Polyelectrolytes Based on Speek/TiO_2 Nanocomposites for Direct Ethanol Fuel Cells Applications

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Summary. *Proton-conducting nanocomposite membranes consisting of poly(ether ether ketone) sulfonated (SPEEK) and titanium oxide (TiO_2) were prepared by sol-gel technique. The TiO_2 incorporation effect on membrane properties such as ethanol uptake, pervaporation and proton conductivity was investigated.*

1 INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have been considered as promising alternative and clean power sources due to the high conversion efficiency of the fuel chemical energy to electric energy with low pollutants emission [1].

Among the types of PEFCs, direct ethanol fuel cells (DEFCs) have recently gained a great deal of attention for their highly potential applications in electric vehicles, stationary applications, and portable power sources, such as mobile phones and laptops, etc [2].

Currently, one of the biggest challenges when alcohols were used in moderate temperature polymer electrolyte fuel cells (PEFCs) is high liquid fuel crossover and low proton conductivity. In order to minimize these limitations, organic-inorganic nanocomposites have been widely studied for direct methanol fuel cells (DMFCs).

In the present work, polymer electrolyte membranes containing SPEEK with 58% of sulfonation degree (SD) and TiO_2 were prepared for direct ethanol fuel cells (DEFC) applications.

2 EXPERIMENTAL

PEEK was sulfonated (SD = 58%) according to literature [3] and dissolved in NMP (1-methyl 2-pirrolidone) under heating at 70 °C and magnetic stirring. Then, tetrabutyl titanate ($Ti(BuO_4)$/acetylacetone (ACAC) (molar ratio 1:2.2) at 0 °C were quickly added in SPEEK solutions at room temperature under magnetic stirring either. Finally, the membranes were prepared by solution casting method. All the membranes presented thickness around 120 μm.

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3 RESULTS

The hybrid nanostructured polyelectrolytes were characterized by X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Infrared Spectroscopy (FTIR-ATR), Ethanol Uptake, Pervaporation, Scanning Electron Microscopy (SEM) and Electrochemical Impedance Spectroscopy (EIS). By infrared spectroscopy was possible to observe that PEEK was sulfonated and possibly occurred TiO_2 incorporation, mainly due to assignments suppression of SPEEK characteristic bands. TGA thermographs of nanocomposite polymer membranes showed an increase of first degradation temperature with increasing of TiO_2 amount (associated to SO_3H groups). This increase suggests that the TiO_2 was incorporated and interacted with SPEEK sulfonic domains. Ethanol uptake and ethanol pervaporation results corroborated with previous observations. Proton-conductivity measurements showed values above 0.1 $S.cm^{-1}$ and the best conductivity was 0.172 $S.cm^{-1}$ in ethanol solution at 80 °C.

4 CONCLUSIONS

The membranes structure based on SPEEK is strongly affected by the nature of the solvent and incorporation of an inorganic oxide in SPEEK polymer. The size of the SO_3H-rich primary nanodomains (ionic clusters), the connectivity between domains, the interdomain distance and the size of the possible aggregates strongly depends on the membranes chemical composition and are directly correlated to membranes performance. This study shows that is possible to optimize future membranes base don SPEEK for direct ethanol fuel cells applications (DEFC) by material structure control at nanometer scale, and chemical additives incorporation of adequate polarity and hidrophilicity.

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