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FREE RADICALS STABILITY INVESTIGATION BY ELETRON PARAMAGNETIC RESONANCE (EPR) OF ELETRON-BEAM IRRADIATED FLUOROPOLYMER FOR FUEL CELL PRODUCTION

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ABSTRACT

The alkaline anion exchange membranes (AAEM) have been produced from the irradiation method to graft functional monomers into polymer films via copolymerization by using either simultaneous or pre-irradiation methods, by means of gamma rays or electron-beam. The pre-irradiation method has been widely used due to a reduced formation of homopolymers. The graft also may be carried out at any moment after free radicals formation. Lifetime of the active species formed during polymer irradiation (radicals, ions and peroxides) is very important and may be controlled either by temperature reduction or vacuum use. In high temperatures, active species undergo decay as a result of recombination in the amorphous phase. The loss of radicals during storage affects the graft reaction, such as reduction of active centers, graft yield and membrane properties. Storage of pre-irradiated polymer is an important factor to be considered when preparing membranes for alkaline fuel cells. For during two months, the free radical decay time of polymeric films storage at ambient and low temperature was studied by Electron Paramagnetic Resonance (EPR): the films radicals hold at low temperature showed good stability and grafting yield even after two months of irradiation. This preliminary result indicates that graft of monomer onto the polymeric irradiated film can be done some time later after irradiation. Further tests in membranes and under different conditions will be carried out for more consistent and reliable results.

1. INTRODUCTION

Fuel cells are electrochemical systems that convert chemical energy into electrical energy through continuous feeding fuel. These systems represents an alternative technology of electricity with great efficiency and large applicability in the areas of portable, stationary, and automotive powers [1,2].

Solid electrolytes, more specifically, anion exchange membranes (AME) are a promising alternative to the development of more efficient electrolytes for alkaline fuel cells (AAME). In general, the AAME are produced from irradiation-grafting method to graft functional monomers into polymers films via copolymerization using either simultaneous or pre-irradiated methods, by means of gamma rays and electron-beam [3-5].

The pre-irradiation method has been widely used due to a reduced formation of homopolymers and the possibility of grafting to be carried out at any time, however lifetime of the active species formed during the polymer irradiation (radicals, ions and peroxides) is very important and may be controlled either by temperature variation or vacuum use. The loss of radicals during storage affects the grafting reaction, such as reduction of active centers, grafting yield and membranes properties [6,7]. Several studies show the stability of radicals storage at -36±2^{o}C and used within 12 months after irradiation [6-8].

During two months, the stability of radicals on electron-beam irradiated ethylene-tetrafluoroethylene (ETFE) film storage at ambient and -70±4^{o}C was studied by Electron Paramagnetic Resonance (EPR) in order to improve quality and reproducibility of the membranes by defining a minimum handle time and storage conditions,

2. EXPERIMENTAL

2.1. Electron-Beam Irradiation and membrane synthesis

2.1.1 Electron-Beam irradiation (EB)

Samples of ETFE (ethylene-tetrafluoroethylene) films of 125μm thickness FP361125 supplied by Goodfellow Cambridge Limited (UK) were prepared for ERP analyses (2.5 cm × 3.0 cm) and grafting irradiation (3.0 cm × 5.0 cm). Samples were irradiated using EB at a radiation absorbed dose of 70 kGy at IPEN–CNEN/SP, Brazil, using the Electron Beam Acelerator Dynamitron (E = 1.5 MeV) from Radiation Dynamics, Inc. and stored in a freezer at -70±4◦C until the use [7].

The EPR analyses were carried out one hour after irradiation and grafting was performed after two months of storage at low temperature (-70±4 ^{o}C).

2.1.2 Synthesis of the Membrane

The membrane was prepared by pre-irradiation grafting technique similar to those described in previous papers [4,6-9],

2.1.2.1 Monomer grafting: Pieces of pre-irradiated ETFE polymer were initially weighed and then rolled up into a cylindrical vessel and filled with monomer solution styrene and isopropanol (40:60 v:v%) until the complete roll was saturated and covered. The oxygen in the vessel was then removed by purging with nitrogen. The grafting reaction was carried out in a inert atmosphere for 24 hours at 60 ^{o}C. Film was washed with xylene to remove any homopolymer and dried on oven at 60 ^{o}C to constant weight. The degree of grafting (DOG) of membranes, which represents the proportion of the grafted polymer in the membrane, was calculated using the following formula

$$DOG(\%) = \frac{m_g - m_0}{m_0} \quad (1)$$

m_g and m_0, are the membrane weight before and after grating irradiation respectively. The DOG obtained in this study was DOG = 78% , consists of 78% of the grafted monomer and 22 % original polymer.

2.1.2.2 Sulfonation: Chlorosulfonic acid introduces sulfonic groups onto the styrene residue of grafted films, providing inexpensive AEM materials. Sulfonation of ETFE-grafted film was carried out by immersing the films in a 0,2 M chorosulfonic acid solution in dichoromethane for a period of 12 hours at ambient temperature . The film was washed to neutrality in de-ionized water.

2.1.2.3 Quaternization and alkalization: In order to impart functionality on the grafted copolymer, the intermediated membrane obtained was reacted in a trimethylamine aqueous solution (Sigma,45 wt%) for 48 hours at ambient temperature, washed in water and heated in fresh water for 1 hour to remove any amine excess. Subsequently, films were treated with hydrochloric acid (1 mol L^{-1}) for 12 hours at ambient temperature and washed to neutrality and stored in de-ionized water until its use. The AEMs were converted to the hydroxide-form alkalized immediately before use and testing by submerging in a aqueous potassium hydroxide (1 mol L^{-1}) for 1 hour at room temperature (changing the solution twice during this period to ensure complete ion-exchange), followed by washing with de-ionized water for several times and kept in de-ionized water [9].

The ion exchange capacities (IEC) of AEMs were performed by a black titration method. A piece of dried hydroxyl formed membrane were soaked into a 0,1 mol L^{-1} hydrochloric acid solution (25 ml, V_{HCL}, the volume for membrane soaking) for 24 hours at room temperature to undergo ionic exchange process. The solution was then black titrated with a 0,025 mol L^{-1} sodium hydroxyl solution (V_{NAOH}, the volume for black titration). The membrane were washed with de-ionized water and dried on oven at 60ºC until constant weight. The IEC (mmol g^{-1}) were calculated as below

$$IEC(mmol\ g-1) = \frac{(V_{HCL}\ x\ C_1 - V_{NAOH}\ x\ C_2)}{M} \quad (2)$$

C1 and C2 are the concentration of HCL and NAOH solutions respectively, and M is the weight of the dried membrane.
The IEC of AEMs obtained in this study was 2,0.mmol g^{-1}.

2.2 EPR procedure

Electron Paramagnetic Resonance (EPR) spectroscopy is a technique for studying materials with unpaired electrons. The basic concepts of EPR are similar to nuclear magnetic resonance (NMR), however it is electron spins that are excited instead of the spins of atomic nuclei [10].

Experimentally, spectra were obtained by measuring the attenuation versus frequency (or wavelength) of a beam of electromagnetic radiation as it passes through a sample of matter. Lines or bonds in a spectrum represent transition between energy levels of the absorbing species. The frequency of each line or band measures the energy separation of two levels [10]. EPR spectroscopy can be applied only to systems in which the balance between radical decay and radical formation keeps the free-radicals concentration above the detection limit of the spectrometer used, in this study the effect of extensive storage (-70±4 ªC and ambient) temperature on electron-beam ETFE was monitoring for two months.

Electron Paramagnetic Resonance (EPR) spectroscopy was performed at room temperature using a Bruker EMX plus model, X band. The frequency of the applied electromagnetic radiation was fixed at 10 GHz, microwave power was fixed at 20 mW and magnetic field was varied in order to generate the EPR spectra. The samples were contained in a quartz tube. All spectra were recorded at room temperature. 10 scans were accumulated for each spectrum. The spectra were recorded in the magnetic-field range from 3300 G to 3700 G [7].

3. Results and Discussion

The effect of two months storage at room and low temperature (-70±4 ºC) on reducing multiple grafted branches and the ion-exchange capacities of producing membrane from electron-beamed ETFE film was evaluated by EPR, DOG and ion-exchange capacities (IEC).

The resonance of the film radicals appears as a singlet and the species giving rise to this signal is likely to be a peroxy radical ($ROO^{\cdot}$, magnetic field range 3450 – 3548) rather than an alkyl radical ($R^{\cdot}$, magnetic field 3527- 3548) was reported by Mitov et al. The value of g determined for the peroxy radical signal of samples storage at cold temperature in the present work were 1.912242 – 2.145325, are slightly superior of values reported to Mitov (2.012 – 2.013) et al and Larsen et al (2.01545 ± 0.00010) for terminal peroxy radicals.

3.1.1 Samples stored at ambient temperature

Fig 1shows the intensity variation within the range of 0 to 60 days after irradiation of samples stored at ambient temperature. The spectra indicate the presence of peroxides (magnetic field 3450 -3548) and alky radicals (magnetic range 3527 - 3548) which disapeared after 7 days. The peroxy radicals showed an expressive reduction during 60 days.

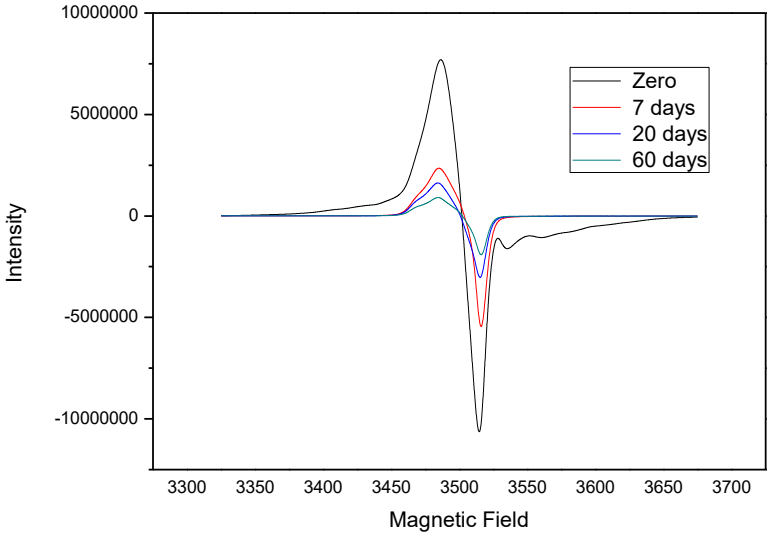

Figure 1: EPR spectra of an electron-beam irradiated ETFE film sample. The spectra were recorded at three different times within the range of 0 – 60 days. Dose of radiation: 70 kGy. Samples storage at ambient temperature.

3.1.2 Samples storage at -70±4◦C

Fig 2 shows the intensity variation within the range of 0 to 60 days after irradiation of samples stored at -70±4 ºC. The effect of low temperature storage on electron-beamed ETFE not produced a significant reduction in the peroxy radicals (magnetic field 3483 – 3515) after two months as observed by the DOG and IEC of the resulting membranes. The alky radicals (magnetic field 3527 - 3547) also despaired after 7 days.

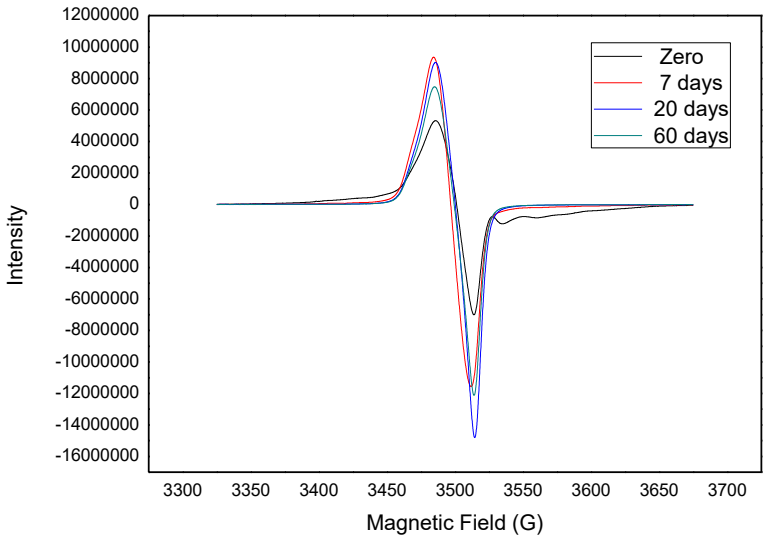

Figure 2: EPR spectra of electron-beam irradiated ETFE film sample recorded at three different times within the range of 0 – 60 days. Dose of irradiation: 70 kGy. Samples stored at -70±4◦C.

Mitov, S. and Larsen, M. J. [6,7], studied the peroxy radical sign decrease of ETFE films pre-irradiated with EB at doses 40 kGy and 1.8 – 2.8 kGy respectively storage at ambient and in liquid nitrogen for different periods of time. Results showed a rapid decrease in the ETFE peroxy radical sign for storage time and temperatures increases, which indicate pronounced temperature dependence. These effects were also observed in the present study, however less pronounced.

3.1.3 Membrane Characterization

The degree of grafting (DOG), water uptake (WU), Ion Exchange Conversion (IEC) and conductivity have been evaluated.

Initial results show a degree of grafting of 78% after 24 hours at 60◦C, membranes thickness changed from 0.125 to 0.298 µm, water uptake of 122 % and IEC= 2.0 mequiv g^{-1}, indicating the presence of large content of ions in the synthesized membrane

3. CONCLUSIONS

The EPR methodology used in the present study allowed the observation of ETFE electron-beamed radicals stability at different storage and temperature conditions by monitoring peroxy radical decrease , meaning the technique is adequate to be used for planning grafting processes. Through the study of the radicals decay it was possible to establish process parameters to ensure an effective graft yield.

EPR results indicate that the radicals formed during the pre-irradiation could be preserved for further graft of functional monomers into polymer films via copolymerization by storage at low temperature (-70±4◦C) at least for two months, as observed by the membranes DOG and IEC. Further tests in different membranes and under different conditions will be carried out for more consistent and reliable results.

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