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Zirconium Phosphate Based Inorganic Direct Methanol Fuel Cell

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A new nano structured and fully inorganic composite zirconium phosphate proton conducting material was synthesized by support impregnation with zirconium oxide suspensions or sols and subsequent phosphorization. The composite inorganic zirconium phosphate membranes prepared using the zirconium oxide suspension were found to give rise to high proton conductivity. The proton conductivity obtained was in the order of 10^{-2} S/cm at room temperature (RH = 100 %), which is comparable to Nafion proton conductivity. An inorganic membrane based direct methanol fuel cell was tested and efficiency equivalent to more than 50 % of the Nafion efficiency was obtained when using standard platinum catalyst inks.

Keywords: direct methanol fuel cell, zirconium phosphate, zirconium oxide nanoparticles, inorganic membrane.

INTRODUCTION

A fuel cell (FC) is an electrochemical device that generates electricity from chemical reactions. Most fuel cells use hydrogen as their fuel and release water as their only waste product. In 1978, Bragi Arnason, a professor of chemistry at the University of Iceland in Reykjavik, proposed that Iceland could be a "Hydrogen Society"- that is, a society entirely free from the use of fossil fuels - by the year 2030 – 40 [1 – 2]. The advantages of the hydrogen economy include: 1) the elimination of pollution caused by fossil fuels; 2) the elimination of greenhouse gases; 3) the elimination of economic dependence; 4) distributed production. In 2003, Daimler Chrysler, Norsk Hydro and Shell Hydrogen, entered into a joint venture with Vistorka (Eco Energy Ltd.), an Icelandic holding company, to create the Icelandic New Energy, which aims to research hydrogen FC technology. In three years, hydrogen powered private cars will reach the Icelandic market [3]. In 2015, the Icelandic government is scheduled to begin renewing the Icelandic fishing fleet using FC`s [3]. At this moment, the problem with putting pure-hydrogen vehicles on the road is the storage/transportation problem. FC users are concentrating on direct type FC`s that use fuels such as methanol since a liquid fuel is best transported and converted into energy from the liquid state.

Direct methanol fuel cells (DMFCs) utilize methanol, in gaseous or liquid form as a fuel. This allows for a substantial system simplification relative to reformate-based FC`s and it has a higher energy density than that is presently available with hydrogen-based systems. However, conventional DMFC`s suffer from methanol crossover due to the permeation of methanol through the polymer membrane [4]. The methanol that permeates through the membrane then typically reacts with the oxidant at the cathode, resulting in significant fuel inefficiency and reduced cell voltage at higher current, which causes a significant loss in overall cell efficiency. The reduction of methanol crossover has therefore received a lot of attention recently [5]. To reduce crossover, very dilute solutions of methanol are typically used as fuel streams. Recent accomplishments include the development of improved membranes with lower cross-over and with higher selectivity (ratio of conductivity to cross-over rate) [6 – 11]. An alternative is to use both inorganic substrate and inorganic filler instead of the traditional organic polymer membrane. Zirconium (IV) phosphate (denoted as ZP) or alfa-$Zr(HPO_4)_2 \cdot H_2O$ could be the material of choice as a filler for large scale applications due to its stability in a hydrogen/oxygen atmosphere, its low cost and low toxicity [12].

ZP has the ability to increase proton conductivity as a result of high proton mobility on the surface of ZP particles and it also has good water retention capabilities. In comparison, reduced methanol efficiencies and significant catalyst poisoning occur as a result of the high methanol permeability of commercially available Nafion, a perfluorosulfonate polymer and the current benchmark proton conducting membrane in DMFC applications. The composite approach has recently been used to obtain reduced methanol permeability of the Nafion membrane while maintaining high power density [4, 9, 12]. Yang et al. [4] have introduced ZP into Nafion through ion exchange of Zr^{4+} followed by the precipitation of ZP by treatment with phosphoric acid. A Pt/ZP/Nafion composite membrane showed improved water retention properties at increased cell temperatures [5 – 6]. The performance of FC`s with Pt-ZP membranes indicated that DMFC`s could be operated without a humidification subsystem. Work done by Jones and Roziere [8] demonstrated that hybrid inorganic-organic membranes could have lower methanol crossover than commercial perfluorinated membranes. Si et al. [9] investigated composite membranes comprised of

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Nafion-ZP. These membranes exhibited low resistance and methanol crossover at elevated temperature and at a low relative humidity. However, the amounts of ZP present in the membranes did not affect methanol crossover. This result is in contrast with the study reported by Grot [7]. This may be due to the different approaches used for preparing the composite membranes. Haufe and Stimming [10] used polysulfone and microglass fibre fleeces as microporous supports for electrolyte based composites. The membranes were prepared by impregnating the matrix with various inorganic acids (H_2SO_4) as well as with a Nafion solution. The surface of the composite had to be sealed in order to avoid leakage of sulfuric acid.

Another interesting property of metal (IV) phosphates is their ability to undergo infinite swelling in appropriate solvents, thus forming colloidal dispersions of delaminated layers. It was pointed out by Alberti et al. [11] that the transfer of the colloidal dispersion into a polymer solution should enable inorganic particles to be dispersed in the polymeric membrane. A variety of ZP based functionalized materials were recently surveyed by Clearfield et al. [13] and Pavlova et al. [14]. Szirtes et al. [15] have prepared transition metal containing alfa-ZP in order to improve the stability and proton conductivity of the material. Hyuk-nyun Kim et al. [16] reports a detailed study of the growth and characterization of films prepared from ZP and exfoliated ZP. Bedilo and Klabunde [17] synthesized high surface area (565 m^2/g) zirconium oxide aerogels.

The objective of the research undertaken by the research team from the University of the Western Cape was to develop a methanol FC prototype based upon an inorganic, zirconium phosphate proton conducting membrane suitable for full-scale application, with performance characteristics that exceed those of Nafion based methanol FC`s. In addition, high material cost and difficulties with water management in current fuel cells, was also to be addressed.

EXPERIMENTAL

New fully inorganic membranes based upon an elastic inorganic matrix, impregnated with zirconium phosphate were developed for application in a FC. The method for crack-free membrane production was developed in a way that allows upscaling of the membrane area. For laboratory applications the membrane area was limited to 100 cm^2, because production of larger areas would increase research costs.

Glass composite fibre supports (with a pore diameter of 240 nm) were used as a support or substrate membrane. Novel techniques for impregnating the substrate membrane with zirconium phosphate materials were developed using two different types of ZrO_2. The procedures were as follows:

I. A sol of crystalline zirconium oxide was prepared according to the method described in [18].

II. Water suspension (5 wt.%) of crystalline zirconium oxide nanoparticles

The ZrO_2 membranes were repeatedly impregnated (up to 5 times) with the ZrO_2 sol or suspension and then phosphorized. The membranes were immersed in a ZrO_2 sol or suspension at room temperature. In order to remove any air from the membrane pores, the sol and immersed membranes were heated up to 98 – 99 °C, then slowly cooled down to room temperature and kept in the sol for 24 hours. After drying at 90 °C, the sol-treated membranes were immersed in an 8 wt.% solution of phosphoric acid, heated to 95 – 97 °C and slowly cooled down to room temperature. After removal from the acid solution the membranes were thoroughly washed with distilled water and dried at 100 – 110 °C. Prior to determining the conductivity the membranes were pre-conditioned at 25 °C for 24 hrs under ambient conditions. Conductivity measurements were carried out after each impregnation.

A cell with a serpentine flow field was used to characterize the performance of the membrane. The following operational parameters were applied: anode (1 M methanol water solution, temperature 80 °C, flow rate between 2 – 20 ml/min), cell temperature 80 °C, atmospheric pressure for cathode and anode, cathode (air flow rate between 2 – 5 l/min). The electrodes were prepared by using a commercial *Johnson Matthey* carbon supported Pt catalyst for the cathode and Pt-Ru for the anode. The ink composition was: 0.125 g catalyst, 0.25 g Nafion (from 5 wt.% solution) and 3.45 g water. The mixture was stirred on a magnetic stirrer for 24 hours. The prepared catalytic ink was spray coated onto a carbon cloth and left overnight at room temperature to dry. The Membrane Electrode Assembly (MEA) was prepared by hot-pressing carbon cloth electrodes (Pt: 2 mg/cm^2) on the membrane at 140 °C for 2 minutes. An experimental set-up for the DMFC testing is shown in Figure 1.

Impedance measurements of each membrane were conducted using an *Autolab* potentiostat/galvanostat PGSTAT30 in combination with the computer controlled frequency response analyzer over a frequency range between 0.1 Hz and 100 kHz.

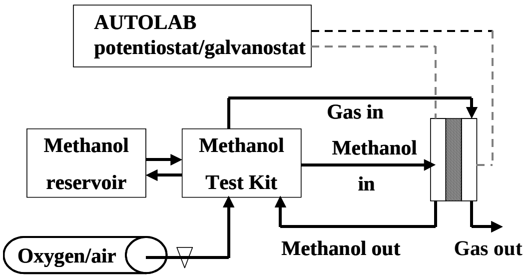

Fig. 1. Experimental set-up for DMFC testing

The membrane (5 cm^2) to be characterized was pressed between two carbon gas diffusion layers, which were used as electrodes. The volume resistance (Fig. 2) was obtained from the Cole-Cole plot by extrapolating to high frequencies using the *Autolab* software (linear regression analysis).

The conductivity of the membrane was calculated using the following equation:

$$\sigma = \frac{l}{RS} ,$$

where σ – proton conductivity, S/cm; l – membrane thickness, cm; S – electrode area, cm^2; R – volume resistance, Ohm.

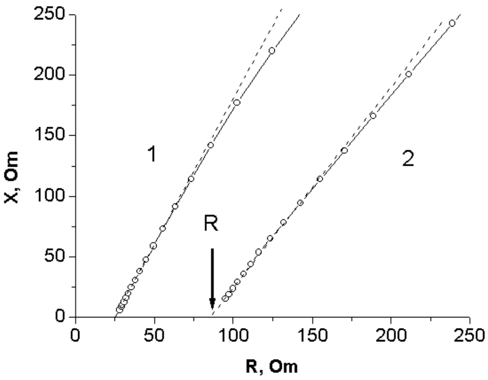

Fig. 2. Cole-Cole plots for membrane after 3rd (2) and 4th (1) impregnation with zirconium phosphate from ZrO_2 sol (where R- volume resistance)

Thermogravimetric determinations were carried out in nitrogen using a Simultaneous Thermal Analyzer STA 1500) at a heating rate of 5 °C·min^{-1}.

The impregnated membranes were further characterized with scanning electron microscopy (SEM). SEM images were obtained on a *Hitachi* x650 (working resolution 6 nm, accelerating voltage 25 kV) attached to an energy-dispersive X-ray analyser system (EDAX) equipped with a tungsten filament and CDU "LEAP" detector. The samples were prepared for analysis by breaking the membranes into small pieces, drying these pieces for 24 hours at 80 °C and sputter coating with gold. Analysis was undertaken on a cross-section of the membrane.

RESULTS AND DISCUSSION

It was calculated that the cost of a 10-cell FC stack constructed in a laboratory would be about 3000 U.S. dollars (see Table 1). The catalyst is only 3 % of all expenses, but it is notable that the Nafion based polymer membrane contributes the major cost item – 63 %. Once mass production is possible, the cost of each component will decrease. It is evident that the membrane is the most challenging part, which shows the greatest potential for radically decreasing the expense. An inorganic low cost composite membrane could be a long awaited alternative to the expensive, environmentally polluting, fluorine based Nafion membranes used so far.

Table 1. Total cost of Nafion based DMFC

Material	Price
Nafion membrane	63 %
Supported Pt catalyst	3 %
Mechanical parts, components and chemicals	34 %
Total cost:	100 %

Experimental results showed that the inorganic ZP composite membranes prepared in this study could provide a proton conductivity that is comparable to that of Nafion (10^{-2} S/cm at room temperature and RH = 100 %). The results presented in Table 2 show that ZP based membranes with conductive properties higher than that of Nafion could be prepared from phosphorized ZrO_2 nanoparticles. The measured conductivity values of the ZrO_2 nanoparticle impregnated membrane were 24 – 60 mS/cm at room temperature and RH = 100 %.

It is well known that the proton conductivity of ZP depends on the crystallinity and surface morphology. ZP is a typical surface conductor and the formation of a highly developed surface is crucial to increase the proton conductivity [19]. It was found (using the BET technique) that the surface area of the newly developed highly conductive membrane was increased by two orders of magnitude. Thus the enhanced ZP surface that was obtained may have directly enhanced the proton conductivity.

Table 2. Proton conductivity of ZP and Nafion based membranes (laboratory test) at room temperature and RH = 100 %

Membrane	Conductivity, mS · cm^{-1}, ±2
Nafion 117	14 – 16
ZP impregnated material	24 – 60

During drying at 80 °C, the proton conductivity was decreased by a few orders of magnitude. However, the proton conductivity was completely restored after 20 – 30 minutes exposure to air. Reversible water loss is important for practical application of the membrane in a FC: the water released during the FC performance could provide the necessary self-humidifying effect [20]. The DMFC operates at RH = 100 % and this characteristic will prevent the membrane from drying out. It was demonstrated using thermogravimetric techniques that the water content in the composite membranes impregnated with ZP using ZrO_2 suspensions was higher compared with membranes impregnated using ZrO_2 sols (Fig. 3). The higher water content could thus also correlate with higher conductivity for the composite inorganic ZP material impregnated using the ZrO_2 suspension.

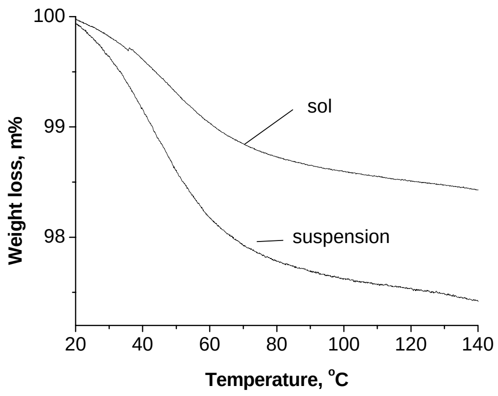

Fig. 3. Thermogravimetric analysis of the membrane impregnated with zirconium phosphate from ZrO_2 sol and suspension

As can be seen in the micrographs presented in Fig. 4, the structure of the impregnated composite inorganic ZP membranes (bottom micrograph), produced from ZrO_2 nanoparticle suspensions, consisted of well-defined crystalline ZP particles, whereas inorganic composites impregnated from sols formed a dense amorphous structure, which was confirmed by XRD measurements.

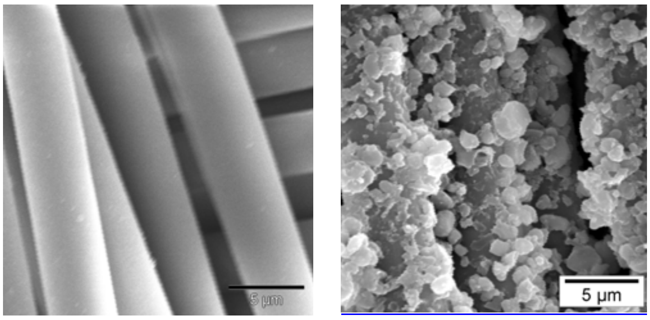

Fig. 4. SEM micrographs of proton conducting membranes (taken from edge): Glass composite membrane: blank (left micrograph) and after impregnation with ZP (right micrograph)

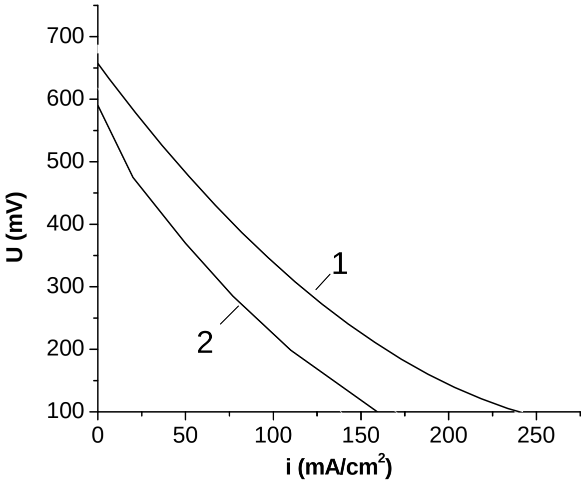

Fig. 5. Performance of DMFC: 1 – with NAFION membrane, 2 – with inorganic membrane

The new composite inorganic ZP membranes were tested in a DMFC. For comparison purposes, standard Nafion 117 membranes were also tested under exactly the same conditions. Current densities of between 150 to 200 mA/cm^2 (at 0.2 V) were obtained by using the standard Nafion 117 membranes and these values are comparable with the current densities obtained by other authors using methanol/air as fuel at lower operating pressures. Current densities obtained for the newly prepared composite inorganic ZP membranes were about 100 mA. The measured current densities that were achieved were more than 50 % of the Nafion standard (Fig. 5).

CONCLUSIONS

A new nano structured and fully inorganic composite ZP proton conducting material was synthesized by support impregnation with zirconium oxide suspensions or sols and subsequent phosphorization. The composite inorganic ZP membranes prepared using the ZrO_2 suspension were found to give rise to high proton conductivity. The proton conductivity obtained was in the order of 10^{-2} S/cm at room temperature (RH = 100 %), which is comparable to Nafion proton conductivity. An inorganic membrane based direct methanol fuel cell was tested and efficiency equivalent to more than 50 % of the Nafion efficiency was obtained when using standard platinum catalyst inks.

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