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Post-irradiation time effects on the graft of poly(ethylene-alt-tetrafluoroethylene) (ETFE) films for ion exchange membrane application

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ABSTRACT

Grafting of styrene followed by sulfonation onto poly(ethylene-alt-tetrafluoroethylene) (ETFE) was studied for synthesis of ion exchange membranes. Radiation-induced grafting of styrene onto ETFE films was investigated after simultaneous irradiation (in post-irradiation condition) using a ^{60}Co source. The ETFE films were irradiated at 20 kGy dose at room temperature and chemical changes were monitored after contact with styrene for grafting. The post-irradiation time was established at 14 days when the films were remained in styrene/toluene 1:1 v/v. After this period the grafting degree was evaluated in the samples. The grafted films were sulfonated using chlorosulfonic acid and 1, 2-dichloroethane 20:80 (v/v) at room temperature for 5 h. The membranes were analyzed by infrared spectroscopy (FTIR), differential scanning calorimeter (DSC), thermogravimetric measurements (TG) and degree of grafting (DOG). The ion exchange capacity (IEC) of membranes was determined by acid–base titration and the values for ETFE membranes were achieved higher than Nafion® films. Preliminary single cell performance was made using pure H_2 and O_2 as reactants at a cell temperature of 80 °C and atmospheric gas pressure. The fuel cell performance of ETFE films was satisfactory when compared to state-of-art Nafion® membranes.

1. Introduction

Among the different technological solutions for sustainable and clean energy generation, fuel cells have had a deserved importance. In general, these devices work by converting chemical fuel, with prominence to hydrogen, in electrical energy. Although there are several different types of fuel cells, proton exchange membrane fuel cells (PEMFC's) have figured among the most prominent ones, especially for automotive and small stationary applications (Kundu et al., 2007).

The development of PEMFC's has been strongly related to improvements in performance of the proton exchange membrane (PEM). This membrane is considered the core component in the PEMFC system that is used to avoid the mix of the fuel and oxidant and allow the transport of the protons from one electrode to other. For high performance of the PEMFC's the membrane has to possess certain requirements, as high proton conductivity, low water permeability, adequate mechanical strength, thermal stability, impermeable to gases, non-electronically conducting and moderate price (Smitha et al., 2005; Lee et al., 2006).

Several proton conducting non-fluorinated and fluorinated membranes have been studied (Souzy and Ameduri, 2005). Nevertheless, due to the latter presents the high chemical and thermal stability it has become the best potential candidate for the application in PEMFC's (Dargaville et al., 2003).

One of the ways to develop cheaper alternatives to commercial membranes is by modification of polymers films using the radiation grafting method (Bhattacharya and Misra, 2004). When the polymer backbone is exposed to radiation, such as γ-rays and electron-beams, the radicals generated on the macromolecular chain initiate the grafting polymerization of a monomer onto polymer. This kind of polymerization reaction can be initiated by pre-irradiation or simultaneous irradiation methods (Chapiro, 2002).

Many studies have reported the use of fluorinated, partially fluorinated and hydrocarbon polymers as in the form of films to obtain PEM using the radiation grafting method. However, fluorine-containing polymers have drawn much attention and are extensively used as base polymers due to their excellent thermal, chemical and mechanical properties (Gubler et al., 2005a, b).

Various research groups have investigated mainly the preparation and the physical–chemical properties of PEM obtained by radiation grafting. The grafting condition using the simultaneous

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irradiation technique such as styrene concentration, irradiation dose and solvent effect on the degree of grafting onto poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP), polytetrafluoroethylene (PTFE) and poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) PFA films has studied by many researchers (Nasef, 2001; Nasef et al., 2000; Nasef and Saidi, 2000). Membranes based on FEP and poly(ethylene-alt-tetrafluoroethylene (ETFE) have been systematically investigated via pre-irradiation method, especially preparing a PEM by grafting styrene and using divinylbenzene (DVB) as crosslinking agent. (Brack et al., 2000; Gubler et al., 2005b, 2008).

Grafting conditions are playing an important role when determining the degree of grafting and the structure built up inside the grafted polymer. In our recent study polystyrene grafted and sulfonated onto PVDF and PTFE membranes were prepared by simultaneous radiation-induced grafting at room temperature. The membranes were characterized by evaluation of their thermal stability and surface structural properties. The grafting yield and surface morphology were found to be dependent mainly on the radiation dose and solvent. (Geraldes et al., 2007).

The radicals in fluorinated polymer backbone remain trapped after radiation during several days. So, the grafting reaction continuously occurs while these radicals are accessible and recombining with the radicals of the monomer. This behaviour after post-irradiation simultaneous process was analyzed in this work and it was verified that the degree of grafting did not change enough during the period studied and the thermal properties of these grafted films, after each period, were not affected then it was chosen the highest DOG to carry on this work that is the sample kept at room temperature for 14 days.

The present work reports studies on radiation grafted and sulfonated fuel cell membranes based on ETFE film by a simultaneous radiation. After the radiation process the samples were kept sealed for 7, 14, 21 and 28 days in order to evaluate the grafting yield in this period of the post-irradiation simultaneous process. The degree of grafting (DOG), ion exchange capacity (IEC) and preliminary single cell performance were evaluated.

2. Experimental

2.1. Membrane preparation

ETFE films with 125 μm thickness purchased from Goodfellow Ltd. were used in this study. The graft solution used was styrene monomer mixed with toluene in a proportion of 1:1 (v/v), without purification. Samples with 18 cm^2 in triplicate were used to prepare material for chemical characterization and a membrane of 144 cm^2 was made to apply in the single cell test.

The films and graft solution were put into a glass tube and nitrogen was bubbled to guarantee inert atmosphere. The tube was sealed and submitted to gamma radiation at 20 kGy dose at 5 kGy h^{-1}. After simultaneous irradiation process the samples were kept in the tube at room temperature for periods of 7, 14, 21 and 28 days in order to evaluate the grafting behaviour. In the sequence, at the end of each period, thermal treatment of the irradiated samples were made in vacuum oven for 4 h at 70 °C.

The sulfonation reaction was carried out with the grafted polymer immersed in a solution of chlorosulfonic acid and 1, 2-dichloroethane for 5 h at room temperature.

2.2. Characterization

The original, grafted and sulfonated ETFE films were characterized by degree of grafting (DOG), ion exchange capacity (IEC), thermogravimetric measurement (TG), differential scanning calorimeter (DSC) and infrared spectroscopy (FTIR).

2.3. Single cell test

The membrane–electrode-assembly (MEA) was prepared with the sulfonated membrane hotpressed with the electrodes at 125 °C and compaction pressure of 22 bar for 2 min.

The single cell test was performed in a single cell with 5 cm^2 of area using Nafion® and ETFE as electrolytes and electrodes from E-TEK with Pt loading of 0.4 mg cm^{-2} (20% Pt on carbon). The fuel cell polarization curves for both Nafion® and ETFE membranes were obtained at a cell temperature of 80 °C, oxygen (O_2) at 85 °C and hydrogen (H_2) at 80 °C, both reactant gases saturated with ultra-pure water at a H_2/O_2 flow stoichiometry of 2.0/4.0. In order to avail the durability the single cell was performed with H_2/O_2 flow stoichiometry of 1.5/1.5 and dried O_2.

3. Results and discussion

The first step of this work was to determine the highest degree of grafting (DOG) as function of time after simultaneous irradiation at room temperature to prepare an electrolyte membrane using ETFE as base polymer. The DOG was very similar for all different periods of the polymerization reaction (around 27%), except for the 14 days, which showed a slightly higher level (32%). This decrease after 14 days occurs probably due to degradation reactions like scission of backbone chain and of the grafted styrene, both as effect of the irradiation. As the membrane obtained after 14 days of the polymerization reaction presented the highest DOG, it was chosen for the study of the physicochemical properties and for test in the fuel cell.

FTIR spectra were obtained for original and grafted ETFE films (these spectra are not showed). The presence of aromatic rings due to grafted styrene was confirmed by the =C–H stretching vibration at 3060 cm^{-1} and the C–C in-plane stretching vibrations at 1550 and 1600 cm^{-1}, respectively. The characteristic absorption peaks of the ETFE macromolecules at 1453 and 1140 cm^{-1} also can be observed.

The thermal stabilities of the ETFE membranes were determined by TG, Fig. 1. The original ETFE has only one sharp weight loss that was ascribed to the decomposition of polymer main

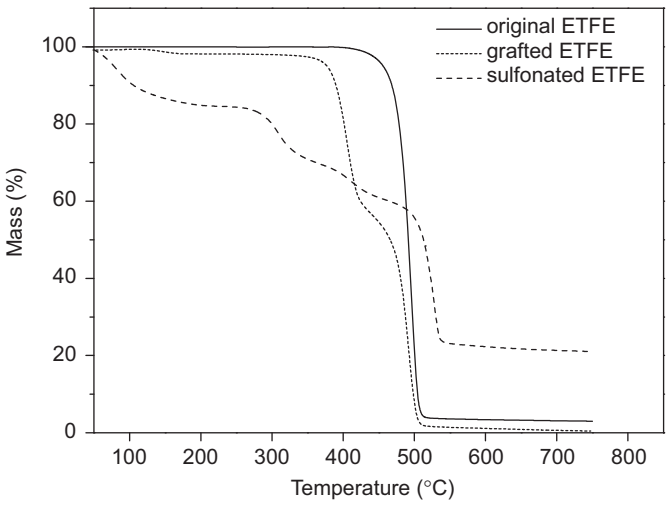

Fig. 1. TG curves for original, grafted and sulfonated ETFE films, in N_2 atmosphere, from 25 up to 700 °C at a heating rate of 10 °C min^{-1}.

chain, at 420 °C. For the grafted ETFE there are two decomposition steps the first one is attributed to grafted styrene that the decomposition begins at 402 °C and the second is the polymer chain decomposition that arises about 20°C in relation with the original polymer.

The sulfonated membranes exhibit four different steps of thermal degradation: (1) around 100 °C is the desorption of water bonded to the sulfonic groups; (2) the second occurs between 240 and 350 °C and is related with the sulfonic acid groups decomposition; (3) the step between 370 and 450 °C is the styrene grafted degradation and (4) the last thermal degradation that starts at 480 °C was assigned to the polymer main chain degradation.

The initial degradation temperature for the original polymer is 420 °C and for the polymer matrix in the sulfonated membrane is 480 °C. This increase indicates that the main chain of sulfonated ETFE has slightly higher thermal stability than the original ETFE and then it is speculated that the main chain structure of sulfonated, after $-SO_3H$ groups were split off, is not identical to the original polymer.

Fig. 2 shows DSC curves of original, grafted and sulfonated ETFE films. As it can be observed, the original ETFE film presents a transition at 263.8 °C, which can be assigned to the melting temperature (T_m). Although the radiation grafting of styrene followed by sulfonation causes some structural changes in the polymer film, the T_m of the grafted (262.6 °C) and sulfonated (263.7 °C) films are enough similar to that of the original film. This melting behaviour suggests that the effect of the radiation grafting is not effective to change the crystalline structure of the polymer matrix.

The experimental IEC of the grafted ETFE film (1.98 meq g^{-1}) obtained is lower than the theoretical (3.04 meq g^{-1}). This may be due to a deviation from the assumption that each styrene unit was bonded to one sulfonic acid group. The high degree of sulfonation calculated (65%) shows that the sulfonation reaction was successfully carried out.

In Figs. 3 and 4 are demonstrated the fuel cell polarization curves for both Nafion® and ETFE membranes. In general, the fuel cell polarization response is associated with irreversible processes. In this sense, three processes are usually identified: activation, ohmic drop and mass-transfer limitations. The activation overpotential (0–0.2 A cm^{-2}) is mainly dependent of the kinetic of the oxygen reduction reaction (ORR), which is considered as the rate determining step in the fuel cell

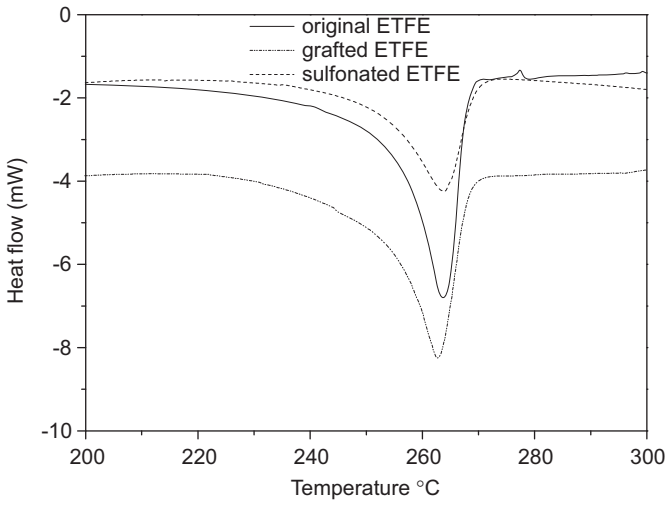

Fig. 2. DSC curves for original, grafted and sulfonated ETFE films, in nitrogen atmosphere, from 30 up to 350 °C at a heating rate of 10 °C min^{-1}.

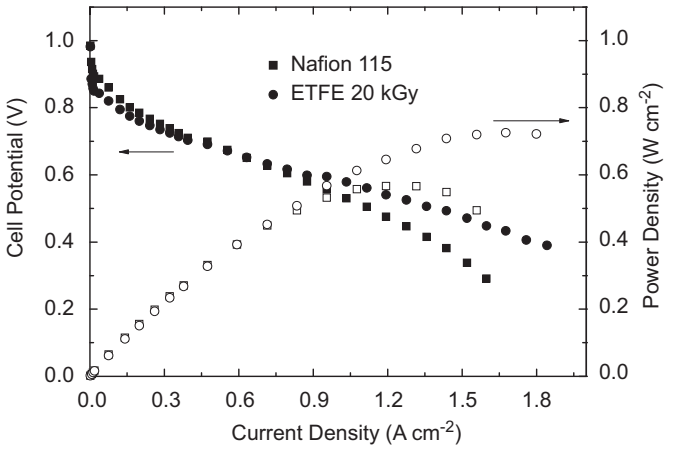

Fig. 3. MEAs performance at a stoichiometry flow of 2.0/4.0 and O_2 humidified at 85 °C.

electrochemical processes. The ohmic drop overpotential (0.2–~1 A cm^{-2}) is associated with resistances of the electrodes and electrolyte. Taking into account that the electrodes are the same, any deviation in the ohmic drop overpotential should be attributed to the electrolyte. Finally, the mass-transfer overpotential is related to the diffusion limitation of the gas reactants to catalyst surface (Ticianelli and Gonzalez, 2005).

Fig. 3 shows the polarization curves for MEAs using both Nafion® and ETFE as electrolyte in humidified conditions (water-saturated H_2 and O_2 reactants). In the activation region a decrease of the ETFE performance is observed when compared to that Nafion®, possibly, due to a flooding of the electrode even at intermediate currents. On the other hand, the ETFE performance tends to increase in the ohmic drop region. Such effect should be attributed to a higher conductance of the ETFE films in comparison to Nafion®. It is relevant to mention that the thickness of both membranes is similar. Considering the maximum power density response (*Y* right axis), the performance of the ETFE membranes is 25% superior to Nafion®. Long-time experiments reveal a rapid decrease of the performance of the fuel cell using ETFE after 6 h of operation. This result is consistent with the formation of flooding zones in the electrodes (cathode), which might affect the electrode process.

In Fig. 4 is demonstrated the polarization and power densities curves as function of the operation time for single fuel cells fed with water-saturated H_2 and dried O_2 are presented. The overall performance of the ETFE after 2 h is slightly lower to that of Nafion® at the same conditions. After this time, an oscillatory performance profile is observed for ETFE membrane. In fact, the performance tends to decrease till 12 h of operation, after 14 h an increase of the maximum power density is evident (Fig. 4a) and the measurements obtained at times superior to 18 h reveal a diminishing in the overall performance. A decrease of the performance seems to be irreversible after 26 h of operation. Such oscillatory behaviour suggests non-equilibrium in the water management processes, i.e., back-diffusion and electroosmotic drag, caused by the formation of dryness and flooding zones, could affect strongly the mechanical and conductivity properties of the membrane (Gubler et al., 2005a, b).

4. Conclusion

Polymer electrolyte membrane has been prepared under controlled conditions using the radiation-induced grafting of

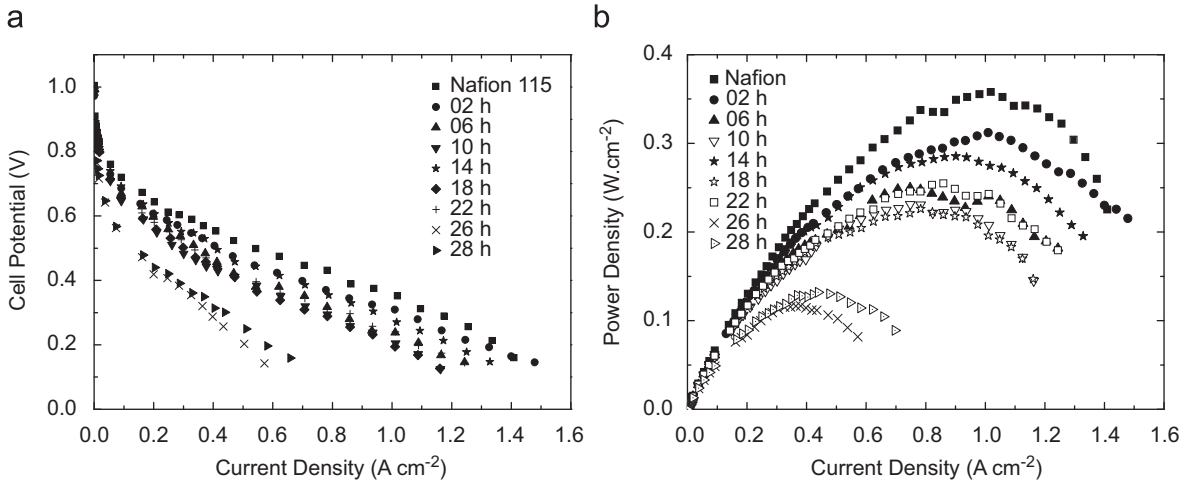

Fig. 4. MEAs performance at a stoichiometry flow of 1.5/1.5 and O_2 dry. (a) Polarization curves and (b) the power density curves. Nafion® 115 performance after 2 h was used for comparison.

styrene onto ETFE followed by sulfonation by a simultaneous method. The effect of post-irradiation time was investigated and no drastic change in the thermal properties or in the degree of grafting was found in this experiment. By means of the FTIR and TG/ DSC measurements, it proved that the sulfonated styrene was grafted into the ETFE film. The performance of MEA with sulfonated ETFE was somewhat superior compared to a Nafion® 115-based MEA.

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