



Electric response and conductivity mechanism reciprocity in H_3PO_4 -doped Polybenzimidazole-4N-ZrO₂ nanocomposite membranes

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ABSTRACT

The electrical response of zirconia composite polybenzimidazole membranes $[\text{PBI4N}(\text{ZrO}_2)_x](\text{H}_3\text{PO}_4)_y$ is studied by Broadband Electrical Spectroscopy (BES), and correlated with our previous Dynamic Mechanical Analysis (DMA) and Modulated Differential Scanning Calorimetry (MDSC) measurements. The presence of nanofiller in the PBI4N polymer matrix is shown to plasticize the membrane, with a maximum effect observed at a nanofiller loading level of $x \approx 0.13$. The disrupting effect of the nanofiller on the interchain dipole interactions modulates the overall electrical response of the materials. Following acid doping, a marked increase in conductivity is observed as new chemistry is installed at the interfaces between polymer and nanofiller that facilitates dipolar fluctuations and segmental motions of the polymer chains. In these composite membranes, two mechanisms of conductivity are postulated based on BES analysis; i) proton hopping between binding sites, and ii) proton hopping at the interfaces between $\text{H}_n\text{PBI4N}^{n+}/\text{H}_n\text{PBI4N}^{n+}$ and $\text{H}_n\text{PBI4N}^{n+}/\text{H}_m\text{ZrO}_2^{m+}$. The results here presented demonstrate the effect of zirconia nanofiller and subsequent acid doping on the conductivity properties of composite PBI4N membranes. Of note, at 100 °C for $[\text{PBI4N}(\text{ZrO}_2)_{0.132}](\text{H}_3\text{PO}_4)_{11}$, conductivity as high as 0.035 S/cm is achieved.

1. Introduction

The use of inorganic-organic composite membranes consisting of polymers modified with inorganic additives such as SiO₂, TiO₂, ZrO₂, Zeolites and Zirconium phosphate, are promising electrolytes for application in high temperature proton exchange membrane fuel cells (HT-PEMFCs) [1]. Composite membranes of this nature have significant advantages over “traditional” membranes, such as reduced reagent crossover and improved water retention at temperatures above 100 °C [2,3]. Over the last decade, new classes of proton-conducting membranes have been proposed to overcome the drawbacks of using perfluorinated polymer electrolytes. Acid doped polybenzimidazole (PBI) membranes have become common place in HT-PMFCs and the doping of them with inorganic additives is one strategic way to increase overall performance [4].

Elucidating the conductivity mechanisms within polymer electrolytes is fundamental in order to fully understand performance. The electrical response of a material is accurately obtained using Broadband Electric Spectroscopy (BES) as a function of temperature and frequency. When an external electric field is applied, the consequent interaction with the electric dipole moments of the sample can be studied in terms of permittivity and conductivity parameters [5,6]. Parallel to the electrical properties, the mechanical and thermal response of a material provides further crucial information. Dynamic Mechanical Analysis (DMA) and Modulated Differential Scanning Calorimetry (MDSC) are the leading techniques for this purpose, allowing for the identification of numerous temperature dependent transitions, e.g. glass transition (T_g). In this paper BES measurements are linked with previous DMA and MDSC results for a series of anhydrous polybenzimidazole membranes that are prepared with different amounts of ZrO₂ nanofiller [PBI4N

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(ZrO₂)_x], and subsequently doped with phosphoric acid [PBI4N(ZrO₂)_x](H₃PO₄)_y [7–9]. The removal of water from the membranes is vital in order to study the effect of phosphoric acid on the electrical response of the membranes in anhydrous conditions, mimicking the conditions of HT-PEMFCs where the presence of water will be negligible.

2. Experimental section

2.1. Materials and sample preparation

The zirconia nanofiller, the undoped PBI4N membrane, the composite [PBI4N(ZrO₂)_x] membranes, and the phosphoric acid doped derivatives [PBI4N(ZrO₂)_x](H₃PO₄)_y are all prepared in an analogous manner to that which we have reported previously [7–11]. All the membranes were dried under vacuum at 120 °C for 12 h and stored under an argon atmosphere (dry box) in order to remove all traces of water (gauged by HR-TGA and ATR-FTIR analysis). In the formula [PBI4N(ZrO₂)_x](H₃PO₄)_y, *x* is defined as the number of moles of zirconia per PBI4N repeat unit ($0 \leq x \leq 0.770$ for undoped membranes and $0 \leq x \leq 0.549$ for phosphoric acid doped membranes), *y* denotes the number of moles of H₃PO₄ per PBI4N repeat unit ($9 \leq y \leq 13$).

2.2. Instrumentation

The electrical response of the membranes is measured by Broadband Electrical Spectroscopy (BES) in the 0.1 Hz ÷ 1 MHz frequency range, using a Novocontrol Alpha-A Analyzer. The BES spectra are recorded from –105 to 195 °C for the undoped membranes, and from –105 to 225 °C for the acid-doped membranes, an interval of 10 °C is used for all trials. The temperature is controlled using a homemade cryostat operating with a N₂ gas jet heating and control system with an accuracy of ± 0.1 °C. Circular samples of a diameter of 13 mm are sandwiched between two cylindrical platinum electrodes that are kept apart by an optical fiber separator of thickness equal to 0.126 mm. The sample and electrodes are sealed inside a cylindrical Teflon cell which is prepared in an argon filled glove-box (MBraun). The geometrical cell constant is determined from the electrode-electrolyte contact surface; the distance between electrodes is the thickness of the optical fiber separator. Corrections for thermal expansion of the cell are not adopted. Descriptions of other instrumentation (DMA, MDSC, WAXS, ATR-FTIR, HR-TGA) can be found in our previously published works on these materials [7–9].

3. Results and discussion

The mechanical and thermal proprieties of the composite membranes have previously been investigated by DMA and MDSC, and so for in-depth analyses we refer to our previous publications [7,8], with discussion relevant to the focus of this manuscript included below. At a constant temperature, the storage modulus (*E'*) of undoped [PBI4N(ZrO₂)_x] membranes is significantly affected by *x* (Fig. S1). An initial decrease in *E'* is observed that reaches a minima at approximately $0.1 < x < 0.2$. At this nanofiller level the defects created by the zirconia that disrupt the interchain dipole interaction are at a maximum, and this renders the polymer matrix more flexible in nature. As the nanofiller content increases, the material becomes stiffer, with *E'* reaching a maximum at ca. $0.2 \leq x < 0.3$. At this point the formation of zirconia crosslinks restrict the mobility of polymer chains. Indeed we have observed these same effects in PBI4N composite membranes of hafnia at similar loading levels [8]. At higher nanofiller loading levels ($x \geq 0.3$) the abundance of nanofiller is too high for efficient interaction with the polymer matrix, and the density of PBI4N-ZrO₂-PBI4N crosslinks is reduced. Nanofiller–nanofiller interactions evolve and form zirconia “cluster bridges” between polymer chains PBI4N–(ZrO₂)_n–PBI4N that decrease the cohesiveness of the membranes. From the tan δ (equal to ϵ''/ϵ') profiles of the composite materials (Fig. 1) four

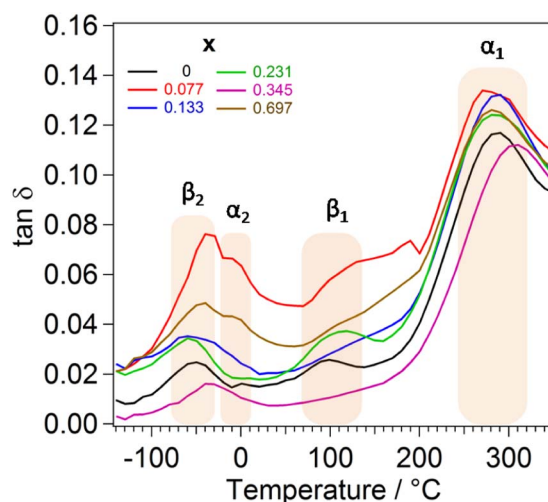


Fig. 1. DMA temperature spectra of [PBI4N(ZrO₂)_x] composite membranes ($0 \leq x \leq 0.549$) in terms of tan δ, showing the four mechanical transitions (α₁, α₂, β₁, β₂).

maxima can be observed which, on the basis of HR-TGA and MDSC analyses [7], are assigned as the α₁, α₂, β₁ and β₂ mechanical relaxation processes [7–9].

The alpha-mode relaxations occur owing to the long-range (α₁) and the short-range (α₂) segmental motions of the PBI4N chains. Whereas the beta relaxations arise from the interchain interactions involving the dipole moments associated with the phenyl benzimidazole units (β₁) and the bibenzimidazole units (β₂) of PBI4N (Fig. S2) [6,7]. The fact that these relaxation phenomena are affected by nanofiller loading level highlights how the nanofiller modulates the dynamics of the composite membranes. Indeed our previous in-depth WAXS and ATR-FTIR measurements demonstrated how the nanofiller loading level modulates the chain freedom in the polymer matrix, and facilitates the conformational reorganization of the aromatic units and resulting interchain distances [7,8].

Unfortunately, following the acid doping of the composite membranes, the surfaces of the membranes are rendered too slick for DMA. Therefore in order to understand the effects of acid doping on the thermal properties of [PBI4N(ZrO₂)_x](H₃PO₄)_y membranes we turned to MDSC [7]. We have previously demonstrated how in the undoped material the zirconia nanofiller acts to plasticize the membranes by reducing the density and strength of PBI4N-PBI4N interchain interactions, resulting in a decrease in crystallinity of nano- and micro-domains, in good agreement with the DMA, WAXS and ATR-FTIR experiments [7]. The presence of the phosphoric acid doping has a much more notable effect on the membrane properties. A significant plasticizing effect on the membranes is demonstrated by a strong glass transition (*T_g*) observed in the range of $-46 \div -56$ °C. The acid breaks the Zr–PBI4N interactions and protonates the Lewis basic nitrogen atoms of the aromatic ring systems. This gives rise to uniformly distributed PBI4NH⁺ chains and, in addition, facilitates the formation of a layer of zirconium dihydrogen phosphate on the surface of the zirconia nanoparticles leading to new interactions at the interface between nanofiller and polymer chains [7].

An extensive BES study of the electrical response of [PBI4N(ZrO₂)_x](H₃PO₄)_y membranes is carried out by analyzing the real and imaginary components of the complex conductivity ($\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega)$) and complex permittivity ($\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$) spectra as a function of frequency ($\omega = 2\pi f$), in terms of dielectric relaxation events and polarization phenomena [5,12–16]. The temperature spectra of tan δ(ω) (equal to $\epsilon''(\omega)/\epsilon'(\omega)$) for [PBI4N(ZrO₂)_x]/(H₃PO₄)_y, recorded at *f* = 1 Hz, 1 kHz and 10 kHz show four dielectric relaxations: α₁, α₂, β₁ and β₂ (Fig. S3). These correspond to the four mechanical events

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