



Material properties

Electrochemical and structural characterization of sulfonated polysulfone

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ABSTRACT

We describe the synthesis, as well as the electrochemical and structural characterization, of sulfonated polysulfone intended for use in PEM fuel cells. Starting from a commercial polysulfone, we assessed the performance of these prepared ionomers using synthesis protocols compatible with industrial production. The efficiency of the trimethylsilyl chlorosulfonate and chlorosulfonic acid reagents in the sulfonation process was confirmed by ¹H NMR, FTIR, elemental analysis, chemical titration and thermal analysis (DSC and TGA). Chlorosulfonic acid was the most effective sulfonation reagent. However, based on SEC-MALLS, this reagent induced degradation of the backbone that is detrimental to the thermo-mechanical stability and lifespan of the membranes. The electrical characterization of the membranes was undertaken using impedance spectroscopy in contact with different HCl aqueous solutions at various temperatures. The activation energies, which ranged from 8.2 to 11 kJ/mol, were in agreement with the prevailing proton vehicular mechanism.

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1. Introduction

Fuel cells, which are the most efficient electrochemical energy conversion sources, are perfectly compatible with other renewable energy sources (i.e., solar and wind energy). The proton exchange membrane fuel cell (PEMFC) has attracted much interest because it is capable of producing high power densities at low temperatures [1]. In addition, its modularity allows for its use as an energy source in various applications from portable electronics to electric cars and stationary applications. Currently, perfluorosulfonated polymer electrolytes, such as Nafion[®] from Dupont or Aquivion[®] from Solvay, are the most widely used electrolytes in PEMFCs due to their high proton conductivity, mechanical properties up to 80 °C and chemical and electrochemical stability. However, this type of membrane also exhibits some drawbacks, which are primarily high cost, low stability at high temperatures, low conductivity at low humidity or high temperature and high methanol crossover in direct methanol fuel cells (DMFCs) [2]. Therefore, extensive studies have been focused on developing alternatives to these perfluorosulfonated membranes [3]. In particular, different polymers

that adopt the sulfonated aromatic hydrocarbon structure have been tested, including poly(arylene ether sulfone)s [4], poly(ether ether ketone)s [5], poly(sulfide sulfone)s [6], polyimides [7], polyphosphazenes [8] and polybenzimidazoles [9].

Among these polymers, polysulfone (PSU) has attracted considerable interest due to its excellent thermomechanical stability, moderate cost and commercial availability. In addition, PSU exhibits resistance to both hydrolysis and oxidizing agents. The diphenylene sulfone endows the polymer backbone with insensitivity to hydrogenation, thermal stability and oxidative resistance [10]. A comparative electrochemical study (i) of model molecules mimicking the backbone of high performance polymers and (ii) their sulfonated form confirmed that the polysulfone ionomers have a wider electrochemical stability window than that of polyether-ether ketone and polyphenylene sulfide ionomers [11]. Therefore, sulfonated polysulfone (SPSU) ionomeric membranes have been extensively studied and tested for fuel cell applications [12,13].

In general, two approaches have been used to introduce sulfonic acid groups to these polymers, including the sulfonation of commercial polymers and the polycondensation of sulfonated monomers [4]. The first approach leads to randomly sulfonated polymers and uses polymers that are fairly cheap with high performance. The second approach provides multiblock ionomers. These ionomers

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have alternating hydrophobic blocks, which provide good mechanical strength, and hydrophilic ones which provide protonic conductivity. Although the nanostructure of the multi-block ionomers is an asset, industrial-scale production is challenging. In addition, as in any step-growth polymerization, the chain length will strongly depend on the purity of all of the monomers (i.e., the sulfonated monomers).

Because sulfonation proceeds through an electrophilic substitution, it occurs on the electron-rich positions of the aromatic rings (i.e., in the ortho position of the ether functions (electron-donating resonance effect of oxygen) of the dioxy-2,2-diphenylpropane moiety). Sulfonation on an electron-poor position (i.e., diphenylsulfone rings) must allow for a decrease in the de-sulfonation of the ionomers and a slight increase in the dissociation of the sulfonic acids. Kerres et al. [14] previously proposed a 3-step reaction that leads to these alternative ionomers. This clever approach led to a wide variety of structured polysulfone ionomers. However, sulfonating polysulfone in this position requires the use of highly concentrated solutions of butyllithium, which makes large-scale production of the ionomer questionable. Currently, the easiest and cheapest upscaling process involves electrophilic substitution of commercially available high performance polymers. Sulfonation of bisphenol-A based poly(ether sulfone) (PES) by chlorosulfonic acid was first reported by Quentin [15]. Noshay and Robeson demonstrated PSU sulfonation using the sulfur trioxide/triethyl phosphate complex [10]. Then, this complex [16], chlorosulfonic acid [13,17], and trimethylsilyl chlorosulfonate ($\text{ClSO}_3\text{Si}(\text{CH}_3)_3$) [12,18] were studied as sulfonating agents in electrophilic substitution. However, sulfuric acid failed because the polymer was neither swelled nor dissolved in the strong acid solvent [17].

In this study, we compare the sulfonation of PSU using two sulfonating reagents (i.e., the industrial route (ClSO_3H) compared to the laboratory one ($\text{ClSO}_3\text{Si}(\text{CH}_3)_3$). The degree of sulfonation (DS) was estimated by ^1H NMR, elemental analysis, ion-exchange capacity (IEC) and thermogravimetric analysis. Special attention was paid to the determination of the actual molecular weights that govern the membrane brittleness. Irrespective of the sulfonation protocol, the concentration in the sulfonic groups, which is expressed by the DS, determines the performance (e.g., mechanical and thermal properties, water uptake, IEC and proton conductivities) of sulfonated polysulfones in membrane applications.

Electrochemical impedance spectroscopy (EIS) was used to study the electrical properties of the membranes. The measurements were carried out with the membranes in contact with HCl aqueous solutions at different concentrations. The analysis of the impedance plots using equivalent circuits as models identified the different contributions to the total conductivity. The study of the conductivity at different temperatures allowed us to obtain the activation energy associated with the membrane, as well as determining the primary mechanism involved in the diffusion process.

2. Experimental

2.1. Materials

Polysulfone ($M_n = 26,000$ g/mol), chlorosulfonic acid (ClSO_3H , 98%), trimethylsilyl chlorosulfonate ($\text{ClSO}_3\text{Si}(\text{CH}_3)_3$, TMSCS, 99%), N,N-dimethylacetamide (DMAc), 1,2-dichloroethane (DCE), DMF- d_7 and DMSO- d_6 were supplied by Sigma–Aldrich (Saint Louis, USA). The solvents were high-grade reagents and used as received.

2.2. Sulfonation of PSU

First, the sulfonation process was carried out in anhydrous

conditions under N_2 following the method described by Chao et al. [19]. Therefore, the solution of PSU in DCE was treated with TMSCS or ClSO_3H diluted in DCE. The mixture was maintained under magnetic stirring for 24 h using TMSCS and 4 h using ClSO_3H at room temperature. Once the reaction was complete, the sulfonated polymer (SPSU) was purified until a neutral pH was achieved. Finally, the obtained polymer was dried at room temperature. The PSU:TMSCS molar ratios were 1:1, 1:3 and 1:6, and the PSU: ClSO_3H molar ratios were 1:1 and 1:3.

2.3. Membrane preparation

The SPSU in the salt form was dissolved in DMAc to prepare a 5 wt % solution under magnetic stirring for 24 h at room temperature. The polymeric solution was cast on a Petri glass dish and dried in an oven using the following thermal cycle: 60 °C for 24 h, 90 °C for 1 h, 120 °C for 1 h and 165 °C for 1 h. Finally, the membranes were immersed in water to eliminate possible traces of the solvent, followed by drying at room temperature. The thickness of the obtained membranes was in the range of 50–100 μm .

2.4. Characterization and measurements

2.4.1. ^1H NMR analysis

The liquid ^1H NMR spectra of polymers were recorded on a Bruker Avance DPX 300 MHz spectrometer. DMF- d_7 was used as the solvent for PSU, and DMSO- d_6 was used as the solvent for SPSU. In addition, tetramethylsilane was used as the internal reference.

2.4.2. FT-IR analysis

The Fourier transform infrared spectra of the polymers were recorded on an FTIR spectrometer Perkin–Elmer Spectrum GX in the 4000–400 cm^{-1} range using 16 scans at a resolution of 4 cm^{-1} .

2.4.3. Size-exclusion chromatography

Size-exclusion chromatography (SEC) was performed on a modular system equipped with an HPLC pump 515 Series, PolarGel-M-D column, refractive index (RI) detector 2000 and DAWN light scattering (LS) detector. LS and viscosity measurements of the ionomers required the use of a solvent with a specific ionic strength to avoid effects from dilution on ionic polymer dissociation, which modifies the chain-solvent interaction. Therefore, the samples (Na^+ form) were dissolved in an eluent (i.e., 0.1 M solution of NaNO_3 in DMF) at a flow rate of 1.0 ml/min. The dn/dc (specific refractive index increment) values were calculated from the measurements assuming 100% mass recovery ($\text{dn}/\text{dc} = 0.13\text{--}0.17$ ml/g). The molecular weights were determined from the LS signal using the Astra 6 software (Wyatt Tech, USA). The fit of the molecular weight/elution volume dependence in the complete range of the RI signal was used to estimate the distribution of the lower molecular weight species that cannot be detected by the LS detector but are visible in the RI signal [20].

2.4.4. Elemental analysis

Elemental analysis (EA) of the polymers based on the sulfur to carbon ratio was performed with a manual FlashEA elemental analyser. C, H, N and S were converted to CO_2 , H_2O and N_2 at 900 °C in a column containing an oxidizing agent. These molecules were separated in a GC column containing molecular sieves and detected by a thermal conductivity detector (TCD). The percentages of C, H, N and S were determined after elaboration of the respective calibration curves for different standards.

2.4.5. Ion-exchange capacity

The IEC values of the membranes were determined by classical

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