer subsystem. Unlike solid state batteries, in a VRFB the energy is carried by vanadium redox couples dissolved in electrolyte solutions, often with excess sulfuric acid.[5] The energy-converting cell interconverts energy between chemical and electrical forms. The VRFB cell includes positive and negative electrodes and an electrolyte separator, which is generally an ion conducting membrane. During battery operation, redox reactions between $V^{2+}/V^{3+}$and VO^{2+}/VO_2^+ couples respectively occur on the surface of negative and positive electrodes. The polymer electrolyte separator is between them to conduct charge and segregate negative and positive electrolyte solutions. The essential function of the separator requires that it has high conductivity to minimize ohmic loss under current.[6]

Cation exchange membranes, such as Nafion, are widely used in proton exchange membrane fuel cells, which have a similar cell structure to the VRFB cell.[5–8] Nafion and similar perfluorosulfonic acids exhibit high conductivity when hydrated and possess excellent chemical and mechanical stability. Nafion has also been introduced into the VRFB system as an electrolyte separator. However, reports in the literature suggest an area specific resistance, or ASR of 0.5 to 6 $\Omega \cdot cm^2$ in VRB cell, in contrast to typical ASR values of 0.05∼0.18 $\Omega \cdot cm^2$ with Nafion in PEMFC.[9–13] While much of this can be ascribed to contact resistance and aspects of cell design,[11] the membrane resistance must also be considered.

Recently, significant VRFB performance improvement has been achieved using a zero-gap battery cell design in combination with Nafion membranes.[6,11,14,15] A maximum limiting current density, 994 $mA \cdot cm^{-2}$ was reported on a battery using a Nafion 115 membrane, accompanied by areal specific resistance of 399–467 $m\Omega \cdot cm^2$.[14] In this cell, the membrane is the primary source of ASR. Such a high internal resistance significantly limits battery performance at high current density; this ASR entails voltage losses of roughly 400 to 500 mV at 1 $A \cdot cm^{-2}$.[6]

In a VRFB, the membrane is exposed to a much more complicated working environment than that in a PEMFC. During battery operation, the membrane is directly exposed to electrolyte solutions that contain sulfuric acid and vanadium ions concentrated at 1 $mol \cdot dm^{-3}$ level. For Nafion, this is substantially higher than the effective anion concentration range for anion equilibrium dominated by Donnan exclusion, roughly 0.4 $mol \cdot dm^{-3}$ level or lower[16,17] based on the approximate fixed anionic site concentration in the membrane. At low electrolyte concentration in contact with the membrane, anions, and therefore excess salt or acid, can be kept out of membrane by an electrostatic repulsion from negatively charged sulfonate fixed-sites, a phenomenon referred to as Donnan exclusion.[18] We refer to uptake of anionic species present at higher concentrations as 'Donnan breakthrough'. Thus all of the electrolyte species can enter the nanopores in the membrane and can alter the microenvironment for proton and cation transport.[16,19,20] Furthermore, the electrolyte composition ensures 'concentrated solution' behavior, and thus a complex transport regime and a situation in which the activity coefficients of all species, including water, vary substantially. Clearly, we must quantitatively describe the uptake of species into the membrane and, eventually, how this depends on membrane composition as well as how it affects transport.

Though there are several 'practical' studies of the properties of membranes in the presence of VRB electrolyte components, those studies fail to identify and isolate critical contributors to observable membrane performance. Furthermore, there is not an extensive body of literature describing the behavior of ion exchange membranes under conditions of exposure to high acid or transition metal ion concentration. Some literature regarding the influence of the presence of acid on membrane performance has been published in the context of PEMFC performance. Verbrugge et al. studied the impact of sulfuric acid on Nafion properties experimentally and mathematically.[21,22] With exposure to sulfuric acid solution, Nafion can suffer remarkable de-swelling and, it is proposed, ionic cluster channel compression, leading to lowered membrane porosity. Acid uptake by membranes can also contribute to significant water loss with equilibration in concentrated sulfuric acid solution. The influence of temperature on Nafion's ionic transport properties was also investigated in a similar experimental and theoretical framework.[23] The transport behavior of different acids in Nafion and other alternative membranes has been studied by several groups.[16,17,20,24] Although acid uptake and dissociation in Nafion can be significant enough to influence its conductivity, the anion transference number was no more than 0.016 when the external equilibrating sulfuric acid concentration was elevated to 4 $mol \cdot dm^{-3}$.[16] In addition, phosphoric acid and sulfuric acid dissociation can be constrained in membrane nanopores because of the presence of sulfonic acid groups and limited amount of waters. Lawton et al. found vanadyl diffusivity in Nafion to be controlled by the sulfuric acid concentration in electrolyte solutions.[25]

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Due to the slow motion of metal cations in Nafion membranes, cationic contaminants can severely affect transport properties, reducing membrane conductivity even under well hydrated conditions.[26–30] Membrane sulfonic acid groups demonstrated a high preference to interact with some cations other than protons,[30] and cationic occupancy on sulfonates can result in a reduced proton concentration. Some transition metal ions, such as Fe^{3+}, lower proton mobility by an unknown interaction with protons.[30] Nevertheless, water is the most important mediator for proton transport in sulfonated membranes.[31,32] Equilibration in dilute acid with some cations, such as K^+ Cs^+, Ni^{2+} and Fe^{3+}, can cause water content loss in Nafion, because their hydration energy is lower than that of a proton.[27–29,33,34] All these observations cited above are helpful for understanding proton exchange membrane performance in vanadium redox flow batteries, but a definitive understanding of membrane-electrolyte interactions in VRFBs is still not available.

To provide a solid basis in physical principles for membrane development in redox flow batteries, we have undertaken a systematic study of composition and transport in membranes exposed to the environment of VRFB. Here, we report a study of uptake behavior of vanadium/sulfuric acid electrolyte solutions in Nafion, as well as the influence of bathing solution composition on membrane conductivity. The dependence of the sulfuric acid and vanadyl ion uptake by the membrane on electrolyte solution condition is described. A correlation between Nafion conductivity and composition is built on a basis of component and thermodynamic analysis. This work is partly built on our previous reports of thermodynamics of water uptake and conductivity in Nafion.[19] Finally, the membrane resistance upon equilibration in electrolyte solutions is also compared to the measured internal resistance of several recently reported batteries.

Experimental

Membrane pretreatment.— Nafion 117 supplied by Ion Power Inc. was treated to obtain uniform initial conditions prior to all experiments reported below. The as-received membrane was cut into 1 × 5 cm strips. The membrane samples were sequentially boiled in 3% hydrogen peroxide (Fisher Scientific), deionized water (Milli Q, 18.2 MΩ · cm), 1 $\text{mol} \cdot \text{dm}^{-3}$ sulfuric acid and deionized (DI) water for at least 1 hour each step at 85°C. The sulfuric acid was prepared from 96% concentrated sulfuric acid (Alfa Aesar). After membrane pretreatment, the membrane samples were stored in DI water for future use.

Membrane uptake measurement.— Before the water and sulfuric acid uptake and conductivity measurements, pretreated membrane samples were soaked in sulfuric acid solutions with concentration ranging from 0.5 to 17.4 $\text{mol} \cdot \text{kg}^{-1}$ for 72 hours to achieve water and sulfuric acid equilibration at 22°C. After equilibration with aqueous sulfuric acid solutions, membrane samples were taken out of bathing solutions, liquid droplets were removed from the surface with Kimwipes and the 'soaked' weight of membrane, m_1, was measured. This step was performed very quickly to avoid weight change caused by fast water exchange between membrane and air. Here, m_1 includes the mass of the dry membrane, water and sulfuric acid. To remove imbibed sulfuric acid, the acid-equilibrated membrane was boiled in DI water for at least 1 hour. The amount of acid removed into the water was determined by titration with a Mettler Toledo DL 15 auto-titrator using 0.01 $\text{mol} \cdot \text{dm}^{-3}$ NaOH aqueous titrant. The weight of the dry membrane was determined by measuring the membrane weight after dehydration in a vacuum oven at 90°C for at least 3 hours after boiling in DI water. Water weight inside the membrane then can be calculated by subtracting weights of sulfuric acid and membrane from m_1:

$$m_{\text{water}} = m_1 - m_{\text{acid}} - m_{\text{membrane}} \qquad [1]$$

Membrane density measurement.— The membrane density was measured using a Micromeritics AccuPyc 1340 pycnometer and Sartorius CPA224s analytical balance. The principle of this method is reported in ref. 35. Before the density measurement, the membrane was soaked in electrolyte solution with the same protocol mentioned in membrane uptake measurement section. Sample weight was measured using the analytical balance immediately after emersion and surface liquid removal. The volume of the membrane sample was measured using a pycnometer with helium. Sample density was calculated by using the measured sample volume and sample weight.

Vanadyl uptake measurement.— The sample equilibrating method applied to vanadium uptake measurements was identical to that used for the acid uptake measurement. Pretreated membrane samples were equilibrated in $VOSO_4/H_2SO_4$ solutions with 0.1 $\text{mol} \cdot \text{dm}^{-3}$ total sulfate/bisulfate concentration. We expect that 0.1 $\text{mol} \cdot \text{dm}^{-3}$ total sulfate and bisulfate concentration is low enough to prevent substantial anion uptake given the Donnan potential effect in Nafion.[18] After solution equilibration, the membrane was removed, blotted and weighed. Then the membrane was immersed into 20 mL 3% (v/v) nitric acid to extract vanadyl ions for no less than 72 hours. The vanadyl content in nitric acid was measured using a Perkin Elmer 2100 DV inductively couple plasma optical emission spectrometer (ICP-OES) relative to vanadium calibration standards (Ricca Chemical). After nitric acid soaking, the membrane was boiled in DI water to remove all residual vanadyl and acid. The membrane weight was measured after at least 3 hours dehydration in a vacuum oven at 90°C. Water content in the membrane can be calculated as above. To illustrate vanadyl's relative concentration in the membrane or solution phase, its content fraction is expressed as $x_{VO^{2+}} = 2c(VO^{2+})_{membrane}/c(-SO_3H)$ or $c(VO^{2+})/c(SO_4^{2-})$.

Concentrated vanadium/sulfuric acid solution preparation.— Concentrated vanadium/sulfuric acid solutions were used to simulate the electrolyte solution environment for the membrane in a vanadium redox flow battery. 1 $\text{mol} \cdot \text{dm}^{-3}$ VO^{2+} and 5 $\text{mol} \cdot \text{dm}^{-3}$ SO_4^{2-} solution was first made from $VOSO_4 \cdot 3.23H_2O$ powder and 96% sulfuric acid supplied by (Alfa Aesar). V^{3+} and VO_2^+ solutions were prepared by electrolysis of 1 $\text{mol} \cdot \text{dm}^{-3}$ $VO^{2+}$and 5 $\text{mol} \cdot \text{dm}^{-3}$ SO_4^{2-} solution with a 5 cm^2 battery setup and method described elsewhere.[11]

Membrane conductivity measurement.— Membrane resistance was measured on a four electrode conductivity cell by electrochemical impedance spectroscopy with a Bio-Logic SP200 potentiostat. The same membrane equilibration strategy as above was used in conductivity sample preparation before conductivity measurement. After wiping liquid droplets from the surface, each membrane sample was quickly mounted onto the four-point conductivity cell. The EIS spectrum of the equilibrated membrane was taken from 200 kHz to 1 Hz with a 30 mV potential amplitude at 22°C. The membrane resistance between two sense electrodes was determined from the high frequency intercept of the impedance curve with the real impedance axis in a Nyquist plot. Membrane conductivity was calculated from measured membrane resistance and the length between the two sense electrodes:

$$\sigma = \frac{L}{RW\delta} \qquad [2]$$

R is the measured membrane resistance between two electrodes; L is the distance between the electrodes; W and δ are width and thickness of the membrane sample, respectively measured by a Fisher Scientific digital caliper and Mitutoyo 543–696 micrometer after impedance taking.

Results and Discussion

Water and acid uptake in aulfuric acid solutions.— As is shown in Figure 1, the presence of a high concentration of sulfuric acid in the bathing electrolyte solution causes significant reduction in membrane water content and sulfuric acid presence in membrane. In aqueous sulfuric acid solution, the water concentration and activity are reduced as acid concentration increases. The water content of Nafion as parameterized by $\lambda = n(H_2O)/n(-SO_3H)$, is known to depend on the

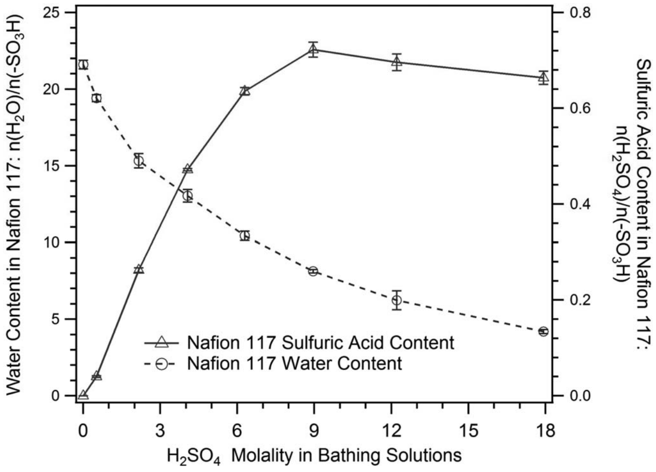

Figure 1. Water and sulfuric acid uptake by Nafion 117 in aqueous sulfuric acid solutions within concentration range from 0 to 17.4 $\mathrm{mol \cdot kg^{-1}}$. Acid existence can lead lowered water content in Nafion, and propel sulfuric acid overcome Donnan potential to enter membrane's ionic domain.

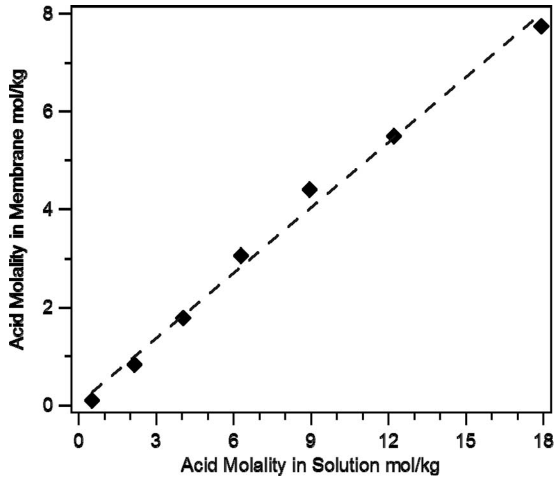

Figure 3. Sulfuric acid concentration in the membrane versus sulfuric acid concentration in bathing solution. The ratio of membrane sulfuric acid to environmental sulfuric acid is roughly 1:2.5.

water activity with equilibration in water vapor.[32,34] Upon equilibration with aqueous sulfuric acid, the water content in Nafion shows a dependence on water activity similar to that observed with water vapor equilibration, though the data for the solution equilibration shows a systematically larger magnitude of λ (Figure 2). Considering the presence of sulfuric acid in the membrane, another water content indicator λ′ can be defined as $\lambda' = \mathrm{n(H_2O)/(n\left(-SO_3^-\right) + n(H_2SO_4))}$ based on the total amount of sulfonic acid group and uptaken sulfuric acid. By incorporating the sulfuric acid content in the membrane into the determination of λ′, the water content in Nafion with sulfuric acid equilibration is much closer to the λ-a_w relation in water vapor equilibrated Nafion. That suggests that sulfuric acid and the sulfonic acid group have similar hydration behavior in the ionic clusters, channels and/or pores of the membrane. The inflated water content in the membrane was brought up by water associated with sulfuric acid. In both water vapor and sulfuric acid equilibrations, two distinct regions of water uptake can be observed, discriminated by an activity less or greater than approximately 0.8. When water activity is below 0.8, membrane water content is roughly linearly proportional to water activity. Once water activity exceeds 0.8, substantial increase in the water uptake per fractional increase in activity occurs in the membrane. In general, the water uptake at low water activity is usually associated with water of hydration of fixed acid sites in the membrane.[36] At high water activity, the chemical energy provided is sufficient to partly overcome the restoring force associated with the polymer matrix, resulting in extra membrane swelling associated with micropore expansion.[32] Within whole water activity range $0 < a_{\mathrm{water}} < 1$, water content difference between acid equilibrated membrane and water vapor equilibrated membrane might be attributed to Schroeder's paradox, based on the experimental observation that polymers take up less water from water vapor than liquid phase.[37,38]

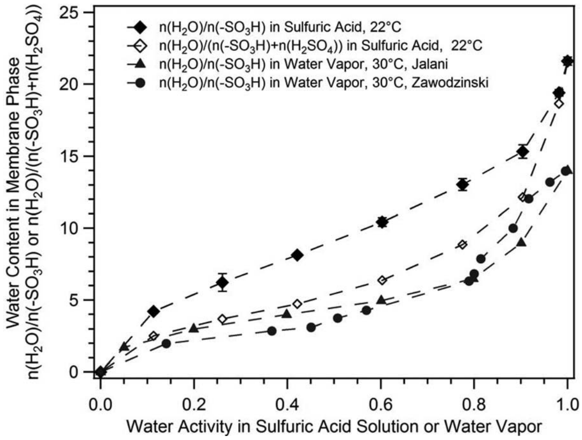

Figure 2. Water uptake in Nafion 117 vs. water activity in equilibrium between membrane and sulfuric acid solution. The water content dependence on water activity in sulfuric acid is very similar to that in water vapor.[32,34]

In Figure 1, the acid uptake in Nafion 117 shows very different response to acid concentration variation when equilibrating acid molality is above or below 9 $\mathrm{mol \cdot kg^{-1}}$. The acid content in Nafion is roughly linearly dependent on acid concentration for acid concentrations lower than 9 $\mathrm{mol \cdot kg^{-1}}$. In this concentration range, the acid uptake by the membrane should be simply dominated by the acid concentration difference between the solution phase and membrane phase. Once acid concentration exceeds 9 $\mathrm{mol \cdot kg^{-1}}$, acid content in the membrane slightly decreases with increasing solution acid concentration. However, this may be an artifact of the way the data are represented in Figure 2. As shown in Figure 3, the ratio of acid to water content in the membrane, i.e. the sulfuric acid molality inside the membrane, is proportional to the acid concentration in the equilibrating solution. Sulfuric acid molality inside membrane is calculated from uptake data in Figure 1:

$$m_{\mathrm{H_2SO_4,membrane}} = \frac{n(H_2SO_4)}{n(-SO_3H)}/\lambda \times \frac{1000}{18} \qquad [3]$$

This suggests that the solution is simply imbibed into the membrane, albeit with some degree of exclusion of acid. Although the acid concentrations used in this research are mostly beyond the concentration limit of Donnan exclusion, fixed sulfonic acid groups still create a barrier to uptake of sulfuric acid or sulfate anions, thereby lowering their content inside membrane. A concentration ratio about 1 to 2.5 was observed between sulfuric acid concentrations inside the membrane compared to that in solution.

Membrane deswelling in acid solutions.— Analysis of the membrane density after sulfuric acid soaking illustrates that Nafion suffers severe deswelling while being exposed to the concentrated acid environment. The density measurement results in Figure 4 clearly show a monotonic increase in density upon equilibration with increasingly concentrated sulfuric acid. The measured density of dehydrated Nafion 117 was 2.10 ± 0.10 $\mathrm{g \cdot cm^{-3}}$. Verbrugge and Hill suggested that Nafion 117's porosity can decrease from 30% to 15% upon equilibration with sulfuric acid over the concentration range 0.001 to 10 $\mathrm{mol \cdot dm^{-3}}$ by experiment.[21] The membrane porosity is calculated

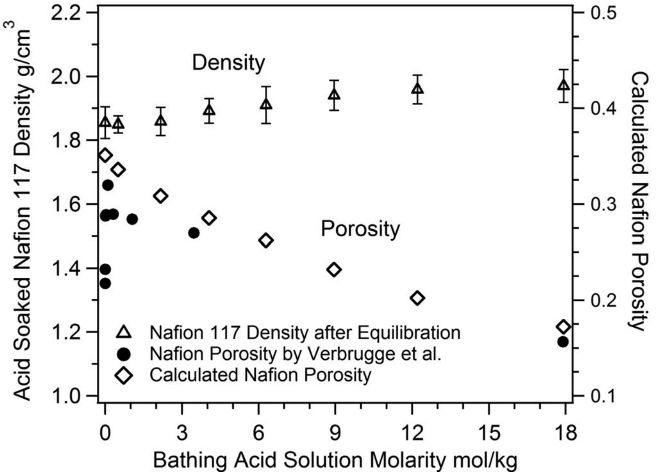

Figure 4. Measured density and calculated porosity of Nafion 117 with respect to sulfuric acid concentration in bathing solution. The declining density dependence on acid concentration in solution is indicating membrane deswells in acid solution.

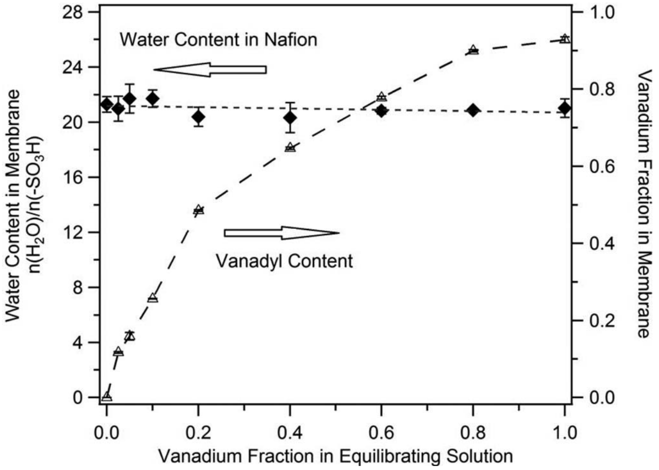

Figure 5. Water and vanadyl content in Nafion 117 equilibrated with vanadyl sulfate/sulfuric acid solutions of 0.1 mol $\cdot$ dm^{-3} total sulfate background. Vanadyl presence in membrane has barely effect on membrane's water content; Vanadyl is preferred by sulfonate to proton in Nafion.

by:

$$\theta = \frac{V_{wet} - V_{Dry,\mathrm{H}^+}}{V_{wet}} \qquad [4]$$

Where V_{wet} and V_{Dry,H^+} are membrane volume per mole of sulfonic acid group, respectively in the sulfuric acid equilibrated state and the dehydrated state in proton form. V_{wet} is calculated from water and acid contents in membrane and measured membrane density, by:

$$V_{wet} = \left(EW + 18\lambda + 98\frac{n_{\mathrm{H_2SO_4}}}{n_{-\mathrm{SO_3H}}}\right) \Big/ \rho_{\mathrm{Membrane}} \qquad [5]$$

The calculated Nafion porosity is presented in Figure 4 as well, showing a good agreement in general trend over the acid concentration range with porosity reported.[21] The porosity loss in Nafion after being exposed to acidic solution illustrates that the acidic environment can cause significant deswelling of Nafion. The internal pore space reduction in concentrated acid is also coincident with the species uptake reduction discussed above.

Vanadyl and water uptake in membranes.— VO^{2+} and water uptake for membranes exposed to vanadium/acid solutions are shown in Figure 5. In this experiment, the total sulfate concentration was maintained at 0.1 mol $\cdot$ dm^{-3} and the vanadium to proton mole fraction was varied. The water content in the membrane was not strongly related to the vanadium concentration in the equilibrating solutions. Neither vanadyl nor sulfuric acid concentration in bathing solution was high enough to reduce water activity in the equilibrium. The high water activity in the membrane results in high and fairly constant water content in the equilibrated membrane with varying vanadyl/sulfate fraction. The vanadyl fraction in the membrane phase was typically higher than its fraction in the solution phase, i.e. vanadyl preferentially was taken into the membrane relative to protons. The membrane has a stronger affinity to vanadyl most likely because vanadyl is a divalent ion which can have a stronger electrostatic attraction with sulfonic acid group than a monovalent ion. Although Pintauro and co-workers showed that several factors other than ionic valence can influence ion partitioning in Nafion,[39–41] especially when high surface charge density monovalent ions are present in the system, the vanadyl/proton partitioning observed in this study behaved more similarly to the partitioning competition between a low surface charge density monovalent and divalent ions, such as Li^+/Ni^{2+} pair.[40] The surprise here is the lack of a concomitant decrease in the water content expected if the vanadyl is strongly ion pairing with the sulfonate.[29,30] Nafion's hydration level highly relies on the hydration energy of the cation.[27,34] Since the vanadium atom in a vanadyl-aqua complex has +4 valence, its electrostatic attraction to water molecules should be stronger than cations with lower valence to maintain a more stable water shell over the entire vanadyl content range.

In the real battery environment, other oxidation states, including V^{3+}, also can enter the membrane and bond to sulfonic acid groups, possibly with a stronger or weaker electrostatic attractive force. Further investigation of the partitioning competition among vanadium ions and proton is needed but that is beyond the scope of the present work, which only focuses on vanadyl ions.

Analysis of acid uptake influence on membrane conductivity.— The conductivity of the membrane as a function of concentration of bathing sulfuric acid solution is shown in Figure 6. The data shows a change in conductivity behavior between low and high acid concentrations. The membrane conductivity enhancement or reduction can be considered as a trade-off between proton concentration increase and proton mobility loss caused by acid presence in environment. In membrane, the sulfuric acid can provide excess protons by its ionization, while it also reduces membrane's water content.

To qualitatively analyze the impact of sulfuric acid uptake on proton concentration and mobility in the membrane, a model was developed based on measured Nafion uptake and conductivity results.

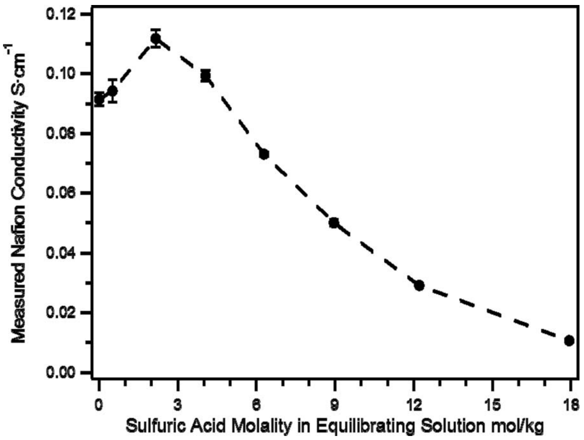

Figure 6. Sulfuric acid presence in equilibrium can enhance membrane's conductivity when sulfuric acid is no more concentrated than 5 mol $\cdot$ kg^{-1} in environment; Acid can reduce membrane's conductivity when its concentration is over 5 mol $\cdot$ kg^{-1} in equilibrium.

In sulfuric acid solutions with concentration up to 40 $mol \cdot kg^{-1}$, all sulfuric acid molecules in solution can complete their first dissociation.[42,43] Sulfonic acid groups in Nafion also have been shown to be dissociated even at low hydration level.[36,44] We propose a simple model of Nafion conductivity with sulfuric acid equilibrium under the assumption that all sulfonic acid groups dissociate and sulfuric acid molecules accomplish their first dissociation. By assuming a bisulfate dissociation constant ($pK_{a,2}$) of 2,[45] it is straightforward to balance proton, bisulfate and sulfate in a dissociation equilibrium:

$$n(H^+)n(SO_4^{2-})/n(HSO_4^-) = K_{a,2} \quad [6]$$

The total concentration of bisulfate and sulfate equals the measured concentration of sulfuric acid in the membrane:

$$n(SO_4^{2-}) + n(HSO_4^-) = n(H_2SO_4)_{measured} \quad [7]$$

The membrane proton concentration is balanced by ionic electrical neutrality inside the membrane:

$$n(H^+) = n(-SO_3^-) + n(HSO_4^-) + 2n(SO_4^{2-}) \quad [8]$$

By solving equations 6–8, the proton content in the membrane is proved to be equal to the total amount of sulfonic acid group and imbibed sulfuric acid. Dissociated sulfuric acid in the membrane is able to provide abundant additional protons to carry charge. Extra protons in the membrane are overwhelmingly generated by sulfuric acid molecule ionization rather than dissociation of bisulfate, because bisulfate's dissociation is completely suppressed by the high proton concentration from ionization of both sulfuric acid molecules and sulfonic acid groups. Combining the density and uptake measurements presented above, the actual sulfonate concentration can be calculated and proton concentration can be derived:

$$c_{-SO_3H} = \rho_{membrane} \Big/ \left[EW + 18\lambda + \frac{98n(H_2SO_4)}{n(-SO_3H)} \right] \quad [9]$$

$$c_{H^+} = \frac{n(H^+)}{n(-SO_3H)} c_{-SO_3H} = \frac{n(-SO_3H) + n(H_2SO_4)}{n(-SO_3H)} c_{-SO_3H} \quad [10]$$

The proton mobility can be precisely calculated from membrane conductivity and the calculated proton concentration in the membrane, by assuming that bisulfate contribution is trivial to the membrane conductivity. Based on previous findings in the literature, the anion transference number is extremely low compared to that of the proton.[16,17] Accordingly, our assumption is safe and proton mobility can be determined by the relation:

$$\sigma_{membrane} = z_{H^+} F u_{H^+} c_{H^+} \quad [11]$$

The calculated proton concentration and mobility with respect to the bathing sulfuric acid concentration are presented in Figure 7. A significant amount of excess protons in the membrane can be generated by sulfuric acid molecule dissociation, while the proton mobility appears to be drastically reduced. Since the first dissociation of sulfuric acid dominates excess proton generation, excess proton content is equal to acid uptake. The peak in membrane conductivity observed in Figure 6 is thus a consequence of the simultaneous increase in proton availability combined with the corresponding decrease in proton mobility.

Proton mobility in Nafion is highly dependent on water content. Water is the most important proton transport mediator in acid equilibrated membrane as well as hydrated Nafion.[31,32,46] In the presence of sulfuric acid, proton mobility increases with membrane water content in two different regimes, demarcated by $\lambda' = 12$ (Figure 8). The turning point of proton mobility dependence on water content at $\lambda' = 12$ suggests that the membrane, sulfuric acid and water reach a critical equilibrium for proton transport at this point. At this equilibrium, water is present in a sufficient quantity to facilitate effectively the proton transport. At this level of water content, proton transport in Nafion is enhanced by the Grotthus mechanism, which provides relatively fast proton diffusion across the water network.[32,46] Although the membrane still suffers water loss when $\lambda' > 12$, bisulfate could facilitate proton transfer by bridging among sulfonates. In these cases, proton mobility is not sensitive to modest water content variations in membrane. At water contents below that corresponding to the peak of conductivity, significant proton mobility loss is caused by major water-sulfuric acid content changes in the membrane. At low hydration level, the proton 'hopping' probability is further reduced because of lower water availability to serve as proton transfer mediator. Facilitation from bisulfate can no longer compensate for the effect of the loss of water on proton mobility. Bisulfate may even have an adverse effect at low hydration level, because it has high affinity to water molecules to restrict their motion. According to Lawton et al.'s observation on the sulfuric acid influence on ion transport in Nafion, ion transport can be slowed down due to increased solution viscosity which is primarily contributed by sulfuric acid.[25]

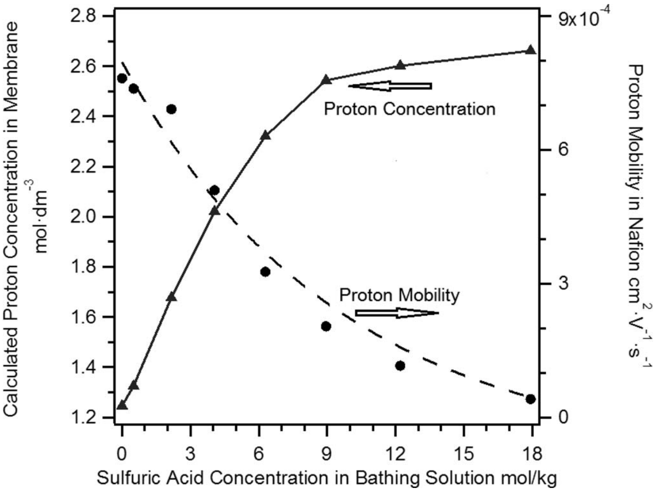

Figure 7. Calculated proton concentration and mobility are presented as functions of sulfuric acid concentration in bathing solution. By being exposed to acidic environment, membrane can gain an elevated proton concentration, but loss proton mobility. The two factors contribute comprehensively to enhanced or lowered membrane conductivity.

In Figure 9, we show that proton mobility in acid-equilibrated membranes can be represented by a power law dependence on water activity given by $u_{H^+} = 7.61 \times 10^{-4} cm^2 \cdot V^{-1} \cdot s^{-1} \times a_{water}^{1.5}$. Water activity in the membrane is determined by the sulfuric acid concentration with the activity-concentration relationship in aqueous sulfuric

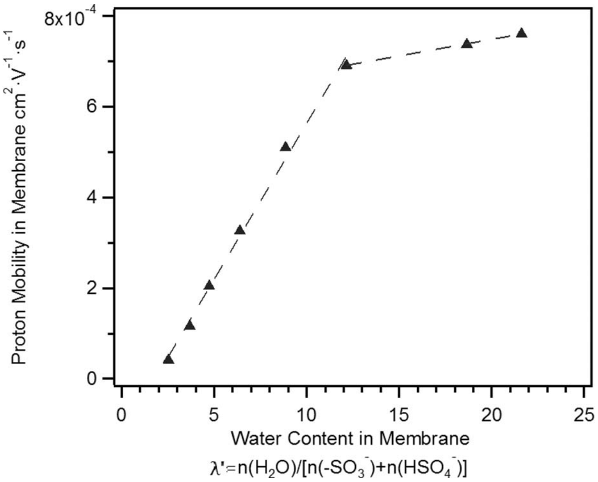

Figure 8. Proton's mobility relies on water/acid content ration in two different ways. At high water content, proton mobility is fairly constant; when water content is lower than 12 water molecules per acid, proton mobility decreases severely with decreasing water content in a linear pattern.

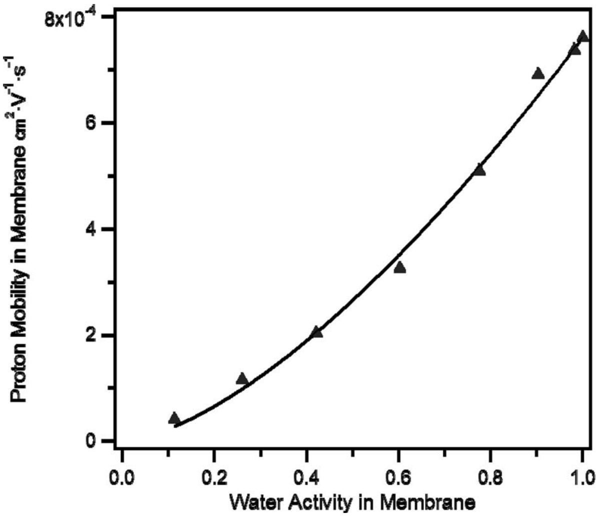

Figure 9. In Nafion membrane, proton mobility is dependent on water activity according to a power law, $u_{H^+} = 7.61 \times 10^{-4} cm^2 \cdot V^{-1} \cdot s^{-1} \times a_{water}^{1.5}$. The mobility dependence on water activity implies that proton transfer involves one to two water molecules.

acid solution recommended by Staples.[47] With equilibration in water vapor, membrane conductivity is a function of water activity.[32,48,49] In the membrane-water-sulfuric acid equilibrium, proton mobility dependence on water activity is similar to its conductivity dependence on water activity with equilibration in water vapor. In both cases, higher water activity can guarantee a larger quantity of water molecules that can participate in proton transport reaction.

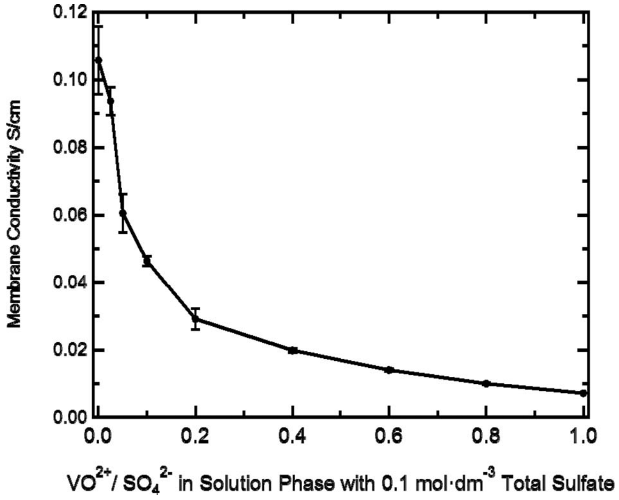

Figure 10. Conductivity of Nafion 117 equilibrated with vanadyl sulfate/sulfuric acid solution with 0.1 mol · dm^{-3} total sulfate background. The vanadyl has a decreasing effect on Nafion's conductivity.

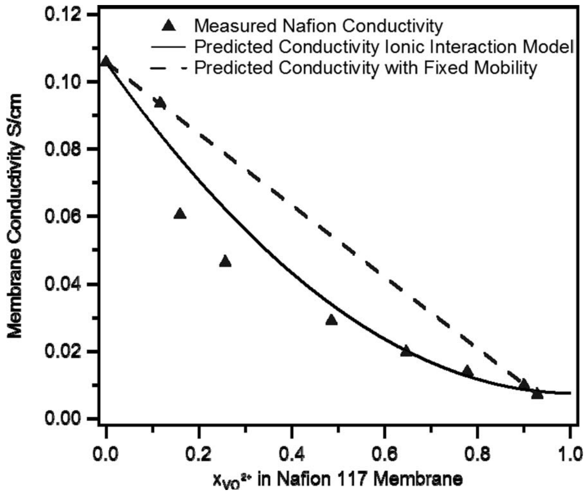

Figure 11. Measured conductivity for Nafion 117 with different vanadyl relative concentration in Membrane in comparison with predicted conductivity from ionic interaction model and fixed mobility model. The analysis illustrates that vanadyl has a much slower motion than proton in transferring inside Nafion, and it can also slow down proton's transport in a linear relation of unrevealed mechanism.

Vanadyl influence on membrane's conductivity.— The conductivity of Nafion was measured after membrane samples were equilibrated in 0.1 mol · dm^{-3} total sulfate solutions of different vanadyl/proton fractions (Figure 10). Clearly, with increasing vanadyl fraction in the bathing solution and thus the membrane, decreased conductivity suggests that vanadyl ion most likely has a substantially lower mobility than the proton. Since the total concentration of sulfate and bisulfate in this set of solutions was 0.1 mol · dm^{-3}, i.e. not high enough to overcome the Donnan potential of the membrane, only a trace amount of anion can get into the membrane. Thus, the influence of sulfuric acid on membrane conductivity can be neglected. As is presented in Figure 5, the water content of Nafion equilibrated with the different acid-salt compositions was essentially constant. Therefore, water content variation in the membrane should not be a factor influencing membrane conductivity. In Figure 11, a strong decrease of membrane conductivity is observed upon vanadium existence in the membrane. Since the concentrations of vanadyl ions and protons in the membrane are balanced by the number of sulfonic acid groups, uptake of vanadyl can reduce the proton concentration. Because metallic cations have much lower mobility than protons in fully hydrated Nafion, membranes containing cations generally have much lower conductivity than unexchanged proton-form membranes.[29,30] In Figure 11, the measured membrane conductivity is obviously lower than the conductivity projected from proton-form and fully exchanged vanadyl-form membrane conductivity based on a linear interpolation with the assumption of fixed proton and vanadyl mobility. This deviation suggests that there must be some interaction between proton and vanadyl to slow proton's motion in the membrane.

To quantify the vanadyl ion influence on proton mobility and membrane conductivity, a model was constructed based on an ionic interaction hypothesis. In our system, since vanadyl-Nafion was as well hydrated as it was fully saturated by pure water, we expect that the Grotthus mechanism dominates proton transport through the hydration networks in ionic cluster channels. Some transition metals have been shown to interact with protons in membranes causing proton mobility reductions without a significant change in the mobility of the metallic ion.[30] To achieve a concise model, it is assumed that vanadyl has a constant mobility while proton mobility is changed by vanadyl. Using the Nernst-Einstein equation, the conductivity of Nafion in mixed vanadyl/proton form is a function of mobility and concentration of vanadyl and proton in membrane:

$$\sigma_{\mathrm{membrane}} = \mathrm{F}(z_{\mathrm{H^+}} c_{\mathrm{H^+}} u_{\mathrm{H^+}} + z_{\mathrm{VO^{2+}}} c_{\mathrm{VO^{2+}}} u_{\mathrm{VO^{2+}}}) \qquad [12]$$

Here, $\sigma_{\mathrm{membrane}}$ is the membrane's conductivity; F is the Faraday constant, 96500 C · mol^{-1}; z, c and u are the respective charge number, concentration and mobility of proton and vanadyl. Because of electrical neutrality in membrane, proton and vanadyl's concentrations are balanced by sulfonic acid group's concentration in membrane, as is presented in eq. 13:

$$z_{-SO_3H} c_{-SO_3H} + z_{H^+} c_{H^+} + z_{VO^{2+}} c_{VO^{2+}} = 0 \qquad [13]$$

To simplify our analysis process, we define proton and vanadyl's relative concentration in membrane as $x_{\mathrm{H^+}} = z_{\mathrm{H^+}} c_{\mathrm{H^+}} / z_{\mathrm{-SO_3H}} c_{\mathrm{-SO_3H}}$

and $x_{VO^{2+}} = z_{VO^{2+}}c_{VO^{2+}}/z_{-SO_3H}c_{-SO_3H}$. Then eq. 13 was reduced to $x_{H^+} + x_{VO^{2+}} = 1$. With definitions introduced, eq. 12 can also be simplified as:

$$\sigma_{membrane} = Fc_{-SO_3H}(x_{H^+}u_{H^+} + x_{VO^{2+}}u_{VO^{2+}}) \qquad [14]$$

The sulfonic acid group concentration is estimated from water-saturated Nafion 117 density and equivalent weight and water uptake: $c_{-SO_3H} = \frac{EW+18\lambda}{\rho_{Nafion,Water}} = 1.25 \times 10^{-3}$ mol · cm^{-3}. Because the constant water content implies only minor membrane deswelling caused by vanadyl uptake, it is proper to assume a constant sulfonate concentration for different proton/vanadyl ratios. Here, proton mobility loss is assumed to be proportional to vanadyl's concentration in membrane:

$$u_{H^+} = u^*_{H^+} - kx_{VO^{2+}} \qquad [15]$$

Where, k is an undetermined coefficient; $u^*_{H^+}$ is proton mobility in fully saturated H-form Nafion. Its value is 8.79×10^{-4} cm^2 · s^{-1} · V^{-1}, scalculated form water saturated Nafion 117's conductivity. By combining eq. 14, eq. 15 can be derived as:

$$\frac{\kappa_{membrane}}{F \cdot c_{-SO_3H}} - u^*_{H^+} = k{x_{VO^{2+}}}^2 + (u_{VO^{2+}} - k - u^*_{H^+})x_{VO^{2+}} \qquad [16]$$

Then k and $u_{VO^{2+}}$ can be calculated from the polynomial coefficients of quadratic curve by fitting the left side of eq. 16 as a function of $x_{VO^{2+}}$. The quadratic curve was fitted by least square polynomial fitting from measured conductivity-vanadyl content data presented in Figure 11. The results are $k = 8.04 \times 10^{-4}$ cm^2 · s^{-1} · V^{-1} and $u_{VO^{2+}} = 6.28 \times 10^{-5}$ cm^2 · s^{-1} · V^{-1}. Compared to proton mobility in H-form Nafion, the vanadyl ion exhibits more than 10 times slower mobility, comparable to reported mobility of Fe^{3+}, 5.3×10^{-5} cm^2 · s^{-1} · V^{-1}.[30] In Figure 11, the predicted conductivity for Nafion 117 by the ionic interaction model is in qualitative agreement with measured conductivity.

The agreement of modeled and experimental conductivity implies that there is a decrease in proton mobility caused by the presence of the vanadyl ion in the membrane. Proton mobility decreases in proportion to the vanadyl content inside the membrane. This result is similar to the iron-proton interaction reported by Okada etc., although vanadyl does not lead to a water content loss in Nafion.[30] As has been stated in ref. 30, the cation-proton interaction is implemented through cation's constraint on water molecule self-exchange to participate proton hopping intermediation near cation exchange site, rather than direct cation-cation interaction. The vanadyl ion has a very stable hydration shell, which seems to be maintained even in the presence of the anions of this system. The strong constraint on water in the vanadyl-aqua complex can restrict coordinated water motion and availability for proton hopping. By this means, the presence of vanadyl ion promotes a higher barrier to proton transport than would be expected at the given water content.

Nafion 117's conductivity in practical electrolyte solutions.— In Figure 12, the Nafion 117 conductivity after 72 hours equilibration in solutions of 5 mol · dm^{-3} total sulfate and varying vanadyl concentration is presented. This is a typical composition of the VRB feed. With more concentrated acid in electrolyte solution, the inhibitive effect of vanadyl on membrane conductivity was less than observed in a low concentration measurement. Even though the concentration of vanadyl in the equilibration solution increased from 0.25 to 1.75 mol · dm^{-3}, the Nafion conductivity only decreased from 0.051 to 0.34 S · cm^{-1}. Only a 30% conductivity loss on Nafion 117 was brought about by an increase of seven times the vanadyl concentration in these high vanadyl/acid concentration solutions. In the lower concentration investigation described above, membrane conductivity was reduced from 0.60 to 0.20 S · cm^{-1}, with the same vanadyl/sulfate concentration ratio elevation. The conductivity reduction caused by the presence of vanadyl was partly inhibited by the presence of concentrated sulfuric acid in the electrolyte solution. The lowered vanadyl uptake impact on Nafion's conductivity indicates that there is a more complicated situation for equilibrium amongst vanadyl, sulfuric acid and sulfonic acid groups under these conditions of high concentrations of all components, with a substantial effect of ion 'competition' for partitioning into the Nafion.

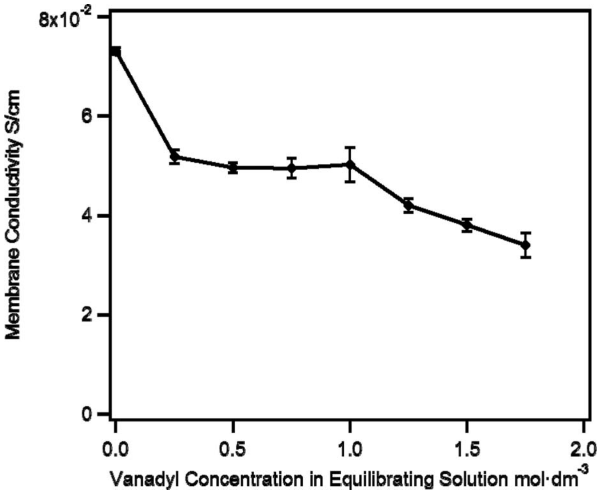

Figure 12. Nafion 117 conductivity upon equilibration in vanadyl sulfate/sulfuric acid solutions of 0 to 1.75 mol · dm^{-3} vanadyl in 5 mol · dm^{-3} sulfate background.

As a component of the measured internal resistances of non-gap battery system, membrane resistance contributes significantly to battery internal resistance. The equivalent areal specific resistance of a single layer Nafion 117 equilibrated with 1 mol · dm^{-3} vanadium / 5 mol · dm^{-3} sulfate with valence states of +3 to +5 was circa 0.37 to 0.40 Ω · cm^{-2}. Several measured internal areal specific resistances of non-gap architecture batteries employing a single layer of Nafion 117, are also listed in Table I, ranging from 0.5 to 0.687 Ω · cm^{-2}. The internal resistance of the battery cell reported here includes the resistance of every cell components and contact resistance on respective interface. Equilibrated Nafion 117's equivalent ASR, which is much higher than any other part of IR, can amount up to 50 to 80% of battery IR loss. To remedy this, we must understand fully the implications of studies such as that described above.

Table I. Conductivity and Equivalent ASR of Nafion 117 Equilibrated in Vanadium/Acid Solutions with Comparison to Internal Resistance of Nafion 117 Installed Battery Systems.

Test Type	Electrolyte	Electrode (compression)	Conductivity S · cm^{-1}	ASR ohm · cm^{-2}	Reference
Conductivity test	5 mol · dm^{-3} Sulfuric acid	–	0.073	0.27	
Conductivity test	1 mol · dm^{-3} V^{3+}/5 mol · dm^{-3} sulfate	–	0.055	0.37	
Conductivity test	1 mol · dm^{-3} V^{4+}/5 mol · dm^{-3} sulfate	–	0.050	0.40	
Conductivity test	1 mol · dm^{-3} V^{5+}/5 mol · dm^{-3} sulfate	–	0.054	0.37	
Non-gap Battery	1 mol · dm^{-3} V^{x+}/5 mol · dm^{-3} sulfate	Toray carbon paper 200 μm (25%)	–	0.63~0.65	11
Non-gap Battery	1 mol · dm^{-3} V^{x+}/5 mol · dm^{-3} sulfate	SGL 10AA CP 400 μm (19–25%)	–	0.5	15
Non-gap Battery	1 mol · dm^{-3} $VOSO_4$/5 mol · dm^{-3} H_2SO_4	SGL 10AA CP 400 μm (20%)	–	0.606~0.687	14

As has been discussed above, electrolyte species in the vanadium redox flow battery can affect Nafion properties as an electrolyte separator. The membrane conductivity can be enhanced or reduced by sulfuric acid in electrolyte, depending on the surrounding concentration. Vanadium ion in the electrolyte is another essential factor leading to lowered Nafion conductivity in a VRFB. When vanadium displaces protons in the membrane, conductivity can be reduced by both lowered proton concentration and slowed proton motion. Vanadyl in an electrolyte with high acid concentration can also enter membrane and cause conductivity reduction. We have conclusively shown that the membrane can lose its conductivity upon exposure to concentrated electrolyte which is necessary to improve battery energy density. Moreover, high membrane resistance also decreases high battery efficiency, especially in the recently achieved high operating current density.[6] To optimize battery system performance, membrane performance and electrolyte composition, or battery energy density should be well balanced in battery design. Our observations also support new electrolyte separator development based on cation exchange polymer membrane. Sulfuric acid and vanadium uptake should be suppressed to keep high proton concentration and mobility to maintain conductivity in future sulfonated polymer electrolyte separator.

Conclusions

The membrane-electrolyte equilibrium and its impact on ionic transport in Nafion have been discussed. Uptake behavior of the membrane in contact with sulfuric acid is comprehensively dependent on the equilibrium between sulfuric acid solution and membrane. From our sulfuric acid influence study, sulfuric acid is concentrated enough to overcome Donnan exclusion to enter nanopores in the membrane. Low water activity in membrane-electrolyte equilibrium can lead lowered membrane water content. Membrane dehydration caused by low water activity in the equilibrating solution can prevent incremental acid uptake by the membrane at a relatively high acid concentration. Sulfuric acid in the membrane can have an enhancing or reducing impact on membrane conductivity, depending on acid and water contents in membrane. Acid in the membrane can enhance membrane conductivity by increasing proton concentration in membrane. However proton mobility can significantly decrease with water loss in membrane. When vanadyl ion is present in the membrane equilibrated in dilute acid, it can reduce membrane conductivity by reducing proton concentration and mobility. Two effects contribute to this: vanadyl mobility is much lower than that of proton in membrane, and it can slow down the proton dynamics in spite of the fact that it does not reduce membrane water content. In a membrane with equilibration in electrolyte with practical composition for VRFB operation, vanadyl and acid also contribute to a reduction of membrane conductivity, but not to the extent observed in the case of the vanadyl/proton form Nafion formed upon equilibration with dilute solutions. This suggests a more complicated equilibrium and partitioning competition between protons and vanadyl for a membrane soaked in concentrated electrolyte.

Acknowledgment

The authors gratefully acknowledge the GCEP program and the NSF-funded TN-SCORE program, NSF EPS-1004083, under Thrust 2 program for their support of this work.

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