

**Figure 2.** Surface morphologies of the argon-plasma-treated Nafion membranes: (a) plain Nafion; (b) 10 W and 240 s; (c) 50 W and 300 s; (d) 200 W and 300 s.

## Experimental Section

**Modification of the Nafion Membranes by Plasma Irradiation.** Nafion 115 was purchased from E.I. du Pont de Nemours and was pretreated by boiling it in 5 wt % peroxide solution, 1 M aqueous sulfuric acid solution, and deionized water, in that order. Figure 1 shows the structural formula of the Nafion membrane. The surface modification of the Nafion membrane was conducted in a plasma reactor with a radio frequency (RF) power generator (model R300A, maximum power 300 W, 13.56 MHz, Autoelectronic Co., Korea) and an automatching network (model LC1000A, Autoelectronic Co., Korea). The pressure in the reactor was measured with a vacuum gauge (275 Mini-convectron gauge, Granville-Phillips helix technology, U.S.A.). Details of the plasma treatment equipment are described elsewhere.<sup>18</sup> To investigate the effect of surface modification by plasma, the conditions of plasma treatment were changed by adjusting the plasma generation power (from 5 to 200 W) and irradiation time (from 60 to 300 s).

**Characterization of the Modified Membranes.** The chemical structures of the plasma-modified Nafion membranes were analyzed by attenuated total reflection (ATR)–FTIR (IFS 66/s with Hyperion ATR kit, BrukerOptics Co.) with a mercury cadmium telluride (MCT) detector. The spectra were collected by performing 64 scans for each sample at a resolution of 2  $\text{cm}^{-1}$ . X-ray photon spectroscopy (XPS, phi 5800, physical electronics, U.S.A.) was also used to characterize the surface functional groups of the modified membranes. The XPS measurement was performed using an Al K monochromator (1486.6 eV) in a constant analyzer energy mode, and a pass energy of 23.5 eV was used for the narrow scan of the C1s, F1s, O1s, N1s, and S2p peaks with a 45° takeoff angle. The peak position of the XPS spectra was calibrated using the binding energy data recommended by Beamson et al.<sup>19</sup> The atomic ratio of each sample was calculated from the sensitivity factor of each component provided by the supplier. The cross-sectional morphologies and roughnesses of the membranes were analyzed using a scanning electron microscope (s-4200, Hitachi, Japan) and an atomic force microscope (CP research, Thermo-Microscopes, U.S.A.), respectively. The water contact angle was

measured by means of a goniometer (model Cam-micro, Tanteq, U.S.A.) with the half-angle method, and each measurement was repeated 10 times to obtain an average value.

To measure the water uptake of a membrane precisely, the membrane was dried at room temperature in a desiccator containing  $\text{P}_2\text{O}_5$  powder for a week to eliminate the possibility of any morphological change in the membrane during drying.<sup>20</sup> The water uptake of a membrane was obtained from the weight gain after soaking it in deionized water for 1 day.

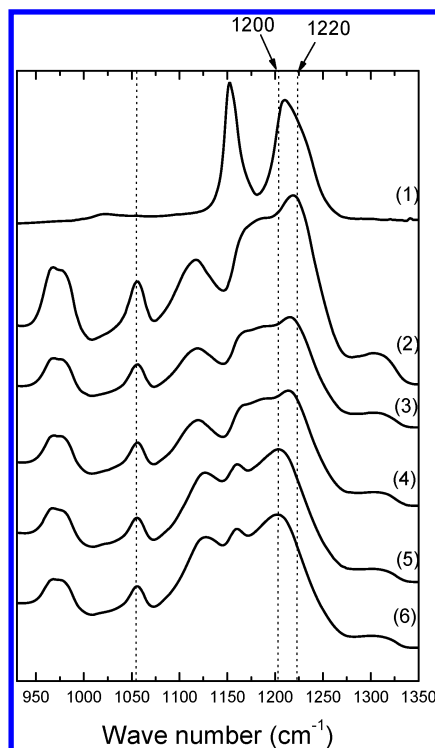
The proton conductivity of a membrane was measured in its fully hydrated form using an impedance spectroscope (IM6, Zahner, Germany) with a glass cell which was made to measure the proton conductance along the cross-sectional direction, as suggested by Slade et al.<sup>21</sup> The proton conducting resistance ( $R_{\text{membrane}}$ ) was determined from a Nyquist impedance plot obtained at room temperature (25 °C) in the frequency range  $10^2$ – $10^6$  Hz. The proton conductivity ( $\sigma$ ) was calculated using the equation  $\sigma = l/A \cdot R_{\text{membrane}}$ , where  $A$  and  $l$  are the conducting area and film thickness, respectively. The methanol permeability was measured using a diffusion cell with a refractive index detector (RI 750F, Younglin, Korea) to monitor the variation in the methanol concentration in the permeate compartment.<sup>22</sup> The methanol permeability was calculated using eq 1.

$$C_b = \frac{A}{V_b} \frac{DK}{l} C_a (t - t_0) \quad (1)$$

where  $C_a$  and  $C_b$  are the methanol concentrations on the feed and permeate sides, respectively, and  $t_0$  and  $V_b$  are the time lag and volume of the permeate compartment,  $A$  and  $l$  are the membrane area and thickness, and  $D$  and  $K$  are the methanol diffusion coefficient and partition coefficient between the membrane and adjacent solution, respectively. The product of  $D$  and  $K$  is thus the methanol permeability ( $P$ ) of a membrane.<sup>23</sup>

## Results and Discussion

**Surface Analysis of the Modified Nafion Membranes.** The surface morphologies of the modified membranes were investigated by using SEM, as shown in Figure 2. No morphological



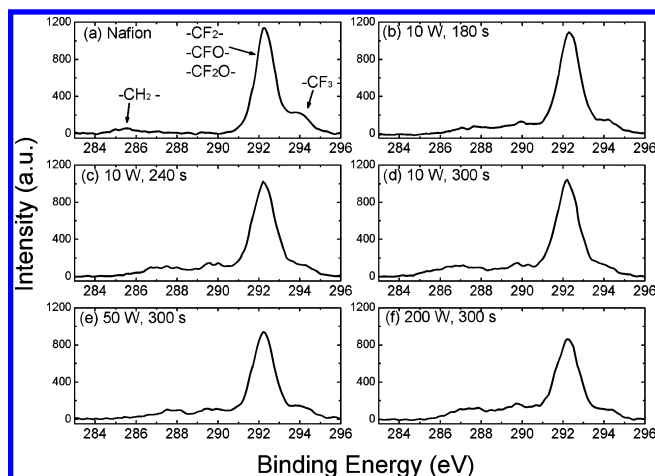
**Figure 3.** ATR-FTIR spectra of various polymers including plasma-modified Nafion membranes according to time and power: (1) PTFE; (2) plain Nafion; (3) 10 W for 180 s; (4) 10 W for 300 s; (5) 50 W for 300 s; (6) 200 W for 300 s.

**TABLE 1: Peak Assignment of ATR-FTIR Spectra for the Nafion Membrane**

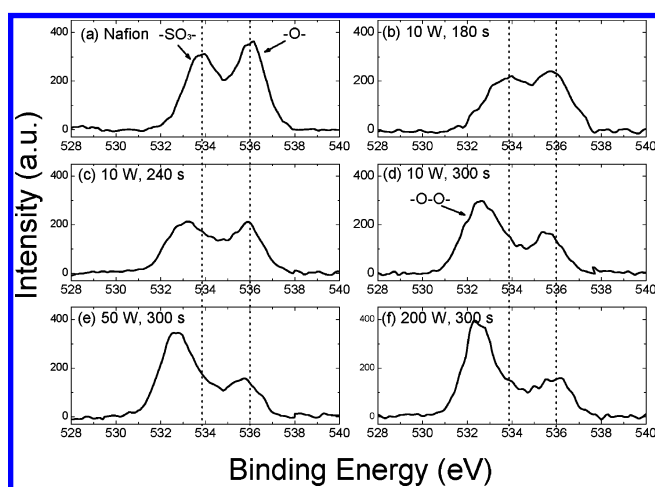
wavenumber (cm <sup>-1</sup> )	assignment
980	symmetric stretching of $-\text{COC}-^{15,25}$
1055	symmetric stretching of $-\text{SO}_3-^{26,27}$
1160, 1200	symmetric stretching of $-\text{CF}_2-^{15}$
1220	asymmetric stretching of $-\text{SO}_3-^{15,25}$
1305	stretching of $-\text{CF}_3^{27}$

changes were found at a low plasma power of around 10 W, whereas at powers higher than 50 W the surface roughness increased due to the etching effect of the plasma treatment and, consequently, the surface area was enlarged.<sup>24</sup> The surface roughness of the membranes was also estimated using AFM, and the corresponding root-mean-squared (rms) roughness factors were found to be 2.842, 6.048, and 14.23 nm for the plain Nafion membrane, the membrane treated with a power of 50 W for 300 s, and the membrane treated with a power of 200 W for 300 s, respectively.

The ATR-FTIR spectra of the plasma-modified Nafion membranes are shown in Figure 3, and the functional groups corresponding to the individual peaks are listed in Table 1.<sup>15,25–27</sup> The most significant feature of the spectra is the decreasing intensity of the sulfonic acid group with increasing time and power of the plasma treatment: an asymmetric stretching of the sulfonic acid group occurs at 1220 cm<sup>-1</sup>. This indicates the degradation of the sulfonic acid group by the plasma treatment, and the results are similar to those obtained from the electron beam treatment of the Nafion membrane.<sup>15</sup> It has also been reported that the peak position of the symmetric stretching of the sulfonic acid group at 1055 cm<sup>-1</sup> shifted, depending on the adjacent environment around the sulfonic acid group.<sup>26,27</sup> This peak position, however, is invariant in the present study, as shown in Figure 3, indicating that the plasma treatment does not cause any appreciable interaction between



**Figure 4.** C1s XPS spectra of the modified Nafion membranes: (a) plain Nafion; (b) 180 s and 10 W; (c) 240 s and 10 W; (d) 300 s and 10 W; (e) 300 s and 50 W; (f) 300 s and 200 W.



**Figure 5.** O1s XPS spectra of the modified Nafion membranes: (a) plain Nafion; (b) 180 s and 10 W; (c) 240 s and 10 W; (d) 300 s and 10 W; (e) 300 s and 50 W; (f) 300 s and 200 W.

the sulfonic acid groups and the adjacent polymer chains or functional groups.

Instead, we can observe the changes in the relative peak heights at 1220 and 1200 cm<sup>-1</sup> and the eruption of a peak at 1160 cm<sup>-1</sup> as the plasma power increases. This change in the peak intensity indicates the degradation of PFSA to poly-(tetrafluoroethylene) (PTFE) by plasma irradiation. We can also see that the stretching band of  $-\text{CF}_3$  at around 1305 cm<sup>-1</sup> and the symmetric stretching from  $-\text{COC}-$  at around 980 cm<sup>-1</sup> decrease following the plasma treatment. There are two kinds of  $-\text{COC}-$  linkages in the Nafion repeating unit, which are designated as 1 and 2 in Figure 1. Although it is difficult to determine which group is more vulnerable to scission, it can be inferred that the breakage of the  $-\text{COC}-$  linkage might lower the content of the sulfonic acid group.

To analyze the surface properties more precisely, XPS technique was employed, and the spectra are shown in Figures 4 and 5. The C1s spectra of the plasma-modified Nafion are shown in Figure 4, and the atomic compositions calculated from the spectra are listed in Table 2. The plain Nafion shows a similar atomic ratio to the value calculated from the chemical formula shown in Figure 1. Fluorine containing C1s peaks are mostly found in the region above 290 eV:  $-\text{CF}_2-$ ,  $-\text{CFO}-$ , and  $-\text{CF}_2\text{O}-$  at around 292 eV,  $-\text{CF}-\text{CF}_2-$  at around 290 eV, and  $-\text{CF}_3$  at around 294 eV.<sup>19,28–30</sup> The highest peak at



**TABLE 2: Atomic Ratio of the Plasma-Treated Nafion and Relative Amounts with Respect to Carbon Obtained from XPS**

sample	atomic ratio (%)					
	C1s	O1s	F1s	N1s	S2p	[C]/[O]/[F]/[S]
Nafion	28.9 (30.4) <sup>a</sup>	8.3 (7.2)	61.2 (59.4)	0	1.6 (1.5)	1:0.29:2.1:0.06
10 W, 180 s	31.9	5.8	61.3	0	1.0	1:0.18:1.9:0.03
10 W, 240 s	35.0	6.2	58.2	0	0.6	1:0.18:1.7:0.02
10 W, 300 s	35.4	6.7	57.5	0	0.4	1:0.19:1.6:0.01
50 W, 300 s	33.2	7.3	58.0	1.4	0.1	1:0.22:1.7:0.003
200 W, 300 s	33.6	8.1	55.7	2.6	0	1:0.24:1.7:0

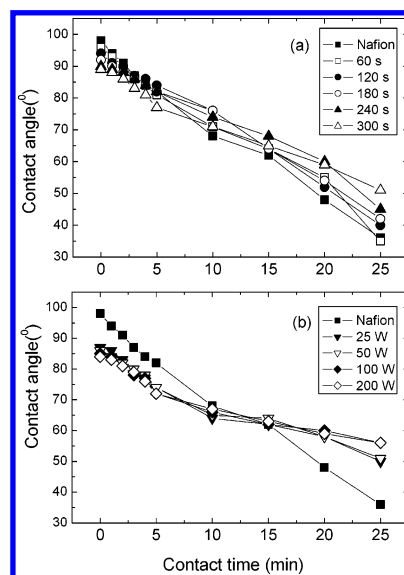
<sup>a</sup> Theoretical value from the chemical formula of the Nafion membrane, assuming  $x = 7$  and  $y = 1$  in Figure 1.<sup>41</sup>

292.2 eV is reduced and slightly broadened with increasing plasma power, reflecting the variation in the relative amount of the fluorine groups, including  $-\text{CF}_2-$ ,  $-\text{CFO}-$ , and  $-\text{CF}_2\text{O}-$ . From Table 2, it is confirmed that the atomic ratio of  $[\text{F}]/[\text{C}]$  decreases from 2.1 to 1.7. The reduction of the fluorine content in fluorinated polymers such as tetrafluoroethylene and perfluoroalkoxyvinyl ether (PFA) polymer, when treated with an argon plasma, was found in the literature.<sup>31,32</sup>

On the other hand, new peaks appear in the region from 286 to 290 eV after the plasma treatment. These C1s peaks presumably originate from carbon groups containing oxygen and fluorine, namely,  $-\text{C}-\text{OH}$  and  $-\text{C}-\text{CF}-$  (286–287 eV),  $-\text{C}=\text{O}$  and  $-\text{CF}-$  (287–288 eV), and  $-\text{O}-\text{C}=\text{O}$  (289–290 eV).<sup>19,33</sup> These peaks indicate that the oxygen containing carbon groups are newly formed on the surface of the Nafion membrane by the plasma treatment.

The O1s spectra of the plasma-modified Nafion are also shown in Figure 5. Two kinds of O1s peaks are available in the plain Nafion, one from the sulfonic acid (around 533.7 eV) and the other from the ether linkage (around 536 eV).<sup>29</sup> As the time and power of the plasma treatment were increased, the intensity of the peak at 533.7 eV representing the  $-\text{SO}_3-$  group decreased, but the peak at 532.5 eV representing the  $-\text{O}-\text{O}-$  group increased. For samples b and c that were treated with a low plasma power, the atomic ratio of  $[\text{O}]/[\text{C}]$  decreased from 0.29 for the plain Nafion to 0.18, probably because of the reduced population of the sulfonic acid group. This ratio, however, increased again with increasing plasma power. This increase in the oxygen concentration may be attributed to the formation of peroxide groups, as indicated by the increased peak intensity at around 532.5 eV.<sup>33</sup>

It is well-known that an argon plasma can break the chemical bonds of a polymer chain and generate peroxide groups or oxidize the broken chains in PTFE and PFA.<sup>24,31,33</sup> Since the ionization energy of argon gas is in the range 11.5–15.8 eV, an argon plasma can easily attack the chemical bonds of a Nafion membrane, which have much lower bonding energies than the ionization energy of argon. For example, the dissociation energies of the chemical bonds in the Nafion structure are 4.86 eV for C–F, 3.64 eV for S–O, 3.6 eV for C–C, 3.58 eV for C–O, and 2.72 eV for the C–S bond.<sup>34</sup> As a result, the chemical bonds of the Nafion can be broken to generate radicals when it is irradiated with argon plasma, followed by reactions between the radicals in the polymer chain that consequently lead to surface cross-linking and the formation of new functional groups.<sup>35–37</sup> The unreacted radicals can also bind with oxygen to make oxygen containing functional groups, such as peroxide, on the Nafion surface when exposed to the ambient air. In view of the relative amount of sulfur with respect to carbon given in Table 2 and the O1s XPS peak of the sulfonic acid (at around 533.7 eV) in Figure 5, one can see that the sulfur content decreases with increasing plasma power. This may be attributed to two kinds of chemical bond breakages. The first one is the



**Figure 6.** Water contact angle as a function of contact time according to (a) plasma treatment time with a fixed plasma power of 10 W and (b) plasma treatment power for a fixed time of 300 s.

breakage of the ether linkage ( $-\text{COC}-$ ) as confirmed by ATR–FTIR and XPS, and the second one is the breakage of the carbon–sulfur linkage (C–S) due to its low dissociation energy. Therefore, the intensity of the S2p and O1s peaks originating from the sulfonic acid group decreases significantly as the plasma power is raised. Nitrogen incorporation was also noticed after the plasma treatment and the atomic ratio of  $[\text{N}]/[\text{C}]$  was 1.4 for 50 W and 2.6 for 200 W. The nitrogen, however, does not appear to have any appreciable influence on the surface properties of the membranes.

#### Water Contact Angle of the Modified Nafion Membranes.

The water contact angle of the membrane surface was also found to be influenced by the plasma treatment. Figure 6 shows the time-dependent contact angles of water as a function of the contact time for the membranes modified with a fixed RF power of 10 W for varying treatment time (Figure 6a) and with varying RF power for a fixed treatment time of 300 s (Figure 6b). In this experiment, all of the membrane samples were initially in a dry state. The plain Nafion membrane shows an incident water contact angle of  $98^\circ$ , which is somewhat smaller than that of a pure PTFE sheet whose water contact angle is approximately  $110^\circ$  under ambient conditions.<sup>38</sup> In this experiment, the change in the contact angle was recorded for 25 min from the start of the measurement. In view of Figure 6, at time zero, the contact angle decreases with the increasing extent of the plasma treatment. This indicates that the plasma-modified membrane is more hydrophilic than the plain Nafion membrane. That is, the greater the plasma power, the smaller the initial contact angle of the modified membrane.

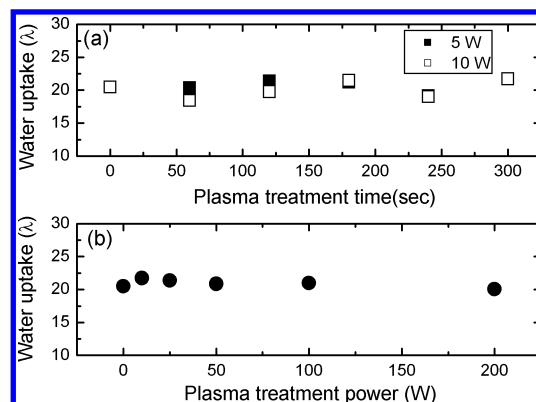
However, all of the membranes experienced a gradual drop in their contact angle with increasing contact time, and the final

values (at 25 min) were in the opposite order of the initial ones. Therefore, the contact angle increases with increasing plasma treatment time and RF power, and the plain Nafion membrane shows the lowest contact angle at a time of 25 min, the point at which its value is only one-third of the initial value. That is, the greater the plasma power, the larger the ultimate contact angle.

The variation in the contact angle with time is attributed to the unique properties of the Nafion membrane. When the incident contact angle of water was measured, the plain Nafion membrane was in a dry state. In the dry state, the surface of the Nafion membrane is highly hydrophobic, because the fluorocarbon region is dominant and the hydrophilic sulfonic acid groups occupy only a small portion of the surface, due to the limited amount of water available for expanding the region of hydrophilic ionic clusters. However, when the membrane is in contact with water, the hydrophilic region expands due to water absorption of the ionic clusters; consequently, the hydrophilicity of the membrane surface increases as time elapses.

From these experiments, one could find that the plasma-modified membranes undergo almost the same change in contact angle as the plain Nafion membrane, but the rate of change is different because of the modified surface properties. The incident contact angle of a polymer surface is known to be highly related to its hydrophilicity and roughness (Wenzel angle).<sup>24,39</sup> When argon plasma is applied to the Nafion surface, the polymer chains are broken and new hydrophilic functional groups such as peroxide are created in the fluorocarbon region of the membrane (Figure 4), while simultaneously the surface is etched to form a rugged morphology (Figure 2). The enhanced plasma treatment increases the population of the hydrophilic peroxide groups, and thus, the hydrophilicity of the membrane in the dry state improves, despite the reduced amount of sulfonic acid groups on the surface, as can be inferred from the FTIR and XPS analyses (Figures 3–6). Moreover, the surface roughness increases with enhanced plasma treatment, as shown in the SEM micrographs and AFM data. Consequently, the initial contact angle of the membrane in a dry state decreases with an increasing extent of plasma treatment. On the other hand, when the membrane is in contact with water for a longer time, the ionic clusters of the membrane which consist of sulfonic acid groups absorb water, thereby increasing the hydrophilicity and decreasing the contact angle, as shown in Figure 6. In addition, since the ultimate water contact angle at  $t = 25$  min is proportional to the degree of water absorption on the surface of the membrane and, in turn, the water absorption is determined by the content of sulfonic acid groups, the ultimate contact angle or the hydrophobicity of the membrane surface increases with increasing plasma treatment.

**Equilibrium Water Uptake and Transport Properties of the Modified Nafion Membrane.** To find the relationship between the surface and bulk properties of the modified membranes, the equilibrium water uptake, methanol permeability, and proton conductivity were investigated. Figure 7 shows the water uptake ( $\lambda$  = [number of water molecules]/[number of sulfonic acid groups]) as a function of the plasma treatment time at a fixed plasma power (5 and 10 W) and as a function of the plasma power at a fixed plasma treatment time (300 s). The water uptake was calculated by assuming that the plasma-modified membrane has the same number of sulfonic acid groups as the plain Nafion membrane because the plasma modification is confined within a very thin skin layer. The plain Nafion membrane had a value of 20.5, and the water uptakes of the modified membranes were also around 20 and did not



**Figure 7.** Equilibrium water uptake of the modified Nafion membranes as a function of (a) plasma treatment time with a fixed plasma power of 5 or 10 W and (b) plasma treatment power for a fixed time of 300 s.

change regardless of the extent of the plasma treatment. This means that although the surface properties of the membranes were significantly changed through plasma treatment, the equilibrium water uptake remained unchanged. This is because the modified layer is thinner than 0.1  $\mu\text{m}$ ,<sup>24,40</sup> which is negligible when compared with the total thickness of Nafion 115 (125 m in the dry state), and thus, the plasma treatment does not have any appreciable effect on the equilibrium water uptake of the bulk membrane.

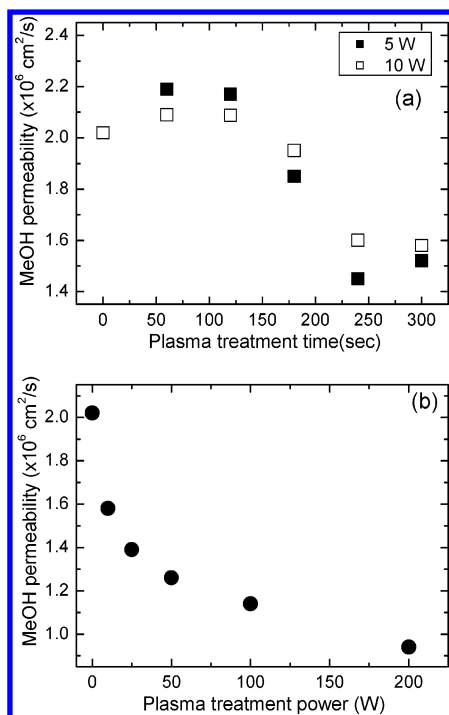
In contrast to the equilibrium water uptake, however, the transport properties were significantly influenced by the plasma treatment. This observation is similar to that of the electron beam treatment of Nafion membranes.<sup>15</sup> The variations in the transport properties are thought to originate from the surface properties of the modified Nafion membrane, which are much different from those of the plain ones in terms of the content of sulfonic acid groups and the possible formation of cross-linking. Figures 8 and 9 respectively show that the methanol permeability and proton conductivity decrease with increasing time and power of the plasma treatment. When the membrane was exposed to plasma irradiation with a low power (5 and 10 W) for less than 150 s, the proton conductivity and methanol permeability increased slightly, as shown in Figures 8a and 9a, respectively. Under weak plasma conditions, the oxygen groups might be incorporated onto the membrane surface without any appreciable reduction in the content of the sulfonic acid groups. This favorable change in the surface chemical moieties might have improved the hydrophilicity and, thus, the methanol permeability and proton conductivity. However, the plasma treatment with higher powers resulted in significant deterioration of the transport properties, presumably due to the substantial drop in the content of sulfonic acid groups and the likely formation of cross-linking between the polymer chains in the membrane surface, leading to increasing resistance against mass transport (i.e., proton or methanol) through the membrane surface.

Since the concentration of sulfonic acid groups on the surface of the membrane varies with the extent of plasma treatment, it would be desirable to estimate the membrane properties as a function of the concentration of the sulfonic acid groups. Experiments were carried out to quantify the concentration of the sulfonic acid groups using the XPS technique. The equivalent weight (EW, g/equiv) of the modified skin layer of the membrane could be calculated using the sulfonic acid concentration: the molecular weight of the polymer electrolyte per one sulfur atom can be considered as an EW of the electrolyte. The estimated EW of plain Nafion 115 was found to be 1059 from the XPS analysis, which is comparable to the theoretical

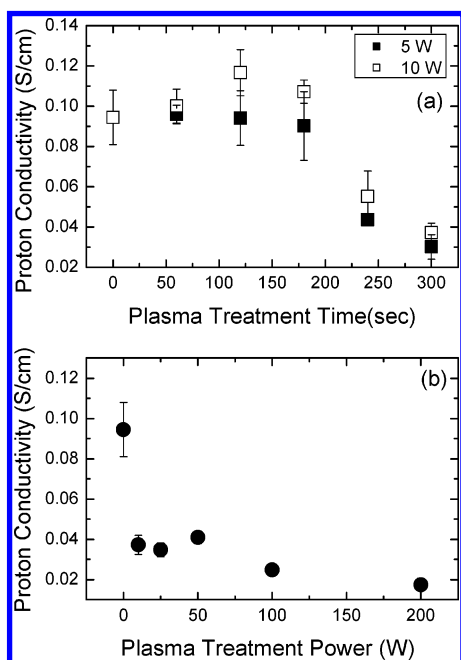
**TABLE 3: Equivalent Weight of the Plasma-Treated Nafion from the XPS Results**

membrane	Nafion	10 W, 180 s	10 W, 240 s	10 W, 300 s	50 W, 300 s	200 W, 300 s
EW (g/equiv)	1059 (1146) <sup>a</sup>	1672	2740	4093	16400	N/A

<sup>a</sup> Theoretical value from the chemical formula of the Nafion membrane.

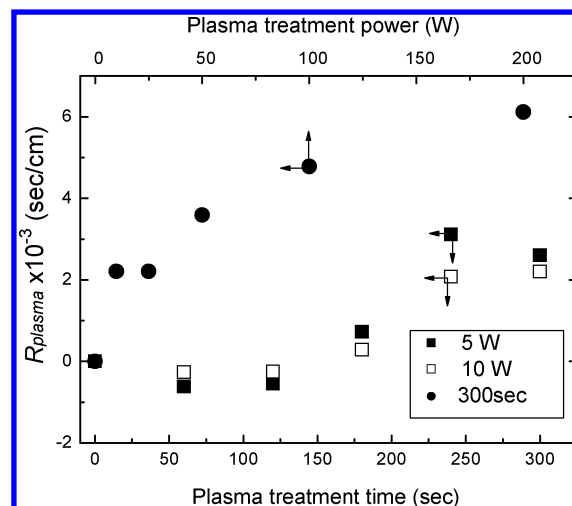


**Figure 8.** Methanol permeability of the modified Nafion membranes as a function of (a) plasma treatment time with a fixed plasma power of 5 or 10 W and (b) plasma treatment power for a fixed time of 300 s.



**Figure 9.** Proton conductivity of the modified Nafion membranes as a function of (a) plasma treatment time with a fixed plasma power of 5 or 10 W and (b) plasma treatment power for a fixed time of 300 s.

value of 1146 obtained from its chemical formula.<sup>41</sup> This difference between the theoretical and estimated values may be due to degradation of the polymer samples through the irradiation of X-rays during the XPS analysis.<sup>29</sup> The EW of the modified skin layer increased as a consequence of the increasing



**Figure 10.** Methanol resistance of the surface layer from plasma treatment as a function of plasma treatment time and power. The treatment time increased at a fixed power of 5 W (■) and 10 W (□). The power increased at a fixed time of 300 s (●).

extent of the plasma treatment, with the values being 1672 for 180 s, 2740 for 240 s, and 4093 for 300 s at 10 W, as listed in Table 3. The increased EW as well as the possible cross-linking of the polymer chains definitely restricts the water swelling of the membrane, by reducing the size of the ionic clusters in the skin layer through which the methanol molecules and protons have to pass.

The modified membrane consists of two parts, namely, the bulk membrane and the modified skin layer, and the methanol permeabilities of these two components differ from each other. Therefore, the total methanol permeability of the modified membrane is considered to be the sum of the contributions from these two components. Therefore, we have constructed an equation to describe the methanol permeability by using the concept of resistance to methanol permeation. The resistance ( $R$ ) can be expressed in terms of the permeability, as shown in eq 2.<sup>42</sup>

$$R = \frac{l}{P} \quad (2)$$

Assuming that the two resistances are connected in series, the total methanol resistance of the modified membrane can be expressed as the sum of the two resistance components, as shown in eq 3.

$$R_{\text{total}} = R_{\text{Nafion}} + R_{\text{plasma}} \quad (3)$$

where  $R_{\text{total}}$ ,  $R_{\text{Nafion}}$ , and  $R_{\text{plasma}}$  are the methanol resistances of the plasma-treated Nafion, the unmodified bulk Nafion, and the modified skin layer, respectively. The total thickness of the plasma-modified membrane is almost the same as that of the plain Nafion membrane, because the modified skin layer is negligibly thin. Therefore, we could calculate  $R_{\text{plasma}}$  from eq 3 using  $R_{\text{total}}$  and  $R_{\text{Nafion}}$  that were measured experimentally.

The value of  $R_{\text{Nafion}}$  for the plain Nafion membrane is  $7.9 \times 10^3 \text{ s/cm}$ . The variation in the calculated value of  $R_{\text{plasma}}$  with the plasma treatment time and power is shown in Figure 10. As expected from the methanol permeability data, increasing



plasma treatment time and power impart higher methanol blocking properties to the modified layer. The layer functions effectively as a methanol barrier after 180 s of treatment with a power equal or less than 10 W, and the treatment with a power of 200 W for 30 s significantly increases the methanol resistance, amounting to about 77% of that of the plain Nafion membrane ( $6.1 \times 10^3$  s/cm), despite its significantly negligible thickness.

## Conclusion

The argon-plasma treatment has changed the physicochemical properties of the Nafion membrane surface and, thus, changed the transport properties of the membrane. The plasma was found to have a kind of etching function to make the surface morphology rugged, though the modification was confined within a very thin layer of less than  $0.1 \mu\text{m}$  in the membrane surface. The FTIR and XPS data revealed that the plasma treatment could remove sulfonic acid groups on the surface, but it could create peroxide groups by cleaving the C—O—C bonds. The newly generated peroxide groups helped increase the hydrophilicity of the modified membrane surface in the dry state and decreased the initial contact angle below the plain Nafion membrane, but the reduced sulfonic acid group concentration increased the ultimate contact angle. Though the modified skin layer was negligibly thin compared to the bulk membrane thickness, it rendered large resistances against proton and methanol transport and thus decreased the methanol permeability and proton conductivity.

Through this study, we could comprehend the changes in the physicochemical properties of the proton exchange membranes caused by the argon-plasma treatment. As reported by some previous studies, the plasma treatment has the possibility of improving on the membrane properties more suitable for use in DMFC, but further optimization of the plasma treatment process is needed to substantially enhance the membrane performance. In addition to this, the preparation of the membrane-electrode assembly should also be optimized because the properties of the modified layer are vastly different from the plain Nafion membrane and therefore the contact resistance between the membrane and the electrode can be higher than that with the plain membrane.

**Acknowledgment.** This project was financially supported by the Korean Ministry of Commerce, Industry and Energy through Institute of Industrial Technology Evaluation and Planning (ITEP) under the research program of "Development of Core Technologies for Next Generation".

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