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Fabrication and Characterization of Ionic Conducting Nanofibers

Alexis Laforgue,* Lucie Robitaille, Asmae Mokrini, Abdellah Ajji

The electrospinning method was used to fabricate nanostructures of Nafion-poly(vinyl alcohol) (PVA) and Nafion-poly(ethylene oxide) (PEO). Depending on the ratio between the two polymers, nanospheres and/or nanofibers could be obtained in a reproducible manner.

The Nafion-PVA mats were found to be more conductive than the Nafion-PEO ones, possibly because of their better mechanical properties when swollen by water. The fiber morphology was always found to be more conductive than the sphere morphology. However, all electrospun mats presented ionic conductivities slightly lower than extruded Nafion 115 or Nafion-PVA cast films.

Introduction

Electrospinning was first observed by Rayleigh in 1897 and patented by Formhals in 1934,^[1] however, the process was largely forgotten until the work of Doshi and Reneker in the mid-1990s.^[2] With increasing interest in the field of nanoscience and nanotechnology, researchers began new investigations on nanofiber production using electrospinning.^[3] The number of publications and patents related to electrospinning has exploded since 2003.^[3,4] Today, the production of nanofibers with diameters ranging from tens to hundreds of nanometers with controlled morphology and function has been demonstrated using both synthetic and natural polymers.^[5,6] Electrospun fibers are being examined for use in many different applications: healthcare (drug delivery, tissue engineering), biotechnol-

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ogy and environmental engineering (nanosensors, filtration), defense and security (protection clothing, electromagnetic interference shielding), as well as energy storage and production (batteries, capacitors, photovoltaic devices).^[7]

Recently, researchers have explored the possibility of using electrospraying and electrospinning to fabricate polyelectrolyte membranes (PEM) for fuel cell applications. Sanders et al.^[8] fabricated electrosprayed NafionTM membranes and compared the properties with cast films and commercially available extruded membranes (Nafion 117). They concluded that water uptake, dimensional changes, and electrical conductivities were similar, with the exception that the electrosprayed Nafion absorbed 15 wt.-% more water than the other two membranes with only a slight increase in conductivity. On the other hand, Akle et al.^[9] prepared Nafion fibers by electrospinning a solution containing 1 wt.-% of poly(ethylene oxide) and 5 wt.-% of Nafion 1100. They reported that the conductivity of the fibers, with diameters of a few microns, was lower than conventional Nafion membranes. However, they did not report conductivity data for the



equivalent Nafion-poly(ethylene oxide) (PEO) membrane prepared by casting, so no conclusion can be made on the effect of the fibers structure and dimensions. Kim et al.^[10] demonstrated the deposition of electrospun Nafion nanofibers on both sides of a PEM membrane in order to increase the surface area, however, they did not report any conductivity data. Li et al.^[11] reported a proton conductivity of 0.37 S \cdot cm⁻¹ for electrospun mats of sulfonated poly(ether ether ketone ketone) (SPEEKK), 37 times higher than SPEEKK membranes prepared by casting.

Given the conflicting reports on the properties of ionic conducting nanofibers, this work presents an exhaustive study of the processing-morphology-properties (conductivity, water uptake) relationships of Nafion-PEO and Nafion-poly(vinyl alcohol) (PVA) nanofibers prepared by electrospinning. The paper presents the morphology of the non-woven mats of Nafion-based fibers obtained with various electrospinning parameters. Ionic conductivities obtained with different morphologies are compared to equivalent membranes prepared by casting, as well as with commercial Nafion membranes.

Experimental Part

Materials

Nafion 5 wt.-% solution was purchased from Sigma-Aldrich and used as received. PEO (\overline{M}_w 200000) from Polysciences and PVA (Gohsenol GH20, $\overline{M}_w \approx 110000 \text{ g} \cdot \text{mol}^{-1}$, 86.5–89% hydrolyzed) from Nippon Gohsei were used without further purification.

The solutions were prepared by dissolving PEO or PVA in the commercial Nafion solution under gentle heating and stirring. In the sample names used in this paper, the number before each component is related to the weight concentration of this component in the solution. The solutions were filtered through a 0.22 μ m pore size filter before electrospinning.

Electrospinning Process

The polymer solutions were filled into a 1 cm³ plastic syringe (Becton D) equipped with a stainless steel needle (n° 20: $\phi_{\rm ext} =$ 0.91 mm; $\phi_{\rm int} =$ 0.58 mm). The syringe was placed in a automatic pump (Harvard Apparatus PHD4400) and grounded. A stainless steel substrate was connected to a high voltage power supply (Gamma High Voltage Research Model ES75P- 10W). The setup is represented in Figure 1. The rotating and translating capabilities of the fiber collector were not used in this work. For each distance/flow rate combination, the voltage was adjusted to obtain a stable Taylor cone. This means that each time the flow rate or distance was changed, the voltage had to be tuned differently.

Characterization

Diameter analysis: histograms were built using SEM image analysis on a minimum of 50 fibers for each operating condition.

Differential scanning calorimetry (DSC) was performed on a TA Instruments Model Q1000 at 20 $^\circ C \cdot min^{-1}$.

Water uptake: measurements were made by mass difference of wet (soaked for 24 h) and dried samples (at room temperature under active vacuum for at least 24 h). Preliminary studies at different time intervals were carried out to confirm that these conditioning parameters resulted in materials at equilibrium (maximum water incorporation/maximum sample desiccation). The water uptake was calculated using the following equation:

$$WU(\%) = \frac{(m_{wet} - m_{dry})}{m_{dry}} \times 100.$$
⁽¹⁾

Ionic conductivity: in-plane conductivity measurements were performed by 2-probe impedance technique using a VMP3 multipotentiostat (Princeton Applied Research) and a BekkTech conductivity cell. Experiments were done at room temperature in Milli-Q water (18.2 $\Omega \cdot cm$) with membranes equilibrated in water for at least 24 h. The conductivity was then calculated using the following equation:

$$\rho = \frac{1}{R} \cdot \frac{d}{t \times L} \tag{2}$$

where, *R* is the resistance obtained from the impedance analysis, *d* the distance between the electrodes, and, *t* and *L* the thickness and width of the sample, respectively.



Figure 1. Electrospinning setup at NRC-IMI. Inset is a photograph of the Taylor cone and beginning of the polymer jet.



Scanning electron microscopy (SEM) was performed on a Hitachi S4700.

Results and Discussion

Nanofibers Fabrication

A commercial Nafion solution containing 5 wt.-% of the polymer dissolved in a mixture of water and low molecular weight alcohols was used in this study. A schematic representation of the electrospinning setup as well as a picture of the Taylor cone obtained for a Nafion solution are presented in Figure 1.

The first electrospinning attempts using the Nafion solution led to the formation of polymer droplets (electrospraying), generally attributed to a lack of polymer chains entanglement.^[8] One of the possible ways to promote fiber formation is to increase the polymer solution concentration. This was done by gently heating the commercial solution to evaporate the solvents. The solution concentrations were adjusted to 10 and 20 wt.-% of Nafion. The 20 wt.-% solution was too viscous to be processed. The 10 wt.-% solution was also very viscous and resulted in very unstable electrospraying processing conditions.

A second approach that has been explored to assist fiber formation is to add a high molecular weight polymer to the

solution. Two polymers were tested for that purpose: PEO $(200\ 000\ g\cdot mol^{-1})$ and PVA $(110\ 000\ g\cdot mol^{-1})$. All the electrospinning experiments were performed by adjusting the electric field to flow rate ratios in such a way to obtain a perfectly stable electrospinning jet. These conditions were only obtained for a narrow range of flow rates, typically between 0.1 to 0.4 mL \cdot h⁻¹. The ambient relative humidity (RH) was found to also be a critical parameter for the stable formation of nanofibers: above 45% RH, nets of entangled fibers grew in the air, perpendicular to the electric field, from the substrate towards the grounded needle. These fibers then stretched to form aligned bundles of nanofibers electrically attracted by the needle. This behavior has already been observed during the electrospinning of other polyelectrolytes^[12] and can be explained by the ionic conducting nature of the fibers in the presence of a significant amount of water molecules in the air. Indeed, the solvent inside the initial "flying" nanofiber does not evaporate quickly because of the high relative humidity in the surrounding environment. Under these conditions, the nanofiber is conducting enough to be submitted to the force of the electric field. Once such a conducting nanofiber stretches from the substrate into the air, this nanofiber becomes the shortest distance between the grounded needle and the electrified substrate resulting in a preferential deposition of the subsequent fibers



Figure 2. SEM images showing the morphology of the electrospun structures using Nafion-PEO solutions. Distance = 5 cm; flow rate = 0.2-0.3 mL \cdot h⁻¹; voltage = 8-9 kV; Nafion solution concentration: 5 wt.-%; PEO content: a) 0.25, b) 0.5, c) 0.75, and, d) 1 wt.-%. Scale-bars represent 10 μ m. RH = 31%; T = 22 °C.



onto the first one rather than onto the substrate. For all experiments, the relative humidity level was carefully controlled to be lower than 45% to avoid this fiber bundle formation process. Moreover, under 45%, variation of RH was not found to influence the nanofiber morphology.

Morphological Analysis

The morphology of the samples prepared from the Nafion-PEO and Nafion-PVA solutions was determined by SEM. Figure 2 presents the SEM images of the Nafion-PEO structures obtained with increasing PEO contents. At



Figure 3. SEM images showing the morphology of the electrospun structures using Nafion-PVA solutions. Distance = 5 cm; flow rate = 0.15 mL \cdot h⁻¹; voltage = 10–12 kV; Nafion solution concentration: 5 wt.-%; PVA content: a) 0.25, b) 0.5, c) 0.75, d) 1, e) 1.25, f) 1.5, and, g) 2 wt.-%. Scale-bars represent 2 μ m. RH = 15–40%; T = 21-23 °C.



0.25 wt.-% PEO in the solution (i.e., 4.8 wt.-% PEO in the final material), the resulting morphology was an aggregation of spheres with diameters varying between 300 nm and 4 μ m, as well as ultra-thin beaded fibers (diameters 30 ± 10 nm). These results indicate that the addition of a small amount of PEO did not allow the formation of nanofibers but stabilized the electrospraying of the Nafion solution. At 0.5 wt.-% of PEO in the solution (i.e., 9 wt.-% PEO in the final material), both electrospraying and electrospinning processes occurred, resulting in a blend of spheres and beaded nanofibers (cf. Figure 2(b)).

The fiber diameter was determined to be 100 ± 30 nm. At 0.75 wt.-% of PEO in the solution (i.e., 13 wt.-% PEO in the final material), both processes still occurred, but electrospinning dominated and very few spheres could be observed. The fibers presented diameters ranging from 40 to 150 nm. However, the few beads still present on the fibers (Figure 2(c)) indicate that the Rayleigh instability prevailed from time to time, due to a lack of chains entanglement. At 1 wt.-% of PEO in the solution (i.e., 16.7 wt.-% PEO in the final material), perfect nanofibers were obtained, with diameters from 80 to 180 nm and a preponderance around 120 nm. The surface of the fibers was smooth, showing no macro-phase separation between the PEO and Nafion chains. The same study was performed with PVA as the supporting polymer. Figure 3 presents the morphology of Nafion-PVA nanofibers with increasing PVA contents. In a similar manner, increasing the PVA content moved the process from stabilized electrospraying to electrospinning of beaded fibers, and finally to smooth fibers. The average diameter of the fibers is about half of the one obtained for similar quantities of PEO. This seems to reflect the difference in molecular weight between the two co-polymers (100 000 and 200 000 g \cdot mol⁻¹ for PVA and PEO, respectively).

Several parameters influencing the fiber diameter were studied. It was found that the target distance had the most significant impact, as largely reported in the literature.^[4–7] The distribution of the fiber diameters as a function of the target distance are plotted in Figure 4 for Nafion solutions containing 1 wt.-% of PVA (left) or PEO (right). The distribution was determined by measuring a minimum of 50 fibers per sample. As can be observed in Figure 4, the average diameter increased from 40 to 60 nm for the Nafion-PVA fibers and from 100 to 140 nm for the Nafion-PEO fibers when the target distance increased from 3 to 10 cm. Using greater distances typically led to perturbations in the electrospinning process, thus giving irreproducible results.



5Naf-1PVA

5Naf-1PEO

Figure 4. Distribution of the Nafion composite fiber diameters for different target distances. PVA or PEO contents = 1 wt.-%; flow rate = 0.15 and 0.2–0.3 mL \cdot h⁻¹ for Nafion-PVA and Nafion-PEO fibers, respectively; voltage = 8–9 kV and 10–12 kV for Nafion-PVA and Nafion-PEO fibers, respectively.







Figure 5. Distribution of Nafion-PVA fiber diameters for different fiber compositions. Target distance = 5 cm; flow rate = 0.15 mL \cdot h⁻¹; voltage = 10–12 kV; RH = 15–35%; *T* = 21–23 °C.

The fiber diameter was also found to be dependent on the spinable polymer concentration in the solution, as illustrated in Figure 5 for Nafion-PVA fibers. By varying the PVA concentration from 1 to 2 wt.-%, the average fiber diameter could be tuned from 50 to 100 nm.

Thermal and Electrochemical Characterization

A DSC experiment of a 5Naf-1PVA sample was carried out and the exotherm is presented in Figure 6. A first peak around 100 °C can be attributed to the evaporation of the water present in the mat but outside the fiber structures. The glass transition of the PVA can be seen around 60 °C, as a shoulder on the water evaporation peak. The second peak



Figure 6. DSC scan obtained for the Nafion-PVA nanofibers containing 17 wt.-% of PVA (1 wt.-% in the solution). Scan rate $= 20 \text{ °C} \cdot \text{min}^{-1}$.

around 147 °C was attributed to the degassing of the unbound-water located in the hydrophilic channels of the Nafion.^[13] The peaks at 190 and 210 °C were attributed to a crystalline phase transition of the non-polar Nafion backbone.^[14] These results are typical of a Nafion-PVA bulk blend, indicating that the nanofiber morphology did not induce any changes in the thermal properties of the material.

Water uptake measurements were performed on the electrospun/electrosprayed samples as well as cast films of equivalent compositions for the two systems. The results are presented in Table 1. The water uptake values obtained for the Nafion-PEO mats were very high, leading to poor mechanical properties after immersion of the films in water. The samples presenting a high content of fibers presented higher water uptake values than the samples with a predominant sphere morphology. This was expected given the larger accessible surface available to water in the samples showing a nanofiber morphology, as well as the higher content in PEO which is a hydrophilic polymer. The Nafion-PVA mats did not swell as much in water than Nafion-PEO mats but showed the same trends. It is interesting to note that a cast film of Nafion-PVA (1 wt.-%) showed half the water uptake compared to the electrospun/electrosprayed mat of the same composition. This result demonstrates that the morphology plays a crucial role in the water swelling properties of the samples.

Finally, the in-plan conductivities of the mats were determined and are presented in Table 1 and Figure 7. The ionic conductivities were lower for the Nafion-PEO mats than for the Nafion-PVA ones. This can be attributed to the very poor mechanical properties of the Nafion-PEO mats which showed a partial decomposition when dipped in



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Sample Type		Observed Morphology	Conductivity	Water Uptake
			S ⋅ cm ⁻¹	%
Nafion 115 Nafion (5 wt%) + PVA Series		Extruded film	7.3×10^{-2}	36±5
PVA sol. concentration	PVA fiber content			
wt%	wt%			
0.25	4.8	Spheres	3.5×10^{-3}	112 ± 10
0.50	9.1	Spheres + ultrathin fibers	4.3×10^{-3}	115 ± 7
0.75	13.0	Beaded nanofibers	$8.7 imes 10^{-3}$	118 ± 8
1.00	16.7	Nanofibers + few beads	1.7×10^{-2}	125 ± 5
1.00	16.7	Cast film	3.0×10^{-2}	50 ± 7
1.25	20.0	Nanofibers + few beads	$1.6 imes 10^{-2}$	127 ± 6
1.50	23.1	Nanofibers + scarce beads	$1.4 imes 10^{-2}$	140 ± 6
2.00	28.6	Nanofibers	1.0×10^{-2}	155 ± 4
Nafion (5 wt%) + PEO Se	ries			
PEO sol. concentration	PEO fiber content			
wt%	wt%			
0.50	9.1	Spheres + ultrathin fibers	$3.5 imes10^{-3}$	255 ± 15
1.00	16.7	Nanofibers	$5.9 imes 10^{-3}$	400 ± 35

water. On the other hand, the Nafion-PVA mats had always significantly better mechanical properties than the Nafion-PEO ones. They could be easily detached from the substrate and handled as self-standing membranes.

For both types of material, the fiber morphology was systematically more conductive than the sphere or sphere



Figure 7. Ionic conductivity of Nafion-PVA mats at different PVA contents in the fibers.

and fiber morphology. This result can be explained by the barriers to proton conduction that are significantly lower in a fiber mat morphology than in a side-by-side sphere morphology. Indeed, the protons are transported through the hydrophilic channels of the Nafion. The main barriers to the conduction in this kind of non-continuous structures are the transfers of the protons at intersections, from one fiber (or sphere) to another. The number of intersections that the protons encounter being lower by far in the case of a fiber morphology than in the case of a side-by-side sphere morphology, the conductivity is expected to be lower in the last case.

The ionic conductivity data of the Nafion-PVA mats at different PVA contents in the fibers are shown in Figure 7. At low PVA contents, the conductivity is limited by the sphere morphology, as explained above. By increasing the PVA content, beaded fibers are formed and the conductivity is significantly enhanced. Increasing the PVA content further, above a critical point, 16–18% in this case (Figure 7), causes the conductivity to decrease back. This last phenomenon is not believed to be related to the change in morphology (increase in fiber diameter, absence of beads, etc.) but rather to the increase in PVA content that does not participate in the proton conduction process.

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It is interesting to note that recently published work on sulfonated PEEKK electrospun mats reported opposite results, where the spherical morphology was by far more conductive than both the fiber morphology or cast films (those being similarly conductive).^[11] According to the interpretation proposed by the authors, the sulfonate groups were located at the surface of the spheres in the case of the spherical morphology and the conductivity was then only a surface phenomenon. It does not appear to be the case in the present study. As expected from the dilution of the conductive component by PEO or PVA, the ionic conductivities measured for the different electrospun structures were all lower than extruded Nafion 115.

For a similar PVA content, for example 1 wt.-% in the solution (Table 1), the cast film showed a slightly higher conductivity than the electrospun mat, even if this composition resulted in one of the most conductive electrospun structures. These results indicate that the nanostructure did not improve the ionic conductivity which is also in opposition to the results published by Li et al.^[11]

However, it is important to note that the conductivities reported in this paper are only "apparent conductivities" since the formulas used to calculate the data are usually applied for bulk materials and not for highly porous materials as described here. For example, the conductivity for 5Naf-1PVA membrane (fiber morphology) was $1.7 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$, compared to $3.0 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ for a cast film of the same composition and same thickness. This represents only a two-fold conductivity reduction, while the sample weight was four times lower compared to the cast film. This result is a good indication that the fiber morphology presents advantages over the bulk morphology in conducting protons. The structural alignment of the hydrophylic domains along the fiber axis is believed to explain this result.

Conclusion

In summary, the electrospinning method was used to fabricate conductive nanostructures of Nafion-PVA and Nafion-PEO. Depending on the ratio between the two polymers, nanospheres and/or nanofibers could be obtained in a reproducible manner. The Nafion-PVA mats were found to be more conductive than the Nafion-PEO ones, possibly because of their better mechanical properties when swollen by water. The fiber morphology was always found to be more conductive than the sphere morphology. However, all electrospun mats presented ionic conductivities slightly lower than extruded Nafion 115 or Nafion-PVA cast films.

These nanofiber mats could have interesting applications for the development of highly sensitive sensors, improved actuators^[9] or enhanced fuel cells membrane electrode assemblies.

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