New Proton-Conducting PVA/Clay/Ionic Liquid Nanocomposite Membranes for Anhydrous Fuel Cells

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Key words: Nanocomposite, PVA, montmorilonitte, protic ionic liquid.

Summary. *Proton-conducting nanocomposite membranes based on poly(vinyl alcohol) (PVA), acid montmorilonitte (MMT-H^+) and the protic ionic liquid (PIL) diethylmethylammonium trifluoromethanesulfonate ([Dema][TfOH]) were prepared. The [Dema][TfOH] incorporation effect on membrane properties such as proton conductivity was investigated. The structural features of nanocomposite membranes were studied by Small angle X-ray scattering (SAXS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) and correlated to the membranes properties.*

1 INTRODUCTION

The possible shortage of non-renewable resources associated to the reinless consumption of fossil fuels has been forcing the introduction of alternative energy conversion devices, such as fuel cells, for a variety of mobile and stationary applications.

Therefore, 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. PEFCs usually apply water-swollen ion-exchange polymer membranes as proton conducting electrolytes at highly water-swollen state [1].

Aiming to reduce catalyst poisoning phenomena and improve the kinetics for fuel oxidation, several studies involving the use of protic ionic liquids (PILs) instead of water at temperature higher than 100 °C have been performed [2].

On the other hand, PVA/Clay membranes exhibiting high proton conductivity together with high mechanical and thermal resistance at temperature larger than 130 °C have been recently obtained [3]. Furthermore, several recent researches reported the possibility of intercalating ionic liquids into the interlamellar voids of clays [4]. Aiming the obtention of new membranes exhibiting high performance for anhydrous fuel cells applications, the present work reports the preparation and study of polymer electrolyte membranes containing poly(vinyl alcohol) (PVA), MMT-H^+ clay and [Dema][TfOH] ionic liquid.

2 EXPERIMENTAL

Acid montmorilonitte MMT-H^+ was added to dimethyl sulfoxide (DMSO) under ultrasonic stirring at 60 ºC for 2 hours. Then, the solution was heated at 80 °C under magnetic stirring overnight. After that, fully hydrolyzed PVA was added to MMT/DMSO solution to prepare

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PVA/MMT/DMSO mixture by total dissolution at 80 ºC under magnetic stirring overnight either. Therefore, the mixture was cooled to room temperature and melamine fomaldehyde resin was added as crosslinking agent. After acidification with HCl, the membranes were prepared by solution casting method and presented thickness values around 120 µm.

3 RESULTS

The structure of hybrid polyelectrolytes was investigated by X-ray Diffraction (XRD), Small Angle X-ray Scattering (SAXS) and Scanning Electron Microscopy (SEM) whereas the ionic conductivity of the membranes was measured by Electrochemical Impedance Spectroscopy (EIS). XRD and SAXS measurements suggest an opposite structural behavior for membranes prepared with low or high clay contents: while the increase of PIL amount induces a better clay dispersion in 20:1 (PVA:MMT$^+$ ratio) samples leading to a less crystalline character of PVA, it promotes the presence of clay aggregates and consequently a more efficient PVA crystallization for the 50:1 (PVA:MMT$^+$ ratio) material. At high PIL content increasing the MMT-H$^+$ amount leads to an increase of the amorphous character of the membrane while the opposite is observed at low PIL content. The evolution of structural features of the membranes as a function of composition has been explained and strongly affects their proton conductivity which exhibits values above 10^{-3} S.cm^{-1} at temperatures higher than 100 °C.

4 CONCLUSIONS

The PVA/MMT-H$^+$/[Dema][TfOH] membranes structure is strongly influenced by the solvent nature and incorporation of an inorganic filler and a proton ionic liquid in PVA polymer. The size of the protic ionic liquid nanodomains (ionic clusters), the connectivity between domains, the interdomain distance and the size of the possible ionic liquid or clay aggregates strongly depends on the chemical composition of membranes and are directly correlated to membranes performance. This study shows the possibility to optimize future PVA-based membranes for applications in direct ethanol fuel cells (DEFC) by controlling the material structure at nanometer scale, through the incorporation of chemical additives of adequate polarity and hidrophilicity.

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