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Membranes based on carboxyl-containing polyacrylonitrile for applications in vanadium redox-flow batteries

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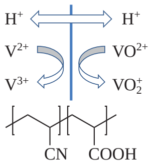
A novel-type ion-exchange membrane has been fabricated by the controlled hydrolysis of a polyacrylonitrile film. The efficiency of this membrane in a model vanadium redox-flow cell has been found comparable to that of a commercial Nafion® membrane.



Due to their advantages (independent power and energy sizing, long cycle life, fast response, and no self-discharge during storage), vanadium redox-flow batteries (VRBs) have been recognized as promising electrochemical energy storage devices.[1] In an electrochemical cell, the anolyte and catholyte solutions are separated by an ion-exchange membrane (IEM). A VRB membrane should be stable against oxidation by VO_2^+ cations and reduction by V^{2+} cations, and it should exhibit high proton conductivity to provide a high voltage efficiency of the battery and low vanadium permeability to ensure a high Coulombic efficiency.

Perfluorinated membranes such as Nafion® and MF-4SC are the most widely used IEMs for VRBs[2,3] due to a combination of excellent mechanical properties, chemical stability, and high proton conductivity. However, Nafion® is an expensive polymer material, and the crossover of vanadium species across the membrane is rather high.

Here, we demonstrate the applicability of the ion-exchange membranes of partially hydrolyzed polyacrylonitrile (PAN)[†] to VBRs. This approach has not been described previously; only the use of porous (nanofiltration) PAN membranes has been reported.[4] A Nafion 115 membrane from Sigma-Aldrich conditioned by a standard procedure[5] was used as a reference.

PAN hydrolysis under the described conditions resulted in the formation of a porous microstructure, as shown in the SEM images (Figure 1).

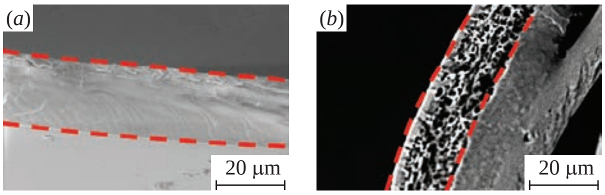


Figure 1 SEM images of the cross-sections of PAN membranes (*a*) before and (*b*) after hydrolysis (dashed lines show the cross-section edges).

The PAN membranes and the reference Nafion 115 membrane were characterized by their ion exchange capacity, through-plane proton conductivity, vanadyl (VO^{2+}) permeability, stability in a $(VO_2)_2SO_4$ solution, and performance in a single-cell model VRB (Table 1).

For the determination of ion-exchange capacity, the dry specimens were kept in 30 ml of a 2 M aqueous NaCl solution for 48 h to replace the membrane protons by sodium ions; then, the released protons in the external solution were titrated with 50.0 (for Nafion 115) or 1.00 mM (for the PAN membrane) aqueous NaOH solution to estimate the amounts of acidic groups in the membranes (SO_3H in Nafion and COOH in PAN membranes).

The through-plane proton conductivity σ (S cm^{-1}) of membranes was determined using an Autolab PGSTAT 302 instrument equipped with a four-electrode cell (a frequency range of 1 to 10^6 Hz at an amplitude of 5 mV) in 2.5 M H_2SO_4: $\sigma = l/(S\Delta R)$ (ΔR is the membrane resistance, l is the specimen thickness, and S is the specimen area).

Vanadium(IV) permeability P through the membranes was found using a two-compartment cell.[6] The cell compartments (of 0.9 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. Vanadium(IV) concentration in the second half-cell $C(t)$ was monitored by measuring absorption at $\lambda = 756$ nm ($\varepsilon_{756} = 16.15 \pm 0.05$ dm^3 mol^{-1} cm^{-1}), and the permeability P was determined by fitting the diffusion rate equation:

$$\ln\left(\frac{C_0}{C_0 - 2C(t)}\right) = \frac{PSt}{lV},$$

where C_0 is the initial V^{IV} concentration in the first half-cell.

The stability of membranes to a strong oxidizer was evaluated by keeping the membranes in a 1 M solution of $(VO_2)_2SO_4$ in 2.5 M H_2SO_4 at 50 °C for a month. Then, the concentration of VO^{2+} ions was determined; their appearance was a sign of ongoing oxidation. The membrane stability was expressed as a residual VO_2^+ concentration in the solution exposed to the membrane, as compared to that in a reference sample (without a membrane).

The model VBR cell consisted of two carbon plates with 8 mm deep milled flow channels, two 2 × 2 cm carbon felt electrodes (10 mm thick), two 1.5 mm thick silicone gaskets, and a polymer membrane placed between the gaskets. Equal amounts (15 ml) of aqueous solutions containing 1.0 M V^{IV} + 2.5 M H_2SO_4 and

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[†] The PAN membranes were prepared by casting a 15 wt% PAN (M_w = = 150000, Aldrich) solution in DMSO on a glass support and leveling with an RDS40 wire wound rod (RD Specialties, USA). The solvent was evaporated at 80 °C, and the films were put into a 4 : 1 (v/v) mixture of DMSO and a 0.25 M aqueous NaOH solution and kept at 50 °C for 2 h. Then, the membranes were washed with water and kept in a 2.5 M aqueous H_2SO_4 solution at room temperature for a day.

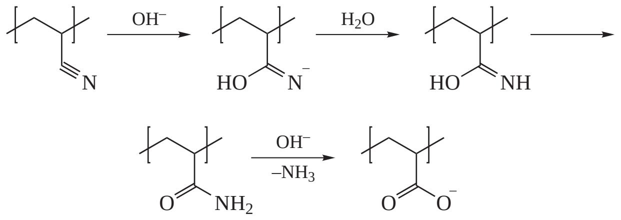
Table 1 Selected characteristics of the PAN and reference Nafion 115 membranes.

Membrane	Ion-exchange capacity/ mol g^{-1}	Proton conductivity/ mS cm^{-1}	Permeability to VO^{2+}/ cm^2 min^{-1}	Stability in $(VO_2)_2SO_4$ (%)	Performance in VBR (10 cycles)	
					CE (%)	EE (%)
Nafion 115	9.0×10^{-4}	40	5×10^{-6}	100	81	66
PAN-based membrane	2.3×10^{-4}	1.7	$\sim 10^{-9}$	100	91	67

1.0 M V^{III} + 2.5 M H_2SO_4 were used as starting anolyte and catholyte, respectively. The electrolytes were stored inside two separate sealed reservoirs in a high-purity argon atmosphere and pumped through the cell by peristaltic pumps (flow rate ~1 ml s^{-1}).

Galvanostatic charge–discharge cycling was performed using an Autolab PGSTAT 302 potentiostat. The cell was charged to 1.7 V and discharged to 1.0 V at a current density of 25 mA cm^{-2}. The Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the cells were calculated as follows: $CE = \tau_d/\tau_c$, $VE = E_d/E_c$, $EE = CE \cdot VE$ (τ is the process duration and E is the average process voltage; the subscripts ‘d’ and ‘c’ refer to discharge and charge stages, respectively).

Table 1 indicates that the modification of a PAN film led to the introduction of a noticeable amount of ionizable groups. Note that the product of the partial PAN hydrolysis contains hydrophilic groups, including carboxylic, amide and imide ones.[7] The subsequent keeping of the membrane in an acidic medium resulted in the further hydrolysis of amide and imide groups (that could be regarded as the stabilization of membrane composition to the action of an acid) (Scheme 1).



Scheme 1

Evidently, mere introduction of carboxylic groups into the PAN structure could hardly lead to a membrane performance comparable to that of Nafion®; the formation of a porous membrane microstructure was essential. Note that pores in the PAN membrane were formed during the hydrolysis rather than as a result of phase separation due to solvent evaporation.[8] Indeed, the membrane was non-porous before hydrolysis [Figure 1(*a*)], and the pores were formed during the membrane conditioning in an alkali solution [Figure 1(*b*)].

Thus, we prepared an ion-exchange membrane *via* the partial hydrolysis of PAN and tested its properties for potential applications in redox-flow batteries (in comparison with a commercial Nafion 115 membrane). The proton conductivity of the PAN-based membrane was 1.7 mS cm^{-1}. The PAN-based membrane was chemically and mechanically stable under the conditions of VBR assembly and operation; moreover, the significantly lower permeability to vanadium ions (three orders of magnitude lower than that for Nafion 115) led to a substantially improved CE of the model cell in the charge–discharge cycle. However, a lower proton conductivity led to a poorer voltage efficiency, and the overall EE was comparable to that of Nafion 115.

Therefore, the membrane of partially hydrolyzed PAN can be regarded as an alternative to commercial perfluorinated Nafion® membranes. The performance of the PAN membrane strongly depends on the preparation conditions (including the concentration of cast solution, the membrane thickness, solvent composition, temperature, alkali concentration, and the duration of membrane hydrolysis). These effects are under study and will be published elsewhere.

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