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Short communication

Fabrication of novel phosphotungstic acid functionalized mesoporous silica composite membrane by alternative gel-casting technique

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HIGHLIGHTS

- HPW/MCM-41 composite membranes have been fabricated by a gel-casting technique.
- HPW/MCM-41 composite membranes can operate stably below 200 °C.
- A single cell can be assembled using the HPW/MCM-41 membrane.
- A maximum output power density of 101 mW cm^{-2} in MeOH/air at 150 °C was observed.

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ABSTRACT

A simple and cost-effective gel-casting technique has been developed to fabricate phosphotungstic acid (HPW) supported on mesoporous silica (MCM-41) electrolyte membrane (HPW/MCM-41) for direct methanol fuel cells (DMFCs). The effect of HPW loading on the stability of MCM-41 structure has been analyzed by small-angle X-ray scattering (SAXS), Fourier transform infrared (FTIR), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) techniques. In particular, the effect of solid state loading and HPW loading on the microstructure, water gain ratio, swelling ratio and conductivity of the HPW/MCM-41 membranes have been studied in detail. The results showed that a large proportion of loaded HPW is anchored in the mesoporous silica matrix, forming an effective proton conduction pathway. The results also showed that the composite membrane can operate successfully at temperatures below 200 °C for a long duration, based on the TGA curve of organic network formed during the gelation stage. The single cell assembled from HPW/MCM-41 membrane with 65 wt.% HPW loading gives a peak power of 101 mW cm^{-2} in methanol/air at 150 °C without any humidification.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) has been proved to be an alternative power source compared to the internal combustion engines, especially for portable power and automobile applications. However, PEMFC relies exclusively on pure hydrogen, which is not readily available for widespread application. Though fuel reforming technology is rather mature, matching of fuel reformer to the fuel cell stack adds on to the cost significantly, especially for subsequent gases cleanup and purification, which would make the PEMFC system very bulky and maintenance hassle. Much different from the direct methanol fuel cell (DMFC) that operates at around the room temperature, high-temperature PEMFC (HT-PEMFC) has evolved very rapidly in recent years. It is seen to be a promising technology that is able to penetrate the market for practical application as methanol/ethanol can be used directly or even logistic fuels that can be applied with a simple fuel reforming technique. The main advantages of operating HT-PEMFC at temperatures above 150 °C include fuel flexibility, improved resistance to carbon monoxide poisoning and the ability of using of non-Pt catalyst. These advantages also prompt some new challenges such as the reliability of conductivity of PEM, low-cost non-

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Pt or low-Pt loading catalyst technology and robust catalyst support resistance to oxidation at elevated temperatures. The proton conductivity of the state-of-the-art perfluorosulfonic acid (PFSA) membranes, such as Nafion, depends strongly on the water content in the membrane. The conductivity decreases with increasing temperature due to the dehumidification effect of the membrane under high temperatures [1–4]. Therefore, the development of proton exchange membranes with high conductivity and stability at high temperature and low humidity form the objective of this study. Many inorganic-based proton conductors have been explored as the electrolytes for HT-PEMFCs, such as heteropoly acid (HPA)-based composite [5–12], ammonium polyphosphate (APP)-based composite [13–24], and doped SnP_2O_7 [25–30]. Among these solid inorganic proton conductive electrolyte materials, HPA, which takes the form of Keggin structure with general formula $H_3MX_{12}O_{40}$ where M = P, Si, etc., and X = W, Mo, V, etc. [7, 31–36]. The highest stability and strongest acidity is observed for phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW). HPW exhibits interesting acid properties due to its easily accessible and reactive protons present in the structure. Although earlier effort on this material as a potential solid electrolyte has failed to meet the requirements due to its high solubility in water and strong humidity-dependent proton conductivity [37], it is interesting to note that the proton conductivity of a well dispersed HPW impregnated into mesoporous silica system by vacuum assisted impregnation method has been quite promising at low humidity [5]. Apart from the conductivity, another technical challenge for the inorganic proton conductive electrolyte is the formation of thin and dense membrane structure with high mechanical strength.

There are various processing techniques available for the fabrication of inorganic proton conductive composite membranes (see Table 1). Till now, there is no report on the inorganic proton conductive composite membrane made by novel ceramic molding technique, i.e., the water-based gel-casting. Gel-casting was first reported by Omatete et al. [38] in 1991. In this technique, slurry of high solid state loading is obtained by dispersing the ceramic powders in the premixed mono-functional and di-functional monomers solution and casted into any desired shape by a mold. By heating or adding catalyst, cross-linking and solidification occur and form a three-dimensional polymeric network structure. Polymerization solidifies and immobilizes the powder into the desired shape. Gel-casting is a low-cost technique commonly used in ceramic industry to fabricate complex three-dimensional ceramic parts [38–40]. Recently, the gel-casting technique has been used to prepare components of solid oxide fuel cells (SOFCs) such as NiO/YSZ (yttria-stabilized zirconia) anode substrates [41]. Due to its simplicity and low-cost, the technique has also been employed in the production of electrode and electrolyte powders for SOFCs [42–47]. It is very inspiring that the phase formation temperature of electrode and electrolyte powders for SOFCs was reported to be considerably lower than that synthesized by conventional solid state reaction route, which is attributed to the uniformly distributed raw particles in a polymeric matrix immobilized during the gelation step. Thus, it is worthwhile to investigate the properties of the HPW/mesoporous silica composite membrane fabricated by the novel ceramic molding technique.

In this paper, a novel HPW-impregnated MCM-41 composite membrane fabricated by an aqueous based gel-casting technique is presented. The effects of HPW loading on the structural stability of MCM-41, the thermal stability of as-assembled powders, the proton conductivity, stability and microstructure of HPW/MCM-41 composite membranes, and the cell performance are investigated in detail.

2. Experimental procedure

2.1. Assembled powders preparation

A large quantity of mesoporous silica MCM-41 was synthesized based on a previously reported procedure [48,49]. Phosphotungstic acid (HPW) was ordered from Sigma–Aldrich. The as-assembled HPW/MCM-41 powders were prepared by a vacuum assisted impregnation method [5]. MCM-41 was treated under vacuum ($<10^{-1}$ Pa) to remove impurities and trapped air in the mesoporous

Table 1
Inorganic proton conductors, fabrication method of composite membranes.

Entry	Proton conductors	Additional organic	Additional inorganic	Fabrication method	Ref.
1	HPW	–	Meso-silica	Pressing	[5]
2	HPW	–	Meso-silica	Pressing	[6]
5	HPW	Polyimide	Meso-silica	Pressing	[12]
6	HPW	Nafion	ZrO_2	Casting	[7]
7	HPW	Polybenzimidazole	Silica	Casting	[8]
8	HPW	Nafion	Silica	Recasting	[9]
9	HPW	Sulfonated poly(ether sulfone)	Silica	Casting	[10]
10	HPW	Perfluorosulfonic acid	Silica	Casting	[11]
11	$(NH_4)_2Si_{1-x}Ti_xP_4O_{13}(0 \leq x \leq 1)$	–	–	Pressing	[14]
12	$(NH_4)_2SnP_4O_{13}$	–	–	Pressing	[15]
13	$2NH_4PO_3$-$(NH_4)_2SiP_4O_{13}$ $2NH_4PO_3$-$(NH_4)_2Mn(PO_3)_4$	–	–	Pressing	[16]
14	NH_4PO_3-$(NH_4)_2Mn(PO_3)_4$	–	–	Pressing	[17]
15	NH_4PO_3	–	Silica	Pressing	[18]
16	NH_4PO_3-$(NH_4)_2SiP_4O_{13}$	–	–	Pressing	[19]
17	$(NH_4)_2SiP_4O_{13}$	–	–	Pressing	[20]
18	NH_4PO_3-$(NH_4)_2SiP_4O_{13}$	–	–	Pressing	[21]
19	NH_4PO_3	Poly(tetrafluoroethylene) (PTFE)	–	Pressing	[22]
20	NH_4PO_3	–	Amorphous oxide $SiO_2 - P_2O_5$	Pressing	[23]
21	$(NH_4)_2TiP_4O_{13}$	–	–	Pressing	[24]
22	$Sn_{0.9}In_{0.1}P_2O_7$	–	–	Pressing	[25]
23	$Sn_{0.9}In_{0.1}P_2O_7$	Poly(tetrafluoroethylene) (PTFE)	–	Cold-rolling	[26]
24	$Sn_{0.9}In_{0.1}P_2O_7$	Poly(tetrafluoroethylene) (PTFE) Polybenzimidazole (PBI)	–	Cold-rolling	[27]
25	$Sn_{0.9}In_{0.1}P_2O_7$	–	–	Pressing	[30]