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Effect of biaxial stretching on the ion-conducting properties of Nafion membranes

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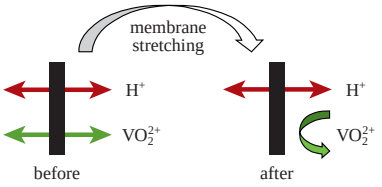
A procedure for Nafion membrane modification *via* stretching has been elaborated. Ion-conducting properties of the modified membranes have been studied in comparison with those of pristine Nafion membrane.



The annealing and stretching of polymer materials often modify their physical properties, in particular, enhance their mechanical, optical, electrical and transport characteristics.[1] A definite advantage of biaxially oriented films over the uniaxially oriented ones is the in-plane isotropy of properties.

The commercial ion-exchange Nafion membrane is a semicrystalline sulfonated fluorine-containing polymer[2] consisting of crystalline and amorphous regions and ionic side chains, the latter aggregating into nanometer-scale hydrophilic clusters. Therefore, it is reasonable to expect that the annealing and stretching of a Nafion film will induce structural rearrangements within the crystalline and amorphous regions. Possible modifications of ionic side chains (and, therefore, changing the ionic channel structure) should also be considered.

This work was aimed at investigating the properties of Nafion membranes subject to annealing at different temperatures and simultaneous biaxial stretching to different draw ratios. If annealing and stretching affected the molecular packing, it would also change the membrane proton conductivity and permeability towards vanadium ions.

Prior to stretching, Nafion 112 membranes (Sigma-Aldrich) were conditioned *via* sequential boiling in distilled water (1 h), aqueous H_2O_2 (3 wt%, 1.5 h), distilled water (1 h), aqueous H_2SO_4 (0.5 mol dm^{-3}, 1.5 h), and distilled water (1 h). Rearrangement of ionic clusters in dry Nafion membrane occurs at $T \geqslant 120$ °C;[3] therefore, the conditioned membranes were biaxially stretched at 120 or 150 °C to a desired draw ratio (DR). The deformation was performed stepwise over 1–2 h. After the stretching, the membranes were slowly cooled to room temperature in a stretched state, conditioned *via* boiling in aqueous H_2O_2 (3 wt%, 1.5 h), and incubated in aqueous H_2SO_4 (0.5 mol dm^{-3}, 24 h). The non-stretched reference membranes (DR ≡ 1) were annealed and conditioned similarly. The DR of stretched membranes was expressed as the final specimen area divided by its initial area.

The uptake of water within an ion-exchange membrane is intimately related to its proton conductivity. We found that Nafion equilibrium water uptake was systematically lowered after the thermal treatment and almost independent of the DR: the water fractions in the membranes equilibrated in water were 29 wt% (pristine Nafion 112), 20 wt% (after treatment at 120 °C), and 23 wt% (after treatment at 150 °C); the reported values being averaged over the samples with different DRs.

A two-compartment dialysis cell was used to determine vanadium(IV) permeability P through the membranes.[4] The cell compartments (0.8 ml each) were loaded with aqueous solutions of 1 M $VOSO_4$ + 2.5 M H_2SO_4 and 1 M $MgSO_4$ + 2.5 M H_2SO_4. The membrane area exposed to the solutions was of 7.85×10^{-5} m^2. The V^{IV} concentration in the second half-cell was monitored hourly by measuring the absorption of solution at λ = 760 nm.

A two-compartment symmetrical cell was used for electrical impedance measurements; each compartment was filled with a 2.5 M aqueous H_2SO_4 solution, and the tested membrane was placed between the compartments. The measurements were performed over a range of 0.1–200 kHz at room temperature. The membrane area resistivity was calculated as $\Omega = S(R_{sample} - R_{ref})$, where S is the membrane area exposed to the solutions, R_{sample} is the resistance of the cell with the membrane specimen, and R_{ref} is the resistance of the cell without the membrane.

Figure 1(*a*) shows the measured P values as a function of the draw ratio of the membranes stretched at 120 and 150 °C. In both cases, even annealing without stretching (DR = 1) decreased the vanadium permeability down to about 55% of that of the pristine membrane. On top of that, the V^{IV} permeability tended to decrease with stretching up to DR ≈ 1.6, slightly growing up with further increased draw ratio. No significant difference in the permeability was observed between the membranes annealed at 120 and 150 °C.

The results of impedance measurements are presented in Figure 1(*b*). Since the electrical conductivity of the membranes was inversely proportional to the proton conductivity under the measurement conditions, the data in Figure 1(*b*) evidenced about a significant decrease in the membrane proton conductivity upon annealing without stretching. Stretching at both of the temperatures (up to DR = 1.5) enhanced the proton transport, and the proton conductivity increased up to that of the pristine Nafion 112 membrane. However, the further stretching of membranes suppressed the proton transport.

One of the emerging areas of Nafion membrane application is the development of all-vanadium redox-flow batteries.[5] The ideal redox-flow battery membrane should be stable under the operation conditions and should exhibit a combination of high

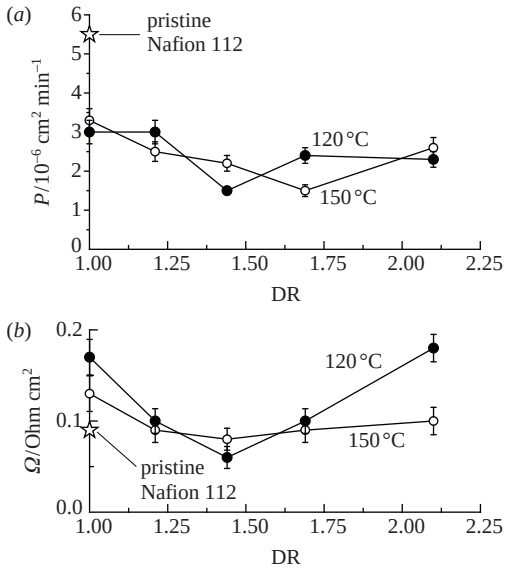


Figure 1 (*a*) V^{IV} permeability *P* and (*b*) through-plane resistance *Ω* of the biaxially stretched, annealed non-stretched (DR = 1), and pristine Nafion 112 membranes.

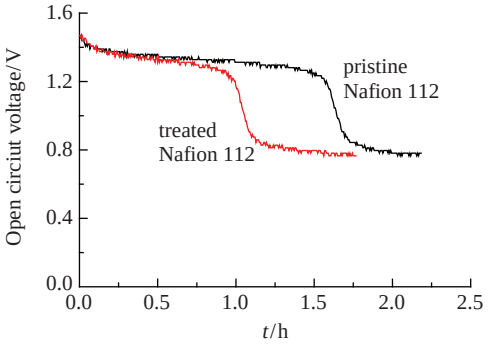


Figure 2 Open circuit voltage of the fully charged battery assembled with pristine Nafion 112 membrane and the membrane biaxially stretched to DR = 1.5 at 150 °C.

proton conductivity and zero vanadium (or other corresponding redox-active) species permeability. The V^{IV} permeability and the proton conductivity data in Figure 1 suggested that the membranes treated at intermediate DR of 1.5–1.75 were optimal in view of the vanadium redox-flow batteries applications.

We performed preliminary tests of the membranes treated as described above using a single vanadium redox-flow cell. The two compartments separated by the tested membrane were filled with carbon felt to ensure the contact of electrolyte solutions with copper current collectors, and the equal volumes of 1.0 M V^{III} and V^{IV} salt solutions in 2.5 M H_2SO_4 were pumped through the compartments. The battery charge was performed at 1.8 V under continuous argon stream to reach a potential of ~1.5 V corresponding to the 100% state of charge of the system. The relatively fast charge cycle (5–6 h) confirmed the sufficiently high proton conductivity of the membranes. Then, the pumps were turned off, and the open circuit voltage was measured during self-discharge of the battery. The results for pristine Nafion 112 membrane and the membrane biaxially stretched to DR of 1.5 at 150 °C are shown in Figure 2.

Surprisingly, the results in Figure 2 indicated that the self-discharge time for the pristine membrane was 75% higher than that for the stretched one, contradicting the above proton conductivity and V^{IV} permeability data. The only reason for that was that the permeability of vanadium species other than V^{IV} was crucial for the self-discharge behavior of the fully charged cell. That could not be attributed to the variation of the ions size since the hydrate shell radii are very close for V^{II}, V^{III}, V^{IV} and V^{V} species.[6] Alternatively, V^{IV} and V^{V} transport within a Nafion membrane could be suppressed due to hydrogen bonding between the oxo group of the vanadium ion and the ester group of a polymer matrix. Unfortunately, only a few studies have reported the permeability of different vanadium species through ion-exchange membranes: the $V^{III} > V^{IV} > V^{V}$ series of decreasing the vanadium species diffusion through Nafion membrane has been revealed,[4,7] and the only report on V^{II} diffusion available so far[8] has demonstrated that V^{II} diffusion in Nafion membrane is the fastest of all the vanadium cationic species.

Accounting for the above-mentioned permeability data and the general reaction scheme,[9] we interpreted the experimental results as follows. In the 100% state of charge, the system contained exclusively V^{II} in the negative electrolyte and V^{V} in the positive electrolyte. The fast diffusion of V^{II} ions in the positive electrolyte half-cell was followed by the reactions with V^{V} ions: $2H^+ + V^{2+} + VO_2^+ \rightarrow V^{3+} + VO^{2+} + H_2O$ and $V^{3+} + VO_2^+ \rightarrow 2VO^{2+}$; that was the major pathway of the cell self-discharge, rather than the slow diffusion of V^{IV} ions. The particular reason for the acceleration of V^{II} diffusion after the membrane stretching requires further experimental confirmation.

Even though the reason for the different diffusion behaviors of the vanadium species in the Nafion matrix has not been unambiguously understood, the results reported in this work have led to a very important conclusion that the measuring of V^{IV} ion permeability through the membrane is not sufficient to estimate the performance of real-life vanadium redox flow batteries, as is commonly accepted.

To summarize, we elaborated and tested a procedure for the biaxial stretching of proton-conductive Nafion membranes in a dry state above the glass transition temperature. The V^{IV} permeability through the modified membranes was lower as compared with that through the pristine Nafion membrane. The membranes through-plane proton conductivity was slightly decreased after the annealing, but it was improved after stretching to a draw ratio of about 1.5. The membrane modified *via* biaxial stretching at 150 °C to DR = 1.5 was tested in a model all-vanadium redox-flow battery; the modification somewhat deteriorated the cell self-discharge performance. That was attributed to the stretching effect on the permeability of V^{II} and/or V^{V} ions.

Detailed studies of the effect of biaxial stretching on the cycling operation of the VRB are under way and will be reported elsewhere.

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