



Proton conducting sol–gel sulfonated membranes produced from 2-allylphenol, 3-glycidoxypropyl trimethoxysilane and tetraethyl orthosilicate

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ABSTRACT

An important research area in proton exchange membrane fuel cells (PEMFC) is devoted to the development of low cost membranes able to work at temperatures higher than 100 °C. In this work, homogeneous, transparent and crack-free hybrid membranes have been synthesized using tetraethyl orthosilicate (TEOS), 3-glycidoxypropyl trimethoxysilane (GPTMS) and 2-allylphenol (AP) as precursors. The synthesis of proton conducting membranes was performed by a post-sulfonation method using trimethylsilyl chlorosulfonate as a mild sulfonating agent. The water retention properties provided by sulfonate and hydroxyl groups and the high porosity leads to relatively high proton conductivity (maximum values around $1.3 \times 10^{-3} \text{ S cm}^{-1}$ at 140 °C and 100% RH) for membranes treated at 180 °C and sulfonated for 2 h.

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1. Introduction

The proton exchange membranes fuel cells (PEMFC) technology is receiving a great deal of attention last years because of their advantages over other type of fuel cells [1–3]. The PEMFCs are at present used at temperatures lower than 80 °C because the perfluorosulfonic acid membranes have to maintain a relative humidity (RH) close to 100%.

One of the important areas of research interest in PEMFC is the development of a low cost membrane for high temperature operation (100–150 °C), with little or null dependence on humidity [4,5] to improve energy conversion efficiency and to avoid CO poisoning of catalysts. Organic–inorganic hybrid materials are viewed as the next generation materials in many applications because they offer the possibility of combining the properties of two components in a unique material at molecular level, hence to develop functional materials with tuned properties [6]. New generation electrolytes must, in fact, meet several requirements: among them, most important are high proton conductivity, sufficient flexibility to make good contacts with electrodes and, at the same time, enough rigidity to support the membrane electrode assembly (MEA), high hydrolytic stability, and low permeability to fuels [7–9]. Modulation of the

properties of the final materials can be achieved by suitable rate of the inorganic and organic components.

Sulfonation is a powerful and versatile process, frequently used for polymer modification to improve hydrophilicity and other membrane properties such as higher water flux, permeability and proton conductivity at the same time [10]. Generally, there are two methods to introduce the sulfonate groups onto polymer chain: post-sulfonation of polymer and direct copolymerization with sulfonated monomers. In the former method, the sulfonate groups can be easily attached onto polymer chains by using appropriate sulfonate agents [11]. Since sulfonation is an aromatic electrophilic substitution reaction (SE_{ar}), electro-donating substituents favour the reaction whereas electron-withdrawing groups do not. 2-allylphenol (AP) is easy to sulfonate because hydroxyl groups activate aromatic ring for electrophilic substitution in ortho- and para-positions, whereas the allyl group activates meta-positions. Sulfonation of AP has been conducted in heterogeneous media with different sulfonation agents, HClSO_3 and $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ in CH_2Cl_2 . HClSO_3 was chosen due to its simplicity, adaptability and reactivity; however, cross-linking and degradation side reactions sometimes happen and sulfonation degree is difficult to control [12]. During the sulfonation reaction, it is possible to affect or even destroy completely the bead morphology due to the action of sulfonating agent and reaction conditions. Trimethylsilyl chlorosulfonate does not usually induce chain cleavage, even at high sulfonation degree, but its efficiency is lower than HClSO_3 .

In this study, we prepared novel organic–inorganic hybrid membranes using a combination of sol–gel route and organic

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