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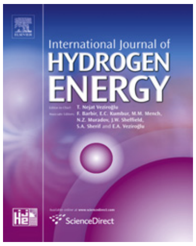

Inorganic–organic membranes based on Nafion, $[(ZrO_2)\cdot(HfO_2)_{0.25}]$ and $[(SiO_2)\cdot(HfO_2)_{0.28}]$ nanoparticles. Part II: Relaxations and conductivity mechanism

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ABSTRACT

Two classes of hybrid inorganic–organic proton-conducting membranes consisting of Nafion and either $[(ZrO_2)\cdot(HfO_2)_{0.25}]$ or $[(SiO_2)\cdot(HfO_2)_{0.28}]$ nanofiller are investigated to elucidate their relaxations and conductivity mechanism and are labeled $[\text{Nafion}/(\text{ZrHf})_x]$ and $[\text{Nafion}/(\text{SiHf})_x]$, respectively. The membranes are studied by dynamic mechanic analysis (DMA) and broadband electric spectroscopy (BES). The latter technique allows a determination of the direct current ionic conductivity (σ_{DC}) and the proton diffusion coefficient (D_{H^+}). Pulse-field-gradient spin-echo nuclear magnetic resonance experiments (PFGSE-NMR) are carried out to determine the water self-diffusion coefficients (D_{H_2O}). D_{H^+} and D_{H_2O} are correlated to obtain insight on the conductivity mechanism of the proposed materials. Results indicate that the nanofiller particles play a major role in the proton conduction mechanism of the proposed materials. It is demonstrated that the basic $[(ZrO_2)\cdot(HfO_2)_{0.25}]$ nanoparticles form Nafion–nanofiller dynamic cross-links with high ionic character. These cross-links improve the mechanical properties and enhance the overall proton conductivity of the membranes at low humidification levels owing to an efficient delocalization of the protons. In $[\text{Nafion}/(\text{SiHf})_x]$ membranes, the dynamic cross-links occur due to dipole–dipole interactions between the side groups of the Nafion host polymer and the quasi-neutral $[(SiO_2)\cdot(HfO_2)_{0.28}]$ nanoparticles. These cross-links significantly reduce the delocalization of the protons, which decreases the overall conductivity of materials.

1. Introduction

During the last decades, investigations in the field of polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) were focused on improving the efficiency of electrode materials and increasing the performance of proton-conducting materials [1–7]. Desirable properties of polymer electrolyte membranes are [4–9]: (a) chemical and electrochemical stability in the operating system; (b) mechanical strength and stability under operating conditions;

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(c) chemical properties of compounds that are compatible with the bonding requirements of the membrane electrode assembly (MEA); (d) extremely low permeability to the reactant species; (e) high electrolyte transport to maintain uniform electrolyte contact and prevent localized drying; (f) high proton conductivity to sustain large current densities with minimal resistive loss and no electronic conductivity; and (g) low production costs compatible with application. Nafion®, whose primary structure consists of acid-tipped side chains dangling from a perfluorinated backbone, is currently the reference among proton-conducting materials even though several other systems including hydrocarbon- or siloxanic-based materials have been examined [1–11].[2] Nevertheless, Nafion is not exempt from drawbacks, which include: (a) the decrease of conductivity due to dehydration; (b) methanol crossover; and (c) high cost [1–9]. Inorganic–organic composite membranes based on Nafion and inorganic fillers with micrometric to nanometric sizes have been intensively studied. These studies demonstrate that inorganic–organic composite membranes are one of the most interesting routes to prepare promising electrolytes for application in fuel cells [12–28]. Therefore, significant efforts have been directed toward the synthesis of Nafion membranes doped with: (a) heteropolyacids, such as silicotungstic acid, phosphotungstic acid, molybdophosphoric acid and others; (b) SiO_2, zirconium phosphate, aerosil-SiO_2; (c) organically modified silicates and silane-based fillers; (d) zeolites; and (e) Pt, Pt–SiO_2 and Pt–TiO_2 [12–25]. The effect of the surface acid–base properties of SiO_2 and Al_2O_3 inorganic fillers on Nafion-based composite membranes was investigated by pulse-field-gradient spin-echo nuclear magnetic resonance (PFGSE-NMR) and demonstrated that acid-silica filler appears to promote proton transport more than basic alumina in the membrane [29,30]. Nevertheless, until now the influence of the chemical and physical properties of inorganic fillers on the structure of composite proton-conducting polymer electrolytes is not well understood. In-depth investigations were conducted on Nafion-based composite membranes with varying compositions of both membranes and nanofillers to elucidate the effect of Nafion–nanofiller interactions on the membrane properties [31–38]. In one of these reports, the effect of nanofillers on the structure and properties of $[\mathrm{Nafion}/(M_xO_y)_n]$ hybrid membranes was described [26]. Particularly interesting properties were exhibited by $[\mathrm{Nafion}/(HfO_2)_n]$ membranes, which were consequently the subject of a more detailed vibrational study [33]. However, the use of bulk hafnium oxide as a membrane filler means application in fuel cells is unfeasible due to its very high cost. In a subsequent paper, a procedure was developed which allowed the preparation of bi-component metal-oxide fillers consisting of a hard oxide "core" and soft oxide "shell" [34]. The procedure was utilized to prepare "core–shell" nanofillers characterized by either a HfO_2 "shell" or "core" with the expectation that the resulting material would have properties similar to bulk hafnium oxide, but with a considerably lower hafnium loading. In the first part of this work, two fillers with formulas $[(SiO_2)\cdot(HfO_2)_{0.28}]$ and $[(ZrO_2)\cdot(HfO_2)_{0.25}]$ were prepared and are labeled SiHf and ZrHf, respectively [39]. These fillers have "cores" consisting of either HfO_2 or ZrO_2. ZrHf and SiHf are A and B-type "core–shell" nanofillers, respectively [39]. A-type "core–shell" nanofillers consist of a "core" with a higher Mohs hardness index or a higher crystallinity that is chemically covered by a "shell" of a softer material characterized by a lower Mohs hardness. The chemical-bonding interaction of the shell with the core material occurs when the two materials have compatible crystal structures and chemical behavior. B-type "core–shell" structures exist when there is the simple adhesion of the soft phase, which has a low Mohs hardness or less crystalline nanoparticles, to the surface of nanoparticles characterized high Mohs hardness to form a physically-interacting shell. This physical interaction is expected when the two materials forming the "core–shell" have very different and incompatible crystal structures. Two series of hybrid membranes, labeled $[\mathrm{Nafion}/(\mathrm{SiHf})_x]$ and $[\mathrm{Nafion}/(\mathrm{ZrHf})_x]$, were prepared and their performance in single fuel cells under operative conditions was extensively studied [39]. It was observed that the chemical properties of the two nanofillers, such as basicity, significantly influenced the overall properties of the hybrid membranes. The more basic nanofiller ZrHf induced an improvement of the fuel cell performance, especially at a low degree of humidification. In contrast, the somewhat neutral SiHf nanofiller caused a reduction in the power density output under all the examined operating conditions. In this report, the two classes of hybrid inorganic–organic proton-conducting membranes $[\mathrm{Nafion}/(\mathrm{ZrHf})_x]$ and $[\mathrm{Nafion}/(\mathrm{SiHf})_x]$, are investigated to elucidate the mechanical and electrical relaxations and the conductivity mechanism. The membranes are studied by dynamic mechanical analysis (DMA), broadband electric spectroscopy (BES) and pulse-field-gradient spin-echo nuclear magnetic resonance (PFGSE-NMR).

2. Experimental section

2.1. Materials

$[\mathrm{Nafion}/(\mathrm{SiHf})_x]$ and $[\mathrm{Nafion}/(\mathrm{ZrHf})_x]$ hybrid membranes with a nanofiller mass fraction x ranging from 0 to 0.15 were prepared as described elsewhere [39]. Reagents and solvents were supplied by Aldrich and further purified by standard methods [40].

2.2. Instruments and methods

Dynamic mechanical analysis (DMA) were carried out with a TA Instruments DMA Q800 instrument using the film/fibre tension clamp. The temperature spectra were measured by subjecting a rectangular dry film sample of ca. 25 (height) × 6 (width) × 0.15 mm (thickness) to an oscillatory sinusoidal tensile deformation at 1 Hz with an amplitude of 4 μm (0.05 N preload force). The measurements are carried out in the temperature range between −10 and 210 °C at a rate of 4 °C min^{-1}. The samples were dried for 24 h in dry air before the measurements. The mechanical response of the materials is analyzed in terms of the elastic (storage) (E') and the viscous

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