

Electrochemical Properties of Polypropylene Membranes Modified by the Plasma Polymerization Coating of SO₂/Acetylene

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ABSTRACT: Polypropylene membranes were modified by the plasma etching of SO₂, SO₂-O₂, or SO₂-H₂O, followed by the plasma polymerization coating of SO₂/acetylene. The conditions for SO₂ plasma etching were optimized by the measurement of the ion-exchange capacity (IEC) as a function of the plasma-etching power (10–30 W), gas pressure (40–60 mTorr), and treatment time (15–120 s). For the plasma etching of SO₂-O₂ and SO₂-H₂O, only the pressure ratio (SO₂/O₂ and SO₂/H₂O) was optimized under the optimized conditions determined from SO₂ plasma etching. Plasma etching was then combined with the plasma polymerization coating of SO₂/acetylene, for which the conditions were again optimized by the measurement of the IEC

as a function of the plasma power (10–40 W), chamber pressure (50–200 mTorr), SO₂/acetylene ratio (15/135–60/90), and treatment time (0–10 min). Next, the electrical resistance and water uptake were evaluated. The modified membranes were also analyzed with scanning electron microscopy, whereas plasma polymer coatings were characterized with Fourier transform infrared/attenuated total reflection. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3692–3699, 2006

Key words: membranes; plasma polymerization; poly(propylene) (PP)

INTRODUCTION

The recent interest in charged membranes used in batteries, fuel cells, sensors, and electrolyzers has led to considerable research into the preparation of high-performance charged membranes.^{1,2} Consequently, a number of researchers have attempted to prepare new polymers for charged membranes, leading to the introduction of polymers such as poly(arylene ether sulfone), polyimides, polybenzimidazoles, and polyphozenes.^{3–7} The difficulty of preparing such polymers, however, has caused researchers to modify existing polymers through a number of techniques. Among these methods, postsulfonation pioneered by Noshay and Robeson⁸ has received great attention and has been used to modify polysulfones,^{9,10} poly(ether ketone)s,¹¹ and polystyrenes.¹²

The process, however, introduces sulfonic acid groups only to the activated position ortho to the aromatic ether bond and also generates acid waste, and it has the difficulty of controlling the degree of sulfonation. Consequently, attention has been paid to other modification methods such as plasma etching,¹³ plasma polymerization coating,^{14–22} graft copolymerization via UV, electron beam, ozone, and plasma,^{23–27} and composite membranes.²⁸ Among them, plasma polymerization is well known as a versatile technique for modifying polymer membranes because it is possible to introduce various functional groups without appreciable damage to the membranes²⁹ and it is an environmentally clean process.

Plasma polymerization has been used to modify membranes with monomers containing SO₃⁻, COO⁻, or PO₃⁻ moieties, whose strong acidity and very low dissociation constant make them very viable choices. Consequently, monomers such as trifluoromethanesulfonic acid,^{18,20} phosphonic acid,²¹ benzene sulfonyl fluoride/benzene sulfonyl chloride,¹⁶ and methyl benzenesulfonate¹⁷ have been used, but together with vinyl-type monomers because they cannot form polymer coatings by themselves. In addition, combinations of SO₂ and C₂H₂¹⁴ and SO₂ and fluorobenzene¹⁵ have been attempted,

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but without a thorough investigation of their electrochemical properties.

In this study, therefore, an attempt was made to modify commercial polypropylene (PP) membranes via the plasma polymerization coating of SO₂/acetylene because acetylene is known to be easily polymerized by plasma energy, whereas SO₂ gas can possibly introduce sulfonic acid moieties. Plasma polymerization conditions such as the plasma power, time, and monomer pressure were optimized by the measurement of the ion-exchange capacity (IEC). In addition, the plasma etching of PP membranes with SO₂, SO₂-O₂, or SO₂-H₂O was combined with the plasma polymerization coating of SO₂/acetylene. Plasma-etching conditions such as the plasma power, time, and gas pressure were again optimized. The modified membranes were subjected to electrical-resistance and water-uptake measurements and were characterized with scanning electron microscopy (SEM), whereas plasma polymer coatings were analyzed with Fourier transform infrared/attenuated total reflection (FTIR/ATR).

EXPERIMENTAL

Materials

A porous PP membrane (Celgard 2500) was obtained from Celgard, Inc. (Charlotte, NC), and was cleaned in *n*-hexane for 7 days. The membrane was then dried at room temperature for 24 h and stored in a desiccator until needed. Sulfur dioxide (99.9%) was purchased from Aldrich (St. Louis, MO), whereas oxygen and acetylene (99%) were supplied by Shin-il (Gwangia, Korea).

Plasma polymerization coating of pp membranes

A radio-frequency (13.56-MHz) plasma generator (HPPS-300, Hanatek Co., Bucheon, Korea), consisting of a bell-jar-type Pyrex chamber, manual impedance matching, and a mass flow controller, was used for plasma etching and plasma polymerization coating. First, the Pyrex chamber was wiped with acetone-soaked Kimwipes and then etched with O₂ plasma (90 W, 30 mTorr) for 10 min before plasma polymerization. Next, a piece of PP membrane (7 × 5 cm) fixed to the aluminum frame was staged vertically in the center of the chamber, which was then vacuumed to 1 mTorr and flushed twice with gas/monomer for plasma etching or plasma polymerization.

The plasma polymerization coating of PP membranes was carried out after the introduction of SO₂/acetylene into the chamber. The conditions were optimized by the variation of the treatment time (2–10 min), plasma power (10–30 W), monomer pressure (50–200 mTorr), and monomer ratio (15/135–60/90)

and by the measurement of the IEC of PP membranes. The plasma-etching conditions were optimized with SO₂ as a function of the etching time (15–120 s), plasma power (10–30 W), and gas pressure (40–60 mTorr) by the measurement of the IEC. However, for the plasma etching of SO₂-O₂ and SO₂-H₂O, only the pressure ratios SO₂/O₂ and SO₂/H₂O were optimized under the optimized conditions determined from SO₂ plasma etching. Finally, the plasma etching of SO₂, SO₂-O₂, or SO₂-H₂O was combined with the plasma polymerization coating of SO₂/acetylene.

Property measurements of modified PP membranes

The modified PP membranes were subjected to measurements of the IEC, electrical resistance, and water uptake. The IEC was calculated from the number of ion-exchange groups in the membrane, which was evaluated by back-titration with a 0.05 N HCl aqueous solution, after the conditioning of the membrane in a 0.1 N NaOH aqueous solution for 24 h.³⁰ The electrical resistance was measured with a clip cell and LCZ meter (2321, NF Electronic Instruments, Yokohama, Japan) at 100 kHz, after the conditioning of the membrane (7 × 5 cm) in 0.5 M NaCl for 24 h. The water uptake of the membranes was also evaluated by a comparison of the weight of the membrane dried at 80°C *in vacuo* for 24 h with the weight of the membrane that was immersed in 0.5 M NaCl for 24 h.

Characterization of plasma polymer coatings

Plasma polymer coatings were characterized by Fourier transform infrared (FTIR) and α step, with samples prepared with silicon wafers instead of PP membranes. FTIR/ATR (460, Jasco, Easton, MD) was used to record 64 scans at a resolution of 4 cm⁻¹. The morphology of the modified membranes was investigated with SEM (JSM-5800, Tokyo, Japan) at 10 kV. The SEM samples were coated with Au/Pd to minimize the charging problem.

RESULTS AND DISCUSSION

Condition optimization of plasma etching with PP membranes

Optimization of so₂-plasma-etching conditions

The SO₂-plasma-etching conditions were optimized by the measurement of the IEC as a function of the plasma power, time, and pressure (Fig. 1). As the plasma power increased from 10 to 30 W, the IEC increased from 0.15 (10 W) to 0.45 (15 W) and 0.65 mequiv/g (20 W), as shown in Figure 1(A). However, the sample treated at 30 W was not tested because it exhibited warping. As the plasma-etching time increased from 15 to 60 s, the IEC value increased from

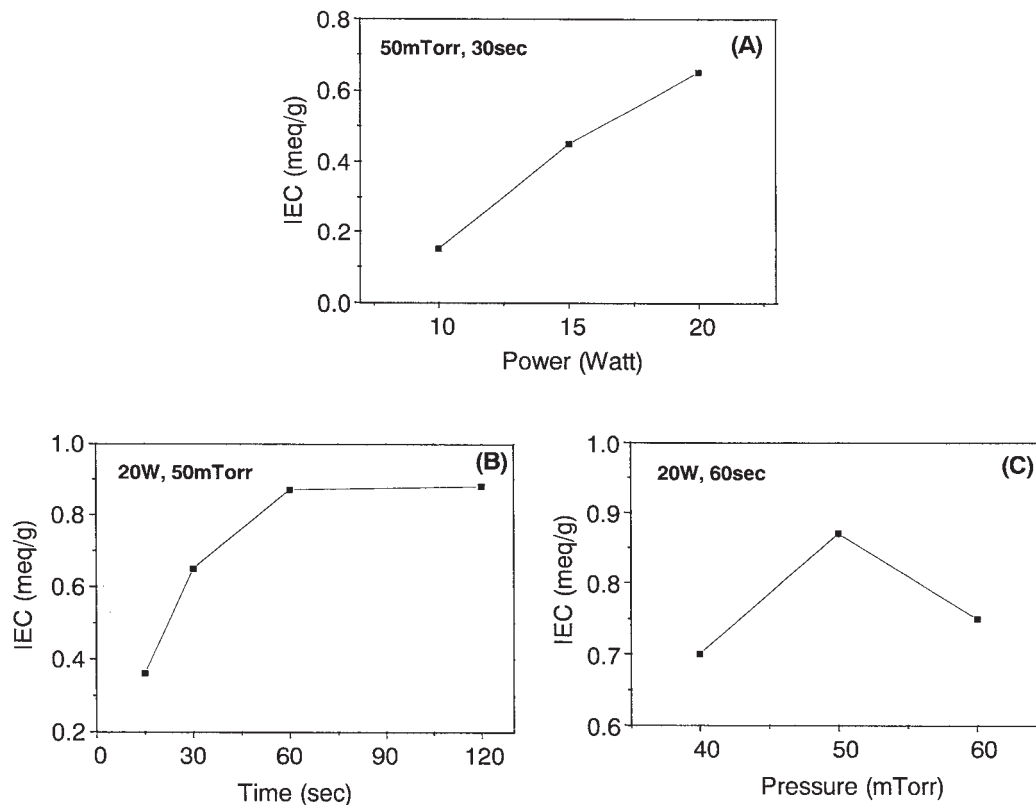


Figure 1 Condition optimization of SO₂ plasma etching: (A) power, (B) time, and (C) pressure.

0.36 to 0.87 mequiv/g and then leveled off [Fig. 1(B)]. Finally, when the SO₂ gas pressure was varied, the highest IEC value of 0.87 mequiv/g was obtained at 50 mTorr, resulting in the optimum conditions of 20 W, 50 mTorr, and 60 s. The enhanced IEC by SO₂ plasma etching can be attributed to the acid-functional moieties introduced by SO₂ plasma etching.

Plasma etching of SO₂-O₂

Because the PP membranes with SO₂ plasma etching exhibited such low IEC values, the plasma etching of SO₂-O₂ was attempted with the hope of accelerating SO₂ oxidation with O₂ and thereby generating more acid-functional groups such as sulfonic acid groups. The same plasma-etching conditions used for the SO₂ etching were used for SO₂-O₂ plasma etching, but the SO₂/O₂ ratio was varied. As shown in Figure 2, the IEC value increased from 0.89 at a 30/20 SO₂/O₂ ratio to 1.18 at 20/30 and then decreased to 0.89 at 10/40. Compared with the value of 0.87 obtained with only SO₂ plasma etching, the IEC was marginally enhanced by the addition of O₂ to SO₂ (but only up to the 20/30 ratio), which aided the oxidation of SO₂ gas to generate more acid-functional groups. However, the lowered IEC value at the 10/40 ratio can be attributed to low SO₂ pressure and a lower number of acid-functional moieties than those at the 20/30 ratio.

Plasma etching of SO₂-H₂O

The final attempt was the modification of PP membranes with SO₂-H₂O plasma etching because H₂O might react with and/or catalyze the oxidation of SO₂, generating strong acid groups such as sulfonic acid moieties, possibly because of radicals containing protons generated by plasma energy. As expected, the IEC increased from 1.11 (30/20) to 1.27 (25/25) and 1.39 mequiv/g (20/30) and then decreased to 1.04 (10/40), as shown in Figure 3. The high IEC value at

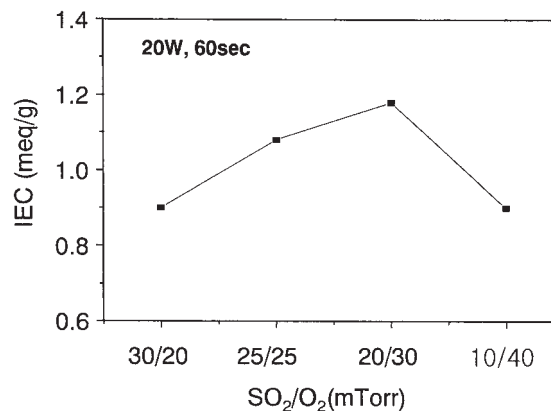


Figure 2 Effect of the SO₂/O₂ ratio on the IEC of PP membranes in SO₂-O₂ plasma etching.

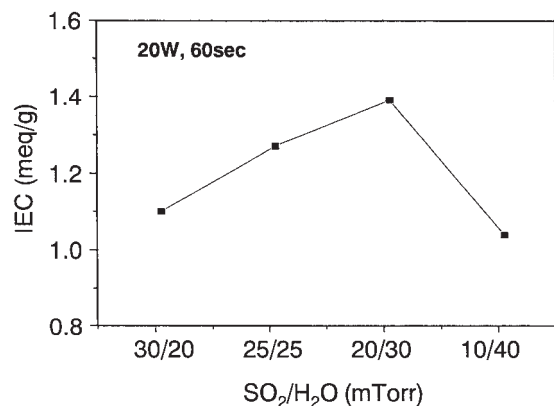


Figure 3 Effect of the SO₂/H₂O ratio on the IEC of PP membranes in SO₂-H₂O plasma etching.

the 20/30 SO₂/H₂O ratio can again be attributed to the enhanced oxidation of SO₂ by H₂O, whereas the low IEC value at the 10/40 ratio can be ascribed to the low SO₂ pressure, which was not sufficient to generate enough acid-functional moieties. It can be said that the plasma etching of SO₂-H₂O is more effective in converting SO₂ to acid groups than the plasma etching of SO₂-O₂.

Optimization of plasma polymerization conditions

Plasma polymerization power

The plasma polymerization power with SO₂/acetylene was optimized under the fixed conditions of 10 min, 100 mTorr, and a 20/80 SO₂/acetylene ratio, as shown in Figure 4(A). As the plasma power increased from 10 to 40 W, the IEC increased from 0.89 (10 W) to 1.12 (20 W) and 1.31 (30 W). Because the warping of PP membranes was observed at 40 W, 30 W was selected as the optimum plasma polymerization power. Increased IEC values with plasma polymerization coating can be attributed to the enhanced polymerization of acetylene monomers, as well as the enhanced conversion of SO₂ gas to acid-functional moieties, with a plasma power increase.¹⁷

SO₂/acetylene pressure

The SO₂/acetylene pressure was also optimized in the range of 50–200 mTorr under the fixed conditions of a 20/80 SO₂/acetylene ratio, 10 min, and 30 W. With increasing pressure, the IEC rose sharply from 0.47 (50 mTorr) to 1.32 mequiv/g (100 mTorr) and then increased slowly to 1.54 mequiv/g (150 mTorr), followed by a decrease to 1.36 mequiv/g (200 mTorr), as

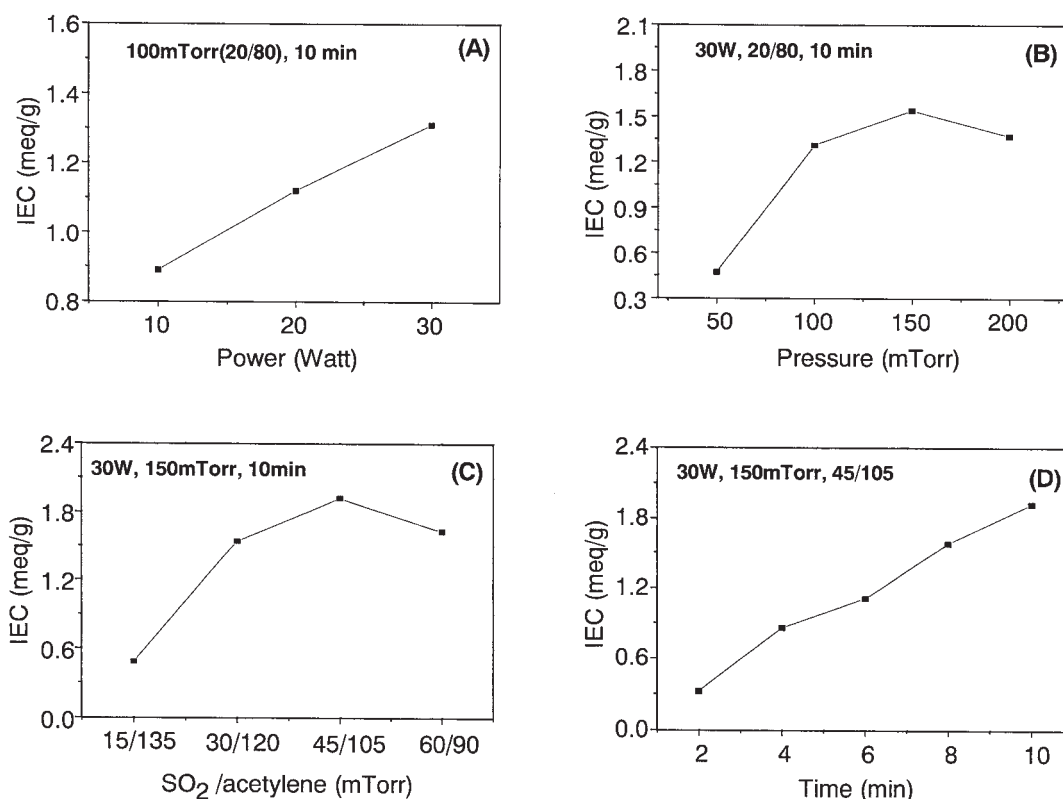


Figure 4 Condition optimization of SO₂/acetylene plasma polymerization: (A) power, (B) pressure, (C) SO₂/acetylene ratio, and (D) time.

shown in Figure 4(B). Such results can be explained by two factors, the power density and coating thickness. As the pressure increases, the power density decreases, but only until it reaches a critical value, at which point all monomers in the chamber are activated, leading to an increase in the coating thickness.²⁹ However, if the power density falls below the critical value, only selected monomers can be activated, and the coating thickness begins to decrease.¹⁷ Thus, the increased IEC with the pressure increasing up to 150 mTorr can be attributed to the increased coating thickness, whereas the opposite is true above 150 mTorr because the IEC is directly related to the number of acid-functional groups, which in turn is proportional to the coating thickness, in general. Therefore, the optimum pressure was determined to be 150 mTorr.

When the SO₂/acetylene pressure ratio was varied at fixed conditions of 30 W, 10 min, and 150 mTorr, the IEC increased rapidly to 1.54 mequiv/g (30/120) and then somewhat slowly to 1.92 (45/105); this was followed by a decrease to 1.63 (60/90), as shown in Figure 4(C). This phenomenon is similar to the IEC variation with pressure and thus can be explained by the coating thickness and acid-functional groups. The former is dependent on the amount of acetylene, whereas the latter is a function of the amount of SO₂. As the SO₂/acetylene ratio is increased, more acid-functional groups are generated but less acetylene polymer is formed, and this results in a decreased coating thickness.¹⁴ Consequently, there should be an optimum ratio of SO₂ to acetylene to maximize the total number of acid moieties in the plasma polymer coating, which was determined to be 45/105 in this study. Above the 45/105 ratio, the IEC would decrease because the total number of acid groups in the coating would decrease on account of the decreased coating thickness.

Plasma polymerization time

The plasma polymerization time was optimized by the measurement of the IEC of plasma-polymer-coated PP membranes at 30 W, 150 mTorr, and a 45/105 ratio, as shown in Figure 4(D). As the time increased, the IEC increased almost linearly to 1.92 mequiv/g at 10 min, and this can be explained by the increased coating thickness and thus increased total number of acid-functional groups in the plasma polymer coating. Therefore, the IEC would continue to increase with time, beyond 10 min. In this study, however, 10 min was chosen as the optimum plasma polymerization time to result in the optimum conditions of 30 W, 150 mTorr (45/105), and 10 min for the plasma polymerization of SO₂/acetylene.

With the plasma polymerization time, the electrical resistance decreased rapidly to 97 ohm cm² after only 2 min of treatment and then leveled off (Fig. 5). These

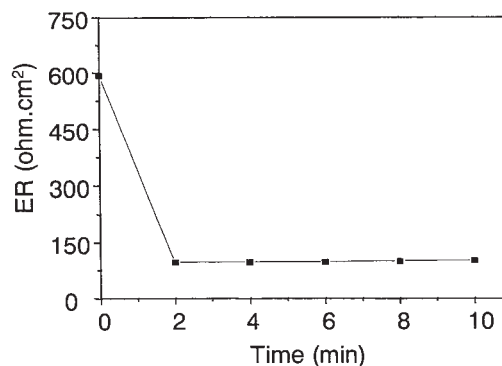


Figure 5 Electrical resistance (ER) of PP membranes with SO₂/acetylene plasma polymer coatings as a function of time.

results can be explained by the acidic moieties that were generated by the plasma modification of SO₂ gas and imbedded into the plasma polymer coating.^{14,15} As the electrical resistance is related to charged ionic groups in the PP membrane, it decreases rapidly as soon as the polymer coating with sulfonic acid groups is formed on the PP membrane surface. Once the membrane surface is completely covered by the coating, the electrical resistance will not change because it is not dependent on the coating thickness. However, the electrical resistance reported in this study is relatively high in comparison with that of other modified charged membranes, and this can be explained by the crosslinked nature of the plasma polymer film.

Combination of plasma etching and plasma polymer coating

The PP membranes modified by SO₂/acetylene plasma polymerization under the optimized conditions (30 W, 150 mTorr, 45/105 SO₂/acetylene, and 10 min) provided excellent electrochemical properties: an IEC of 1.92 mequiv/g and an electrical resistance of 97 ohm cm². Despite the good electrochemical properties, however, the treatment time of 10 min appeared to be too long, and so it was suggested to shorten the SO₂/acetylene plasma polymerization time to 4 min and combine it with plasma etching of SO₂, SO₂-O₂, or SO₂-H₂O.

SO₂ plasma etching and SO₂/acetylene plasma polymerization coating

The IEC values of PP membranes treated with SO₂ plasma etching followed by SO₂/acetylene plasma polymerization (4 min) are listed in Table I. The synergy effect of this combination is demonstrated by a comparison of the IEC of 1.38 (SO₂ plasma etching and SO₂/acetylene plasma polymerization coating) to the IEC of 0.87 obtained from only SO₂ plasma etching or

TABLE I
Combination Effect of Plasma Etching and Plasma Polymerization Coating on the Electrochemical Properties of the PP Membranes

Plasma polymer coating	Plasma etching			
	None	SO ₂	SO ₂ -O ₂	SO ₂ -H ₂ O
None	—	0.87	1.18	1.39
SO ₂ /acetylene, 4 min	0.86	1.38	1.41	1.47
SO ₂ /acetylene, 10 min	1.92	—	—	—

the IEC of 0.86 from SO₂/acetylene plasma polymerization coating (4 min). However, the value was still much lower than the value of 1.92 obtained from 10 min of SO₂/acetylene plasma polymerization coating. On the other hand, the electrical resistance was similar to that from the plasma polymerization coating of SO₂/acetylene at 4 min. Therefore, it can be said that the enhanced IEC via the combination approach can be attributed to the acid-functional groups introduced in the membrane by SO₂ plasma etching, which were preserved by the subsequent plasma polymerization coating of SO₂/acetylene.

SO₂-O₂ plasma etching and SO₂/acetylene plasma polymerization coating

The combination of SO₂-O₂ plasma etching with SO₂/acetylene plasma polymer coating (4 min) resulted in an IEC of 1.41, which was similar to the value of 1.38 obtained from SO₂ plasma etching and SO₂/acetylene plasma polymer coating but much lower than the value of 1.92 from 10 min of SO₂/acetylene plasma polymerization coating (Table I). When this is compared to 1.18 (plasma etching of SO₂-O₂) and 0.86 (SO₂/acetylene plasma polymer coating of 4 min), one can see the synergy effect via the combination of plasma etching and plasma polymerization coating. As explained previously, this can be attributed to the acid-functional moieties that were preserved by the subsequent plasma polymerization coating of SO₂/acetylene. Surprisingly, this approach provided a similar IEC (1.41) to that from the combination of SO₂ plasma etching with 4 min of SO₂/acetylene plasma polymer coating (1.38), even though SO₂-O₂ plasma etching provided a much higher IEC (1.18) than the SO₂ plasma etching (0.87). This phenomenon needs to be investigated further. On the other hand, the electrical resistance was nearly the same as that obtained from SO₂ plasma etching and SO₂/acetylene plasma polymer coating.

SO₂-H₂O plasma etching and SO₂/acetylene plasma polymerization coating

The combination of SO₂-H₂O plasma etching and SO₂/acetylene plasma polymer coating provided an

IEC of 1.47, which was slightly higher than 1.38 (SO₂ plasma etching and SO₂/acetylene plasma polymer coating) and 1.41 (SO₂-O₂ plasma etching and SO₂/acetylene plasma polymer coating) but much lower than the value of 1.92 obtained with 10 min of SO₂/acetylene plasma polymerization coating (Table I). It was also slightly higher than the value obtained from SO₂-H₂O plasma etching (1.39) but much higher than that from 4 min of SO₂/acetylene plasma polymerization coating (0.86). Consequently, it is again believed that the enhanced IEC can be attributed to the synergy effect and that the enhanced electrochemical properties are the result of functional moieties introduced into the membrane. However, the electrical resistance did not change with this combination approach.

Characterization of plasma polymer coatings and coated membranes

FTIR analysis

The FTIR/ATR spectra of modified PP membranes are shown in Figure 6. As expected, as-received PP membranes provided typical peaks at 1370, 1450, and 2900 cm⁻¹, which are well matched to those reported in the handbook.³¹ Upon the plasma polymerization coating

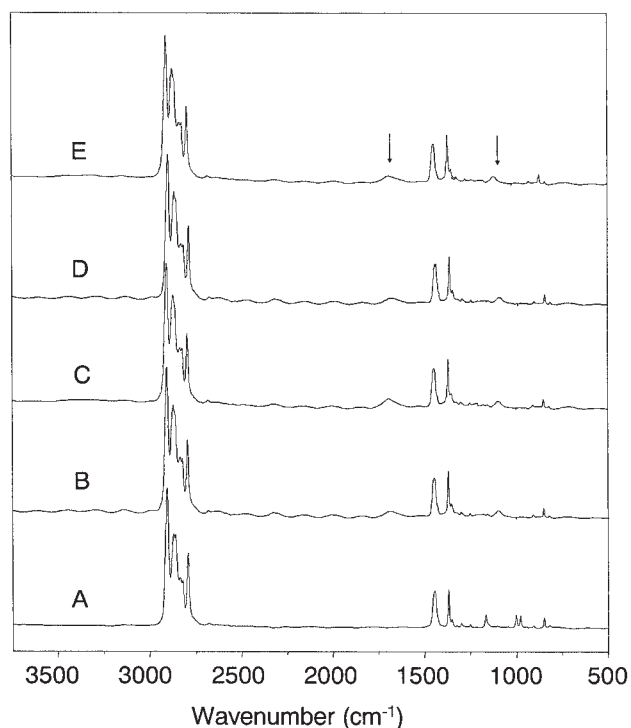


Figure 6 FTIR spectra of plasma-etched and plasma-polymer-coated PP membranes: (A) as-received, (B) SO₂/acetylene-plasma-polymer-coated, (C) SO₂-plasma-etched and SO₂/acetylene-plasma-polymer-coated, (D) SO₂-O₂-plasma-etched and SO₂/acetylene-plasma-polymer-coated, and (E) SO₂-H₂O-plasma-etched and SO₂/acetylene-plasma-polymer-coated.

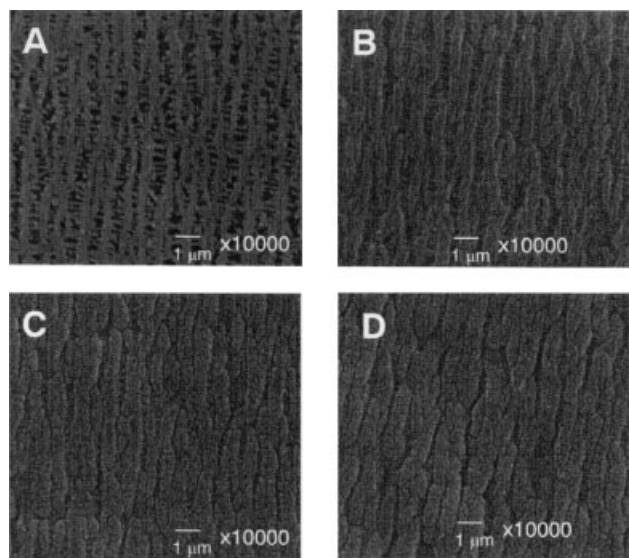


Figure 7 SEM images of PP membranes with SO₂/acetylene plasma polymer coatings: (A) as-received, (B) 2 min, (C) 4 min, and (D) 6 min.

of SO₂/acetylene, two new peaks were detected at 1120 and 1708 cm⁻¹, which could be assigned to SO₃H and C=O, respectively.^{14,32} The former could be attributed to the SO₂ gas, which was converted to sulfonic acid moieties via plasma energy,¹⁴ whereas the latter could be attributed to C=O stretching from the acrylic acid moiety, as reported previously.³² Similar spectra were obtained from PP membranes modified by the plasma etching of SO₂, SO₂-O₂, or SO₂-H₂O, followed by the plasma polymer coating of SO₂/acetylene, which could be attributed to the lack of FTIR sensitivity. Nevertheless, the FTIR analysis clearly demonstrated the existence of sulfonic acid moieties in the modified PP membranes, which led to their enhanced electrochemical properties. The FTIR analysis of plasma-etched membranes was not attempted because there would be large deactivation upon the samples' exposure to open air.

SEM analysis

The plasma-polymer-coated PP membranes were analyzed by SEM to investigate their surface morphology. As shown in Figure 7, the as-received PP membranes showed pores on the surface, which were gradually covered by the plasma polymer coating. After 2 min of plasma polymerization coating, approximately two-thirds of the pores were covered by the plasma polymer, with complete coverage occurring within 4 min. Therefore, the decreased electrical resistance at 2 min can be explained by the coverage of pores in the PP membrane with a plasma polymer coating containing acid-functional groups.

Upon the plasma etching of SO₂ under optimized conditions, the surface morphology did not change appreciably, but with SO₂-O₂ and SO₂-H₂O plasma etching, some fibrils were etched away. However, the PP membranes etched by SO₂, SO₂-O₂, or SO₂-H₂O plasma, followed by 4 min of plasma polymerization coating, exhibited nearly the same morphology as those treated with 4 min of SO₂/acetylene plasma polymerization coating only. Consequently, the enhanced IEC from these combination approaches could be attributed to acid-functional moieties introduced by the plasma etching of SO₂, SO₂-O₂, or SO₂-H₂O. At the same time, the similar electrical-resistance values obtained could be attributed to the complete coverage of PP membranes from the plasma polymer coating of SO₂/acetylene.

Water uptake of modified PP membranes

The water absorption of PP membranes with SO₂/acetylene plasma polymer coating (at 30 W, 150 mTorr, and 45/105) was evaluated as a function of time. The water absorption increased almost linearly with time—0.9 (2 min), 1.5 (4 min), 2.3 (6 min), 3.1 (8 min), and 4.2% (10 min)—demonstrating the introduction of acid-functional groups.²² When SO₂, SO₂-O₂, or SO₂-H₂O plasma etching was carried out before the SO₂/acetylene plasma polymer coating (4 min), the samples exhibited water absorption of 2.5, 2.7, and 3.0%, in comparison with the value of 1.5% obtained with the SO₂/acetylene plasma polymer coating of 4 min (Table II). This behavior could be attributed to the introduction of extra acid-functional groups from the plasma etching of SO₂, SO₂-O₂, and SO₂-H₂O. This trend mirrored the one observed with IEC values in Figure 4(D). Consequently, the results of water-absorption measurements also support the introduction of acid-functional groups into or onto the PP membrane via plasma polymerization coating. However, the water absorption in this study is very low in comparison with other charged membranes, and this can be explained by the crosslinked nature of the plasma polymer film.

TABLE II
Electrochemical Properties and Water Uptake of the Plasma-etched and SO₂/Acetylene-Plasma-Polymer-Coated PP Membranes

Modification	Property	
	Electrical resistance (Ω cm ²)	Water uptake (wt %)
SO ₂ /acetylene PP (4 min)	97	1.5
SO ₂ etching and SO ₂ /acetylene PP	99	2.5
SO ₂ -O ₂ etching and SO ₂ /acetylene PP	98	2.7
SO ₂ -H ₂ O etching and SO ₂ /acetylene PP	101	3.0

CONCLUSIONS

PP membranes were modified by the plasma polymerization coating of SO₂/acetylene in combination with the plasma etching of SO₂, SO₂-O₂, or SO₂-H₂O carried out before the plasma polymerization. The findings are summarized as follows:

1. In plasma etching, SO₂-H₂O plasma etching provided the best results (an IEC of 1.39 and an electrical resistance of 97 ohm cm²), followed by SO₂-O₂ and SO₂ plasma etching.
2. The optimum conditions for the plasma polymerization coating of SO₂/acetylene were 30 W, 150 mTorr, a 45/105 SO₂/acetylene ratio, and 10 min, which provided an IEC of 1.92 mequiv/g and an electrical resistance of 97 ohm cm².
3. Upon the combination of the plasma etching and plasma polymerization of SO₂/acetylene, SO₂-H₂O plasma etching provided the best results, with an IEC of 1.47 and an electrical resistance of 101, followed by SO₂-O₂ and SO₂ plasma etchings.
4. The FTIR analysis demonstrated the presence of sulfonic acids as well as C=O moieties, whereas increased water uptake also supported the presence of acid-functional moieties.
5. The SEM analysis revealed that the plasma etching of SO₂, SO₂-O₂, or SO₂-H₂O did not appreciably damage the PP membranes under the optimized conditions, whereas complete coverage was observed after 4 min of plasma polymerization coating.

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