Novel Bilayer Composite Membrane for Passive Direct Methanol Fuel Cells with Pure Methanol

Li-Duan Tsai[3], Hung-Chung Chien[2,3], Wei-Han Huang[2], Chiu-Ping Huang[2], Chi-yun Kang[2], Jiunn-Nan Lin[2], and Feng-Chih Chang[1,3,4,]*

[1]Department of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, 804, Taiwan
[2]Material and Chemical Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 310, Taiwan
[3]Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan
[4] R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli, Taoyuan, Taiwan
[*]E-mail: changfc1973@gmail.com

The bilayer composite membrane composed of the sulfonated graphene oxide (SGO)/Nafion and sulfonated activated carbon (SAC)/Nafion composite membrane is designed and prepared by repeatedly bar-coating. With the carefully chosen of solvent, the bilayer composite membrane has shown identical thickness on SEM observation. The SGO/Nafion side has a low methanol permeability ascribed to the unique selectivity of the SGO. Moreover, the SAC side has good water retention which can facilitate the back diffusion water produced by the cathode. The unique design of composite membranes confers low methanol crossover and high proton conductivity at the same time. The bilayer composite membrane shows better power density than Nafion 212 and Nafion 115 and the performance monitored for 24h to ensure the stable power density and the durability of the membrane.

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) have attracted considerable attention because of easily manageable liquid methanol fuel with excellent energy storage densities. DMFCs provide uninterrupted, continuous power as long as the methanol fuel is supplied because they are energy conversion devices rather than energy storage devices. Moreover, DMFCs provide higher energy

densities than Li-ion batteries.   DMFCs consist of an anode, a cathode, and a proton-conducting electrolyte membrane, which collectively are called a membrane electrode assembly (MEA). DMFC device is based on polymer electrolyte membranes that provide appropriate fuel cell performance in terms of conductivity, chemical and mechanical stability, durability, and fuel crossover. Among the polymer electrolyte membranes, DuPont's perfluorosulfonic acid, Nafion, is commonly used because of its excellent chemical stability and high proton conductivity. However, Nafion has a methanol permeability problem, referred to as methanol crossover, ascribed to the migration of water together with methanol through the ion clusters [1-3]. To address methanol crossover problems, several groups focused on the modification of Nafion membranes with a variety of organic and inorganic nanofillers, such as SiO_2, zeolites, zirconium, and polypyrrole [4–8]. Carbon materials are potential fillers for proton exchange membranes for their easy surface modification, as long as the composite membranes do not cause short. Carbon nanotubes (CNT)/Nafion composite membrane had shown impressive mechanical properties and good fuel cell performance. However, the low loading ratio of the conductive CNT has limited to mechanical properties and cause extensive swelling ratio. Amorphous carbon made from low temperature has been realized and shows high water retention and proton conductivity. However, the dramatic changes in thickness lower the performance of the fuel cell [9-11].

In this study, a novel bilayer composite membrane, comprised a sulfonated activated carbon (SAC)/Nafion layer and a sulfonated graphene oxide (SGO) layer, is developed by repeating bar-coating with controlled thickness. The bilayer membrane has low methanol crossover and high water retention properties for DMFC.

2. EXPERIMENTAL SECTION

2.1 Materials

Nafion 212 and 18% Nafion DE2020 dispersion were obtained from Ion Power Inc., New Castle, Delaware, U.S. PtRu/C and Pt/C were purchased from Johnson Matthey Inc., and used without further purification.

2.2 Preparation of sulfonated graphene oxide (SGO)

Graphite oxide was prepared from flake graphite powder by a modified Hummers method [12]. In brief, graphite oxide was synthesized by an oxidation of graphite with $KMnO_4$ and $NaNO_3$ in concentrated sulfuric acid. The oxidation was carried out using 25 ml of concentrated sulfuric acid per 1 g of graphite as the dispersion medium. To the graphite dispersion, 0.5 g $NaNO_3$ were added and cooled the dispersion to 0 ^{o}C by using the ice water bath. Then 3 g of $KMnO_4$ were added slowly during 5 hours. When the addition was finished, the resulting mixture was stirred at room temperature for another 5 hours. The reaction was quenched by pouring ice cold water and adding 5% H_2O_2 to destroy unreacted oxidant. The oxidized graphite was collected and washed with $HCl_{(aq)}$ and DI water.

The brown graphite oxide was dried under the vacuum. To prepare graphene oxide (GO), 100 mg graphite oxide was dispersed in 100 ml of DI and ultrasonicated with power 100 W (misonix, sonicator 3000) for hours until the solution became clear. Then, the GO solution was centrifuged with 4000 rpm for 10 min to remove any large and unexfoliated graphite oxide.

To sulfonate the grapheme oxide, 50 mg graphene oxide was added to 8 ml 0.06 M sulfanilic acid solution at 70 $^{\circ}$C. Under continuous stirring, 2 ml 6×10^{-3} M sodium nitrite solution was added dropwise and the mixture held at the 70 $^{\circ}$C for 12h. After the reaction, the mixture was washed collected by centrifuge and washed with water for several times until the pH reached 7. The SGO particles were characterized by XPS (X-ray photoelectron spectroscopy, Thermo VGESCAlab 250).

2.3 Preparation of sulfonated activated carbon

The sulfonated activated carbon was prepared by the same method mentioned in graphene oxide sulfonation. In brief, 1g AC was dispersed at 100 ml DI water and ultrasonicated for 2h. Then, the mixture was heated to 70 oC and 15 mL 0.6M sulfanilic acid was added to the mixture. Under continuous stirring, 5 ml 6×10^{-2} M sodium nitrite solution was added dropwise and the mixture held at the 70 $^{\circ}$C for 12h.

2.4 Manufacture of bilayer composite membranes

Nafion ionomers were transferred to *N,N*-dimethylacetamide (DMAc, Aldrich) by distilling a mixed solution of Nafion DE2020 and DMAc under reduced pressure until the solution temperature reached 70°C, to remove water and solvent. SGO/Nafion solution with 0.1 wt% SGO loading (compared to Nafion) in DMAc was prepared by adding well-dispersed $SGO_{(aq)}$ into the Nafion solution and mixing by mild ultrasonication. Then, the SGO/Nafion solutions were degassed and dispersed with a planetary mixer before casting. The composite membranes were obtained by bar coating with a gap of 300 um and drying at 50°C for 24 h, and post annealing at 140°C for 2 h. The SAC/Nafion solution was prepared by dispersing 10 wt% SAC (compared to Nafion) into Nafion solution (18% dispersion in aqueous alcohol). Then the SAC/Nafion mixture was bar-coating onto the SGO/Nafion film by a smaller bar with a controlled gap of 300 um and drying Nafion composite at 50°C for 24 h, and post annealing at 140°C for 2 h. Then, the membranes were cut into desired sizes and placed into 0.5 M $H_2SO_{4(aq)}$ at 80°C for 1 h to activate the sulfonic acids of the Nafion. Then, the activated membranes were soaked at 80°C in DI water to remove excess acid on the membrane. The cross-section of the bilayer composite membrane was characterized by SEM (Field emission scanning electron microscopy, LEO 1530 FE-SEM).

2.5 Fabrication of membrane electrode assembly (MEA)

PtRu/C catalysts and Pt catalysts were obtained from Johnson Matthey, Inc. Anode ink was made by mixing the supported PtRu/C catalyst, deionized water, and Nafion dispersion. Meanwhile,

the cathode ink was prepared by supported Pt catalysts, deionized water, and Nafion dispersion. The catalyst inks were ultrasonicated until the mixtures became homogenous pastes. The inks were coated onto gas diffusion layers and the loadings of the PtRu for the anode and the Pt for the cathode were 2 mg cm^{-2} each. Membrane electrode assemblies were prepared by hot pressing under a pressure of 25 kg cm^{-2} at 130°C for 3 min.

2.6 Proton conductivity

The impedance spectra of the membranes were measured by a four-point probe unit using a Bio-Logic SP-300 Analyser. The measurements were conducted at room temperature. Ultimately, the proton conductivity σ was calculated based on the equation:

$$\sigma = L/AR \quad (1)$$

Where L is the sample thickness, A is the cross-sectional area, and R is the resistance of the membrane.

2.7 Water uptake and swelling ratio

The water uptakes of the membranes were calculated from the equation:

$$WU = (W_{wet} - W_{dry})/W_{dry} \quad (2)$$

Where W_{wet} and W_{dry} are the weights of the fully hydrated and the anhydrous membranes, respectively. In our protocol, the membranes were first immersed in deionized water (or methanol at 30°C) for 24 h, blotted with an absorbent paper, and then, W_{wet} was measured. Subsequently, the membranes were thoroughly dried in a vacuum oven at 70°C for 24 h; then, W_{dry} was measured. The dimensions of the hydrated and dry membranes were measured by a micrometer (Mitutoyo) that was able to measure the membrane thickness with micrometer resolution.

The volume swelling ratio was used instead of traditional swelling ratio in length. The volume changes according to the changes of the lengths and the thickness. The average thickness was measurement more than four times in different positions.

2.8 Ion exchange capacity and methanol permeability

Ion exchange capacity (IEC) titration was measured with the following procedure. Typically, 0.1g Nafion or AC/Nafion composite membrane was soaked into 50 mL 1M NaCl$_{(aq)}$ for 12 h. The membrane was taken out and titrated the NaCl$_{(aq)}$ with 0.01M NaOH$_{(aq)}$ until the pH value reached 7 (pH meter, Suntex SP-2200). The IEC value was calculated based on the equation.

$$IEC = VC/W \quad (3)$$

Where V is the volume used for titration, C is the concentration of the NaOH$_{(aq)}$ and W is the sample weight. [13]

The methanol permeability of the membrane was determined using a two-chamber liquid permeability cell with 20 v/v% MeOH$_{(aq)}$. The methanol permeability is based on methanol crossover

the membrane for the concentration difference. The methanol permeability is calculated according to the following equation:

$$C_B(t) = (A/V_B) D (K/L) C_A(t - t_0) \quad (4)$$

Where C is concentration, V_B is the volume of the solution in the methanol permeation side, A and L are the membrane area and thickness respectively; D and K, are respectively, the methanol diffusivity and partition coefficient. Assume that D inside the membrane is constant and K is independent to the concentration. The product DK is the membrane permeability. t_0, referred as the time lag, is related to the diffusivity as $t_0 = L^2/6D$. C_B has been monitored by density meter (Auton Paar, DMA 4500). The methanol permeability was calculated from the slope of the straight line plot straight line plot obtained between $C_B(t)$ against time. [14]

3. RESULTS AND DISCUSSION

3.1 Preparation of sulfonated activated carbon and sulfonated graphene oxide

To improve the poor dispersion and proton conductivity of the activated carbon (AC), the submicron sized AC particles was modified by aryl diazonium reaction with sulfanilinic acid. The ratio of the sulfonation was characterized by the XPS as shown in Fig. 1. The ratio of C1s / S2p was 8.31 / 1. The sulfonation of the AC increased the dispersion in the Nafion solution through inter-molecular hydrogen bonding. Moreover, the decorated sulfonic groups on the surface of AC facilitated the proton transport and resulted in higher proton conductivity. Compared to the high sulfonation ratio of the AC, the sulfonation of graphene oxide sheets was lower (C1s/S2p = 39.7/1) as shown in Fig. 1(b). The lower sulfonation ratio was ascribed to the deficiencies of the aromaticity of graphene oxide sheets.
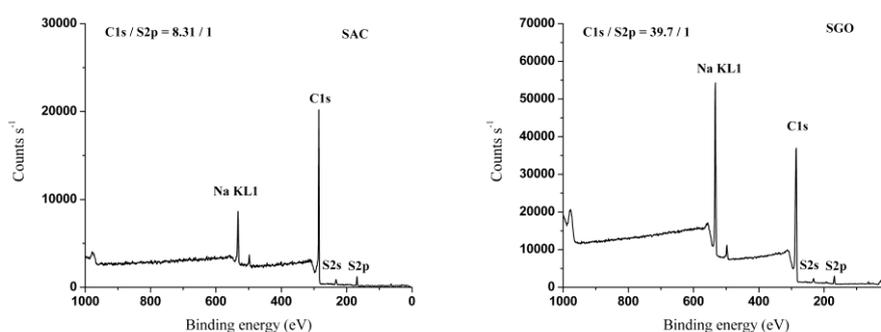
Figure 1. XPS analysis of (a) SAC and (b) SGO

3.2 Preaparation and characterization of the bilayer composite membrane.

The preparation of the bilayer composite membrane was shown in the Fig. 2. The solvent for the coating was carefully chosen and SGO/Nafion DMAc solution was used for the first layer.

Compared to Nafion coated with aqueous alcohol, Nafion coated with higher boiling point has better dimensional stability and mechanical properties. [15] To avoid undesired swelling ratio, the low aliphatic Nafion solution was used for second layer. The SAC/Nafion in aqueous alcohol solution was coated directly onto the SGO/Nafion membrane by a Dr. blade with a gap of 300um. After drying and thermal annealing, the bilayer composite membrane was formed and carefully cut into desired size for further characterization.
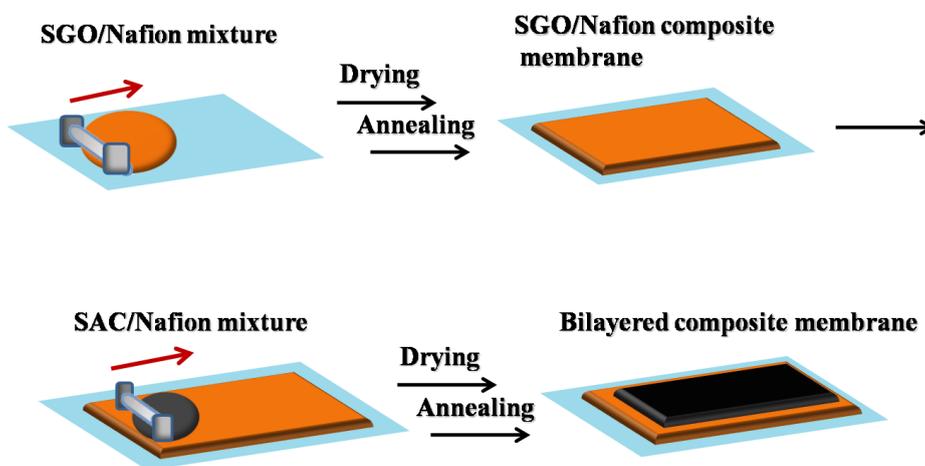
Figure 2. The preparation of the bilayer composite membrane.

The cross-section of the bilayer composite membrane was observed by SEM as shown in Fig. 3. The two layers had identical thickness which were 37.68 um (SGO/Nafion) and 37.02 um (SAC/Nafion). The locally enlargement of SGO/Nafion (Fig. 3(b)) showed an obscure interface between SGO and Nafion matrix. Graphene oxide had been considered as an effective additive in Nafion composite membrane for low methanol permeability and performed excellent DMFC performance. [16] In our previous study, acidified AC was incorporated into Nafion membrane as a water reservoir and showed high performance in proton exchange membrane fuel cell. [17] In this study, sulfonated AC was used instead of acidified AC in order to provide higher proton conductivity. The SAC/Nafion layer (Fig. 3(c)) showed SAC merged into the Nafion matrix without obvious aggregation or pin holes.
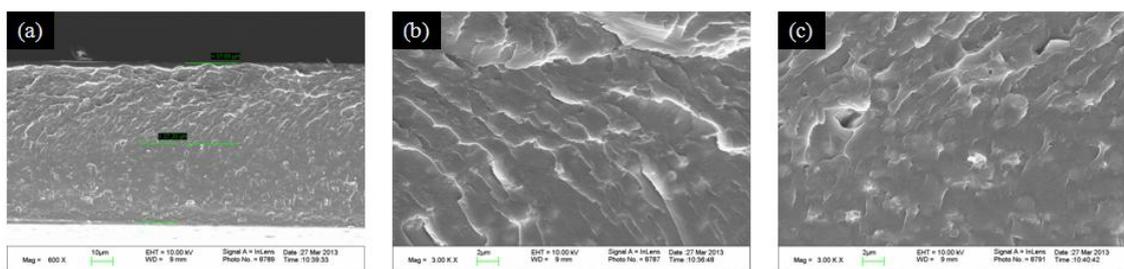
Figure 3. The SEM images of the (a) bilayer, (b) SGO/Nafion and (c) SAC/Nafion composite membrane.

3.3 Water uptakes, and the swelling ratio of the composite membrane

The water uptakes of the composite membranes are listed in Table 1. The water uptakes of recast Nafion and SGO/Nafion composite membrane were 29.7% and 30.8%, respectively. Instead, the AC showed higher water uptake (80.2%) because of the high porosity and surface area of the activated carbon. Moreover, the bilayer composite membrane, composed of SGO/Nafion and SAC/Nafion, had a high water uptake due to the high water storage character of the SAC/Nafion.

The phase separation feature of Nafion membrane is derived from the hydrophilic sulfonic acid side groups and the nonpolar fluorocarbon backbone. The water-swollen ionic domains were treated as inverse micelles—essentially, pools of water—and it was proposed that water and ion transport occurred through narrow interconnecting channels [18]. The swelling ratio was strongly related to the solvent uptake. The swelling ratios of the Nafion composite membranes were determined as listed in Table 1. The recast Nafion membrane showed a high swelling ratio because of the high swelling character of the ionic clusters. Expansion in the ionic channels allows methanol to pass through the membrane much more easily. In contrast, the 1 wt% SGO/Nafion composite membrane exhibited a swelling ratio of 32.2% while the SAC/Nafion composite membrane displayed a swelling ratio 35.7. Nevertheless, the bilayer composite membrane had a higher swelling ratio of 47.8% contributed to the uncertainty of the interfaces between SAC/Nafion and SGO/Nafion. Another important factor for passive DMFC is the proton conductivity of the membrane. As shown in Table 1, all the composite membranes had better proton conductivity than recast Nafion due to the easier proton transfer between sulfonated additives and the ionic clusters of the Nafion.

Table 1. The physical properties of the recast Nafion and composite membranes

	Recast Nafion	**SGO/Nafion**	**SAC/Nafion**	**Bilayer composite membrane**
Conductivity (S/cm)	0.033	0.042	0.060	0.052
Volume swelling ratio (%)	66	32.2	35.7	47.8
Water uptake (%)	29.7	30.8	80.5	75.1

Methanol permeability is an important consideration in passive DMFC applications, since the crossover leads to lower cell voltages and reduced fuel efficiency. The methanol permeabilities of the bilayer composite membrane and commercially available Nafion 212 are shown in Fig. 4. The methanol permeability decreased in the presence of SGO had been described in previous studies for the

grapheme oxide offer unique selectivity between methanol and water molecules which impeded the transport of the methanol.
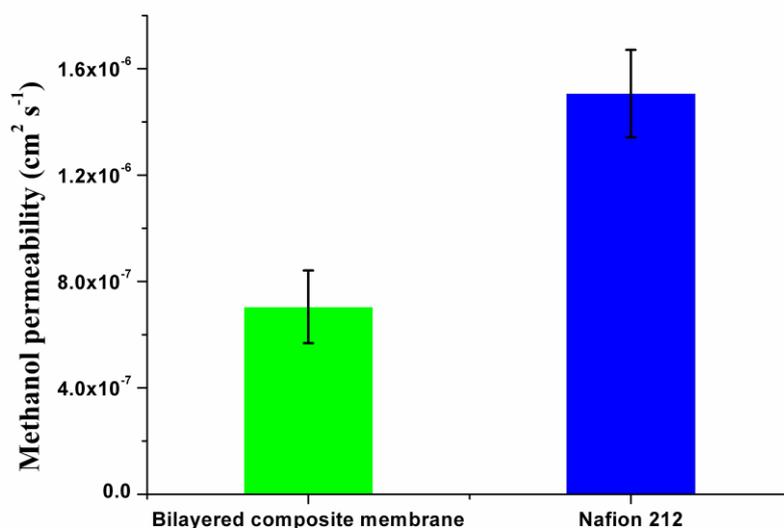
Figure 4. The methanol permeability of the bilayer composite membrane and Nafion 212.

The unique selectivity of graphene oxide was described by the A. K. Geim group [19]. Commercial pristine Nafion 212 exhibited a methanol permeability of 1.32×10^{-6} cm^2 s^{-1} at 30°C, whereas the methanol permeability of bilayer composite membrane was 7.54×10^{-7} cm^2 s^{-1}, about a 2-fold decrease by comparison. Methanol transport strongly depends on the nature of water transport in the Nafion matrix. However, it was clear that the incorporation of well-dispersed SGO reduced methanol permeability because it could impede the methanol from migrating through the membrane with longer routine. The better performance was contributed to the higher water uptake and lower methanol permeability.

3.4 Performance of the DMFC

The actual cell voltages of the DMFCs are lower than the theoretical voltages due to losses involved in fuel cell operation. Major losses are due to methanol crossover from the anode to the cathode [20, 21]. We devised a simple method to mitigate methanol crossover by introducing bilayer composite membrane into the DMFC. The SGO side was designed for anode while the SAC side was used in a cathode as shown in Figure 5. Pure methanol was fed from the anode and generally suffered a high methanol crossover and results in lower performance. During the fuel cell operation, cathode produces water molecules and most of them were carried out by the air. However, some of the water molecules diffused into the membrane, so called as back-diffusion water, and facilitated the hydrated of the membrane. Discharge curves for the commercial Nafion 212 membrane and the bilayer composite membrane with pure methanol as fuel is shown in Fig. 6. The power density at 0.35V was

monitored for 24h to ensure the performance of the cell was stable. From the results, Nafion 212 and Nafion 115 had the power density 27.15 and 26.90 mW/cm^2 (5h, at 0.35V), respectively while the bilayer composite membrane has 29.07 mW/cm^2. The novel bifunctional composite membrane existed a better performance than Nafion 212 and Nafion 115 for the lower methanol permeability, higher water uptake and proton conductivity.
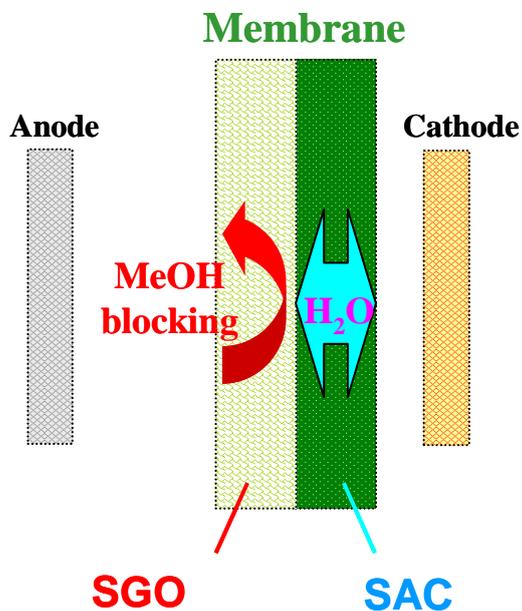
Figure 5. The illustration of the bilayer composite membrane for passive DMFCs.
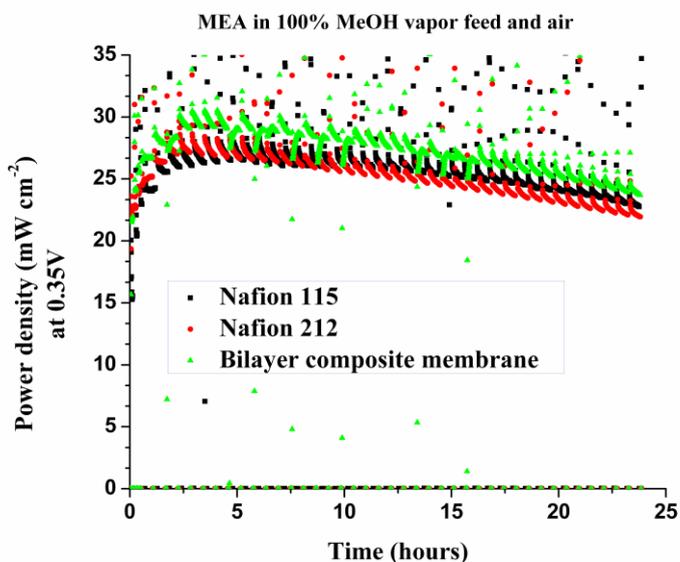
Figure 6. The continuous power density at 0.35V of passive DMFC made of the bilayer composite membrane, Nafion 115 and Nafion 212.

4. CONCLUSIONS

In conclusion, a low methanol crossover and high water uptake composite membrane was developed by simply repeated coating. The SGO/Nafion composite membrane provided lower methanol permeability for its unique selectivity between methanol and water molecules. On the other hand, the SAC/Nafion composite membrane offered a better water retention due to the porosity and surface area of the activated carbon. The bilayer composite membrane had lower methanol permeability than Nafion 212 while maintaining higher water uptake. The power density of passive DMFC made of the bilayer composite membrane was 10% better than Nafion 212 and lasted for 24h. With this method, composite membranes with multi-functions can be easily designed by control casting solvent and the gap of the wet film.

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