

Thermal properties of Nafion–TiO₂ composite electrolytes for PEM fuel cell

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Abstract Thermal analysis has been used to evaluate the stability, glass transition, and water retention of Nafion based polymer–ceramic electrolytes. These electrolytes are envisioned as promising replacement of Nafion in fuel cells operating above 100 °C. The polymeric matrix prepared by casting exhibits lower crystallinity than the extruded Nafion, a feature that affects the water absorption properties. The addition of titania-based nanotubes and nanoparticles to the polymer has enhanced the water retention at high temperatures (~130 °C) and the glass transition temperature, respectively. Such results are important for the design of composite electrolytes for the operation of fuel cells at high temperatures.

Keywords Nafion · Composite · Polymer electrolyte fuel cell

Introduction

The development of proton exchange membrane fuel cell (PEMFC) is facing two crucial issues that inhibit its application as a renewable energy source [1]. The first one concerns the fuel cell operating parameters and the other

one to the fuel cell material components [2]. There is a great interest in the elevation of the PEMFC operating temperature from ~80 to ~130 °C [2]. Such an increase requires modification or substitution of PEMFC materials components to satisfy this new condition [1, 2]. As an electrochemical device, the PEMFC processes are thermally activated, i.e., the increase of the temperature enhances the fuel cell performance and efficiency. However, such a procedure is not straightforward; the increase of the operating temperature is followed by a dramatic loss of performance of the fuel cell. The main reason for such a decrease is the loss of water confined in the structure of the traditionally used polymeric electrolyte, Nafion [3]. To elevate the PEMFC temperature and consequently its performance, it is necessary to develop new materials that are capable of water retention at elevated temperature (~130 °C) [4]. This breakthrough could make PEMFC competitive as an environmentally friendly and efficient power source.

One of the most promising alternatives to such a challenge is the development of Nafion–ceramic composites [4]. High surface inorganic phases, such as titania and silica, have the capacity of water retention at elevated temperatures ($T \sim 130$ °C) [4, 5]. Several inorganic particles have been already used in the fabrication of composite membranes [4–6]. When these membranes are tested in PEMFC, the results have indicated that the surface specific area is an important property that contributes to a better performance of these electrolytes at elevated temperatures [5]. Furthermore, previous results showed that specific particle morphologies have better performance than the commonly used spherical ones [7]. Mesoporous titania and titanate nanotubes have been tested as a second phase in Nafion–ceramic composites and a significant enhancement of the PEMFC

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performance at elevated temperatures (~ 130 °C) has been observed [8, 9].

In the present study, thermal analysis has been used to investigate the main properties that are related to the better performance observed for Nafion–titania composite electrolytes in PEMFC operating at elevated temperatures.

Experimental

Two types of titania were used to fabricate Nafion-based composites: mesoporous titania (TMP) and the titanate nanotubes (TNT). Further details of the preparation of both the TMP and TNT are described elsewhere [9, 10]. A relevant feature of the inorganic phases is that TNT has larger surface specific area ($200\text{--}400\text{ m}^2\text{ g}^{-1}$) than TMP ($115\text{ m}^2\text{ g}^{-1}$).

Composite electrolytes were prepared by the casting method with the addition of titania concentrations: $x = 0, 2.5, 5.0,$ and $10\text{ mass}\%$, as described in [9]. Nafion 115 (DuPont) extruded membrane (Nextr) was used as a reference.

The fabricated membranes were treated in three different solutions: HNO_3 (7 mol L^{-1}), H_2O_2 ($3\text{ vol.}\%$) and H_2SO_4 (0.5 mol L^{-1}) at 80 °C for 1 h with intermediate washings with deionized water to assure the complete removal of organic solvent residues and to assure the protonic (H^+) form of the membrane.

The water uptake (ΔM) of cast membranes, defined as $\Delta M (\%) = (m_S - m_D)/m_D$, was evaluated by weighing both the dry membrane (m_D) after thermal treatment at 110 °C for 3 h and the water saturated membrane (m_S) after boiling in water for 1 h. The equivalent mass (EM) was determined by an exchange of protons with Na^+ ions in solution. The acidic membrane was placed to a NaCl solution (2 mol L^{-1}) and allowed to exchange for 30 min. Then, the sodium form membrane was titrated to the phenolphthalein end point with NaOH (0.025 mol L^{-1}) to determine the quantity of exchanged H^+ ions. The EM was calculated by using the dry mass of the membrane and the quantity of exchanged protons.

Thermogravimetric measurements (Setaram-LabSys) were carried out in the $25\text{--}150$ °C temperature range at a heating rate of 5 °C/min under nitrogen flow. This setting was used to measure the mass loss of water saturated samples. After cooling down to room temperature a second heating to evaluate the thermal stability of the composite membranes was performed at a rate of 10 °C/min in the $25\text{--}600$ °C temperature range under nitrogen flow. Differential Scanning Calorimetry (DSC) scans were performed by using a Metler/Toledo device in the temperature range of $50\text{--}300$ °C with 10 °C/min heating rate under nitrogen atmosphere.

Results and discussion

Figure 1 shows the TG curves of polymers and composites. It can be observed that both the extruded (Nextr) and cast Nafion (Ncast) have similar behaviors (Fig. 1a). The first mass loss onset is at $T \sim 310$ °C for Ncast and $T \sim 325$ °C for Nextr. Such an event is attributed to the degradation of sulfonic acid groups from the polymer side chains [6]. In the range of $T \sim 320\text{--}380$ °C the TG curve presents a shoulder, which precedes the largest mass loss in the $T \sim 400\text{--}500$ °C temperature range [6]. This latter event is assigned to the degradation of Nafion perfluoroether side chains concomitantly with the degradation of Teflon-like polymeric backbone.

Figure 1b presents the TG curves of Nafion-based composites with $10\text{ mass}\%$ of different titania particles (TMP and TNT). Composite samples displayed the same degradation processes as exhibited by the polymeric matrix. However, the mass loss assigned to sulfonic acid groups occurs at a lower temperature ($T \sim 280$ °C) for both TMP and TNT composites. The second degradation process of composite specimens started at the same temperature observed for the polymer. Furthermore, in the $T \sim 450\text{--}500$ °C temperature range an additional mass loss step was observed. Such a mass loss can be assigned to the degradation of Nafion polytetrafluoroethylene backbone; however, further investigations are required.

It is important to note that the degradation processes observed in Fig. 1b occurred at lower temperatures when compared to the ones of Fig. 1a. The decrease of the degradation temperature observed in the Nafion– TiO_2 composites has been associated with a catalytic effect of titania [6]. However, it is important to consider that the temperature in which the degradation processes occur is high enough to prevent any deterioration of the PEMFC performance operating at $T \sim 150$ °C. On the other hand, the glass transition temperature of Nafion is within this temperature range. This transition influences the properties of the polymer and must be considered for the development

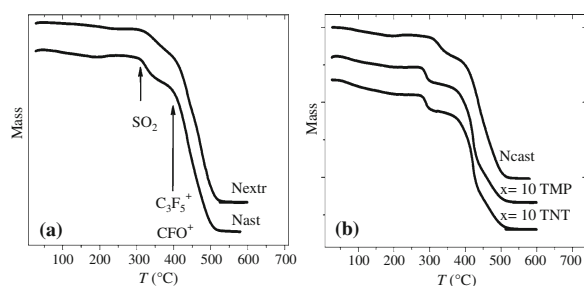


Fig. 1 TG curves of polymers (a) cast (Ncast) and extruded (Nextr); and (b) composite membranes with addition of $x = 10\text{ mass}\%$ of titania

of PEMFC components. Such a property can be analyzed by using differential scanning calorimetry (DSC).

Figures 2 and 3 display DSC scans for the polymer and composites, respectively. The DSC curves for Nafion (Fig. 2a) show two effects. The first one occurs at $T \sim 110$ °C and is attributed to the glass transition of the ionic clusters [11], and the second one is usually ascribed to the melting of Nafion crystallites occurring at $T \sim 210$ °C [12]. The two effects observed for Ncast polymer take place at slightly lower temperatures, compared to the extruded Nafion membrane. Such a characteristic can be associated with the polymer equivalent mass (EM). The calculated EM for Ncast is ~ 941 g mol⁻¹, a value lower than the one found for the Nextr ($\sim 1,070$ g mol⁻¹). A polymer with lower EM has a larger amount of perfluoroether side chains, which can hinder the packing of crystallizable chains segments. This effect can influence directly the water absorption capacity and must be further investigated.

Due to the overlapping of endothermic minima in the DSC curves it is difficult to estimate the degree of crystallinity of the samples. In order to qualitatively evaluate this property polymers were kept at ~ 300 °C for 5 min to promote the degradation of sulfonic acid groups, as inferred from the results shown in the Fig. 1. After the degradation of sulfonic acid groups the DSC scans do not exhibit

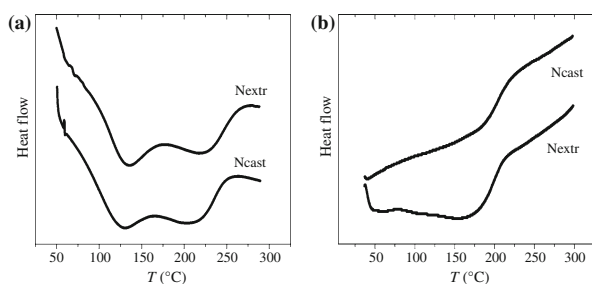


Fig. 2 DSC curves of cast and extruded Nafion

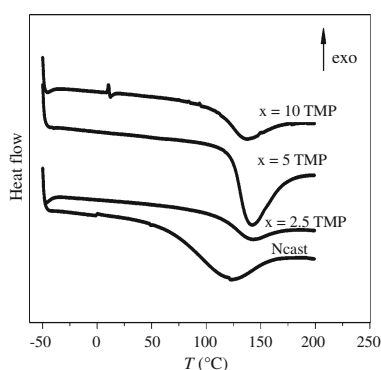


Fig. 3 DSC curves of Nafion-mesoporous titania composite as a function of particle concentration

the glass transition and only one minimum was measured, as displayed in Fig. 2b. It is clearly observed in Fig. 2b that the area of the DSC endothermic peak of the Nextr is larger than the one of Ncast. This result is in agreement with both the calculated EM and previous reports that have shown that the extrusion process provide a higher crystallinity due to the orientation of polymeric chains [13].

Figure 3 shows the DSC scans for the TMP composite with concentration of the inorganic phase in the $x = 2.5$ – 10 mass% range. The addition of the nanoparticles increased the glass transition temperature from $T_g \sim 120$ °C, for the cast Nafion to $T_g \sim 140$ °C for the composites. Such a result suggests that the addition of inorganic particles increases the composite thermal stability, which is an important property for the application in PEMFC operating at elevated temperatures.

The water uptake for the polymers (Ncast and Nextr) and for the TMP and TNT composites was measured as a function of particle concentration, as shown in Fig. 4. The water uptake for Ncast ($x = 0$ mass%) is $\Delta M = 42\%$, which is larger than the one for Nextr ($\Delta M = 34\%$). Such a difference is associated with the crystallinity of the membranes. The water absorption capacity of Nafion is a balance between the hydration of the sulfonic acid groups and the elastic energy imposed by the polymer chains against expansion [14]. A higher degree of crystallinity confers a higher resistance to the expansion of the membrane, limiting the water absorption by the polymer.

Composite samples with the addition of TMP exhibit a slight decrease of water absorption with increasing titania concentration. On the other hand, titania nanotube (TNT) composites show a marked increase in water absorption with increasing particle addition. These results suggest that the surface properties of the inorganic particles, such as the specific surface area, have a strong influence on the properties of the composite electrolytes.

Figure 5 displays the mass loss of water-saturated Nafion membranes (a) and Nafion-based composites (b) measured by TG experiments. The observed water loss is

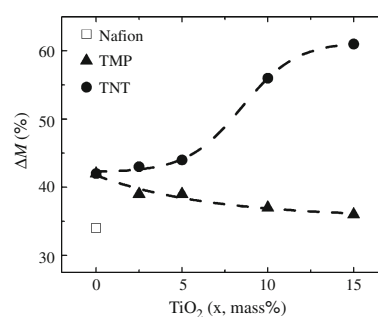


Fig. 4 Water uptake dependence on the titania concentration measured by gravimetry

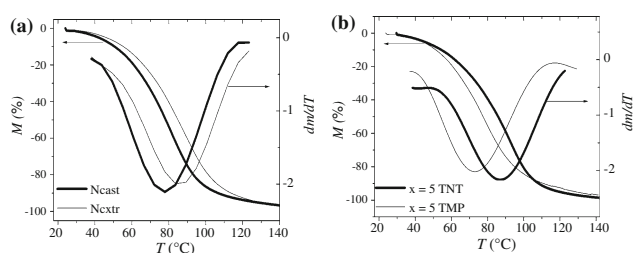


Fig. 5 Water loss of (a) extruded and cast Nafion; and (b) composites with $x = 5.0$ mass% of titania concentration

attributed to the weakly bond water absorbed by the membrane. The DTG curves exhibit a minimum that indicates the temperature of maximum water loss rate. For the Nextr, such a minimum occurs at ~ 90 °C (Fig. 5a), which is ~ 10 °C higher than the one for the Ncast (~ 80 °C). Even though Ncast has higher water absorption than Nextr, the incorporated water is more volatile and evaporates at lower temperatures. The TG curves for the TNT and TMP composites with $x = 5$ mass% are shown in Fig. 5b. It can be noticed that composites with the addition of the inorganic particles TNT show an increased water retention capacity than the TMP ones at the same concentration.

Conclusions

Thermal analyses data of Nafion–titania composite electrolytes were found to be in good agreement with the observed enhancement of the performance of PEM fuel cells at high temperature. In addition to the different properties of cast and extruded Nafion membranes, DSC and TG results of Nafion–titania composites revealed important features concerning the addition of the inorganic phase on the thermal properties of the electrolytes. The particle shape and surface properties of the inorganic phase were found to result in higher glass transition temperatures and higher water retention, which are important characteristics for enhanced performance of the electrolyte at ~ 130 °C. The observed features showed that thermal analyses are a helpful tool to investigate relevant properties of electrolytes aiming at the operation of polymeric fuel cells at high temperature.

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