Short communication

Nafion/polyaniline composite membranes specifically designed to allow proton exchange membrane fuel cells operation at low humidity

Jinyan Yang[a], Pei Kang Shen[a,*], John Varcoe[b], Zidong Wei[c,*]

[a] *The State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University,*
135 Xingang Road, Guangzhou 510275, Guangdong, PR China
[b] *Division of Chemical Sciences, University of Surrey, Guildford GU2 7XH, UK*
[c] *The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, School of Chemistry and Chemical Engineering,*
Chongqing University, Chongqing 400044, China

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ABSTRACT

A Nafion and polyaniline composite membrane (designated Nafion/PANI) was fabricated using an in situ chemical polymerization method. The composite membrane showed a proton conductivity that was superior to that obtained with Nafion® 112 at low humidity (e.g. RH = 60%). Water uptake measurements revealed similarities between the Nafion® 112 and Nafion/PANI membranes at different humidities. The high conductivity of the Nafion/PANI membrane at low humidity is hypothesized to be due to the existence of the extended conjugated bonds in the polyaniline; proton transfer is facilitated via the conjugated bonds in lower humidity environments allowing retention of the relatively high conductivity. Correspondingly, the performance of a single cell fuel cell containing the Nafion/PANI composite membrane is improved compared to a Nafion® 112-containing cell under low humidity conditions. This is important for portable fuel cells, which are required to operate without external humidification.

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1. Introduction

Perfluorosulfonic acid polymer membranes, e.g. Nafion® (DuPont, USA), are widely used as the polymer electrolyte membranes (PEM) in fuel cells. The poly(tetrafluoroethylene) (PTFE) backbone structure imparts thermally and chemically stability. The presence of terminal –SO$_3$H groups allow high proton conductivities but only under well-humidified conditions. A contributing factor to poor fuel cell performance is high membrane (solid electrolyte) derived ionic resistances. Therefore, the proton conductivity related properties of the PEM directly determine the output performance of the fuel cells. However, the Nafion® PEM must be kept well hydrated to retain acceptable proton conductivity. Loss of water content in the PEM leads to a sharp decrease in the proton conductivity and shrinkage of the membrane, which results in mechanical degradation of the membrane–catalyst interface. It is vital to be able to improve PEM proton conductivities under low humidity conditions.

A common strategy that has been adopted to improve the water retention capacity is to integrate hygroscopic materials into the membranes [1–3]. However, the intrinsic conductivities of the resulting composite membranes are reduced with further increases in inorganic additive contents. This article presents the modification of Nafion® PEMs using surface coatings of polyaniline (PANI) specifically to improve proton conductivities at low humidity; the long conjugated PANI chains are expected to promote proton mobility in the composite membrane. PANI is an important electronically conducting polymer [4–6]. Previous work on the use of PANI to modify the properties of Nafion® containing fuel cells mainly focused on the modification of electrode structures to impart mixed electronic/protonic conductivities [7–9]. However, Gharibi et al. [8] investigated membrane electrode assemblies (MEA) containing a Nafion® and PANI composite membrane. The results indicated that the presence of PANI in Nafion® led to reduced polarization resistances. Nagarale and co-workers [10,11] studied the properties of sulfonated poly(ether ether ketone)/PANI composite membranes and found that methanol permeabilities were significantly lower than that of Nafion® 117 PEM. Tan and Bélanger [12] used a chemical polymerization method for in situ modification of a Nafion® membrane and evaluated the resulting performances. They found that with the use of a high concentration of oxidant (e.g. 1 mol dm^{-3} (NH$_4$)$_2$S$_2$O$_8$), PANI was formed primarily at the surface of the Nafion® membrane and with a high proportion of oligomers. On the contrary, the PANI was located inside the ionic domains of Nafion when a lower concentration of oxidant was used (0.1 mol dm^{-3}), which blocked the pathways to ion transport and thus impeded the transport of the cations.

* Corresponding authors. Tel.: +86 20 84036736; fax: +86 20 84113369.
E-mail addresses: stsspk@mail.sysu.edu.cn (P.K. Shen), zdwei@cqu.edu.cn (Z. Wei).

2. Experimental

2.1. Membrane preparation

Nafion® 112 membrane was pretreated in a dilute solution of H_2O_2 (aq, 3 v/v%) and H_2SO_4 (aq, 0.5 mol dm^{-3}) at 80 °C for 1 h, respectively. The resulting decontaminated Nafion® membrane was then stored in HCl until required for use. On modification, the pretreated membrane was immersed in 20 ml of aniline (1 mol dm^{-3}) solution in HCl (aq, 1 mol dm^{-3}) for 2 h and then mixed with 20 ml of $(NH_4)_2S_2O_8$ (0.1 mol dm^{-3}) in HCl (aq, 1 mol dm^{-3}). The reaction was maintained at 5 °C for 1 h using an ice bath. Reaction times of 2 h, 3 h and 4 h were also used to compare the effect of this on the properties of the resulting composite membranes (denoted Nafion®/PANI-1, Nafion®/PANI-2, Nafion®/PANI-3 and Nafion®/PANI-4, respectively). Green PANI powder was also produced during the reactions. These were recovered using filtration, washed thoroughly with aqueous solutions of hydrochloric acid, acetone and deionized water, and dried at 60 °C for 8 h in vacuum oven to enable IR analysis.

2.2. Characterization of the membranes

FT-IR spectra were recorded on a Nicolet 5700 spectrometer with a DTGS detector (Thermo Electron Corporation, USA). The spectra were collected as the average of 32 scans with a resolution of 4 cm^{-1}. Thermogravimetric analysis was carried out to detect the temperature-programmed decomposition (short-term) characteristics of the membrane using a TG 209 (NETZSCH Corporation, Germany) at a rate of 10 °C min^{-1} under N_2 atmosphere. The membrane samples were in the dry state before measurement.

The proton conductivity of the membrane was determined using a standard two probe AC impedance method on an IM6e electrochemical station (Zahner-Electrik, Germany) with a frequency range from 1 Hz to 1 MHz. The AC perturbation signal was 10 mV rms. Membrane samples were cut into strips of dimensions 1 cm wide and 4 cm long. The conductivity cell was placed in a stainless steel chamber where the temperature and humidity of the atmosphere was controlled. For accurate measurements, the samples were equilibrated in the chamber for at least 12 h before the impedance spectra were recorded [13–16]. The water contents of the membranes were measured in parallel under the same environmental conditions; these membrane samples (5 cm × 5 cm) were dried under vacuum at 80 °C for 12 h and weighted prior to testing. The gravimetric water uptakes were calculated using the following equation:

$$W\% = \frac{(W_1 - W_0)}{W_0} \times 100$$

where W_0 and W_1 are the mass of the membrane before and after water absorption.

2.3. Single PEM fuel cell test

2.3.1. Preparation of membrane electrode assembly (MEA)

The membrane electrode assembly was prepared by hot pressing the anode and cathode to the membrane at 10 MPa pressure and 135 °C for 3 min. Carbon paper (180 μm, Toray Industries Inc., Japan) were used as the electrode backing layers. An intermediate gas diffusion layer, located on one side of the carbon paper, was composed of 20 mass% PTFE and geometric loadings of 1.0 mg cm^{-2} carbon powder (Vulcan XC-72R, Cabot Corp., USA). The active surface area of the MEA was 1.5 cm × 1.5 cm and was composed of catalyst layers of geometric loadings of 0.5 mg$_{Pt}$ cm^{-2} (50 mass% Pt/C, Johnson Matthey) in both the anode and cathode.

2.3.2. Single fuel cell performance

The single fuel cells were evaluated by recording the current density vs. cell voltage curves using an Arbin fuel cell test system (Arbin instrument, USA). Dry air and hydrogen, at atmospheric pressure, were supplied to the cathode and anode, respectively with cell temperatures ranging from 45 °C to 65 °C. The flow rate of air was 800 cm^3 min^{-1} and H_2 was operated at a stoichiometry, λ_{H_2}, of 1.5. Polarization curves were recorded after the single fuel cell was activated at 500 mA cm^{-2} for 3 h.

3. Results and discussion

The as-prepared Nafion®/PANI-1 and Nafion®/PANI-2 composite membranes compared show uniform green in color. Fig. 1 shows the FT-IR absorbance spectra of PANI and Nafion®/PANI-2 composite membranes. Characteristic bands at 1559 cm^{-1} and 1483 cm^{-1} are attributed to the quinoid and benzenoid stretching modes of the pure polyaniline sample [12,17,18]. Other characteristic bands at 1294 cm^{-1}, 1243 cm^{-1} and 1113 cm^{-1} are assigned to the C–N stretching, C–N$^{\bullet+}$ stretching and –NH$^+$=-stretching vibrations, respectively, of PANI in the emeraldine form (protonated by HCl). The band at 797 cm^{-1} is assigned to the C–H bending vibration of the benzene. Fig. 1b shows the FT-IR absorbance spectra of Nafion® 112 and Nafion®/PANI-2. It is clear that the bands at 1585 cm^{-1} and 1491 cm^{-1}, 1302 cm^{-1}, and 805 cm^{-1} indicate the presence of PANI in the composite membrane.

The thermal properties of the Nafion®/PANI composite membranes were probed using TG-DTG measurements and compared with the Nafion® 112 membrane (Fig. 2). The sharp DTG peak at
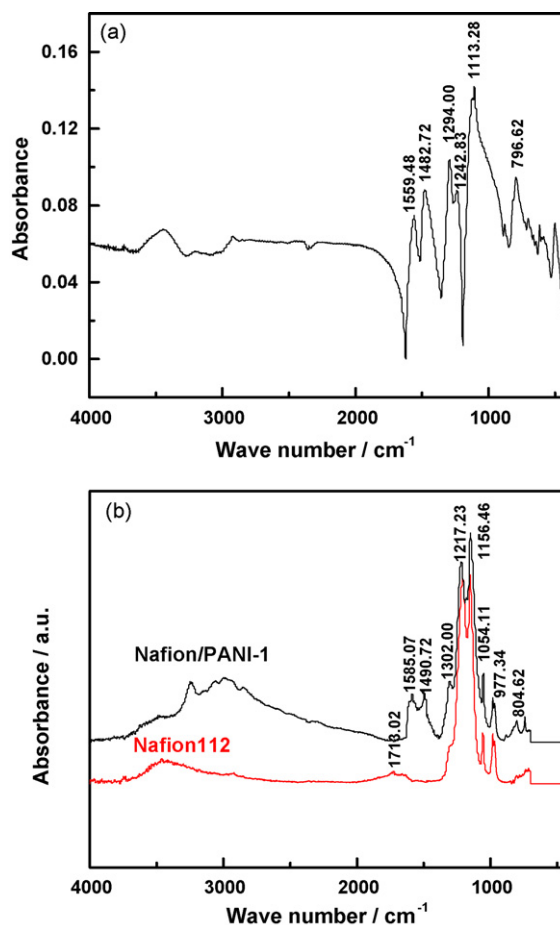

Fig. 1. FT-IR spectra of (a) PANI and (b) Nafion® 112 and Nafion®/PANI–2 composite membranes.
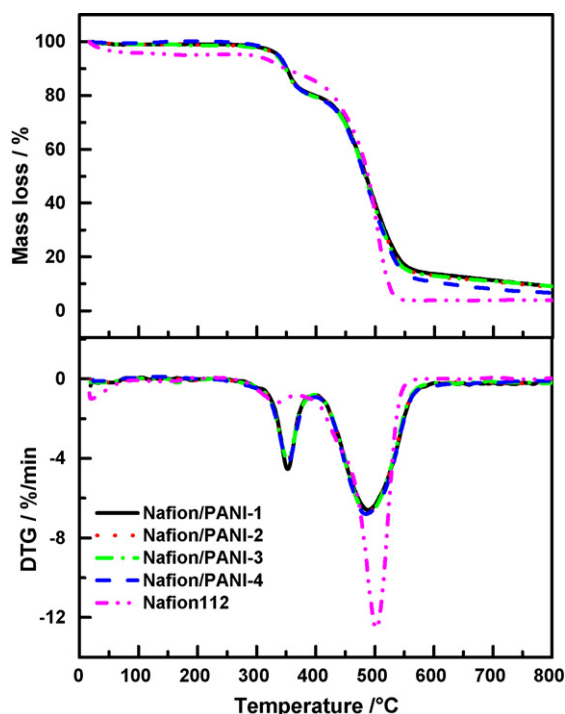
Fig. 2. Thermal gravimetric profiles of composite membranes and unmodified Nafion® 112.

Fig. 3. (a) Proton conductivity as a function of relative humidity at 30 °C and (b) plots of the normalized conductivity against RH = 100% for the different composite membranes and Nafion® 112 benchmark.

~350 °C is associated with the decomposition of the sulfonic acid groups ($-SO_3H$) in the Nafion® 112 [19]. The mass loss for the ether side chains and fluorocarbon polymer backbone are observed at temperatures above 400 °C. Larger sulfonic acid mass losses were observed for the Nafion®/PANI composite membranes. These data support the hypothesis that the aniline was primarily polymerized in the ionic cluster regions of Nafion® 112, which acts as a catalyst for enhanced removal of the sulfonate groups above 300 °C (only possible if there is a specific molecular contact between the sulfonate groups and the PANI surface). The DTG peaks at temperatures below 100 °C, which are associated with the endothermic removal of water from the membranes, are larger for Nafion® 112 membrane than for the composites. This means that the hydrophilicity of the composite membranes is decreased compared to pristine Nafion® 112.

The proton conductivity of the membranes was investigated at different humidities at 30 °C; the proton conductivities of the composite membranes are consistently higher than that of Nafion® 112 membrane (Fig. 3a). The conductivities of all membranes decrease with the decreasing in the humidity. However, the reduction in conductivity is smaller for the Nafion®/PANI membranes. The data was normalized based on the conductivities at RH = 100% (Fig. 3b); this clearly shows the enhancement in conductivities at the lower humidities. Nafion®/PANI-1 and Nafion®/PANI-2 show the best performances. The origin of the improvement at lower humidities with the polyaniline composites may be due to an improvement in the water retention. Water uptake experiments were then performed to provide evidence of this.

The results reveal that all the membranes show the same water uptake tendency at different humidities (Fig. 4). There is no evidence that the composite membranes exhibit improved water retention at lower humidity. A tentative alternative explanation is provided as follows. The ionic clusters in Nafion® have the largest diameters when the PEM is fully humidified and the channels between the clusters allow increased proton transfer. The physical hydrated connections between clusters are collapsed at lower humidities, resulting in a sharp reduction in the ionic con-
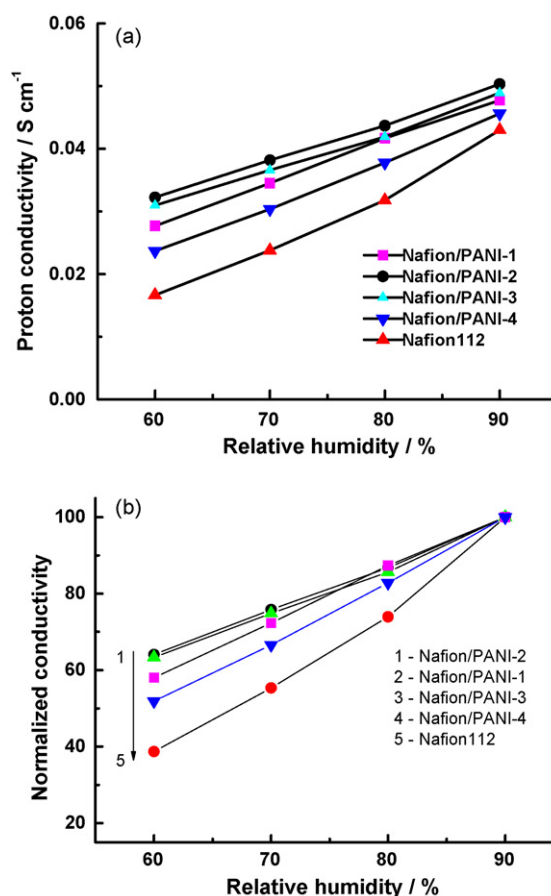
ductivity. As discussed above, there is thermogravimetric-derived evidence of strong interactions between polyaniline and sulfonic acid groups. The conjugated nature of the bonds in the polyaniline makes it highly conductive both electronically and ionically. The improved proton mobility is hypothesized to be due to improved proton transfer is association with the conjugated bonds at lower humidities. This has been evidenced by a recent report. Choi et al. reported the chemical *in situ* synthesis of Nafion/polyaniline composite membranes. They found that the improvement in the fuel cell
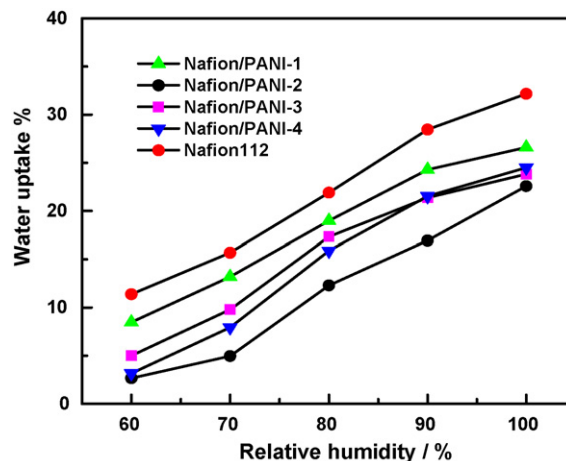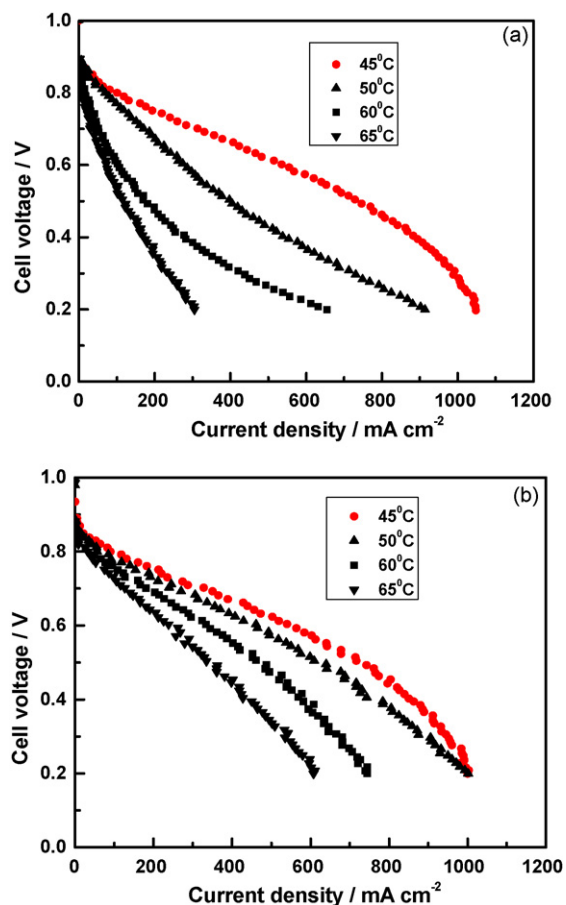

Fig. 4. Water uptake as a function of relative humidity for the different composite membranes and Nafion® 112 at 30 °C.

Fig. 5. Pseudo steady-state current–voltage curves for single cell fuel cells containing (a) Nafion®112 PEM and (b) Nafion®/PANI-2 composite PEM at increasing temperatures in dry H_2/air conditions. Scan rate = 10 mV s^{-1}.

performance by using Nafion/polyaniline composite membrane is due to the favorable interactions between ionic channels and PANIs [20].

The composite membranes were tested in single fuel cells using unhumidified gas supplies. The fuel cells with Nafion® 112 membrane and Nafion®/PANI-2 composite show high open circuit potentials of 0.91 V and 0.95 V, respectively (Fig. 5). The high open circuit potential with Nafion®/PANI-2 provides corroborative evidence of the absence of polyaniline-derived electronic short-circuits. The performance of the single fuel cell with Nafion® 112 membrane degrades rapidly with an increase in fuel cell temperature indicating the performance is seriously affected by water loss from the PEM. In the case of the single fuel cell with Nafion®/PANI-2, the reduction in the performance is observed to be slower. The results show that the Nafion®/PANI membranes appear promising for use in fuel cells operating at reduced humidities.

4. Conclusions

An in situ polymerization method was used to fabricate Nafion®/polyaniline composite membranes. The composite membrane is exclusively ionically conducting (no electronic short circuits due to PANI penetration through the membrane). The composite membranes were characterized by physical and electrochemical methods. The results showed that the proton conductivity of the composite membrane was superior to that of the Nafion® 112 membrane at low humidities. The superior conductivity of the Nafion®/PANI membrane at low humidities was hypothesized to be due to the existence of the conjugated bonds in the polyaniline that facilitated proton transfer and electronic conductivity at the PEM electrode interface, i.e. the proton transfer via the conjugated bonds at lower humidity retaining high conductivities. As expected from the above, the performance of the single fuel cell with a select Nafion®/PANI composite membrane was superior to that of Nafion® 112 membrane when operated with unpressurized dry gas feeds. This is important for portable fuel cells operating without external humidification and/or at low humidity conditions.

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