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Novel Nafion–zirconium phosphate nanocomposite membranes with enhanced stability of proton conductivity at medium temperature and high relative humidity

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Abstract

In order to increase the stability of Nafion conductivity at temperatures higher than 100 °C, composite membranes made of recast Nafion filled with different percentages of zirconium phosphate (ZrP) were investigated. The membrane preparation was carried out by a simple synthetic procedure based on the use of solutions of ZrP precursors in dimethylformamide. The formation of insoluble α-type ZrP nanoparticles within the Nafion matrix was proved by ^{31}P-MAS NMR and X-ray diffractometry. The membranes were characterized by TEM microscopy, ion-exchange capacity determinations, static stress–strain mechanical tests and conductivity measurements as a function of filler loading, at controlled relative humidity (r.h.) and temperature. An increasing filler loading results in enhanced membrane stiffness and in lower conductivity compared with pure recast Nafion. At 90% r.h. and 100 °C, the conductivity decreases from ≈0.07 S cm^{-1} for pure Nafion to ≈0.03 S cm^{-1} for the composite membrane containing 25 wt.% ZrP. Systematic conductivity measurements as a function of r.h. and temperature were carried out to draw a stability map for the conductivity of pure recast Nafion and of a composite membrane filled with 10 wt.% ZrP. These maps provide for each r.h. value the maximum temperature at which the conductivity remains stable for at least 150 h. The effect of zirconium phosphate is to increase the stability of conductivity at high temperature, with a gain up to 20 °C. This stability enhancement has been ascribed to the higher stiffness of the composite membrane.

Keywords: Nanocomposite membrane; Proton conductivity; Medium temperature; Nafion; Zirconium phosphate

1. Introduction

Perfluorosulfonic acid (PFSA) membranes (e.g. Nafion) are the most used polyelectrolytes in polymer electrolyte membrane fuel cells (PEM FCs) [1–5]. These membranes exhibit excellent properties up to about 90 °C in terms of proton conductivity, mechanical stability and chemical inertia, but show high permeability towards hydrogenated fuels such as methanol. Moreover, the conductivity of PFSA membranes at low relative humidity (r.h.) is not sufficient for fuel cell applications requiring high current densities, while at temperature above 100 °C and r.h. close to 100% the anisotropic membrane swelling, occurring when the membrane is pressed between the electrodes, provokes an irreversible conductivity decay [6,7].

The possibility to modify physical and chemical properties of a polymer by dispersing inorganic nanoparticles in the polymeric matrix [8–11] encouraged the development of proton conducting composite membranes suitable for PEM FCs working at temperatures above 100 °C [12,13].

Layered zirconium phosphate ($Zr(O_3POH)_2$, hereafter ZrP) [14–33] and phosphonates [14,34–40] were already used as fillers of proton conducting polymeric membranes because they are proton conductors with good chemical and thermal stability. Under the most favourable conditions, their conductivity is ~10^{-2} S cm^{-1} for high surface ZrP [30,41] and ~10^{-1} S cm^{-1} for zirconium phosphate sulfophenylenphosphonates [35,42]. The presence of ZrP nanoparticles improves the Nafion mechanical properties [23,33] and the fuel cell per-

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formances at temperatures above 100 °C [15,17,19,22,24,30], while reducing methanol cross-over [23,30].

Three main synthetic procedures were used to insert zirconium phosphate and zirconium phosphonates in ionomeric and polymeric matrices. The first method is based on the dispersion of pre-formed filler particles in the polymer solution [20,43]. The second procedure (hereafter called the "exchange method"), developed by Grot and Rajendran [44] for cation exchange membranes, consists of two-steps: first, the cations of the ionomer are exchanged with zirconium cationic species, and then the membrane is treated with phosphoric acid in order to precipitate zirconium phosphate within the hydrophilic regions of the ionomer.

A third approach (hereafter the "precursor solution" method) was discovered in our laboratory [29,38] and is based on the experimental observation that soluble precursors of ZrP and zirconium phosphonates can be formed in proton acceptor organic solvents. These soluble precursors are transformed into the final zirconium salts just by heating to dryness at 100–130 °C. As a consequence, a composite membrane can be easily obtained by casting a mixture of the polymer solution and the precursor solution, in the same solvent, followed by solvent evaporation.

In the present work, the precursor solution method was successfully used to prepare Nafion membranes loaded with ZrP nanoparticles. These membranes were characterized by electron microscopy, solid state NMR, X-ray diffraction, thermal analysis and determinations of the ion-exchange capacity (iec). Conductivity measurements, as a function of r.h. and temperature, and static stress–strain mechanical tests were performed on samples with ZrP loading up to 30 wt.%. Attention was focused on the ability of the filler to increase the dimensional stability of the membrane and to shift the threshold of the irreversible conductivity decay, mentioned above, to higher temperature and r.h. values.

2. Experimental

2.1. Chemicals

Zirconyl propionate ($ZrO_{1.27}(C_2H_5COO)_{1.46}$, MW = 218 Da) was supplied by Magnesium Elektron Ltd., England. Ortho Phosphoric Acid (99%) was supplied by Fluka. The Nafion dispersion (EW = 1100, 20 wt.% in a mixture of aliphatic alcohols and water) and all other reagents were supplied by Aldrich. The concentration of the Nafion dispersion was accurately determined by potentiometric titration with 0.1 M NaOH.

2.2. Solution of ZrP precursors in dimethylformamide (DMF)

A solution of ZrP precursors in DMF was prepared according to Ref. [29]. Specifically, 0.10 g of zirconyl propionate were dissolved in 4.3 ml of DMF. Separately, 0.18 g of phosphoric acid were dissolved in 4.3 ml of DMF. The first solution was added to the second one under stirring at room temperature, thus obtaining a clear solution (P/Zr = 4, [Zr] ≈ 0.05 M).

2.3. Preparation of Nafion/ZrP composite membranes

Recast Nafion membranes filled with ZrP were prepared according to Ref. [29]. Typically, 5 g of the commercial Nafion dispersion were concentrated at 80 °C so as to reduce the volume by 90%. About 10 ml of DMF were added to the remaining solution and the volume was reduced again. The procedure was repeated several times in order to assure the complete removal of water and alcohols. The final dispersion contained about 15 wt.% Nafion in DMF. A weighed amount of the ZrP solution in DMF was added to the Nafion dispersion in the same solvent so that the ratio (R) between the Zr moles and the Nafion equivalents was in the range 0.2–1.7. The mixture was held under stirring at room temperature for about 15 min and cast on a Petri dish. The solvent was evaporated at 100 °C overnight. Transparent membranes were obtained for $R \leq 1$. The samples were then equilibrated with a 1 M NaCl solution at 80 °C for 4 h to exchange sodium ions for protons, rinsed in water at room temperature and then heated at 140 °C for 4 h. The replacement of H^+ with Na^+ is expected to make the membrane more resistant to the thermal treatment at 140 °C. Finally, the membranes underwent the following standard treatment: 1 h in boiling 3% H_2O_2, 1 h in boiling 0.5 M H_2SO_4, 1 h in boiling H_2O, 3 washings with H_2O followed by drying in air.

The same conditions were also used to prepare pure recast Nafion membranes.

2.4. Techniques

X-ray patterns of powders and membranes were collected with a Philips X-Pert PW 3710 powder diffractometer using the Cu Kα radiation source.

Thermogravimetric determinations were carried out by a NETZSCH STA 449 Jupiter thermal analyser connected to a NETZSCH TASC 414/3 A controller at a heating rate of 10 °C min^{-1}, with an air flow of about 30 ml min^{-1}.

Titration curves of solids and membranes were obtained by a Radiometer automatic titrimeter (TIM900 Titrilab and ABU91 Burette) operating at the equilibrium point method. Before titrations, the membranes were heated at 140 °C for 1 h in order to eliminate water and to determine the weight of the anhydrous sample. The dry membranes were equilibrated overnight, at 80 °C, with a 1:1 (v/v) water/ethanol solution containing 1 M NaCl in order to exchange Na^+ ions for the membrane protons. The solutions were then titrated under stirring with 0.1 M NaOH without removing the membranes.

Solid state ^{31}P-MAS NMR spectra were performed at 81.08 MHz on a Bruker ASX-200 spectrometer. The spin rate was 8 kHz. The $\pi/2$ pulse width was 3.5 μs, and the recycle delay was 140 s; 1200 scans were collected for each spectrum. Powdered samples were packed into 4 mm zirconia rotors and sealed with Kel-F caps. Spectra were acquired using 1024 data points in the time domain, zero filled and Fourier transformed. The chemical shift was externally referred to H_3PO_4 85%.

TEM analysis was carried out by an HRTEM JEOL, JEM-2010 high-resolution transmission microscope.