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Sulfonic acid-functionalized hybrid organic–inorganic proton exchange membranes synthesized by sol–gel using 3-mercaptopropyl trimethoxysilane (MPTMS)

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HIGHLIGHTS

- Sulfonic acid-functionalized hybrid membrane using MPTMS were successfully obtained.
- Hybrid membranes are thermally stable up to 350 °C.
- SH groups are mostly oxidized to SO_3^-.
- Proton conductivity increases with SO_3^- groups (0.097 S cm^{-1}, 120 °C).
- Methanol permeability is much lower than Nafion® 117.

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ABSTRACT

Organic/inorganic hybrid membranes based on (3-glycidoxypropyl) trimethoxysilane (GPTMS) and 3-mercaptopropyl trimethoxysilane (MPTMS) have been prepared by sol–gel method and organic polymerisation, as candidate materials for proton exchange membranes in direct alcohol fuel cell (DMFC) applications. The –SH groups of MPTMS are oxidized to sulfonic acid groups, which are attributed to enhance the proton conductivity of hybrid membranes. FTIR, XPS and contact angle were used to characterize and confirm the hybrid structure and oxidation reaction progress. Membranes characterization also includes ion exchange capacity, water uptake, methanol permeability and proton conductivity to confirm their applicability in fuel cells. All the membranes were homogeneous and thermally and chemically resistant. In particular, the hybrid membranes demonstrated proton conductivities as high as 0.16 S cm^{-1} at high temperature, while exhibiting a low methanol permeability as compared to Nafion®. These results are associated with proton conducting paths through the silica pseudo-PEO network in which sulfonic acid groups work as proton donor.

1. Introduction

Direct methanol fuel cells (DMFC) are extensively investigated for use in portable and distributed electrical power generation because of the high cell efficiencies. The high volumetric and specific energy density of methanol, low CO_2 emissions, easy refill options and extended life-times between refills of DMFC system offer several advantages over existing battery technology. The use of methanol as fuel also offers several advantages over the use of hydrogen, the existing infrastructure can be easily adapted to accommodate methanol, and safety concerns over hydrogen storage are removed. Commercialisation of DMFC systems has been hindered somewhat by the slow rate of methanol oxidation at the anode catalyst sites, the cost of the polymer electrolyte membrane and the methanol crossover through the membrane. DuPont Nafion® is the most widely utilized proton exchange membrane (PEM) for DMFC applications because of the excellent mechanical properties and high proton conductivity when is fully hydrated [1]. However, methanol diffusion through a Nafion membrane is high in comparison with other PEM materials, but alternative materials do not exhibit proton conductivity comparable to that of Nafion [2]. The incorporation of methanol blocking materials into the water channels of Nafion decreases methanol permeation. Thus, fuel cell

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performance is improved because methanol moves through a tortuous pathway to reach the cathode, while protons use alternative fast pathways created by the proton conducting material [3]. The appearance of nanometre pinholes at the interface between the organic and inorganic components also facilitates methanol transport [4,5]. In an attempt to overcome this problem, alternative materials such as sulfonated polymers were developed [6–8]. They present excellent mechanical and thermal stabilities and high conductivity but only at high degree of sulfonation. Increasing the degree of sulfonation enhances the conductivity of the membrane, but also increases methanol permeability and deteriorates the mechanical properties due to a large hydrophilicity of the membrane [9]. Crosslinking is a powerful and simple method to suppress the methanol crossover and water swelling of PEMs. However, in most of the cases, proton conductivity decreases significantly due to diminishing the free protons of conductive materials. Another approach to reduce methanol crossover is the development of hybrid organic–inorganic materials with covalent bond between components, using the sol–gel method [10–14]. Incorporation of inorganic components in a nanometre size has several attributes of interest, including decreased membrane swelling, reduced permeability towards methanol and improved morphological stability without compromising the proton conductivity at high sulfonation degree [15–17]. Our group has synthesized several hybrid membranes via direct polycondensation of alkoxides and alkylalkoxides with monomers, further using sulfonation processes to provide high proton conductivity [18–22]. Generally, sulfonation is a strong process able to produce side reactions including crosslinking and cleavage of the polymer chains still at low degree of sulfonation. The sulfonation of these membranes make them swollable in aqueous solutions and even soluble in aqueous methanol solutions at high sulfonation degree. Moreover, it is necessary a multiple-step synthesis: formation of the hybrid network through sol–gel and organic polymerization, consolidation of the hybrid material with a thermal treatment and, further sulfonation of the material. In this paper, the main objective was to develop an alternative sulfonation route using a direct synthesis to generate hydrophilic surfaces by using mercapto-functionalized silica. Several studies have reported that the introduction of silica-based inorganic components derived from (3-mercapto-propyl) trimethoxysilane (MPTMS) generate homogeneous nanocomposite membranes with enhanced physicochemical stability and performance [23–28]. Many silane monomers were incorporated to hybrid materials showing good proton conductivity and greatly decreased methanol permeability [26,29,30]. Glass hybrid membranes based on TEOS-GPTMS-MPTMS were reported, filtering the sol into a fibre glass matrix in order to obtained free standing membranes that then were calcined up to225 °C, getting a glass material. Conversion of thiol groups to sulfonic acid have been detailed, obtaining a balance between proton conductivity and methanol permeability [26]. H. Lin and coworkers [10] reported a crosslinked hybrid material based on MPTMS precursor and a polymer with a carboxyl group and sulfonic acid groups (SPAEK) that allows high proton conductivity and low methanol permeability. Y.-I. Park [25] also reported high proton conducting GPTMS-MPTMS hybrid membranes with enhancing chemical stability comparing with previously works that used heteropolyacids as proton source [31,32]. However, the sulfonation degree analyses as a function of oxidation time, methanol permeability and long-term stability test have not been reported. Here, we report chemically stable MPTMS-GPTMS hybrid materials with high concentration of sulfonic acid groups firmly bonded to the hybrid structure. GPTMS was used as hybrid precursor bridging the inorganic and organic components. On one hand, organic polymerization generates PEO (polyethylene oxide) crosslinked chains that provide flexibility and proton conducting paths. On the other hand, the network can co-condensate with the silica part of MPTMS, producing stable Si–O–Si bonding. GMPTS could provide low methanol permeability because generates a crosslinked hybrid network at molecular level. MPTMS was used to provide stable proton conducting paths to the hybrid network. MPTMS contains thiol groups, a stable propyl spacer and a hydrolysable $Si(OCH_3)_3$ moiety susceptible to copolymerize with Si branches of GPTMS. The thiol groups of MPTMS were *in situ* oxidized to sulfonic acid groups by mild oxidation with hydrogen peroxide under acidic conditions. The inorganic network can enhance the chemical and dimensional stabilities, and also the proton conductivity based on a high concentration of hydroxyl groups and its water sorption capability. An illustration of a possible hybrid structure can be observed in Fig. 1, showing the sulfonic acid groups grafted to the hybrid structure and the movement of protons jumping from one hoping site to another. It was expected that a high proton conductivity would be afforded by the addition of the sulfonic acid groups while low methanol permeability and durability would result from the combination of crosslinking and covalent bonds of hybrid components. The water absorption, ion exchange capacity and proton conductivity of hybrid membranes with different degrees of sulfonation have been studied in detail.

2. Experimental

2.1. Materials

Mercaptopropyl trimethoxysilane from Aldrich and 3-glycidoxipropyl trimetoxysilane from ABCR, were used as precursors. Molar ratios of MPTMS/GPTMS 60/40 and 70/30 were used. Ethanol was used as a solvent (Aldrich) and *hydrochloric acid* (Aldrich) as catalyst of sol–gel reaction.

2.2. Synthesis

The sols were prepared by mixing two solutions. Solution A was prepared by mixing MPTMS, half amount of absolute ethanol (molar ratio of ethanol/(MPTMS + GPTMS) = 4) and half amount of H_2O (HCl 0.5 N) (molar ratio of water/(MPTMS + GPTMS) = 3), stirring at room temperature for 2 h. Solution B was prepared by stirring at room temperature for 2 h a mixture of GPTMS, half amount of absolute ethanol and acidulated water. Both solutions were mixed and stirred at room temperature for another 60 min. Sols were cast in polytetrafluoroethylene moulds and left at 50 °C for obtaining homogeneous gels through organic polymerisation of GPTMS, and simultaneous sol–gel reactions of GPTMS and MPTMS. Dried hybrid membranes were peeled off from the moulds and were additionally treated at 150 °C (heating rate 0.1 $°C\ min^{-1}$) in air for 24 h to complete the drying and curing processes. Then, the crosslinked hybrid membranes were placed in a 10% hydrogen peroxide solution at 50 °C for different times (2, 4, 6, 8, 24 and 30 h) after oxidation treatment; the hybrid membranes were washed with water. The wet material was immersed again in acidified H_2O (H_2SO_4, 0.1 M) for another 4 h. Finally, the materials were extensively washed with H_2O and dried in vacuum at 60 °C for 24 h.

2.3. Analytical methods

The fracture surface of the membranes was examined with a HITACHI S-4700 field emission scanning electron microscope (FE-SEM). Elemental analysis by EDX (NORAN system six) was used to study the distribution of elements across the membrane thickness. Thermal stability of the membranes dried at 150 °C was studied by Thermogravimetric and Differential Thermal Analysis (TGA- DTA)