

Short communication

## Sulfated zirconia–Nafion composite membranes for higher temperature direct methanol fuel cells

Suzhen Ren<sup>a,b,\*</sup>, Gongquan Sun<sup>a</sup>, Chennan Li<sup>a</sup>,  
Shuqin Song<sup>a</sup>, Qin Xin<sup>a</sup>, Xuefeng Yang<sup>b</sup>

<sup>a</sup> Direct Alcohol Fuel Cells Laboratory, Dalian Institute of Chemical Physics,  
Chinese Academy of Sciences, China

<sup>b</sup> Laboratory of Plasma Physical Chemistry, Box 288, Dalian University of Technology, Dalian 116023, China

Received 30 September 2005; accepted 2 January 2006

Available online 21 February 2006

### Abstract

A sulfated zirconia/Nafion<sup>®</sup> 115 nanocomposite membrane is prepared by ion-exchange of zirconium ions into the Nafion followed by precipitation of sulphated ZrO<sub>2</sub> by treatment in 5 M H<sub>2</sub>SO<sub>4</sub> at 80 °C. The incorporation of sulfated zirconia increases water uptake by the Nafion membrane, and importantly, more water is absorbed than by an unmodified membrane at high temperatures. The proton conductivity of the composite membrane is evaluated and compared with that of an unmodified Nafion<sup>®</sup> 115 membrane. The nanocomposite membrane experiences a smaller decrease in proton conductivity than the Nafion<sup>®</sup> 115 membrane at high temperatures.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Direct methanol fuel cell (DMFC); Sulfated zirconia; Proton conductivity; Water uptake retention; Nafion<sup>®</sup>; Composite membrane

### 1. Introduction

World-wide effort is currently underway to find suitable alternatives to Nafion<sup>®</sup> membranes that might allow direct methanol fuel cells (DMFCs). The main approach is to improve the water retention characteristics of Nafion<sup>®</sup> membranes by the addition of inorganic materials. The so-called ‘high-temperature membranes’ can be developed via modification of the polymer host membranes with (i) hygroscopic oxides such as SiO<sub>2</sub> and TiO<sub>2</sub> to increase water uptake; (ii) inorganic solid acids such as ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> to increase the water uptake as well as the concentration of acid sites; and (iii) inorganic proton conductors such as heteropoly acids to enhance further proton conductivity using inorganic-assisted proton transport together with high water uptake and high acid concentration in the membrane [1–4]. Zirconium oxide or zirconium phosphate modified Nafion<sup>®</sup> membranes have been investigated and shown to exhibit good performance at operating temperatures up to ~150 °C [5–7]. In the present study, an attempt is made to

incorporate sulfated zirconia, a superacid [8], into Nafion to improve its proton conductivity and water retention characteristics.

### 2. Experimental

#### 2.1. Membrane preparation

A sulfated zirconia/Nafion<sup>®</sup> 115 nanocomposite membrane was prepared by means of ion-exchange of zirconium ions into the Nafion<sup>®</sup> 115, followed by precipitation of sulfated ZrO<sub>2</sub> by treatment in 5 M H<sub>2</sub>SO<sub>4</sub> at 80 °C. Nafion<sup>®</sup> 115 serves as a template that directs the morphology and particle size of the oxide in the PEM matrix. As-received Nafion<sup>®</sup> 115 was purified by (i) heating in pure water at 60–70 °C for 30 min; (ii) treatment in 3 wt.% H<sub>2</sub>O<sub>2</sub> solution at 60–70 °C for 30 min; and (iii) washing with de-ionized water at 60–70 °C for 30 min. The Nafion membrane was then soaked in ZrOCl<sub>2</sub>/2-propanol solution at 75 °C for 24 h. The membrane was removed, blotted, and placed in 2-propanol/H<sub>2</sub>O solution for 2 h at 80 °C. After the acid-hydrolysis and condensation reactions, the membrane was removed and vacuum-dried thoroughly at 80 °C for 24 h and then at 110 °C

\* Corresponding author. Tel.: +86 411 84379310; fax: +86 411 84379063.  
E-mail address: [rensz@dicp.ac.cn](mailto:rensz@dicp.ac.cn) (S. Ren).

for 2 h. The membrane was then boiled in 5 M  $\text{H}_2\text{SO}_4$  solution at  $60^\circ\text{C}$  for 1 h to sulfate the  $\text{ZrO}_2$  nanoparticles, and finally rinsed in water.

## 2.2. Water uptake and proton conductivity measurements

The experimental details of water uptake and proton conductivity have been reported elsewhere [9,10]. The proton conductivity of samples in the traverse direction was measured in a measurement cell using a.c. impedance spectroscopy with a potentiostat (EG&G Model 280A) and Lock-in (EG&G Model 5210). The proton conductivity,  $\sigma$ , was calculated from the impedance data, using the relation  $\sigma = l/RS$ , where  $l$  and  $S$  are the thickness and area of the membrane, respectively, and  $R$  was derived from the low intersect of the high frequency semicircle on a complex impedance plane with the  $Re(z)$  axis.

The performance of the use membrane–electrode assembly (MEA) was determined at 90 and  $105^\circ\text{C}$  under ambient pressure with an in-house electrochemical test station that was equipped with an Arbin system [9,10]. Oxygen was used at the cathode at a flow rate of  $100\text{ mL min}^{-1}$  and 1 M methanol solution was used at the anode with a flow rate of  $1\text{ mL min}^{-1}$ .

## 3. Results and discussion

Water sorption data for Nafion<sup>®</sup>115 and sulphated  $\text{ZrO}_2/\text{Nafion}$  nanocomposite membranes in the temperature range  $25\text{--}120^\circ\text{C}$  are presented in Fig. 1. The incorporation of  $\text{ZrO}_2/\text{SO}_4^{2-}$  increases the water uptake of the Nafion<sup>®</sup>115 membrane, and importantly, more water is absorbed than by an unmodified membrane at high temperature. The composite membranes exhibit enhanced hydration under conditions that dehydrate unmodified Nafion membranes because  $\text{ZrO}_2/\text{SO}_4^{2-}$  nanoparticles contribute additional hydrogen bonding sites and displace the more volatile bulk water. Perhaps, the  $\text{ZrO}_2/\text{SO}_4^{2-}$  particles provide new acid sites for absorption of water and proton transport. The structure of  $\text{ZrO}_2/\text{SO}_4^{2-}$  solid acid is shown in Fig. 2 [4,11].

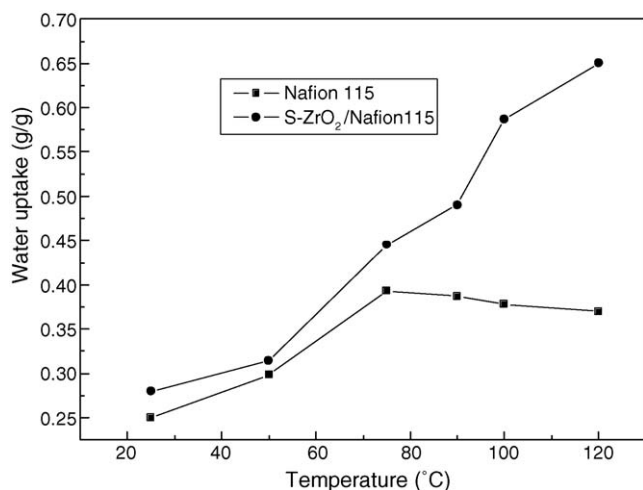


Fig. 1. Water uptake of Nafion<sup>®</sup>115 and sulfated  $\text{ZrO}_2/\text{Nafion}$ <sup>®</sup>115 membranes at different temperatures.

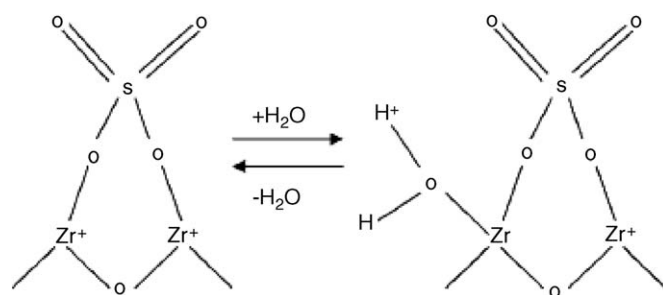


Fig. 2. Structure of  $\text{ZrO}_2/\text{SO}_4^{2-}$  solid acid.

Since the proton conductivity of Nafion<sup>®</sup>115 is closely related to the content of water and the majority of the composites are still Nafion resin [12], a smaller proton conductivity of the composite membranes compared with the Nafion<sup>®</sup>115 membrane is expected from the results of the water uptake test. The conductivities of sulfated  $\text{ZrO}_2/\text{Nafion}$  and Nafion<sup>®</sup>115 membranes are given in Fig. 3. The membrane proton conductivity is decreased slightly by  $\text{ZrO}_2$  impregnation. The proton conductivity of Nafion<sup>®</sup>115 membrane is  $1.5 \times 10^{-2}\text{ S cm}^{-1}$  at  $25^\circ\text{C}$ , while that of the  $\text{S-ZrO}_2/\text{Nafion}$ <sup>®</sup>115 membrane is decreased to  $5.0 \times 10^{-3}\text{ S cm}^{-1}$  at  $25^\circ\text{C}$ . At or above  $110^\circ\text{C}$ , the proton conductivity of the  $\text{S-ZrO}_2/\text{Nafion}$ <sup>®</sup>115 membrane is more than one-half that of the Nafion<sup>®</sup>115 membrane.

From the data in Fig. 3, it is concluded that the composite membrane is less susceptible than unmodified Nafion membranes to high-temperature damage. Loss of water from unmodified Nafion membranes irreversibly collapses their pores and subsequently leads to the loss of the conductivity of the nanopores. The presence of the sulfated zirconia in the membrane prevents these temperature-related structural changes and maintains conductivity even after thermal cycling above the dehydration temperature. Sulfated  $\text{ZrO}_2$  appears to be a useful bifunctional additive to a Nafion membrane—it improves water retention characteristics and maintains proton conductivity for higher temperature operation of DMFCs.

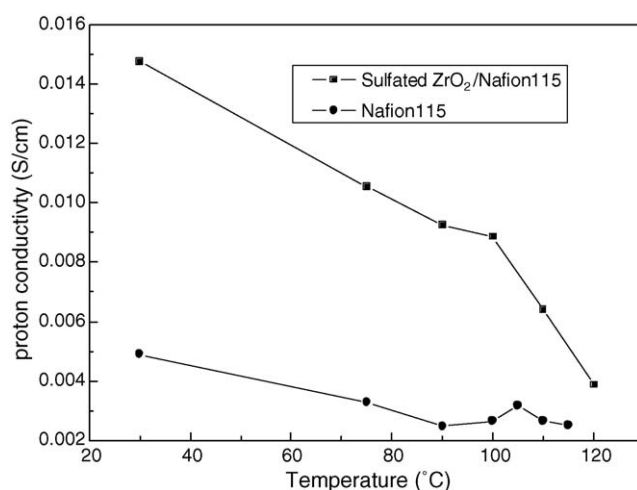


Fig. 3. Proton conductivity of sulfated  $\text{ZrO}_2/\text{Nafion}$  and Nafion<sup>®</sup>115 at different temperatures.

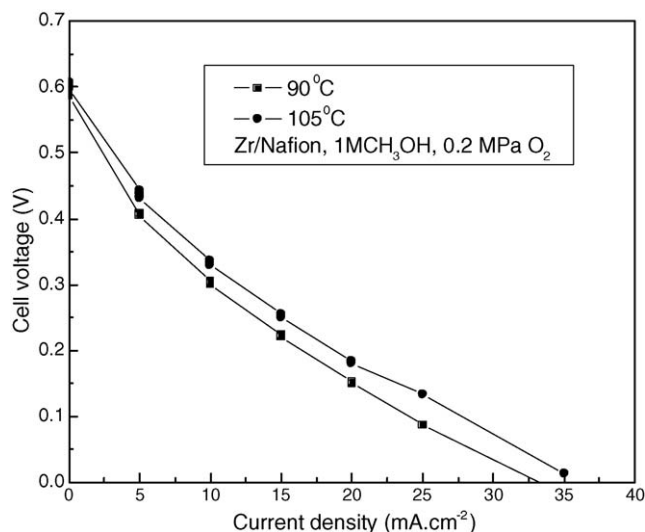


Fig. 4. Current–voltage curves for a DMFC with a S–ZrO<sub>2</sub>/Nafion<sup>®</sup> membrane.

Membrane properties in the DMFC are evaluated by measuring water uptake, proton conductivity, and cell performance. In low-temperature DMFCs, a modest temperature of around 60 °C is usually applied as the cell operation temperature. In addition, an ambient cell temperature of around 20 °C is also attractive for a power supply of portable devices. To minimize the efficiency loss due to methanol cross-over, the methanol concentrations used for DMFCs are usually lower than 2 M. A higher methanol concentration is desirable due to higher specific energy if the problem of methanol cross-over through the membrane can be suppressed. In this work, the behaviour of the S–ZrO<sub>2</sub>/Nafion<sup>®</sup> membranes are evaluated at 90 and 105 °C. A lower methanol concentration, 1 M, is applied as the fuel. The performance of a DMFC with a S–ZrO<sub>2</sub>/Nafion<sup>®</sup> membrane is shown in Fig. 4. The slope of curve indicates that the proton conductivity of the S–ZrO<sub>2</sub>/Nafion<sup>®</sup> membrane is very small.

The presence of the inorganic compound decreases the proton conductivity in all cases. At high humidity, the conductivity first increases from 80 to 100 °C and decreases at 130 °C. This behaviour has already been described by Alberti et al. [13] for Nafion<sup>®</sup>117 [13]. The decrease in conductivity is more pronounced at temperatures above 100 °C.

The measured values for the inorganically-modified Nafion<sup>®</sup> membrane are basic information for improving DMFC performance. The method of in situ synthesis of nanoparticles via sol–gel processing in recast or commercial Nafion membranes may result in a lower performance of the membrane in a DMFC than the method of mixing Nafion gel and inorganic particles followed by membrane casting.

#### 4. Conclusions

The incorporation of sulfated zirconia into Nafion<sup>®</sup> membrane increases the amount of water uptake and provides additional acid sites for proton transportation, which results in higher proton conductivity compared with the host membrane at higher temperature. Polymer/inorganic nanocomposite membranes can be considered as promising alternative PEMs for fuel cells.

#### References

- [1] T.M. Thampan, N.H. Jalani, P. Choi, R. Datta, J. Electrochem. Soc. 152 (2) (2005) A316–A325.
- [2] P. Choi, N.H. Jalani, R. Datta, J. Electrochem. Soc. 152 (3) (2005) E84–E89.
- [3] P. Choi, N.H. Jalani, R. Datta, J. Electrochem. Soc. 152 (3) (2005) E123–E130.
- [4] P. Choi, N.H. Jalani, R. Datta, J. Electrochem. Soc. 152 (8) (2005) A1548–A1554.
- [5] C. Yang, S. Srinivasan, A.S. Arico, P. Creti, V. Baglio, V. Antonucci, Electrochem. Solid State Lett. 4 (4) (2001) A31–A34.
- [6] N.H. Jalani, K. Dunn, R. Datta, Electrochim. Acta 51 (3) (2005) 553–560.
- [7] F. Bauer, M. Willert-Porada, J. Power Sources 145 (2005) 101–107.
- [8] S. Hara, M. Miyayama, Solid State Ionics 68 (2004) 111–116.
- [9] S. Ren, C. Li, X. Zhao, Z. Wu, S. Wang, G. Sun, Q. Xin, X. Yang, J. Membr. Sci. 247 (1–2) (2005) 59–63.
- [10] C. Li, G. Sun, S. Ren, J. Liu, Q. Wang, Z. Wu, H. Sun, W. Jin, J. Membr. Sci. 272 (1–2) (2006) 50–57.
- [11] K. Arata, M. Hino, Mater. Chem. Phys. 26 (1990) 213–237.
- [12] S. Hietala, S.L. Maunu, F. Sundholm, J. Polym. Sci., Part B: Polym. Phys. 38 (2000) 3277–3284.
- [13] G. Alberti, M. Casciola, L. Massinelli, B. Bauer, J. Membr. Sci. 185 (2001) 73–81.