

Polymer communication

Highly hydrated Nafion/activated carbon hybrids

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ABSTRACT

The incorporation of highly porous activated carbon (aC) to Nafion membranes confers unprecedented levels of water uptake (4 times higher for 10 wt% aC compared to neat Nafion) at a minimal dimensional swelling and results in dramatic enhancements in ionic conductivity at low relative humidity. This behavior reveals the development of a robust network of water nanochannels formed by the carbon pores and the polymeric ionic domains which are structurally stabilized by the rigid Nafion backbone and the non-deformable aC particles.

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1. Introduction

Nafion membranes are widespread in fuel cell electrode assemblies because they combine the remarkable chemical stability of their Teflon-like backbone with their unique proton-conducting properties stemming from the sulfonated side chains [1]. The energy efficiency of a fuel cell is maximized at elevated temperatures mainly due to the acceleration of the cathodic oxygen reduction reaction and the enhanced CO tolerance by the anode electrocatalyst [2]. However, at elevated temperatures extensive dehydration of Nafion membrane undermines its performance, longevity and reliability given that proton conduction is strictly restricted through the ionic nanochannels that can expand reversibly to accommodate water. The development of ionomer membranes with enhanced water retention capacity and, thus, improved ionic conductivity even under low humidity levels remains a major challenge for the advancement of the fuel cell technology [3].

A common approach to address this problem is the incorporation of hygroscopic particles (smectic clays, inorganic oxides, zirconium phosphates, or heteropolyacids) [4–7], water-filled porous or hollow additives [8,9] and self-humidifying particles

(e.g. SiO₂ supported platinum catalyst nanoparticles) [10]. The hybrid membranes show improved hydration, but oftentimes they suffer from poor dispersion [11], leaching [7], extensive swelling [11], reduced ionic conductivity (as a result of the low intrinsic conductivity of the additives) [12], not to mention their substantial economic cost [12].

In this work we focus on the preparation and characterization of hybrid Nafion membranes containing highly porous activated carbon (aC) particles that not only play the role of the hygroscopic additives, but also function as compact water reservoirs. The cost-effective hybrid membranes exhibit unprecedented levels of water retention and, by doing so, they demonstrate dramatic enhancements in ionic conductivity at a minimal dimensional swelling.

2. Experimental section

The activated carbon (aC) was purchased from Osaka Gas and milled with fused zirconia powder for 72 h (Supporting Information (S.I.) Figure S1). The milled aC was oxidized by refluxing in a mixture of HNO₃/H₂SO₄ at 80 °C for 24 h. Following oxidation the aC particles were extensively washed on a filter with deionized water until the pH of the filtrate water became neutral and then dried at 100 °C. Nafion DE2020 (18 wt% in lower aliphatic alcohols and water) was obtained from Ion Power Inc. The Nafion/aC dispersion was stirred for 12 h, then dried in an oven for 24 h ($T = 50\text{ }^{\circ}\text{C}$) and post annealed at 140 °C for 2 h. The cast membrane

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was activated by 1 M H₂SO₄ at 80 °C for 1 h and then rinsed in distilled water (80 °C for 1 h).

The impedance spectra of the membranes at various humidity levels were measured by a four-point probe unit in a temperature and humidity test chamber (MHK, TERCHY) using a Solartron 1260 Analyzer within the range 1 MHz–0.1 Hz with (voltage amplitude 0.01 V). The resistance of the membranes was calculated from the intercept of the real axis in the intermediate frequency domain of the impedance spectrum (Z'' vs Z'). The impedance measurements were conducted at 30 °C and the membranes were equilibrated for 1 h at each humidity level. For the pristine Nafion membranes the error of resistance determination was calculated to be $\pm 5\%$. Ultimately, the ionic conductivity σ was calculated based on the equation $\sigma = L/AR$, where L is the sample thickness (length parallel to current flow), A is the cross-sectional area (perpendicular to the current flow) and R is the resistance of the membrane.

The liquid-equilibrated water uptake (WU) of the membranes was calculated from the equation: $WU = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}$ where W_{wet} and W_{dry} are the weights of the fully hydrated and the anhydrous membranes, respectively. In our protocol, the membranes were first immersed to deionized water at two different temperatures (30 and 80 °C) for 24 h, blotted by an absorbent paper and the W_{wet} was measured. Subsequently, the membranes were thoroughly dried in a vacuum oven at 70 °C for 24 h and then the W_{dry} was measured. The dimensions of the hydrated and dry membranes were measured by a micrometer (Mitutoyo) that is able to measure the membrane thickness at micrometer resolution. Each membrane was cut into 5×5 cm [2] and the swelling ratio was conducted at 30 °C for 24 h and calculated according to the volume changes. Dynamic mechanical analysis (DMA) of rectangular films was carried out on an Instron TAQ800 using the film/fiber tension clamp within the temperature range from 35 °C to 150 °C (scanning rate 3 °C/min, applied strain 0.3%, single frequency 10 Hz).

The membrane morphologies were characterized using SEM (Scanning electron microscope, JSM-6500F, JEOL Ltd., Japan) and TEM (Transmission electron microscope, JEM-2100F, JEOL Ltd., Japan). To stain the hydrophilic domains, the membranes were converted into their Pb²⁺ forms by immersing in Pb(AC)₂ (lead acetate, 1 N) solution overnight and then rinsing with water. Membranes were dried under vacuum at 80 °C for 12 h and then sectioned into 50 nm slices using an ultramicrotome. The slices were picked up with 200 mesh copper grids for TEM observation.

3. Results and discussion

Taken into account the poor dispersion of the as received, micron sized aC particles within the Nafion matrix, we have focused on their mechanically milled submicron derivatives and surface acidification. BET surface analysis (based on nitrogen absorption/desorption isotherms) indicated that milling and acidifying treatments do not compromise the high surface area of the particles that remain close to 1800 m²/g.

The SEM images shown in Fig. 1a confirm the homogenous distribution of the submicron aC particles within the membrane, while the continuous dark lines along their periphery (seen in TEM images in Fig. 1b) point to the dense population of sulfonic groups in the matrix/hydrophilic filler interface. The TEM images also reveal the formation of discrete polar (dark spots, sulfonic groups) and non polar (light spots, PTFE backbone) domains as expected for a phase-separated system. Several models proposed to explain the morphological features of Nafion membranes underscore the significance of the interconnectivity and tortuosity of ionic clusters to the transport properties of the membranes and the dominant role of the crystalline phase to the structural integrity of the membranes [1].

The introduction of aC particles to the dry Nafion membranes affords significant mechanical reinforcement as evident by the

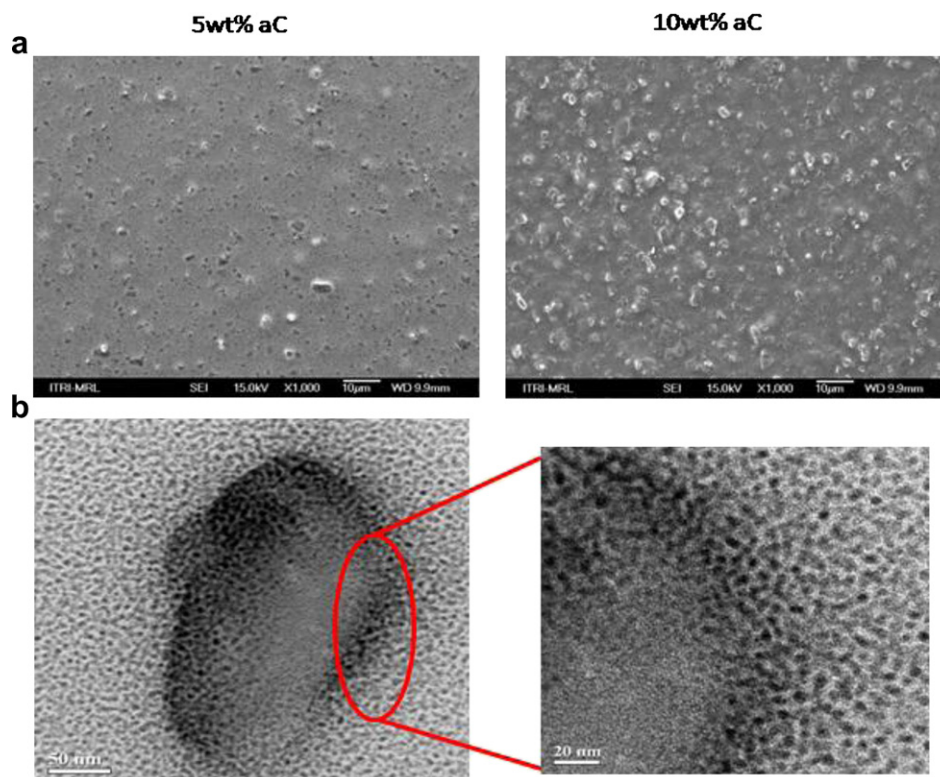


Fig. 1. SEM (a) and TEM (b) images of Nafion/activated carbon composites membranes.

DMA traces shown in Fig. 2a. Compared to pristine Nafion, the storage modulus of 10 wt% aC/Nafion membranes is higher by a factor of 1.5 and 2.5 at 30 and 80 °C, respectively. Although, the mechanical properties of all membranes tend to decline with increasing humidity, the storage modulus of the 10 wt% and 20 wt% aC/Nafion membranes remains substantially higher compared to pristine Nafion within the entire temperature window considered (S.I. Figure S2). Substantial mechanical enhancements have been previously reported for various types of Nafion based hybrids, including systems based on silica, CNT, clays and graphite oxide [13–17]. In fuel cell applications, the stiffer ion conductive materials allow the use of thinner membranes with reduced internal resistance, without the risk of structural failure.

At the same time, the $\tan\delta$ curves (Fig. 2b) indicate that the introduction of aC particles causes only a minor displacement of the high temperature α relaxation. The α relaxation has been assigned to the onset of long range mobility of the polymeric chains (both backbone and side chain) resulting in the gradual collapse of the static network [18,19]. We note that the low temperature β relaxation that corresponds to the genuine glass transition of Nafion (e.g. the onset of segmental mobility) falls outside the temperature range considered. Unlike the aC/Nafion hybrids, the Nafion nanocomposites typically display a profound displacement and suppression of the α relaxation $\tan\delta$ peak due to the polymer confinement in the vicinity of organic–inorganic interface [13–16,20]. The minor effect seen in Fig. 2b points out to the limited Nafion–aC interface, as a direct consequence of the submicron (rather than nano) size of the aC particles.

In considering the water uptake (WU) of the Nafion membranes it is important to recognize that the large discrepancies encountered in literature are rationalized due to variations of the membrane pretreatment (critical for the morphology evolution) and the hydration process [21,22]. In the present study all membranes have been subjected to an identical hydration/dehydration protocol (from liquid water) at two different immersion temperatures 30 and 80 °C (see Experimental section for details).

At immersion temperature 30 °C, the WU of the pristine Nafion is 30% and it monotonically increases with aC content to 45, 81, 135 and 190% for the 2.5, 5, 10 and 20 wt% composite, respectively (Fig. 3). At immersion temperature 80 °C, the WU of the pristine Nafion approaches 50%, an effect that has been attributed to the weaker stresses experienced by the ionic clusters due to the softening of the neighbor crystalline domains [23] (see also Fig. 2a). Improved WU was also obtained for the 2.5 and 5 wt% hybrids, but the trend diminishes at higher aC content, since an increasing number of carbon pores become available to accommodate water.

In other words, the temperature profile of the WU of the hybrid membranes reflects a change in the nature of the dominant water reservoirs, upon increasing the aC content, from the ionic domains of Nafion to the carbon pores.

The introduction of hygroscopic or water-filled porous particles typically improves the hydration of Nafion membranes; however to a much lesser extent compared to the behavior observed for the present system. For reference, the highest value $WU = 87\%$ has been determined for the 10 wt% laponite/Nafion [24], $WU = 56\%$ for the 13 wt% sulfonated mesoporous silica [6], $WU = 47\%$ for 5 wt% superacid-Zirconia [25], $WU = 40\%$ for 7 wt% of bifunctional silica nanoparticles (bearing hydrophilic Si-OH and proton conductive SO_3H groups) [26]. To our knowledge, the exceptional hydration characteristics observed for aC/Nafion membranes ($WU = 146\%$ for 10 wt% aC) have not been reported for any other Nafion based system.

Despite the unprecedented hydration level of the aC/Nafion membranes, their dimensional swelling tends to decline with aC content. In particular, the swelling of pristine Nafion is 40%, it remains essentially unaltered for the 2.5 and 5 wt% hybrid, but decreases to 32 and 27% for 10 and 20 wt% hybrids, respectively. Dimensional stability upon hydration is highly desirable for a proton conducting membrane, since uncontrolled swelling is detrimental for the integrity of the membrane and leads to internal stresses, pinhole formation and contact loss in the membrane/electrode interface.

The unique hydration/swelling characteristics observed for aC/Nafion membranes reveal the built up of a robust network of nanochannels that can accommodate extensive amounts of water. The nanochannels are formed by the carbon pores and the ionic clusters and exhibit minimal swelling due to the non-expandable nature of aC particles [27]. In analogy, addition of sulfonated mesoporous silica effectively suppresses swelling [6]. However, porosity alone fails to provide such attractive hydration characteristics to Nafion membranes. For example, $WU = 120\%$ has been reported for mesoporous Nafion membranes, but this effect is accompanied by extreme dimensional swelling 100% due to the lack of a robust scaffold to afford structural stability [28]. There is no general trend established on the effect of hydroscopic particles to Nafion membranes; inclusion of hollow silica nanoparticles reduces swelling [29], but addition of 10 wt% TiO_2 results in swelling in excess of 300% [11].

It is well established that the ionic conductivity (κ) of pristine Nafion membranes increases with relative humidity (RH) because proton transfer takes place through the polar domains that tend to absorb more water in the high RH limit [1]. In Fig. 4, it can be seen

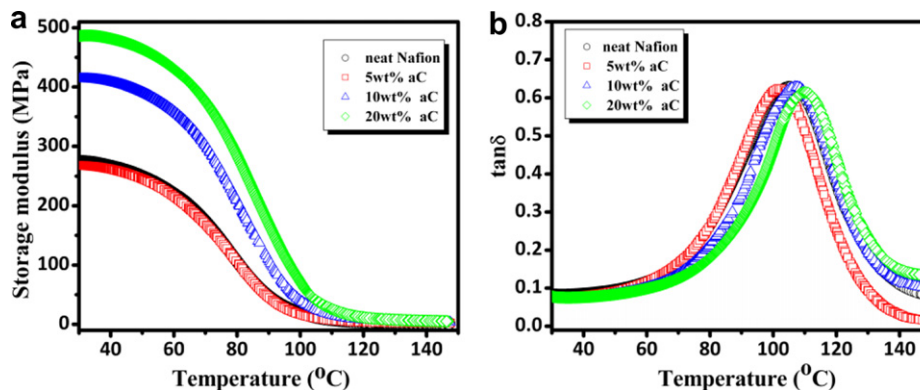


Fig. 2. DMA traces of Nafion/activated carbon composites membranes; a) storage modulus and b) $\tan\delta$. Symbols denote; neat Nafion (black circles), 5 wt% aC (red squares), 10 wt% aC (blue triangles) and 20 wt% aC (green diamonds). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

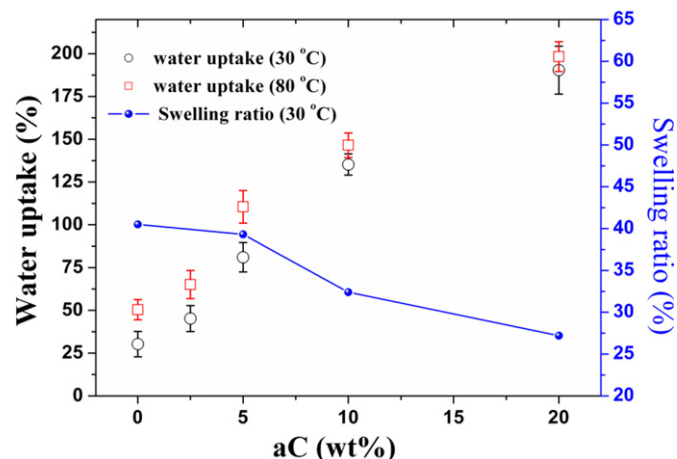


Fig. 3. Water uptake and swelling ratio of Nafion/activated carbon composite membranes; immersion temperature 30 (black circles and blue spheres) and 80 °C (red squares). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

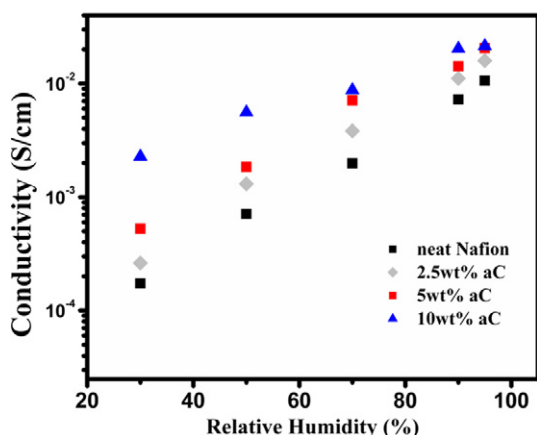


Fig. 4. Ionic conductivity of Nafion/activated carbon composite membranes as a function of relative humidity; neat Nafion (black circles), 2.5 wt% aC (gray diamonds), 5 wt% aC (red squares) and 10 wt% aC (blue triangles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that incorporation of aC systematically enhances κ throughout the entire RH range considered, but the effect is more pronounced in the low RH (The 20 wt% hybrid showed somewhat lower κ compared to 10 wt% and is not included in the plot for clarity). We note that the Ion Exchange Capacity of the membranes marginally decreases upon the addition of the filler (S.I. Table S1), indicating that the contribution of any possible ionic interactions induced by the aC particles to the conductivity are not significant. Those observations point out that the improved proton conduction of the hybrid membranes can be traced back to their superior water retention capability, an effect that has stronger impact at low humidity environments.

At RH = 30% the conductivity increases by a factor of 1.5, 3, 13 for the 2.5, 5 and 10 aC wt% hybrids, respectively. In contrast, at RH = 95% the conductivity of the hybrids is at most twice higher

compared to neat Nafion. In a similar manner, more pronounced enhancements in κ at low RH have been reported for mesoporous Nafion membranes [28] and hybrids containing mesoporous silica [6] or mesoporous zirconium phosphate [30]. In contrast, addition of nanoclays [13,14], silica nanoparticles [31] or zirconium phosphate [32] adversely affects conductivity of the Nafion membranes due to the low intrinsic conductivity of the embedded particles.

In conclusion, we demonstrate that the hydration characteristics of aC/Nafion hybrid membranes are very attractive for fuel cell applications. The hybrid membranes show unprecedented levels of water uptake and minimal dimensional swelling due to the presence of a robust network of water nanochannels formed by the non-expandable carbon pores and the polymeric ionic domains. This aqueous network facilitates proton transfer and gives rise to an order of magnitude enhancement in ionic conductivity at low humidity.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.polymer.2012.08.061>.

References

- [1] Mauritz KA, Moore RB. *Chem Rev* 2004;104:4535–85.
- [2] Li Q, He R, Jensen JO, Bjerrum NJ. *Chem Mater* 2003;15:4896–915.
- [3] Yang C, Costamagna P, Srinivasan S, Benziger J, Bocarsly AB. *J Power Sourc* 2001;103:1–9.
- [4] Alberti G, Casciola M. *Annu Rev Mater Res* 2003;33:129–54.
- [5] Laberty-Robert C, Vallé K, Pereira F, Sanchez C. *Chem Soc Rev* 2011;40:961–1005.
- [6] Pereira F, Valle K, Belleville P, Morin A, Lambert S, Sanchez C. *Chem Mater* 2008;20:1710–8.
- [7] Ramani V, Kunz HR, Fenton JM. *Electrochim Acta* 2005;50:1181–7.
- [8] Pu H, Wang D, Yang Z. *J Memb Sci* 2010;360:123–9.
- [9] Baglio V, Di Blasi A, Arico AS, Antonucci V, Antonucci PT, Trakanprapai C, et al. *J Electrochem Soc* 2005;152:A1373–7.
- [10] Watanabe M, Uchida H, Seki Y, Emori M, Stonehart P. *J Electrochem Soc* 1996;143:3847–52.
- [11] Slade SM, Smith JR, Campbell SA, Ralph TR, Ponce de Leon C, Walsh FC. *Electrochim Acta* 2010;55:6818–29.
- [12] Peighambaridoust SJ, Rowshanzamir S, Amjadi M. *Int J Hydrogen Energy* 2010;35:9349–84.
- [13] Cele N, Ray SS. *Macromol Mater Eng* 2009;294:719–38.
- [14] Burgaz E, Lian H, Alonso RH, Estevez L, Kellarakis A, Giannelis EP. *Polymer* 2009;50:2348–92.
- [15] Alonso RH, Estevez L, Lian H, Kellarakis A, Giannelis EP. *Polymer* 2009;50:2402–10.
- [16] Ansari S, Kellarakis A, Estevez L, Giannelis EP. *Small* 2010;6:205–9.
- [17] Thomassin JM, Koller J, Caldarella G, Germain A, Jerome R, Detrembleur C. *J Memb Sci* 2007;303:252.
- [18] Page KA, Cable KM, Moore RB. *Macromolecules* 2005;38:6472–84.
- [19] Obsorn SJ, Hassan MK, Divoux GM, Rhoades DW, Mauritz KA, Moore RB. *Macromolecules* 2007;40:3886–90.
- [20] Jalani NH, Dunn K, Datta R. *Electrochim Acta* 2005;51:553–60.
- [21] Hinatsu JT, Mizuhata M, Takenaka H. *J Electrochem Soc* 1994;141:1493–8.
- [22] Onishi LM, Prausnitz JM, Newman J. *J Phys Chem B* 2007;111:10166–73.
- [23] Jalani NH, Datta R. *J Memb Sci* 2005;264:167–75.
- [24] Bebin P, Caravanier M, Galiano H. *J Memb Sci* 2006;278:35–42.
- [25] Navarra MA, Croce F, Scrosati B. *J Mater Chem* 2007;17:3210–5.
- [26] Wang H, Holmberg BA, Huang L, Wang Z, Mitra A, Norbeck JM, et al. *J Mater Chem* 2002;12:834–7.
- [27] Balzer C, Wildhage T, Braxmeier S, Reichenauer G, Olivier JP. *Langmuir* 2011;27:2553–60.
- [28] Lu J, Tang H, Xu C, Jiang SP. *J Mater Chem* 2012;22:5810–9.
- [29] Yuan J, Zhou G, Pu H. *J Memb Sci* 2008;325:742–8.
- [30] Sahu AK, Pitchumani S, Sridhar P, Shukla AK. *Fuel Cell* 2009;9:139–47.
- [31] Jiang R, Kunz HR, Fenton JM. *J Memb Sci* 2006;272:116–24.
- [32] Casciola M, Capitani D, Comite A, Donnadio A, Frittella V, Pica M, et al. *Fuel Cell* 2008;3–4:217–24.