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Short communication

Fabrication of phosphotungstic acid functionalized mesoporous silica composite membrane by alternative tape-casting incorporating phase inversion technique

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HIGHLIGHTS

- Composite membranes have been fabricated by tape-casting & phase inversion technique.
- Such thin inorganic proton exchange membranes can be easily scaled up.
- The TGA results demonstrated that the composite membranes can operate stably below 200 °C.

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ABSTRACT

Meso-porous silica (MCM-41) membranes functionalized by phosphotungstic acid (HPW) for high temperature proton exchange membrane fuel cells (HT-PEMFCs) are successfully developed by a cost-effective tape-casting incorporating phase inversion and vacuum assisted wet impregnation techniques. The microstructure of the membrane is characterized by field emission scanning electron microscopy (FESEM). The effect of MCM-41 content on the tensile strength, ultimate elongation, and weight gain ratio and swelling ratio in water/methanol of the membranes are investigated in detail. The thermal stability of MCM-41 membrane with/without HPW is analyzed by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) techniques. In particular, the effects of HPW loading and MCM-41 content on the proton conductivity of HPW/MCM-41 membranes are studied comprehensively. The results on the swelling ratio and tensile tension show that the developed membranes can be applied as an electrolyte membrane for HT-PEMFCs. The developed MCM-41 membrane, in which polyethersulfone (PESf) is used as the supporting backbone, is able to operate up to 200 °C. The single cell assembled from HPW/MCM-41 membrane with 70 wt.% HPW loading gives a peak output power of ~230 mW cm^{-2} and ~125 mW cm^{-2} in H_2/air at 90 °C and in methanol/air at 150 °C without any humidification, respectively.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) attract considerable attention to power various applications, such as, electric vehicle, domestic power generation, portable and stationary power source [1,2] due to their advantages in high-energy conversion efficiency, high power density, simplicity of operation and eco-friendly nature [3–7]. The polymer electrolyte membrane, a key component of the PEMFC, acts as both a separator and an electrolyte in the fuel cell. The membrane must satisfy a number of criterion: a) high ionic conductivity, b) zero electronic conductivity, c) high mechanical strength, d) low gas permeability, e) high cation transport number, f) mechanical and chemical stability at the operating temperature, and g) acceptable water transport characteristics. Ideally, it should also be easy and cheap to manufacture. Our technology scan in the field of polymer electrolyte for PEMFCs finds that perfluorosulphonic acid (PFSA) based Nafion membranes from DuPont Company are the de facto standard [8]. PFSA Nafion membranes offer a relatively high ionic conductivity, a cation

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transport number near unity, zero electronic conductivity, and relatively low gas permeability [1].

It is well-known that the efficiency of PEMFCs can be further improved by increasing the operating temperature of the fuel cells up to 120 °C due to the enhanced electrodes reaction kinetics and improved CO tolerance [9,10]. However, the proton conductivity of Nafion membrane depends strongly on the water content of the membrane and decreases significantly with increasing temperature or decreasing relative humidity because of the loss of water from the membrane under conditions of high temperature or low humidities [11–13]. Therefore, the development of proton exchange membranes with high conductivity, and performance stability at high temperature and low humidity is a very critical component in this area.

Many inorganic-based proton conductors have been explored as the electrolytes for HT-PEMFCs, such as heteropoly acid (HPA)-based composite [14,15], ammonium polyphosphate (APP)-based composite [16], and doped SnP_2O_7 [17,18]. Among these solid inorganic proton conductive electrolyte materials, phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW), one kind of HPAs with Keggin structure shows the highest stability and strongest acidity. 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 [19]. In recent years, researchers have paid more attention on the immobilization of HPA. For example, Tang and co-workers reported to the use of a one-step self assembled method to immobilize the HPW molecular inside the mesoporous silica structure via a hydrogen-bond and electrostatic self-assembly assisted with a structure-directing surfactant (a non-ionic triblock copolymer $EO_{20}PO_{70}EO_{20}$) [20,21]. A fuel cell based on a 165 μm thick HPW–silica nanocomposite membrane achieved a maximum power output of 128.5 and 112.0 mW cm^{-2} for direct methanol and ethanol fuel cells, respectively, at 200 °C [20]. Lu and co-workers reported the immobilization of HPW molecules inside the mesoporous silica structure by using a novel and cost-effective vacuum-assisted wet impregnation method. And the cell fabricated from such HPW-impregnated meso-silica membrane demonstrated a peak power density of 90 mW cm^{-2} in methanol/O_2 at 150 °C and an extremely low relative humidity of 0.67% [14].

Apart from the performance of HPW/MCM-41 composite membrane, another technical challenge for such HPW-based inorganic proton conductive electrolyte relates to the feasibility of forming of thin and dense membrane structure with high mechanical strength without sintering treatment.

There are various processing techniques available for the fabrication of inorganic proton conductive composite membranes, such as die-pressing [14], casting [15], recasting [13], and cold-rolling [18]. Novel ceramic moulding technique, e.g., the water-based gel-casting has also been introduced to fabricate inorganic proton conductive composite membranes in our group recently [22]. Gel-casting is a low-cost technique commonly used in ceramic industry to fabricate complex three-dimensional ceramic parts [23], and has been successfully used to prepare components and synthesize electrode and electrolyte powders for solid oxide fuel cells (SOFCs) [24–30]. However, until now it is difficult to further decrease the thickness of the HPW functionalized mesoporous silica fabricated by gel-casting technique at the current stage. It has been reported that the cell resistance decreases with the reduction in electrolyte thickness [31], which implies that the cell performance depends on the thickness of electrolyte membrane. This means that the key contributor for the development of high performance HT-PEMFC lies in creating thin composite electrolyte membranes.

Tape casting is a well known colloidal shaping technique utilized to produce flat, and large-area ceramic tapes in a thickness range of 10–1000 μm, which can be difficult to achieve with other methods, such as pressing and extruding [32–34]. Using the tape casting technique, a pristine MCM-41 membrane has been successfully fabricated in our laboratory (see Fig. 1a). However, the chemical stability of membrane fabricated by non-aqueous based tape-casting emerges as an issue when methanol/ethanol is used as fuel. The other problem relates to the thermal stability of the membrane resulting from the thermal decomposition of organic additives ~150 °C (refer to Fig. 1b). These two technical problems serve as the motivation to develop the existing tape-casting technique to fabricate thin HPW/meso-porous silica composite membrane with good chemical and thermal stability.

In this paper, the organic–inorganic composite membranes with various mesoporous silica MCM-41 contents were fabricated by the tape-casting incorporating phase inversion techniques. The properties of MCM-41 membranes were studied by field emission scanning electron microscopy (FESEM), tensile strength test, and water/methanol uptake and swelling tests. HPW was impregnated into MCM-41 composite membranes by the method of vacuum assisted wet impregnation to enforce proton conductivity. The thermal stability of membrane with/without HPW impregnation treatment was characterized by TGA/DTG technique. The effect of MCM-41 content on the proton conductivity and single cell performance were investigated in detail.

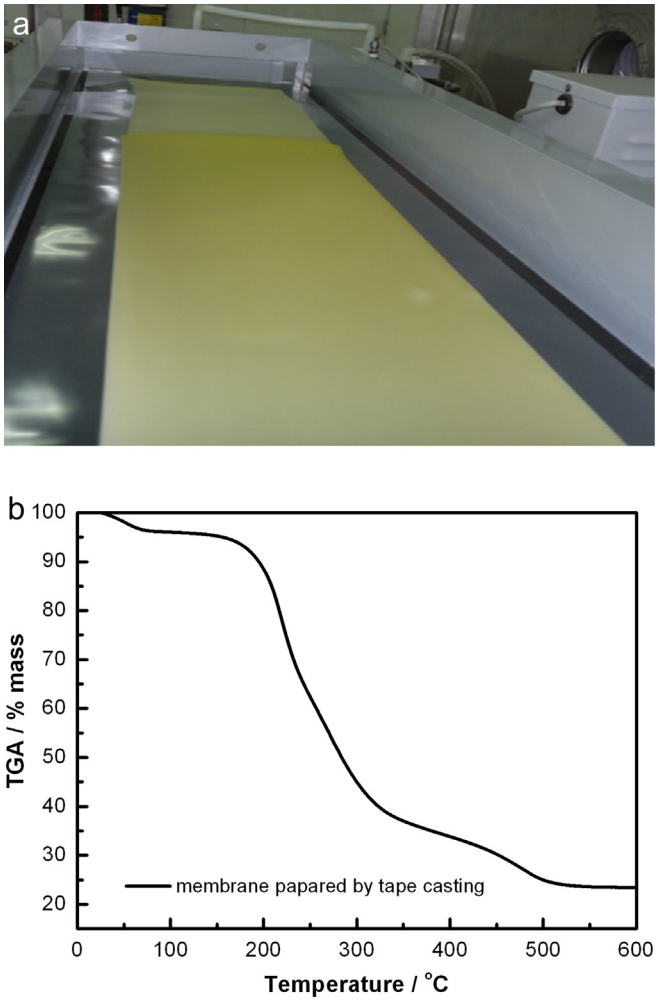

Fig. 1. (a) Optical picture of the pristine MCM-41-m membrane fabricated by tape-casting & phase inversion process, (b) thermogravimetric analysis (TGA) of this pristine membrane.