

Sulphonated Poly Ether Ether Ketone/Amino-diphenylsilandiol Composite Electrolyte for PEM Fuel Cells

Z. Ahmed,^{1,2} S. Belitto,³ M. L. Di Vona,³ M. Trombetta,⁴ E. Traversa,⁵ S. Licoccia³

¹National center for research and materials sciences, Cedria Science and Technology Park, Route Touristique Borj Cédria, B.P 174, 1164 Hammam-Chatt, Tunisia

²High School of Sciences and Technologies of Hammam Sousse, Rue Lamine Abassi 4011 H. Sousse, Tunisia

³Dipartimento di Scienze e Tecnologie Chimiche & NAST Centre for Nanoscience & Nanotechnology & Innovative Instrumentation, Università di Roma "Tor Vergata," Via della Ricerca Scientifica 1, 00133 Roma, Italy

⁴Università "Campus Bio-Medico di Roma," CIR-Chemistry and Biomaterials Laboratory, Via Alvaro del Portillo 21, 00128 Roma; Italy

⁵International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Received 26 August 2010; accepted 16 May 2011

DOI 10.1002/app.34906

Published online 2 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A composite polymeric membrane to be used as electrolyte in polymer electrolyte membrane fuel cells has been prepared and characterized. The membrane is composed of an acidic polymer, sulfonated polyetheretherketone, and of basic filler, amino-diphenylsilandiol, a functionalized organically modified silane. Attenuated total reflectance (ATR)/fourier transform infrared spectroscopy (FTIR) demonstrated the occurrence of a specific interaction of the polymer $-\text{SO}_3\text{H}$ groups with the basic

function of the filler. Such interaction reflected in reduced swelling, enhanced thermal stability, and good proton conductivity values at intermediate temperatures ($\sigma \approx 10^{-2} \text{ S cm}^{-1}$ at 100°C). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2610–2614, 2012

Key words: acid–base polymer blends; proton conductivity; FTIR; thermal stability

INTRODUCTION

Polymeric electrolyte membranes (PEM) are a critical component both in hydrogen fuelled and direct methanol fuel cells. The PEM serves both as the electrolyte for proton transport from the anode to the cathode and as a separator preventing mixing of the fuel and oxygen from the cathode side of the cell. The most common commercial PEM material is Nafion®, a perfluorosulfonic acid ionomer. Although Nafion® has been used in fuel cells for some 30 years, it has several deficiencies, namely an upper use temperature of about 80°C , poor conductivity at low relative humidity (RH), and poor resistance to fuel transport, that limit its use for the next generation of fuel cells.¹

The research directed to the development of PEM materials alternative to Nafion is very active and,

although it is known that many polymeric materials can be used for proton conductivity applications,² it is widely recognized that a single material does not possess all the requirements needed for applications in FCs. Among the numerous strategies that can be followed to improve the performance of polymeric membranes, a versatile method is the combination of different materials into a composite, thus modulating the morphological and electrical properties of the two components.^{3,4}

Several nonfluorinated polymers have been studied as possible alternatives to Nafion.⁵ We focused our attention on polyetheretherketone (PEEK), which possesses good thermal stability, appropriate mechanical properties,⁶ and interesting conductivity when sulfonated polyetheretherketone (SPEEK).^{7–12} Unfortunately, at high values of the sulfonation degree ($\text{DS} > 0.8$), corresponding to high conductivity, the mechanical properties of SPEEK severely deteriorate.^{4,5,12}

We have previously reported on the use of a sulfonated ormosil (sulfonated diphenylsilandiol, SDPSD) as a filler for both SPEEK and Nafion matrices.^{13,14} The interaction and structural affinities between polymer and filler led to composite membranes showing improved performance in terms of solvent permeability, thermal stability, and proton

Correspondence to: Z. Ahmed (zakarya.ahmed@ufabc.edu.br).

Contract grant sponsor: MiUR: the Italian Ministry of University and Research (FISR 2001 NUME Project Development of composite protonic membranes and innovative electrode configurations for Polymer Electrolyte Fuel Cells).

conductivity. The choice of the filler was based on its structural similarity with arylene main chain polymers such as PEEK, and because of the ease of functionalization of the phenyl rings: the introduction of sulfonic groups was in fact expected to add an extra contribution to conductivity.

In this work, we chose to modify the ormosil introducing a basic function to allow the formation of hydrogen bridges between the acidic and the basic entities,^{15–17} with the aim of producing a thermally and chemically stable composite material with reduced water adsorption characteristics with respect to pure SPEEK membranes.

EXPERIMENTAL

Materials

Diphenylsilandiol (DPSD; Aldrich, Germany) was obtained in the form of powder (95%), sulfuric acid (95–98 wt %), dichloromethane, trifluoroacetic anhydride (TFAA), ammonium nitrate, dimethylacetamide (DMAc), and 2,4-pentanedione (acac) were obtained from Aldrich Chemical Corporation Polyetheretherketone (Victrex, PEEK, 450 P, MW = 38,300), was sulfonated in concentrated sulfuric acid, obtaining a polymer with DS = 1, as confirmed by ¹H-NMR and by titration, according to published procedures.⁹

Amino-diphenylsilanediol (NDPSD) was prepared according to the procedure reported in the literature for aromatic substrates.^{18,19}

Membrane preparation

Composite membranes made of SPEEK/NDPSD 90/10 wt/wt (referred as S10) were prepared by solution casting. In a typical procedure, SPEEK (340 mg) was dissolved in DMAc (30 mL) at 60°C. A solution of NDPSD (60 mg) dissolved in the minimum amount of acac was then added to the polymer solution. The resulting mixture was stirred for 4 h, evaporated to 5 mL at 70°C, then casted onto a glass plate. The samples were dried at 70°C for 4 h and then heated to 100°C under vacuum for 12 h to remove the residual casting solvent. Membranes made of pure SPEEK (S0) and SPEEK/NDPSD 97/3 wt/wt (S3) were also prepared by the same procedure. The membranes thickness was in the range of 150–200 μm.

Characterization

To measure the water uptake, disks with a diameter of 6 mm were cut from the dried membranes and weighted. The films were then soaked in water at room temperature and then weighted after blotting with absorbent paper. Wet weight data were collected

every 10 min in the first hour, then every hour for the following 24 h. The weight gain of absorbed water was calculated referring to the weight of the dry sample: $(W_{\text{wet}}/W_{\text{dry}} - 1) \times 100$.

Thermogravimetric (TG) analysis was carried out using a thermobalance (STA 409, Netzsch, Germany) in air flow with a heating rate of 10°C/min in the range 25–800°C.

The ATR/FTIR spectra were collected in the range 1300–550 cm⁻¹, on a Nicolet (Fitchburg) 870 E.S.P. with a Golden Gate MK2 Diamond Specac cell. Spectra were recorded positioning the samples on a cell platform operating at room temperature (32 scans, 2 cm⁻¹ resolution).

Surface morphology of the polymer membrane was observed using a scanning electron microscope (SEM, Carl Zeiss, Germany; FE-SEM, LEO mod. Supra 35), the electron beam energy being 17 keV. SEM observations were carried out after gold sputtering the samples.

The proton conductivity of the samples was determined as a function of temperature (from 60 to 100°C) and RH (from 35 to 100%) using electrochemical impedance spectroscopy measurements over a frequency range of 1 MHz to 10 Hz at a signal amplitude ≤100 mV with a Solartron (ametek, Hampshire, UK) SI 1260 Impedance/Gain Phase Analyzer. Conductivity measurements were carried out on membranes, sandwiched between gas diffusion layer which were pressed on the membrane faces by means of porous stainless steel discs (two-point probe method). RH was controlled by using a stainless steel cell consisting of two cylindrical compartments connected by a tube and held at different temperatures. One compartment contained water (C₁), while the other compartment housed the membrane under test (C₂). The RH was usually calculated from the ratio between the pressures of saturated water vapor (*p*) at the temperatures of C₁ (T_c) and C₂ (T_h). $RH = p(T_c)/p(T_h) \times 100$. The resistance of the membranes, hence their conductivity, was calculated by a linear fit of the impedance spectra in their linear portion. *R* was obtained from the intersection of the linear fit with the Re(*Z'*) axis of the complex impedance plane. The impedance data were corrected for the contribution of the empty and short-circuited cell. A typical Nyquist plot of the composite is presented in Figure 1.

From the resistance values, we obtained the conductivity (σ) value using the following equation:

$\sigma = d/(R \times A)$, where *R* is the resistance, *d* is the distance between electrodes, and *a* is the electrode area.

RESULTS AND DISCUSSION

Figure 2 shows the ATR/FTIR spectrum of the composite S10 (Trace b) compared with that of a

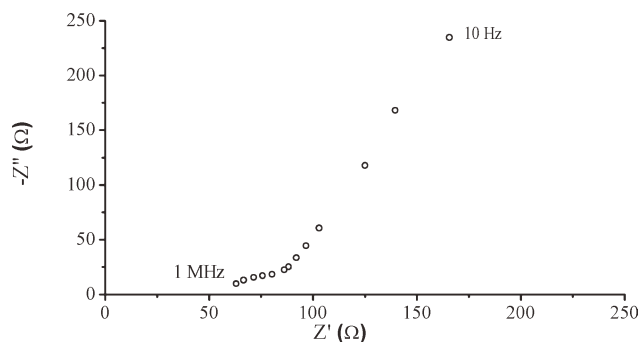


Figure 1 Typical Nyquist impedance diagram for the composite S10 at 80°C and 55% RH.

reference S0 membrane (Trace a). Both spectra are dominated by SPEEK absorptions.^{12,20} To emphasize the difference between the two samples, significant regions of the difference spectrum obtained by subtracting the spectrum of SPEEK from that of SPEEK/NDPSD are shown in the inset (c). The presence of NDPSD is confirmed by the bands at 1605, 1650, and 1775 cm^{-1} that are due to δ N—H of the amino group, and at 1300, 1275 cm^{-1} characteristic of ν C—N of primary aryl amines. Moreover, components at 1240 and 1175 cm^{-1} indicate the presence of 1 : 2-, 1 : 4-substituted phenyl rings characteristic of *ortho*- and *meta*-substituted NDPSD. In the latter signal, there is also a contribution due to ν_s (SO_3^-) that, together with the band at 1195 cm^{-1} typical of ν_{as} (SO_3^-), evidenced SPEEK perturbation due to SPEEK–NDPSD interaction. The absorptions at 1028 cm^{-1} assigned to the sulfonic acid group in SPEEK.²¹ The intensities of this absorption bands decrease and shifted at higher value for S10 sample.

Figure 3 shows the influence of the filler on value of λ , $\lambda = N_{\text{H}_2\text{O}}/N_{[\text{bond}]\text{SO}_3\text{H}'}$ at room temperature of SPEEK-based membranes. Here λ is the molar number of water taken up by each mole of sulfonic acid group. The polymer/filler interaction affects the water uptake behavior of the composites: while the pure S0 membrane dissolves in water after about 2 h, the water uptake of the composite at low NDPSD content (3 wt %) is still quite elevated but reaches an apparent equilibrium after about 2 h at $\lambda = 400$. At higher NDPSD content (10 wt %) the equilibrium is reached almost instantaneously at a $\lambda = 8$. The very low λ value can be correlated with the existence of an acid/base interaction between the polymer and filler.

The reduced swelling observed for the membrane S10 led us to select this sample for further characterization. The thermal stability of the composite membrane was investigated by TG analysis. Figure 4 shows the TG and differential TG (DTG) curves of the composite S10 and of a reference SPEEK membrane. The curves can be divided in regions corresponding to different weight loss ranges. A slight mass loss ($\sim 5\%$) due to desorption of water and residual casting solvent can be observed up to 150°C. The thermal decomposition of SPEEK has been studied by several authors^{9,22,23} and it is known to occur in two steps, the first step associated with splitting off of the sulfonic groups with formation of SO_2 and aromatic products ($144^\circ\text{C} < T < 284^\circ\text{C}$) and the second step associated with decomposition of the main chain groups ($338^\circ\text{C} < T < 391^\circ\text{C}$). The addition of NDPSD to the SPEEK matrix shifts all these processes at higher temperatures indicating an increased thermal stability for the composite.

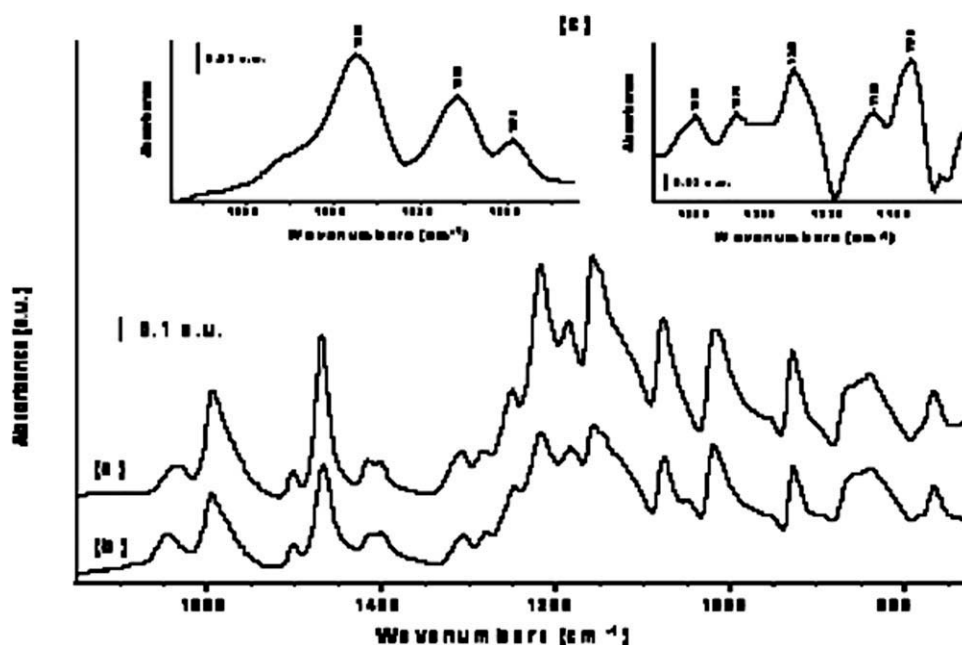


Figure 2 ATR/FTIR spectra of (a) S0, (b) S10, and (c) subtraction spectra [(c,d) = (b) - 1(a)].

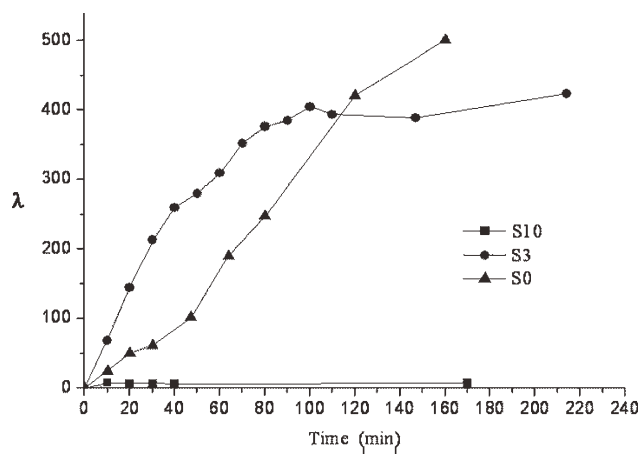


Figure 3 Water uptake ($\lambda = N_{\text{H}_2\text{O}}/N_{[\text{Sbond}]\text{SO}_3\text{H}}$) as a function of time for S3 and S10 and reference SPEEK membranes.

The morphology of the membranes was examined by scanning electron microscopy to examine the influence of the filler in the polymer morphology. Figure 5 shows the SEM micrograph of the S10 composite (a) and S0 membrane (b) for comparison. The presence of NDPSD can be clearly observed in the composite membrane. Although some aggregates are present, the formation of the composite did not introduce in the membrane any porosity in this scale that could negatively influence performance.^{10,13}

The electrochemical performance of the composite membrane was studied by electrochemical impedance spectroscopy (EIS). Figure 6 shows the Arrhenius plot for the S10 membrane. A linear Arrhenius behavior was observed between 25°C and 110°C, and the calculated value of the activation energy for the proton transfer process resulted to be 0.41 eV, in agreement with a proton hopping mechanism.^{24–28}

To verify the membrane stability under controlled humidified condition, the membrane proton conduc-

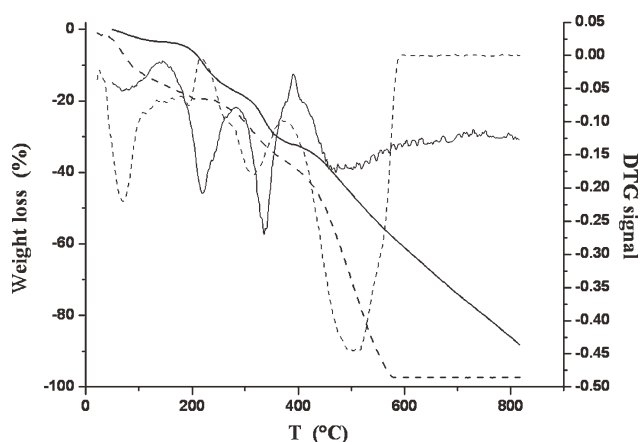


Figure 4 TG/DTG of S10 membrane (solid line) and reference S0 membrane (dotted line).

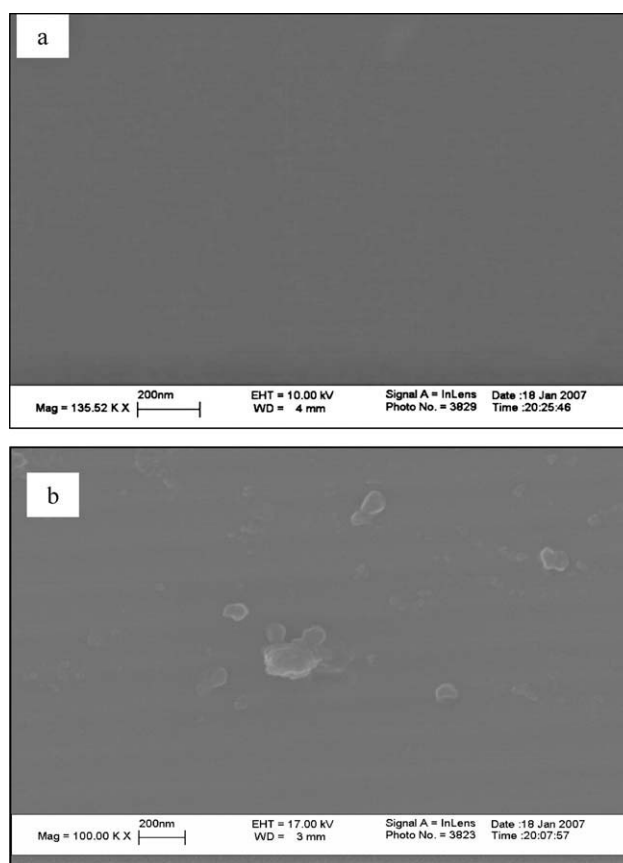


Figure 5 SEM micrograph of S0 (a) and S10 (b) membranes.

tivity was measured as a function of RH. Figure 7 show the data recorded at 60°C, 80°C, and 100°C at different RH. In the whole range of temperature investigated, σ increased with increasing RH, from 10^{-4} to 10^{-2} S cm^{-1} . Figure 7 indicates that the SPEEK-NDPSD membrane have similar proton conductivity value to Nafion (0.02 S cm^{-1} at 80°C and 80% RH).²⁹

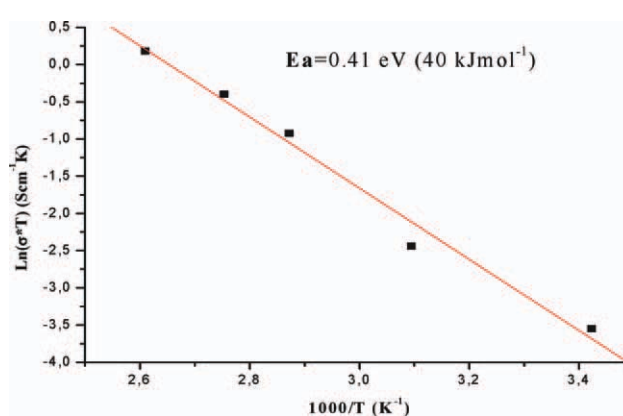


Figure 6 Arrhenius plot for S10 membrane. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

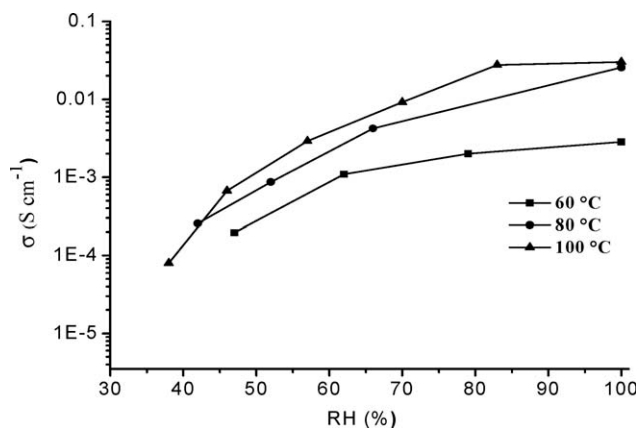


Figure 7 Conductivity as a function of RH determined at different temperatures for the composite S10.

It has to be emphasized that the composite membrane showed a high conductivity at 100°C, especially for large RH values, while the pure SPEEK membrane was not stable at such a temperature. This behavior can be attributed to the increase in membrane water retention at high temperatures (above 100°C) in the presence of the filler (NDPSD). The loss of water observed at elevated temperatures may be caused by a change in polymer structure and not by direct evaporation of water from the electrolyte,³⁰ so in this case the acid–base interaction between filler and SPEEK allows to maintain the SPEEK self-assembled structure through the high values of the operating temperatures studied here (100°C).

CONCLUSIONS

To reduce the water uptake and to increase thermal stability of highly sulfonated PEEK membranes, SPEEK/base polymer, to be used as electrolytes in polymeric fuel cells, have been synthesized and characterized. The introduction of a modified ormosil (NDPSD) in high DS SPEEK-based membranes decreased the water uptake of the polymer. The composite membrane shows better thermal stability than the pure SPEEK and good proton conductivity.

The authors thank Ms. C. D'Ottavi for her valuable technical assistance.

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