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Zirconium phosphate based proton conducting membrane for DMFC application

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ARTICLE INFO

Article history:

Received 9 October 2014

Received in revised form

12 May 2015

Accepted 16 May 2015

Available online xxx

Keywords:

Ion-exchange membrane

Zirconium phosphate

PVDF

Methanol crossover

DMFC

ABSTRACT

A proton conducting poly(vinylidene fluoride) (PVDF) supported zirconium phosphate (ZrP) ion-exchange membrane (ZrP/PVDF) was synthesized for potential application in DMFC by filling the pores of a PVDF film with in-situ grown ZrP particles. Presence of labile protons attached to P=O group was confirmed from ¹H NMR and FT-IR characterizations. SEM micrographs showed defect-free top surface. The thermal stability and mechanical strength of the ZrP/PVDF membrane was better than Nafion-117. Water to methanol uptake ratio was higher while methanol cross-over for ZrP/PVDF membrane was lower than Nafion-117. Membrane possessed fair electrochemical properties; 0.85 static counter-ion transport number, 0.76 meqg⁻¹ ion exchange capacity and 1.25 mScm⁻¹ proton conductivity at 30 °C. DMFC performance of the synthesized membrane at 35 °C was compared with the Nafion-117. DMFC studies were also done at different operating conditions and the maximum peak power density was 32.3 mWcm⁻² at 60 °C, 1 M methanol concentration and 60% relative humidity.

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Introduction

In the recent past, interest in advanced functional materials, like membranes, electro-catalysts, and bipolar plates, has gained much attention due to emergence of various energy devices like fuel cell, batteries, sensors etc. Among all these devices, fuel cell particularly the direct methanol fuel cell (DMFC) has unique features of easy operation, higher energy density with low emission [1]. Membrane's properties considerably affect the DMFC performance. At present, polymeric membranes have been found to be the most appropriate for DMFC applications; however their poor thermal stability

and deterioration in performance at elevated temperature (>80 °C) has led to the search for alternative membranes.

Inorganic-organic ion-exchange membranes composed of organic support with distributed inorganic phase having functional (ionic) groups possess enhanced physical and chemical properties compared to both organic and purely inorganic membranes and have potential to be used in DMFC. The inorganic phase is selected on the basis of its ion exchange capacity (IEC) and proton conductivity. A type of inorganic ion-exchangers, called fast proton conductors have gained interest in recent times. These materials are acid salts of tetravalent metal and their general chemical formula is [M (IV) HPO₄ nH₂O] where, M is the tetravalent metal e.g., Sn, Zr, Ti. Protons (H⁺) of the hydroxyl group (–OH) structurally

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<http://dx.doi.org/10.1016/j.ijhydene.2015.05.117>

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bound to the metal M acts as ion-exchangeable sites [2,3] and enable proton conduction. A number of small cations (Li^+ , Na^+ , Ca^{2+} etc.) can be exchanged with H^+ providing high IEC [4]. Protons can easily move on surface containing hydrated $-\text{OH}$ groups [5]. Zirconium phosphate (ZrP) is one of the most widely studied fast proton conductors because it has high IEC (6.64 meqg^{-1}) [3]. Also, ZrP is thermally stable up to 450°C . However, it has very low proton conductivity, in the range of 10^{-5} – 10^{-6} Scm^{-1} [5].

Recent literature reported synthesis of inorganic-organic composite membranes by impregnation of porous support, of polymeric materials such as poly(vinylidene fluoride) (PVDF), poly(tetrafluoro ethylene) (PTFE), poly(propylene) (PP), poly(ethersulfone) (PES), with a colloidal suspension of inorganic ion exchangers [6]. It was pointed out by Alberti et al. [7] that the transfer of the colloidal dispersion of ZrP particles into a polymeric matrix enables proper dispersion of the inorganic particles due to their small particle size (ranging from nano to micrometers). The advantages of such composite inorganic-organic membranes include low cost, good mechanical strength in both wet as well as dry state, and good thermal stability. In addition, it is possible to obtain membranes much thinner than Nafion-117 ($175 \mu\text{m}$) yet maintaining comparable mechanical strength and methanol crossover. Thinner dimensions leads to lower areal resistance of the membrane. ZrP based membranes have been reported in literature [8–10]. Some of them have shown that hybridization of Nafion membrane with inorganic ZrP reduces methanol crossover of the membrane.

In this work, synthesis of ZrP based proton conducting membrane is described. Synthesis was carried out by impregnating porous polymeric PVDF film of sub-micron pore size with in-situ grown ZrP particles. Synthesized ZrP/PVDF membrane was characterized using various physico-chemical (^1H NMR, XRD, FT-IR, SEM, stability test, water uptake) and electrochemical characterization techniques (Transport number, IEC, proton conductivity). Methanol crossover was measured and the membrane's performance in DMFC was compared with that of Nafion-117.

Experimental

Materials

Porous PVDF film (pore size $0.22 \mu\text{m}$, thickness $50 \mu\text{m}$) was procured from Rankem Pvt. Ltd., India. Zirconyl oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and ortho-phosphoric acid (H_3PO_4) were purchased from Central Drug House (CDH), India. Other chemicals like methanol, sodium chloride, acetone, ethanol, hydrogen peroxide, hydrogen chloride and sulfuric acid were purchased from Merck Ltd., India. All the chemicals were of AR grade and triple de-ionized water was used for all the experiments.

Synthesis

ZrP ion-exchanger

ZrP powder was prepared by adding 10 ml of 5 wt.% zirconyl oxychloride (salt precursor of zirconium ion (Zr^{4+})) to 10 ml of

$0.5 \text{ M H}_3\text{PO}_4$ solution while stirring. A few drops of HCl acid were also added to the solution to maintain the pH between 2 and 3. The prepared solution was stirred for 2 h at room temperature during which it turned milky. It was then filtered (using Whatman filter, Grade 1) to obtain white precipitate. The obtained white precipitate was washed multiple times with water to remove excess acid followed by heating at 120°C for 12 h to get the ZrP powder. The prepared ZrP powder was characterised using FT-IR, particle size analyzer (PSA) and XRD.

ZrP/PVDF membrane

Membrane was synthesized in two steps. First a porous PVDF film was immersed in 5 wt.% ZrOCl_2 aqueous solution at 80°C for 6 h. In the second step, after removing excess solution from the surface, the ZrOCl_2 impregnated PVDF film was immersed in $0.5 \text{ M H}_3\text{PO}_4$ solution containing few drops of HCl for 48 h for the in-situ formation of ZrP inside the pores of the PVDF film. This was followed by heat treatment at 120°C for 12 h.

Characterization

Characterization of ZrP

^1H -MAS NMR spectroscopy of the synthesized ZrP sol was done on a Bruker Electrospin machine (make: Bruker USA, model: 300 MHz) to determine the state of protons (H^+) present in the sol. For this DMSO-d_6 (di-methyl sulphoxide dissolved in deuterated water) was used as an NMR solvent. The chemical shifts (up-fields and down-fields) and peaks were referenced to tetramethoxysilane (TMS) used as an external standard. The particle size distribution (PSD) and zeta potential of ZrP particles of the sol was measured at 30°C and 60% RH on a particle size analyzer (make: Malvern Instruments UK, model: S90). The FT-IR of the ZrP powder, obtained by drying the ZrP sol, was measured on a spectrometer (make: Thermo Nicolet USA, model: 6700) in transmittance mode over wave-number range of 500 – 4000 cm^{-1} . For this purpose, a pellet was made by mixing the powdered sol with KBr and then it was heat treated at 100°C for 2 h to remove the moisture. XRD of the powdered form of the sol was done on an X-ray diffractometer (make: Philips Pro Xpert The Netherlands, model: PW 3040) operated at 45 kV and 40 mA with monochromatic Cu K_α radiation. The two theta (2θ) range was kept between 10 and 60° with step size of 0.02° . Both XRD and FT-IR test were performed at 30°C and 60% RH.

Characterization of ZrP/PVDF membrane

XRD. XRD of the membrane was done in a way similar to that of the powdered sol described above.

Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS)

SEM (make: ZEISS Germany, model: EVO-50) was used to study the surface morphology of PVDF film and ZrP/PVDF membrane. Samples were dried at 150°C for 2 h to remove the moisture and then coated with gold under vacuum before performing the SEM experiment. Elemental composition of the synthesized membrane was determined using EDS.

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