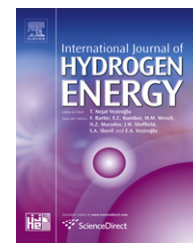


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Sulfonated bisphenol-A-polysulfone based composite PEMs containing tungstophosphoric acid and modified by electron beam irradiation

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ABSTRACT

Composite sulfonated bisphenol-A-polysulfone (SPSF) based PEMs, containing tungstophosphoric acid (TPA) and modified by electron beam (EB) irradiation with doses of 50 and 100 kGy, were prepared and characterized by a number of physico-chemical methods. The probability of the cross-linking was increased by post treatment of the irradiated membranes at 180 °C for 8 h into a vacuum oven. The cross-linking strongly affected membrane properties, reducing their swelling, but at the same time decreasing their proton conductivity. The proton conductivity of the membranes was measured by a two electrode ac impedance technique using a frequency response analyzer. The PEMs performance was tested in H₂/O₂ fuel cell (FC) and found to approach that of Nafion[®] 117 commercial PEM at the same conditions. The PEMs composite stability was adequate at least for 2 days, during which no degradation of the performance was observed.

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1. Introduction

Fuel cells have been given great attention as new energy conversion technologies for their promising applications in new clean power sources were applied. Fuel cell technology is also more efficient in its conversion of chemical energy to electrical energy than present technologies [1]. Among the technology types of fuel cells, proton exchange membrane fuel cell has been receiving great attention due to its highly attractive properties as power sources for both stationary and mobile applications [2–4]. Polymer electrolyte membranes play an important role in the development of the fuel cell technology. Perfluorinated polymer electrolytes such as Nafion[®], Aciplex[®], Flemion[®] and Dow membranes are the most widely used electrolyte in polymer electrolyte fuel cell

(PEFC) due to its high proton conductivity, mechanical, chemical and electrochemical stability. However, this type of membrane also exhibits some drawbacks, mainly the high cost and the operation temperature. Their performance is strongly dependent on their hydration degree and becomes very poor over 90 °C and at a low relative humidity [5]. As a consequence, there are many efforts to find alternatives to these perfluorinated membranes [6–9]. Different ionomers have been explored such as: sulfonated aromatic polymers; composite membranes based on polybenzimidazole and strong acids; composite membranes based on fluorinated polymers and inorganic materials ranging from oxides to lamellar zirconium phosphates or phosphonates; perfluorinated membranes containing proton-conducting ionic liquids (PCILs) and inorganic/organic composite membranes

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based on Nafion and inorganic micrometer to nanometer size fillers [5,10].

Aromatic hydrocarbon provides the opportunity to incorporate sulfonic acid groups by electrophilic substitution reaction. As the pKa of arylsulfonic acids is close to -6 , a fairly good dissociation can therefore be expected [11]. Polysulfone bisphenol-A (PSF) is one of the engineering plastics having aromatic structure in the main chain with excellent mechanical properties and stability at high temperature [12]. To achieve FC conductivity, PSF must be highly sulfonated. As a result, these polymers swell substantially with water uptake and some are even soluble in water [13].

In the present study composite membranes were prepared by incorporation of inorganic filler (TPA) into a polymer matrix (SPSF). The TPA is one of the Keggin-type heteropolyacids with high proton conductivity (between 0.02 and 0.1 S cm^{-1} at 25°C). In the hydrated phase, the proton in TPA molecules as a Bronsted acid is bridged with water by forming hydronium ions such as H_3O^+ , or H_5O_2^+ [14]. So, the incorporation of TPA into SPSF membranes can facilitate the transport of protons into the membrane. However, it was found that embedding a fast proton conductor such as TPA ensures only temporary improvement of the PEM properties. When swollen in the FC hydrothermal environment the composite membranes lose the inorganic phase, gradually transforming into their initial form [14,15]. The EB irradiation cross-linking technique was employed to decrease the water swelling improving the mechanical strength and trap the TPA particles within a sulfonated polysulfone matrix. A significant improvement in PEM's conductivity is attributed to the loading of extremely conductive hydrated TPA, which is found to be less often prone to leaching out of the composite due to restricted mobility of polymer cross-linking chains. The EB process utilizes ionizing radiation in the form of accelerated electrons which interact with matter by transferring energy to the electrons orbiting in the target materials' atomic nuclei. These electrons may then be either released from atoms, yielding positively charged ions and free electrons, or moved to a higher-energy atomic orbital, yielding an excited atom or molecule to form free radical. These ions, electrons and excited species are the precursors of the chemical changes observed in irradiated material. Polymers generally respond to EB processing in one of three ways. The polymer may cross-link in which the molecular weight increases and improves the mechanical properties [16,17]. The polymer may degrade due to chain scission. Finally, the polymer may be radiation resistant where no significant degree of either cross-linking or chain scission occurs. This resistance is attributed to molecular protection typically afforded by means of an aromatic ring. EB cross-linking provides some material advantages, including tensile and impact strength, chemical resistance, and environmental stress crack resistance and barrier properties. The process neither does not require any additives, nor does it generate hazardous chemical by-products.

The proton conductivity, water uptake, thermal properties and chemical structure examined by FTIR were monitored. The performances in the H_2/O_2 FC were tested for these composite membranes in order to reveal a consistent pattern for the SPSF cross-linking and its effect on the properties of the composite PEMs [15].

2. Materials and methods

2.1. Materials

Bisphenol-A-polysulfone (PSF – Ultrason 56010, $M_w = 60,000$) was kindly provided by BASF. SPSF was obtained by mild sulfonation of bisphenol-A-polysulfone with trimethylsilyl chlorosulfonate as sulfonation agent. Tungstophosphoric acid hydrate ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) of reagent grade was purchased commercially from Fluka and used as received.

2.2. Membrane preparation

The membrane was prepared with 20 wt.% SPSF homogeneous solutions in *N-N*-dimethylacetamide (DMAc). The polymer was kept 8 h in contact with the solvent and dissolution was completed with mechanical stirring at 60°C . Composite membranes were prepared adding 8 wt.% of TPA to SPSF solutions before mechanical stirring. Afterward, the solution was cast onto a flat glass and the solvent was slowly evaporated at 60°C for 24 h. Subsequently, the membranes were peeled from the glass in deionized water. Then, to ensure complete solvent removal, the membranes were placed under vacuum at 80°C for 48 h. Thus, membranes of $100 \mu\text{m}$ thickness were obtained [13,18,19].

2.3. Irradiation cross-linking

The EB irradiation was carried out at room temperature and atmospheric air under a Rodotron TT200 electron accelerator with an average dose rate of 630 kGy/min and energy of 10 MeV . The beam was applied in the form of scanning on the samples when they passed through the beam to be transported by the walkways system. EB irradiation was controlled by dosimeters located on the samples. After irradiation, the SPSF films were thermally treated in a vacuum oven at 120°C for 2 h for quenching any residual radicals [2]. Additional thermal cross-linking of the sulfonic acid groups in the irradiated SPSF membranes was carried out in vacuum oven at 180°C for 8 h. The degree of sulfonation of the membrane was determined before and after irradiation by acid–base titration [20].

2.4. Membrane characterization

Fourier transform infrared (FTIR) spectra of the membranes were obtained in the range of wave number $4000\text{--}450 \text{ cm}^{-1}$ using a Perkin Elmer 1720-X FTIR spectrometer by attenuated total reflectance (ATR) techniques.

Thermogravimetric analysis (TGA) was carried out using a TGA Q500 (TA Instruments) under nitrogen atmosphere. Samples ($10\text{--}20 \text{ mg}$) were heated from room temperature up to 700°C at 10°C/min . The glass transition temperatures of the membranes were determined using a TA Instruments DSC Q1000 differential scanning calorimeter at a heating rate of 10°C/min from -40 to 300°C , in a nitrogen atmosphere. Before measurement, the sample was dried under vacuum at 120°C for 24 h.

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