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Inorganic membranes based on zirconium phosphate for fuel cells

Received: 13 January 2003 / Accepted: 2 June 2003 / Published online: 17 July 2004
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Abstract In this paper we report on zirconium phosphate based inorganic membrane preparation and electrochemical characterization. The zirconium oxide microporous membranes were impregnated with colloidal particles of zirconium phosphate and were designed for application in direct methanol fuel cells. Scanning electron microscopy, thermogravimetry and impedance spectroscopy was used for membrane characterization.

Keywords Direct methanol fuel cells · Inorganic membranes · Zirconium phosphate

Introduction

The direct methanol fuel cell (DMFC) is a technology which is receiving attention because it has specific advantages over hydrogen based fuel cell systems. A liquid-feed proton exchange membrane fuel cell (PEMFC) would be more suitable for fuel cells in cars and portable applications due to the simplified handling and increased energy density. At present, almost exclusively perfluorosulphonic membranes (as DuPont Nafion) are used in a PEMFC. Nafion is permeable to methanol transport, thereby reducing fuel cell efficiency. Several researchers have attempted to use modified perfluorosulphonic membranes [1, 2, 3, 4]. However, general opinion is that a membrane without fluorine chemistry, and with higher operating temperatures, higher mechanical strength at lower thickness and a smaller resistance would be useful [5]. New synthetic routes have been developed for hybrid polymer membranes–organic/

inorganic nanocomposites [6, 7] or membranes, which were impregnated with acidic electrolytes [3, 8]. Polysulphone and microglass fibres impregnated with various inorganic acids or Nafion were investigated by Haufe and Stimming [9]. Among other composites, thermostable polymers mixed with phosphoric acid [10], ionomers loaded with an acidic inorganic filler [11] or poly(tetrafluoroethylene) supported materials [12] were tested. In the case of liquid electrolytes the leakage is a problem and additional sealing is necessary. High cost of the membranes, especially Nafion, is limiting for large scale application.

An alternative is to use both inorganic substrate and inorganic filler. It could offer mechanical and chemical stability at higher temperature as well as a moderate cost. Application of fibre substrates could increase the mechanical strength of the membrane. Zirconium phosphate (ZP) could be the material of choice as a filler for large scale applications due to its stability in a hydrogen–oxygen atmosphere, low cost and low toxicity, potentially a very important factor for fuel cells, which are promoted as an environmentally friendly source of energy. For this reason it is not surprising that back in 1961 Dravnieks [13] proposed the application of zirconium phosphate in fuel cells. At the same time glass fibre membranes impregnated with zirconium phosphate were described by Alberti [14]. However, the conductivity and the temperature stability of membranes was not sufficient for fuel cell application. During the last decades the knowledge about electrolytes, the conductivity mechanisms and membrane technology has improved, which has encouraged development of new zirconium phosphate based materials. A composite Nafion–zirconium phosphate membrane exhibited good performance at operating temperatures up to 150 °C [15].

At the temperatures over 100 °C zirconium phosphate dehydrates and loses conductivity. However, temperature stability could be improved by composite forming [16]. Belyakov and Linkov [17] developed a method for membrane impregnation with a crystallized

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sol of zirconium oxide, subsequently treated with phosphoric acid to produce zirconium phosphate. This paper reports results of studying the membranes, which were prepared by Belyakov and Linkov method, using porous ZrO_2 substrate and by using different zirconium oxide particles.

Experimental

Membrane preparation

The ZrO_2 substrate membrane (Inoceramic, Gesellschaft für innovative Keramik mbH, Germany, thickness—1 mm, pore size—5 μm , pore volume—43%) was impregnated with zirconium phosphate as follows. (I) A sol of crystalline zirconium oxide and phosphoric acid was used, according to the method described in [17]. (II) A 5-wt.% water suspension of crystalline zirconium oxide nanoparticles (MarkeTech International Inc., particle size 60 nm) was used instead of sol.

The ZrO_2 membrane was repeatedly impregnated up to 15 times with the ZrO_2 sol or suspension and phosphoric acid. The membranes were immersed in a sol at room temperature. In order to remove any air from membrane pores, the sol and immersed membranes were heated to 98–99 $^{\circ}\text{C}$, then slowly cooled to room temperature and kept in the sol for 24 h. After drying at 90 $^{\circ}\text{C}$, sol-treated membranes were immersed in an 8% solution of phosphoric acid, heated to 95–97 $^{\circ}\text{C}$ and slowly cooled to a room temperature. After removal from the acid solution the membranes were thoroughly washed with distilled water and dried at 100–110 $^{\circ}\text{C}$. For taking conductivity measurements membranes were pre-conditioned at 25 $^{\circ}\text{C}$ for 24 h under ordinary conditions. Conductivity measurements were carried out after each impregnation.

Experimental technique

Impedance measurements of each membrane were conducted using an Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie, The Netherlands) in combination with the computer controlled frequency response analyser over the frequency range 0.1 Hz to 100 kHz according to the impedance technique. The membrane (5 cm^2) was pressed between two carbon gas diffusion layers (Lydall Inc., LyFlex Grade 484C), which were used as electrodes. A typical Cole–Cole plot consists of a semicircle (Fig. 1), which represents the electrode/membrane interface impedance (R2, C1). The volume resistance of membrane R1 (Fig. 1) was obtained by extrapolating to high frequencies using Autolab's software (linear regression analysis).

Thermogravimetric determinations were carried out in nitrogen using a simultaneous thermal analyser STA 1500 (CCI-3, Rheometric Scientific) at a heating rate of 5 $^{\circ}\text{C min}^{-1}$.

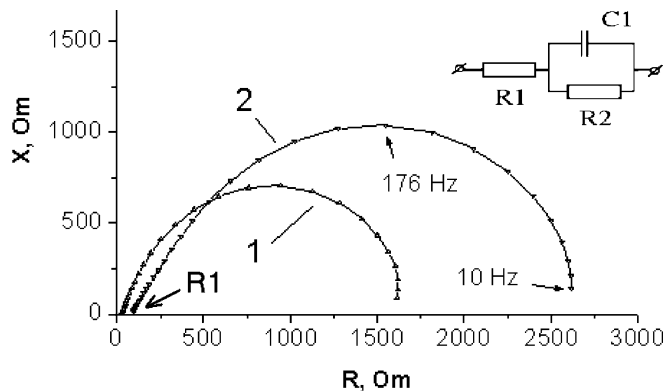


Fig. 1 Cole–Cole plots for membrane after third (1) and fourth (2) impregnation with zirconium phosphate from a ZrO_2 sol

Impregnated membranes were characterized with scanning electron microscopy (SEM). SEM images were obtained on a Hitachi x650 instrument (working resolution 6 nm, accelerating voltage 25 kV) attached to an energy-dispersive X-ray analyser system (EDAX) equipped with tungsten filament and CDU “LEAP” detector. The samples were prepared by breaking the membranes into small pieces, drying them for 24 h at 80 $^{\circ}\text{C}$ and coating with gold. Analyses were undertaken on a cross-section of the membrane.

Results and discussion

Nanocomposite preparation and characterisation

Preliminary investigation showed that at least five impregnations with zirconium phosphate are necessary to produce highly conductive hybrid membranes with low gas and methanol permeability. Figure 2 shows scanning electron micrographs of a zirconium oxide membrane incorporating ZP particles (Fig. 2b, c and d), and that of a non-modified zirconium oxide membrane for comparison (Fig. 2a). The picture is taken from the edge and represents the morphology inside membrane. Membranes, impregnated from sol (Fig. 2b), maintain the same morphology as substrate membranes (Fig. 2a). In the micrographs of the hybrid membrane, impregnated from the nanoparticle suspension (Fig. 2c and d), a homogenous distribution of ZP is observed. The presence of ZP on the pore surface was confirmed by EDAX analysis.

Figure 3 illustrates DSC results for membranes with different impregnation levels. Two endothermic peaks can be seen in the DSC (Fig. 3). The first broad peak at 50 $^{\circ}\text{C}$ is connected with the adsorbed water. The smaller endothermic peak, at temperatures over 150 $^{\circ}\text{C}$ and with an rise in the baseline after the peak, is related to the irreversible loss of absorbed water, probably from the interstitial layers of zirconium phosphate. The position of the second peak strongly depends on the structure of membrane. For samples impregnated

Fig. 2 SEM pictures of a ZrO_2 substrate membrane (taken from the edge) before impregnation (a), impregnated with zirconium phosphate from ZrO_2 sol (b) and impregnated from ZrO_2 nanoparticle suspension (c, d). The magnification is $980\times$ (a–c) and $5,000\times$ (d)

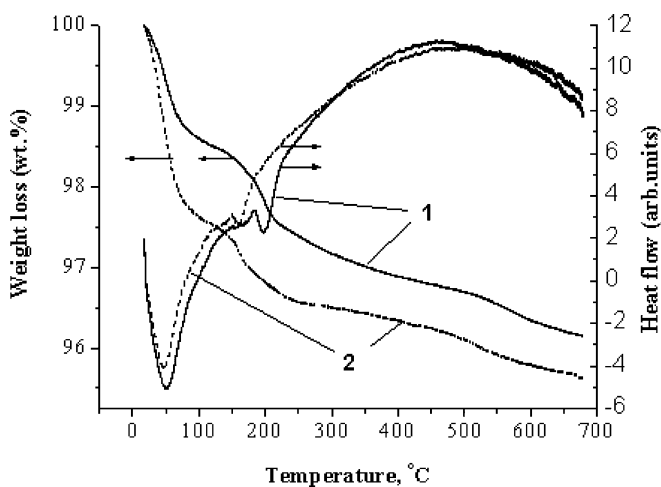
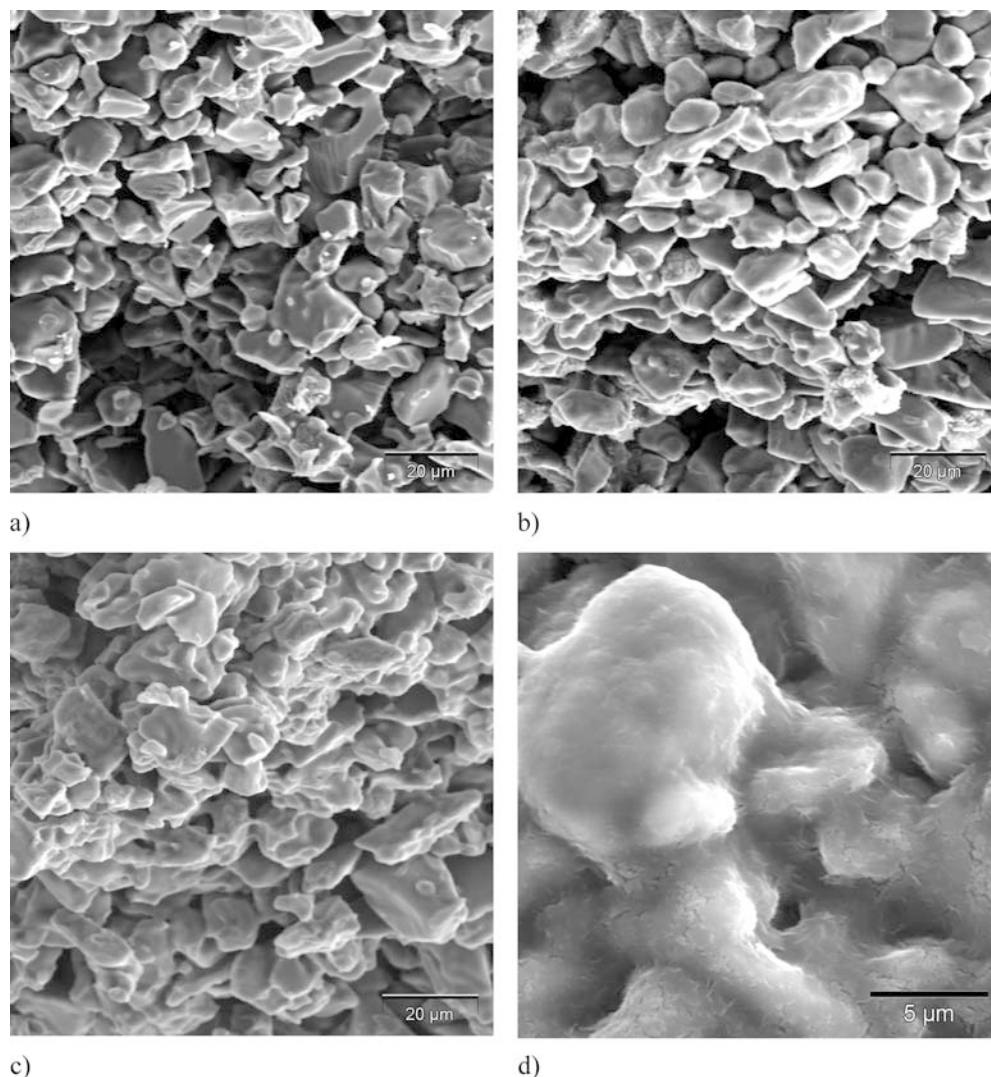


Fig. 3 DSC data for a ZrO_2 substrate membrane impregnated with zirconium phosphate from a ZrO_2 sol (curves 1) and from a ZrO_2 nanoparticle suspension (curves 2)

from the ZrO_2 sol (with morphology as in Fig. 2b), the second peak is observed at the rather higher temperature of 200°C . For samples impregnated from the ZrO_2 nanoparticle suspension (with a morphology identical to that in Fig. 2c), the peak shifts from 200°C to about 160°C . The water content is also different in both cases. Impregnation from the sol formed $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 2.7 \pm 0.2$), but $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n = 3.7 \pm 0.2$) was formed from the nanoparticle suspension. This is consistent with data reported by Vairavars [18] for a powdered zirconium phosphate under similar conditions. The water content of non-exfoliated zirconium phosphate was equal to $n = 3.7$, but after exfoliation by heat treatment or intercalation, it was decreased to $n = 2.9$. We suggest that in the case of the ZrO_2 nanoparticle suspension it was possible to form the layered structure of zirconium phosphate, which has a high capacity to keep water between planes. At the same time, impregnation from a sol forms particles which are similar to the exfoliated particles with a lower capacity to absorb water.

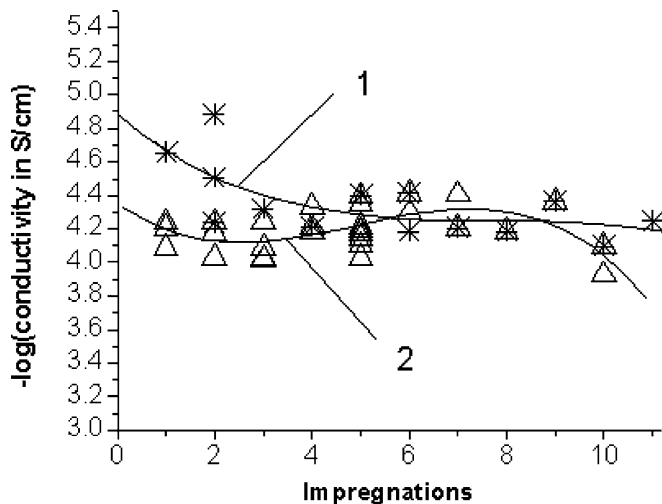


Fig. 4 Proton conductivity of zirconium phosphate/ ZrO_2 membranes impregnated with zirconium phosphate from a ZrO_2 sol (curve 1) (*) and a ZrO_2 nanoparticle suspension (curve 2) (Δ)

Conductivity measurements

Proton conductivity of 10^{-4} S/cm was observed after the first impregnations for the nanoparticle suspension, and further changes were negligible (Fig. 4). Few additional impregnations were needed for sol impregnation. After equilibrating at RH = 100%, the conductivity was increased by one order of magnitude due to the increase of the water content (Fig. 5).

The thermal stability of membranes was tested. During drying at 80°C the conductivity was decreased by one order of magnitude (Fig. 5). However, conductivity was restored after 20–30 min of exposure to air. Reversible water loss is important for practical application of the membrane in a fuel cell: water is released during the fuel cell performance and could provide a self-humidifying effect.

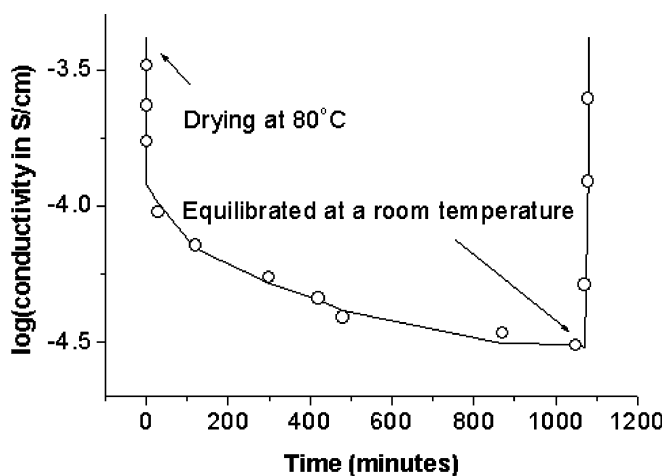


Fig. 5 Drying of the zirconium oxide/zirconium phosphate membrane impregnated from the ZrO_2 sol

Summary

The novel inorganic proton conducting membranes were prepared by impregnating an inorganic porous substrate with zirconium oxide particles and by subsequent phosphorization. Two different methods to impregnate the zirconium oxide membrane with a proton conducting zirconium phosphate were tested. Impregnation using a ZrO_2 nanoparticle suspension is more promising, because it allows the production of a high density structure, which is important in order to decrease the methanol cross-over. Membranes were tested in a direct methanol fuel cell setup and showed long term stability under methanol flow (for at least a few days). However, the cell resistance obtained for the Nafion based fuel cell is around 0.2Ω . To achieve the same cell resistance for a fully inorganic membrane the thickness should be decreased and proton conductivity improved. It is suggested that a membrane with a thickness of 200μ and a conductivity of 10^{-2} S/cm at room temperature might suffice.

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