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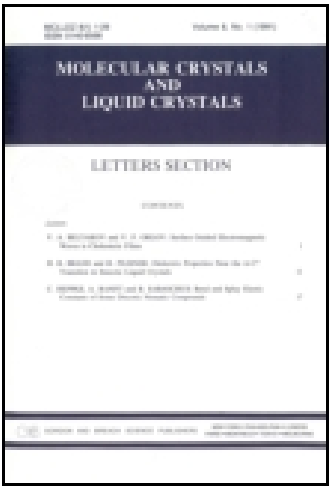

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LbL Assembled sPPO Composite Membrane Containing GO for DMFC Applications

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Multilayered polyelectrolyte membrane was prepared by layer by layer (LbL) method by alternating deposition of poly (diallyl dimethyl ammonium chloride) (PDDA) and an anionic polyelectrolyte chosen from graphene oxide (GO), sulfonated GO (sGO), or sulfonated poly (phenylene oxide) (sPPO). LbL deposited bilayers of {PDDA / GO}$_n$ *and {PDDA / sGO}*$_n$ *were prepared and their accumulation behaviors were studied. After the LbL assembly of the above polyelectrolyte tetra-layers of {PDDA / GO (or sGO) / PDDA / sPPO}*$_n$ *onto the Nafion film, the adaptability as a membrane for direct methanol fuel cell (DMFC) was investigated in terms of proton conductivity and methanol permeability*

Keywords Graphene oxide; layer by layer deposition; proton exchange membrane; direct methanol fuel cell

Introduction

Layer-by-layer (LbL) deposition is a very versatile method to prepare very thin polyelectrolyte multilayer composite films by alternately depositing positively and negatively charged polyelectrolytes [1–2]. During the LbL deposition the polyelectrolyte self-assembles and self-organizes on an oppositely charged substrate via electrostatic or hydrogen bonding interactions, so it is possible to include nanoparticles and biological molecules of different shapes [3]. For the development of polyelectrolyte membrane, LbL method is often used for the surface property modification of a given polymer film. Especially for a direct methanol fuel cell (DMFC) application, there have been many investigations on the LbL modification of Nafion to reduce the methanol permeability of the films [4–7]. But there have been a few attempts on the utilization of inorganic fillers as a component of the LbL polyelectrolyte [8–9].

Graphene oxide (GO) is oxidized form of graphene and usually used as a precursor of graphene [10], and has been known as an excellent amphiphilic material due to several oxygen- containing functional groups in the basal plane and carboxylic acid at the edge positions as shown in Fig. 1a). Similar to inorganic fillers, GO and its derivatives can be used as fillers for polymer composites, and their composites are known to exhibit enhanced

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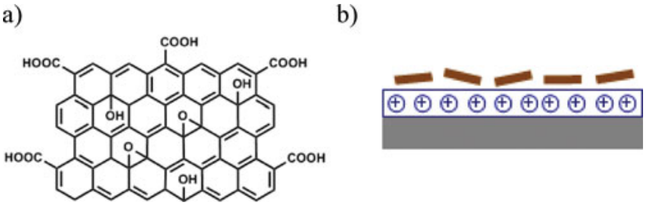

Figure 1. a) A representative molecular structure of GO, and b) a schematic illustration of GO layer on PDDA in LbL deposition.

electrical and mechanical properties [11], and improved thermal stabilities [12–13]. In the composites, however, GO becomes the minor component and it is very difficult to find out the literature on the investigation of the orientations of GO in the polymer composites. Different from this polymer composite approach, two dimensional sheet-like GO can be assembled into a more or less flat object via LbL deposition by using the GO itself as the negatively charged or positively charged polyelectrolyte as shown in Fig. 1b). Through this flat assembling method, GO sheets can be overlapped each other and can show good electrical conductivity. Almost all investigations on GO via LbL depositions are, therefore, targeted for the conducting electrodes, batteries, solar cells, super capacitors, and sensors [14]. In a different aspect, the two dimensional sheet-like nature of GO can be used as an excellent barrier material in proton exchange membrane in which the GO can substantially reduce the methanol cross over in DMFC membrane.

Although GO is easily reduced by thermal or chemical treatments, electrical insulating characteristics of proton exchange membrane can be maintained by incorporating small amount of GO. Also a possible simultaneous reduction in proton conductivity can be minimized or circumvented by the use of sulfonated GO (sGO). Herein, poly(diallyldimethylammonium chloride) (PDDA) and a highly sulfonated poly(phenylene oxide) (sPPO) were used as the positively and negatively charged polyelectrolyte solutions, respectively, as shown in Fig. 2. GO and sulfonated sGO were prepared, and used also as negatively charged species. For a simple comparison, LbL deposited bi-layers of $\{PDDA / GO\}_n$ and $\{PDDA / sGO\}_n$ were prepared and studied, and then similarly deposited tetra-layers of $\{PDDA / GO / PDDA / sPPO\}_n$ and $\{PDDA / sGO / PDDA / sPPO\}_n$ were prepared and studied. After the LbL assembly of the above polyelectrolyte tetra-layers onto the Nafion film, the adaptability as a membrane for DMFC was investigated in terms of proton conductivity and methanol permeability.

Experimental

Materials

GO was prepared by using the modified Hummers method as reported previously [15]. Sulfanilic acid and sodium nitrite were obtained from Sigma Aldrich and used as received.

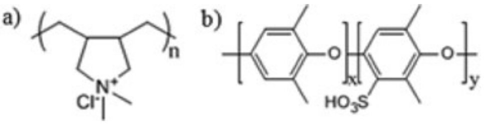

Figure 2. Chemical structures of a) PDDA and b) sPPO.

Concentrated sulfuric acid and hydrochloric acid were obtained from Samchun chemicals (Korea) and used as received. PDDA ($M_n = 200{,}000 \sim 350{,}000$) was obtained from Sigma Aldrich and used as received. Highly sulfonated sPPO with ion exchange capacity of 5.47 meq/g was prepared by following the literature procedure [16]. Other chemicals were obtained from Samchun chemicals and used as received. Nafion 112 was obtained from Alfa Aesar and used after treatment by immersion in 0.5 M boiling sulfuric acid for 2 h, followed by immersion in boiling deionized water for 2 h. Quartz slides or silicon wafers were used as substrates for LbL after cleaning with Piranha solution (98% H_2SO_4 / 30% H_2O_2 = 3/1).

Preparation of sGO

The stability of GO dispersion in water was very good, and no precipitation was observed even after centrifuge at 6000 rpm for 20 min. sGO was obtained by following the literature procedure [17]. Briefly, GO (37.5 mg) was dispersed in water by sonication for 1 h in an ultrasonic bath cleaner. For the sulfonation, aryl diazonium salt was prepared from the reaction of sulfanilic acid (23 mg) and sodium nitrite (9 mg) in water (5 g) with a few drops of 1N HCl solution in an ice bath. Then the aryl diazonium salt solution was added into the GO dispersion in an ice bath with stirring, and reacted for 2 h. After the reaction the solution was dialyzed against water and freeze dried.

LbL Assembly

For LbL film deposition, substrates were immersed in aqueous PDDA solution for 10 min, followed by each 2 min rinses in deionized water three times, and then in aqueous GO dispersion for 10 min followed by each 2 min rinses three times. The concentration of the PDDA or sPPO was 10 mM based on the molecular weight of repeating units of the polymer. The concentration of GO or sGO was 0.1 wt%. This cycle was repeated to obtain the desired number of bilayers.

Characterization

Chemical reactions were monitored by ^{1}H-NMR and FTIR. After LbL assembly, films were soaked in acidic water (pH ∼ 2) for 4 h and washed with deionized water to ensure that the films are protonated. The proton conductivity (in-plane) of the membranes was determined by the two probe AC impedance spectroscopy using HP4192A LF impedance analyzer [18]. The measurement was carried out at room temperature in deionized water (relative humidity 100%). The methanol permeability of the films was determined using a diaphragm glass diffusion cell at 25°C following a previously reported procedure [19]. Scanning electron microscopy (SEM, Nova Nano SEM 450) was used to observe the thickness of the LbL assembled films after liquid nitrogen fracture. Tapping mode atomic force microscopy (AFM, Park system) was used to observe the sGO samples after deposition of sGO over PDDA on silicon wafer substrate.

Results and Discussion

Fig. 3 shows the FTIR spectra of GO and sGO. As shown in the figure, GO shows absorption peaks at 1720 (C=O), 1620 (adsorbed H_2O), and 1100 cm^{-1} (C—O stretching). sGO shows

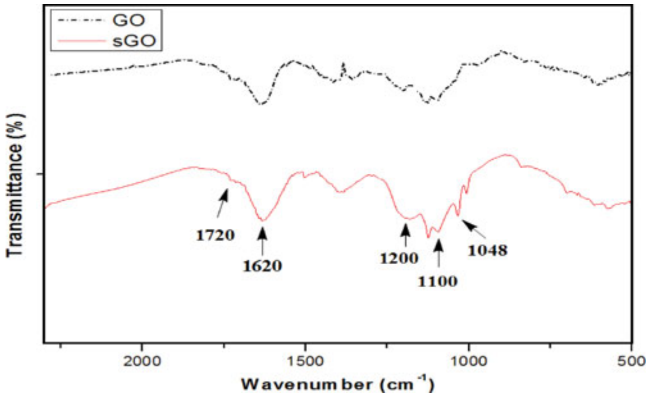

Figure 3. FTIR spectra of GO and sGO.

peaks at 1200 cm^{-1} (SO_2 symmetric stretching) and 1048 cm^{-1} (SO_3 stretch of sulfonic acid). These FTIR spectra show that sulfonation reaction was successfully occurred.

Fig. 4 shows the AFM image of PDDA / sGO bilayer on silicon wafer. sGO dispersion in water was coated on PDDA treated silicon wafer and observed by AFM. The figure shows that the size distribution of sGO is rather broad, but the size of large plate is less than 4 um. The corresponding line profile also shows a thickness of 2 ∼ 4 nm. The thickness of GO or sGO used in this experiment was ∼ 1.2 nm (not shown), and it is reported that the typical thickness is 1 ∼ 1.2 nm for a fully exfoliated GO dispersed in water [20]. So, it is believed that there is a high chance of existing small pieces of sGO under the large sGO plate in this AFM if one do not consider the influence of PDDA layer on the thickness of the bilayer. Also this figure shows that the coverage of sGO on PDDA layer is not compact, but rather shows irregular coverage. This may explain well the observation on the electrical conductivity of LbL deposited GO, which reported that the conductivity was very poor with the low number of deposition, but increased with the high number of deposition [21].

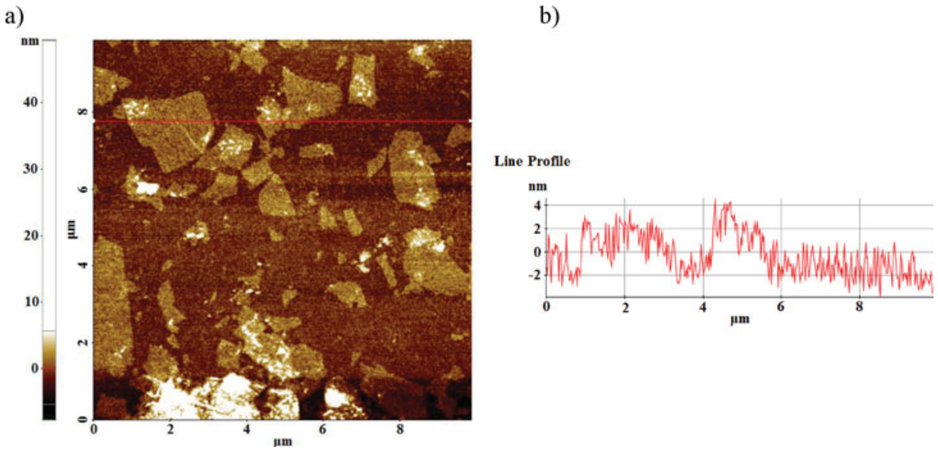

Figure 4. a) A non-contact AFM image of PDDA / sGO bilayer on silicon wafer, and b) its height line profile.

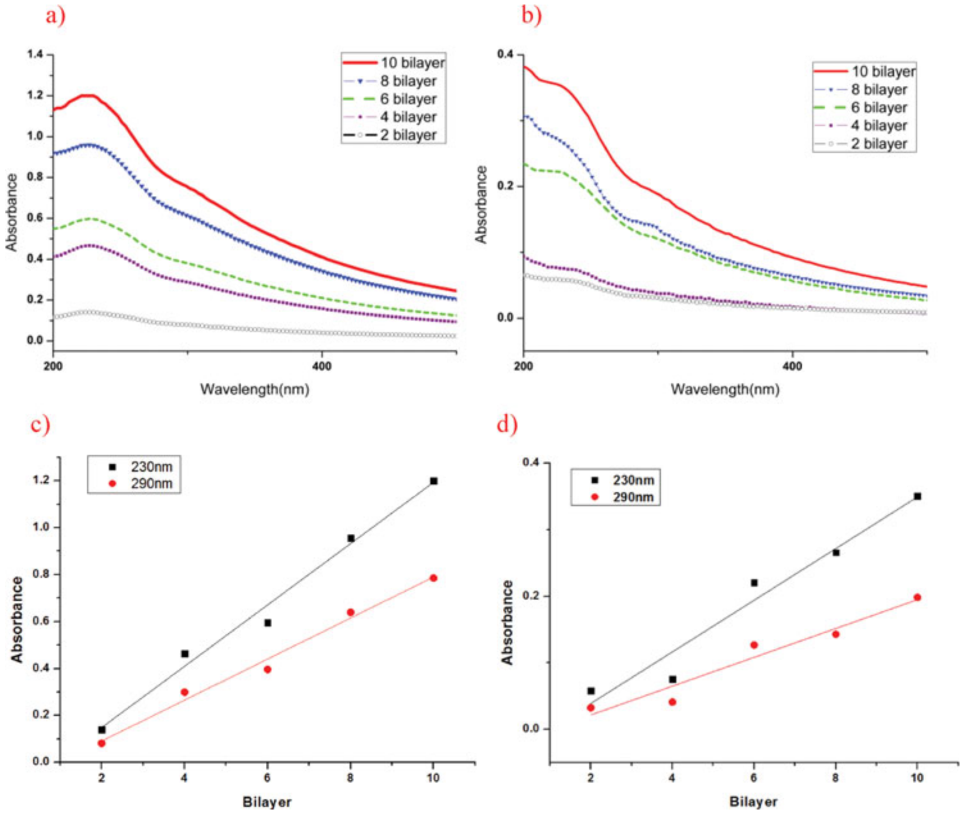

Figure 5. UV absorption spectra of a) PDDA / GO bilayers, b) PDDA / sGO, and c) - d) the corresponding absorbance versus number of bilayers at 230 and 290 nm.

Fig. 5 shows the UV absorption spectra of LbL bilayer films deposited on quartz slide from the cationic PDDA solution and the anionic GO or sGO water dispersion. The absorbance plots show almost linear increases of absorbance at 230 nm and 290 nm, demonstrating that each accumulating bilayer process is reproducible in LbL process.

For the membrane application, LbL films of GO or sGO were prepared on Nafion 112 in the form of 10 tetra-layers (20 bi-layers), i.e., $\{PDDA / GO / PDDA / sPPO\}_n$ on each side of the Nafion for GO. As shown in Table 1, in-plane proton conductivity was changed from 0.021 to 0.032 S/cm by changing from GO to sGO in the $\{PDDA / GO / PDDA / sPPO\}_n$ –Nafion composite membrane. But the value was quite lower than that of Nafion,

Table 1. In-plane proton conductivities of different Nafion membranes

	Proton conductivity (S/cm)	Methanol permeability ($\times 10^{-6}$ cm^2/min)	Selectivity
PDDA/GO/PDDA/sPPO	0.021	1.76	1.19
PDDA/sGO/PDDA/sPPO	0.032	1.56	2.05
Nafion 112	0.091	2.36	3.86

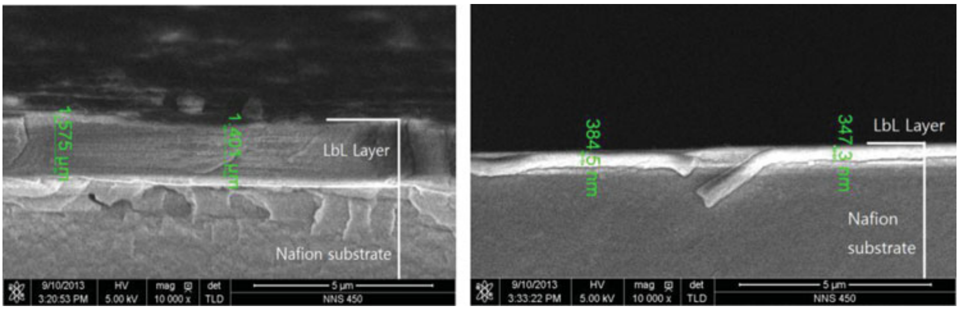

Figure 6. SEM pictures of films showing cross section of 10 LbL tetra-layers on Nafion: a) GO, and b) sGO.

probably due to the presence of cationic PDDA polymer which neutralizes a strong acidic sPPO. Also the conductivity data shows that carboxylic acid in GO may not be good enough for good proton conductivity, but sulfonic acid in sGO is better for the conductivity. The use of NaCl in the sPPO solution usually gives thicker sPPO layer, resulting in increased proton conductivity by making a polymer chain conformation to "coiled" in a strong electrolyte condition. But such attempt was not tried in this study.

LbL-Nafion membranes showed improved methanol barrier properties compared to Nafion 112 as in the Table. The improvements made with the membranes were 25% for GO and 34% for sGO. And these values are rather unsatisfactory when one considers the fact that the reported improvement was around 30% with 8 bilayers of PDDA / sulfonated polystyrene on Nafion [4]. Therefore, the additional existence of GO or sGO seems to influence only marginal effect in the improvement of methanol barrier property in this study. Selectivity which is defined by the ratio of the proton conductivity to the methanol permeability of a film, showed slightly lower values for the LbL-Nafion membranes compared to that of Nafion, due to the low proton conductivities of the LbL membranes.

SEM pictures in Fig. 6 show the cross sectional views of the liquid nitrogen fractured 10 tetra-layer LbL-Nafion films, which show the LbL film thickness of ca. 1.5 um for the LbL film containing GO and ca. 0.35 um for the LbL film containing sGO. The overall thickness of the composite membrane will be 53 or 50.7 um for the one containing GO or sGO, respectively. And this marginal difference in thickness will show only marginal influences in the performance of DMFC. But from the difference in the thickness of LbL layers, one can figure out the packing compactness of the GO nanosheets. If one recalls that the reported thickness of PDDA / sPPO is 6.91 nm per bilayer under the same experimental condition [22], then the calculated thickness of PDDA / GO will be ca. 140 nm per bilayer and that of PDDA / sGO will be ca. 28 nm per bilayer. That means that the thickness of PDDA / GO bilayer is ca. 5 times thicker than that of PDDA / sGO bilayer. And the origin may be the low acidity as well as the location of −COOH groups in GO molecule. Relatively large size (micrometer order) and the size differences of GO may be additional factors to the irregular and loose self assembly of the GO, and the resultant very thick bilayer. The marginal methanol barrier properties of the LbL membranes containing GO and sGO are, therefore, related with the less compactly assembled carbonaceous materials.

Conclusions

LbL films were prepared from PDDA and highly sulfonated sPPO, and GO or sGo were incorporated into the LbL film by the form of tetra-layers of {PDDA / GO (or sGO) / PDDA

/ sPPO}. Both GO and sGO formed LbL films with PDDA which showed good correlations in absorbance versus the number of bilayer relationship. The tetra-layers on Nafion film showed decreased methanol permeability, but the influence of the GO or sGO on the barrier property was marginal, due to the non-compact assembly of the GO or sGO in LbL layers. As a result, the presence of GO or sGO did not provide enough tortuosity in the path of methanol permeation. The thickness of LbL with sGO was about a quarter compared to that of LbL with GO. And a better barrier property is expected with sGO of smaller size and uniform size distribution.

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References

[1] Decher, G. (1997). *Science*, *277*, 1232.
[2] Lyklema, J., & Deschênes, L. (2011). *Adv. Coll. Interface Sci.*, *168*, 135.
[3] Boudou, T., Crouzier, T., Ren, K., Blin, G., & Picart, C. (2010). *Adv. Mater.*, *22*, 441.
[4] Jiang, S. P., Liu, Z., & Tian, Z. Q. (2006). *Adv. Mater.*, *18*, 1068.
[5] Yılmaztürk, S., Deligöz, H., Yılmazoğlu, M., Damyan, H., Öksüzömer, F., Koç, S. N., Durmuş, A., & Gürkaynak, M. A. (2009). *J. Membr. Sci.*, *343*, 137.
[6] Deligöz, H., Yılmaztürk, S., Yılmazoğlu, M., & Damyan, H. (2010). *J. Membr. Sci.*, *351*, 131.
[7] Zhang, H., & Shen, P. K. (2012). *Chem. Soc. Rev.*, *41*, 2382.
[8] Kim, D. W., Choi, H. -S., Lee, C., Blumstein, A., & Kang, Y. (2004). *Electrochim. Acta*, *50*, 659.
[9] Zhao, C., Lin, H., Cui, Z., Li, X., Na, H., & Xing, W. (2009). *J. Power Sources*, *194*, 168.
[10] Compton, O. C., & Nguyen, S. T. (2010). *Small*, *6*, 711.
[11] Stankovich, S., Dikin, D. A., Dommett, G. H. B., Kohlhaas, K. M., Zimney, E. J., Stach, E. A., Piner, R. D., Nguyen, S. T., & Ruoff, R. S. (2006). *Nature*, *442*, 282.
[12] Niranjanmurthi, L., Park, C., & Lim, K. T. (2012). *Mol. Cryst. Liq. Cryst.*, *564*, 206.
[13] Lingappan, N., Kim, D. H., & Lim, K. T. (2013). *Mol. Cryst. Liq. Cryst.*, *580*, 69.
[14] Hong, J., Han, J. Y., Yoon, J., Joo, P., Lee, T., Seo, E., Char, K., & Kim, B.-S. (2011). *Nanoscale*, *3*, 4515.
[15] Hummers W. S., Jr, & Offeman, R. E. (1958). *J. Amer. Chem. Soc.*, *80*, 1339.
[16] Argun, A. A., Ashcraft, J. N., & Hammond, P. T. (2008). *Adv. Mater.*, *20*, 1539.
[17] Si, Y., & Samulski, E. T. (2008). *Nano Lett.*, *8*, 1679.
[18] Kim S. H., & Cho, C. G. (2011). *Macromol. Res.*, *19*, 1142.
[19] Li, G. H., Lee, C. H., Lee, Y. M., & Cho, C. G. (2006). *Solid State Ionics*, *177*, 1083.
[20] Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., & Ruoff, R. S. (2007). *Carbon*, *45*, 1558.
[21] Wu, J., Tang, Q., Sun, H., Lin, J., Ao, H., Huang, M., & Huang, Y. (2008). *Langmuir*, *24*, 4800.
[22] Ashcraft, J. N., Argun, A. A., & Hammond, P. T. (2010). *J. Mat. Chem.*, *20*, 6250.