



Enhancement of fuel cell performance with less-water dependent composite membranes having polyoxometalate anchored nanofibrous interlayer



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HIGHLIGHTS

- Composite membranes consisting ion conductive nanofibers are proposed for PEMFCs.
- Dimensional stability improved and water uptake reduced compared to Nafion 112.
- The proton conductivity at low humidity is improved in composite membranes.
- OCV enhanced by about 100 mV than Nafion 112 when tested at 60 °C and 40% RH.
- Maximum power density increased by 35% in the composite.

ARTICLE INFO

Article history:

Received 31 March 2016

Received in revised form

4 July 2016

Accepted 7 July 2016

Available online 15 July 2016

Keywords:

Polymer electrolyte membrane fuel cells

Conductive nanofibrous membrane

Polyoxometalate

Membrane electrode assembly

High energy density

ABSTRACT

Polyoxometalate immobilized nanofiber was used to fabricate low gas permeable layer for composite membranes designed for proton exchange membrane fuel cell (PEMFC) operating at low relative humidity (RH). The composite membranes revealed enhanced proton conductivity in dry conditions compared with state-of-the-art pristine membrane (Nafion 112, N112). This was coupled with a low fuel crossover inheriting the composite membranes about 100 mV higher OCV than N112 when tested in PEMFC at 60 °C and 40% RH. A maximum power density of up to 930 mW cm⁻² was also achieved which is substantially higher than the N112 under similar conditions (577 mW cm⁻²). Such remarkable performance enhancement along with undetectable leaching of immobilized polyoxometalate, high dimensional stability and low water uptake of the composite membranes suggest a strong potential for PEMFC under low RH operation.

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1. Introduction

Proton Exchange Membrane fuel cell (PEMFC) is one of the key emerging technologies that is attracting remarkable effort with the aim to provide alternative environmentally friendly and efficient power sources. The advances in proton exchange membranes (PEMs) is critical for improving the performance of PEMFC [1–4].

Membranes comprising perfluorosulfonic acid polymers such as Nafion have been used extensively due to their high conductivity and stability. However, these materials need to be saturated with water to obtain practical levels of proton conductivity. Such hydration undermines the permeability of H₂ and O₂ due to the involvement of the formed hydrated ionic clusters in the gas permeation mechanism [5,6]. On the other hand, the retention and management of water within these types of membranes is challenging, costly and in most cases reduce the PEMFC performance. Therefore there is a strong demand for the PEMs to work at lower relative humidity and/or under anhydrous conditions.

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Accelerated electrochemical reactions and simpler water management of fuel cells under lower RH and/or anhydrous conditions is challenged by dramatic losses of proton conductivity of perfluorinated sulfonic acid based membranes [2,7,8]. Typically, N112 losses one order of magnitude of its proton conductivity at around 60% RH which, increases two orders of magnitude with the reduction of RH to 25%. So, it was concluded that the current Nafion based membranes cannot meet the requirements for the practical applications in these conditions.

Various designing strategies and advanced materials have been developed to improve the performance of PEMs operating under low RH [9]. One of the main strategies is based on reduction of the membrane thickness in a way leading to thinner membranes with lower internal resistance and improved water management during operation at lower RH and or elevated temperatures [7]. This is the main reason of progressive reduction in the thickness of commercial Nafion membranes for PEMFC over the past 2 decades (e.g. from ~183 μm in N117 to ~125 μm in N115 and then to 25 μm in N211) [10]. However, the thinner membranes are challenged by high fuel crossover and weak mechanical properties. On the other hand, low open-circuit voltage (OCV) and short PEM lifetime are the major concerns that have arisen on the practical application of 25 μm -thick Nafion membranes in hydrogen fuel cells.

Other strategies of designing less water dependent polymer electrolytes [11–13], modification of available electrolytes with water retention fillers [8,14–18], and introducing anhydrous proton conductive additives are also widely discussed to improve membrane limitations under lower RHs [19–23]. ENREF_15 Particularly, the incorporation of inorganic proton conductors such as heteropolyacids was found to increase the conductivity under dry and humidified conditions [20,24–27]. Heteropolyacids (such as phosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$, PTA) have a very strong Brønsted acidity, higher than both pure sulfuric acid and Nafion and approaching the superacid region. This high acidic strength is accomplished with fast reversible redox transformations under quite mild conditions [28]. In addition, this hydrophilic inorganic metal oxides have a high tendency to strongly accommodate water in their interlayer regions [29,30]. On the other hand, heteropolyacids could improve the stability of membranes by inhibiting the formation of peroxide/or catalyzing its decomposition [31–33]. The latter merit was confirmed by intense reduction in the release rate of F^- originated from fluorinated backbone degradation during PEMFC operating under relatively hot and dry conditions. However, although introducing of PTA to the membranes led to improved properties, yet PTA loading level and its direct contact with water are the serious concerns which need to be addressed. Low amount of PTA could be introduced into the membrane either through impregnation of porous substrate with an aqueous solution of PTA [22,34], or blending of PTA or its derivatives with a polymer followed by casting [35,36]. The composite membranes with PTA showed improved methanol barrier properties and/or water retention in DMFC [37–39], and enhanced PEMFC performance at low humidity and/or elevated temperatures [22,36,40]. However, due to the low level of PTA, loose interactions with polymer substrate and agglomeration, resulting composite membranes show low proton conductivity and PTA leaching during the fuel cell operation [41]. Copolymerization of PTA containing monomers was proposed to increase the loading level and minimize the leaching of PTA [42,43]. Such monomers are commonly prepared in the multi-step synthetic procedure and therefore this method was not used widely.

Recently, we proposed a simple and flexible method to introduce high level of PTA onto membranes [44]. Various amounts up to 50 wt% of PTA could be simply immobilized onto nylon nanofibers by self-immobilization. Such ion conductive nanofibers are capable

of fast proton transport [45]. On the other hand, leaching of PTA was addressed through assembling the membrane in a layered structure with two recast Nafion layers. The membranes showed an improved performance in DMFC and the conductivity remained quite stable even after more than 100 h of continuous testing.

In this work, a modified method was used to immobilize high level of PTA on nanofibrous structure and sandwiched membranes were fabricated for low humidity PEMFC application. The effects of PTA loading level and nanofiber diameter on the water uptake, dimensional stability and proton conductivity were investigated in comparison with commercially available N112. Moreover, the effect of introducing PTA on open-circuit voltage (OCV) as well as single-cell performance under lower RH were also evaluated.

2. Experimental

2.1. Materials

Technical grade nylon-6,6 (medium viscous, DSM Co., The Netherlands) was used to prepare the nanofibrous sheets using Electrospinner (Nanolab Instruments) electrospinning system. Thin Nafion layers with a thickness of 20 μm were prepared by casting a 15% concentrated aqueous solution of Nafion (5%, supplied from DUPONT). $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (98.1%, from Fischer Scientific Company, Fairlawn, NJ) was used for the preparation of Fenton agent for chemical stability test. Commercial catalyst of 40 wt % Pt/C (Johnson Matthey) was used in both the cathode and the anode.

2.2. Characterizations

Transmission electron microscope (TEM) images were obtained with a TECNAI G2 F20 with an accelerating voltage of 200 kV. A piece of the sample was milled at liquid nitrogen using Ika Ultra Turrax tube disperser. The dark areas in the HRTEM images clearly show hydrophilic domains and the light areas represent hydrophobic domains. The atomic force microscope (AFM) images were obtained with a Park NX10 in a non-contact mode. Scanning Electron Microscope (SEM) images of nanofibrous sheets and composite membranes were taken on the Philips XL30 Field Emission Scanning Electron Microscope (FESEM) after coating with 5 nm Au. The cross-sectional morphology was examined using cryofracturing of samples in liquid nitrogen. Fourier transform-infrared attenuated total reflection (FT-IR-ATR) spectra were performed on Agilent Cary 660 spectrometer. X-ray diffraction pattern was obtained on the Philips X'Pert 1 X-ray diffractometer with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5401 \text{ \AA}$) at scanning rate of 2° min^{-1} over a range of $2\theta = 4\text{--}80^\circ$. Thermogravimetric analysis (TGA) was performed on the Perkin Elmer TGA7 under nitrogen atmosphere at a heating rate of $10^\circ \text{C min}^{-1}$. Leaching of the PTA from the membrane was measured by immersing the composite membranes in deionized water at room temperature and monitoring the concentration of PTA in water every 12 h using a UV-1800 UV-vis spectrometer.

The in-plane (σ_{\parallel}) and through-plane (σ_{\perp}) proton conductivities of the membranes were measured by using a four-point probe of Bekk Tech conductivity cells (BT-112) and two-point probe of homemade stainless steel cylindrical electrodes with diameter of 20 mm. The resistance of the membranes was measured by using a DC conductivity testing (Keithley 2400 sourcemeter) controlled by a Labview software. The potentiostat was set to apply a specific voltage between the two inner probes and measure resulting current. The slope of the data from current versus voltage measurement was used to calculate the resistance (R) and proton conductivity (σ) was calculated according to the equation (1):

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