Journal of Membrane Science 474 (2015) 254–262

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Self-humidifying Pt–graphene/SiO_2 composite membrane for polymer electrolyte membrane fuel cell

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ARTICLE INFO

Article history:
Received 6 January 2014
Received in revised form
30 September 2014
Accepted 1 October 2014
Available online 13 October 2014

Keywords:
Pt–graphene content
SiO_2 content
Open circuit voltage
Zero humidity
Cell performance

ABSTRACT

Pt–graphene (Pt–G) is prepared by in-situ reduction of Pt precursor on graphene oxide surface using a microwave method. Various Nafion/xPt–G/$y$$SiO_2$ composite membranes where x is 0.5 wt%, 1.5 wt% and 3.0 wt% and y is 0.0 wt%, 1.5 wt% and 3.0 wt%, respectively are fabricated of which water uptake and proton conductivity show similar trend: that is, those are increased with both Pt–G and SiO_2 contents. The cell performance is significantly affected by relative amount of Pt–G and SiO_2 in composite membrane. Below 1.5 wt% in Pt–G content, the cell performance is increased with SiO_2 due to the excellent retention ability of SiO_2 for water produced from Pt site on graphene. Beyond 1.5 wt% in Pt–G content, however, the cell performance is rather decreased compared to that of 1.5 wt% Pt–G. It is ascribed to the blocking effect for proton conduction due to too much inorganic filler and possible loss of electrons through Pt network. The effect of SiO_2 on cell performance seems to be different depending on Pt–G and relative humidity (RH). Open circuit voltage (OCV) is significantly affected by SiO_2 content and increased with SiO_2 content.

1. Introduction

Recently, the demand of pure and clean power source which could substitute for energy solution has been increased due to energy shortage by gradual depletion of fossil fuel and the rise of environmental consciousness [1]. Proton exchange membrane fuel cells (PEMFCs) have received a huge amount of attention as the best candidate of alternative power sources such as solar cell, biomass, geothermal and wind due to its high power density and rapid adjustment to power demands [2]. Research efforts around the world have been paid to the study of PEMFC regarding their function at relatively low temperatures (80–100 °C) [3,4] and pressures (1–5 bars) [5]. These studies contributed to examine optimal designs of each operating conditions [6–9]. As well known, general PEMFC system needs humidified operating condition because the water content of a membrane is affected by electrical load, thickness of membrane, property of catalyst on electrode and operating conditions such as temperature, pressure and flow rate [10]. Water can be transported by the electro-osmotic drag and back-diffusion from cathode to anode due to the concentration gradient. Since proton is conducted via water molecules existing within the membrane, the water content in membrane has important effect on PEMFC performance. Therefore, fuel gases should be humidified before entering the cell using external humidifying unit which reduces the portability of fuel cell system due to the increase in its size [11–13]. In this reason, many researchers focus on self-humidifying polymer membrane as an alternative humidification of membrane which would remove the need for external humidification of the PEMFC system. These described the use of nano-sized inorganic fillers in the membrane to enhance water retention and even to create in situ water production. Nano-sized fillers such as TiO_2 [14,15], $TiSiO_4$ [16], SiO_2 [17,18], zeolite [19,20], montmorillonite [21] and ZrO_2 [22] were dispersed in Nafion membrane. It has been known that inorganic fillers in polymer inorganic composite membranes contribute to the enhancement of proton conductivity by retaining water within the membrane as well as mechanical and thermal stability [23–25]. Impregnation of Pt nanoparticles to these fillers leads to in situ water production. For examples, Pt nanoparticles impregnated onto SiO_2 provide the sites for both water production and retention: that is, water production on Pt nanoparticles combining H_2 and O_2 coming from anode and cathode and retention on SiO_2 [26]. Recently, polymer/graphene or polymer/graphene variants membrane has been investigated [27–31]. Graphene has a large surface area ($> 2600\ m^2\ g^{-1}$), superior mechanical strength and elasticity, excellent electrical and thermal conductivities, as well as ease of modification. Thus, graphene has considerable potential in molecular engineering, thin films, hybrids, energy production, and analytical fields [32,33]. It was reported that Pt or Pt metal alloy nanocatalysts supported on graphene sheets have higher electrocatalytic activity [34–36]. Due to these properties, graphene could be the promising electrocatalysts support material.

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http://dx.doi.org/10.1016/j.memsci.2014.10.001
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Most recently, Lee et al. [37] reported Nafion/graphene oxide (GO) composite membrane for self-humidifying PEMFC. As of now, however, no Nafion/Pt–graphene/SiO_2 composite membrane has been reported for self-humidifying PEMFC.

In this paper, we report Nafion/Pt–graphene(Pt–G)/SiO_2 composite membranes produced at different doping levels of Pt–G and SiO_2 particles. The membrane electrolyte assembly (MEA) was fabricated and the cell performance was conducted and discussed.

2. Experimental

2.1. Synthesis of GO

GO, the intermediate material of graphene was synthesized by a modified Hummer's method [38–40] using graphite powder as the starting material. 4 g of graphite powder (E-NanoTech. Co., Korea) was dispersed into 100 ml of concentrated H_2SO_4 (Samchun Chemical Co., Korea). 5 g of $K_2S_2O_8$ (Yakuri Pure Chemicals Co., Japan) and 2.5 g of P_2O_5 (Samchun Chemical Co., Korea) was then added to graphite dispersed solution. The dark gray mixture was heated to 80 °C in the oil bath and stirred for 2 h. The mixture was then cooled and kept at room temperature for 10 h. The mixture was washed with deionized (DI) water thoroughly to remove the residual acid. The product was dried at 80 °C in vacuum oven. The pre-oxidized graphite was grounded to powder. 4 g of the pre-oxidized graphite powder was added to 80 ml of concentrated H_2SO_4 (Samchun Chemical Co., Korea) in ice-bath (4 °C) during steady magnetic stirring. Then, 12 g of $KMnO_4$ (Samchun Chemical Co., Korea) was added slowly and kept below 10 °C in ice-bath for 30 min. After oxidation reaction, the dark blue mixture was heated to 35 °C and kept for 30 min under stirring, and then 100 ml of DI water was added to dilute the mixture during which the color of mixture was turned to yellowish brown. The mixture was then stirred at 95 °C for 30 min to which 600 ml of DI water, 20 ml of 30 wt% H_2O_2 aqueous solution and 100 ml of 10 wt% HCl aqueous solutions were added. Finally, the color of the mixture was changed to bright yellow along with bubbling. This solution was sonicated for 2 h to exfoliate graphite layers. The bright yellow solution was centrifugated and washed with DI water to remove metal ions and acid. Centrifugation was processed under 12,000 rpm for 3 min, followed by washing and repeated until the pH became neutral. The resulting GO powder was dried in vacuum oven at 60 °C for 10 h.

2.2. In-situ deposition of Pt nanoparticles onto GO by microwave treatment

Pt-impregnated graphene (Pt–G) were synthesized by in-situ Pt deposition onto GO using microwave treatment [37,41–43]. First, 100 mg of GO was dispersed into the mixture of 75 ml ethylene glycol (EG, Samchun Chemical Co, Korea) and 25 ml isopropyl alcohol (IPA, Samchun Chemical Co., Korea) and sonicated for 10 h to guarantee perfect dispersion. 104 mg of H_2PtCl_6 (Aldrich Co.) as a precursor was added to the above mixture of EG and IPA solution and stirred for 3 h, followed by 2 h sonication for good dispersion of precursor in solution. 1 M NaOH solution was added drop wise to the mixture to adjust pH to 12. The mixture was then heated in a household microwave oven (Samsung, RE-C21AW, operating frequency: 2450 MHz) at an output power of 700 W for 2 min. The heated mixture was cooled to room temperature. Then, 0.5 M HNO_3 solution was added drop wise to the mixture to adjust pH to 4 which would prevent Pt nanoparticle from agglomeration. The obtained Pt–G was washed and filtered with 500 mL of DI water 3 times. It was then dried in vacuum oven at 60 °C for 12 h. Oxygenated functional groups in GO were removed by chemical and thermal reduction during the deposition of Pt nanoparticles which led to Pt deposited multilayer graphene sheets.

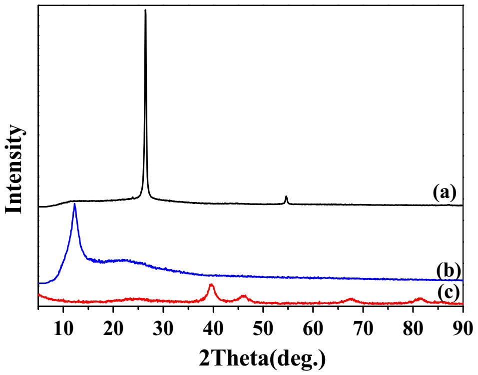

Fig. 1. XRD patterns of (a) graphite, (b) graphene oxide (GO) and (c) Pt–G.

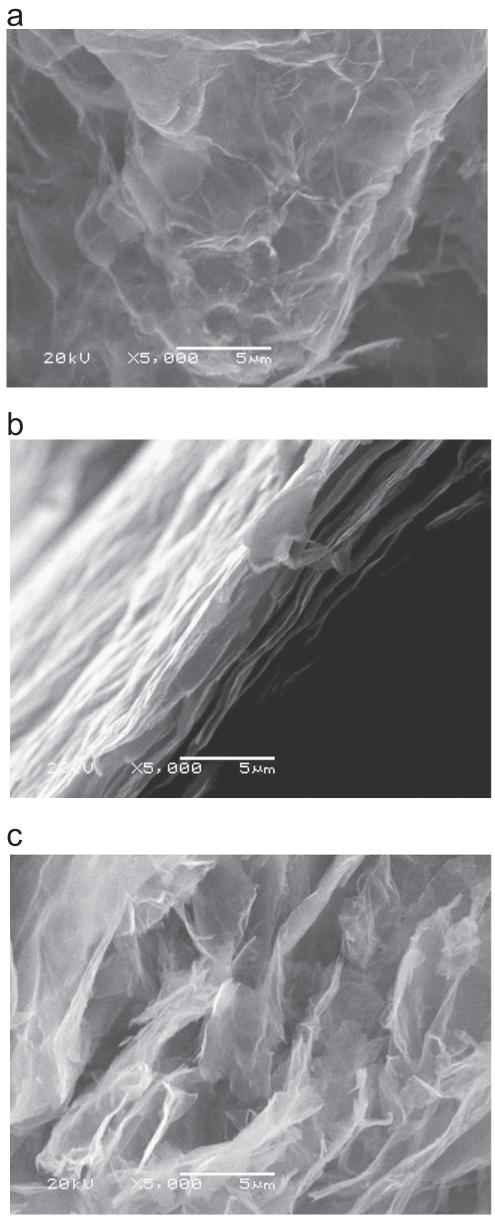

Fig. 2. SEM images of (a) graphite, (b) graphene oxide (GO) and (c) Pt–G.