

## 배터리 분리막을 위한 이온교환형 PVdF 멤브레인의 방사선 그래프트법에 의한 간편한 제조법

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한남대학교 화학과

(2009년 10월 23일 접수, 2009년 11월 26일 수정, 2009년 12월 30일 채택)

### Convenient Preparation of Ion-Exchange PVdF Membranes by a Radiation-Induced Graft Polymerization for a Battery Separator

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(Received October 23, 2009; Revised November 26, 2009; Accepted December 30, 2010)

**초록:** 메탄올 용매에서 고분자 측진 단량체와 소듐 스티렌 술포네이트를 방사선 그래프트 방법으로 양이온 교환 PVdF 멤브레인을 제조하였다. 고분자 측진 단량체로서 스티렌, 아크릴산, 비닐 피롤리돈을 사용하였다. 또한, 음이온 교환 PVdF 멤브레인도 방사선 그래프트 중합법에 의해 제조하였다. 양이온 및 음이온 교환 PVdF 멤브레인은 SEM, XPS 그리고 열분석기기를 통해 특성평가를 하였고 성공적으로 합성됨을 확인할 수 있었다. 그래프트 수율, 이온교환기의 양 및 침투율은 각각 30.0~32.3%, 2.81~3.01 mmol/g 그리고 66.6~147%로 평가되었으며, 20 °C에서 이온 전도도를 측정한 결과 0.020~0.053 S/cm 이었다. 최종적으로, 제조된 양이온 및 음이온교환 PVdF 멤브레인은 전지 격막으로서 충분히 사용될 수 있음을 확인할 수 있었다.

**Abstract:** A cation-exchange nanofiber poly(vinylidene fluoride) (PVdF) membrane was prepared by a radiation-induced graft polymerization (RIGP) of sodium styrene sulfonate (NaSS) in the presence of the polymerizable access agents in methanol solution. The used polymerizable access agents include styrene, acrylic acid, and vinyl pyrrolidone. The anion-exchange nanofiber PVdF membrane was also prepared by RIGP of glycidyl methacrylate (GMA) and its subsequent chemical modification. The successful preparations of cation- and anion-exchange PVdF membranes were confirmed via SEM, XPS and thermal analysis. The content of the grafting yield, ion-exchange group, and water uptake was in the range of 30.0~32.3%, 2.81~3.01 mmol/g and 66.6~147%, respectively. The proton conductivity at 20 °C was in the range of 0.020~0.053 S/cm. From the result, the prepared ion-exchange PVdF membrane can be used as a separator in battery cells.

**Keywords:** PVdF nanofiber membrane, sodium styrene sulfonate, polymerizable access agents, glycidyl methacrylate, radiation-induced graft polymerization, ion-exchange, proton conductivity.

## Introduction

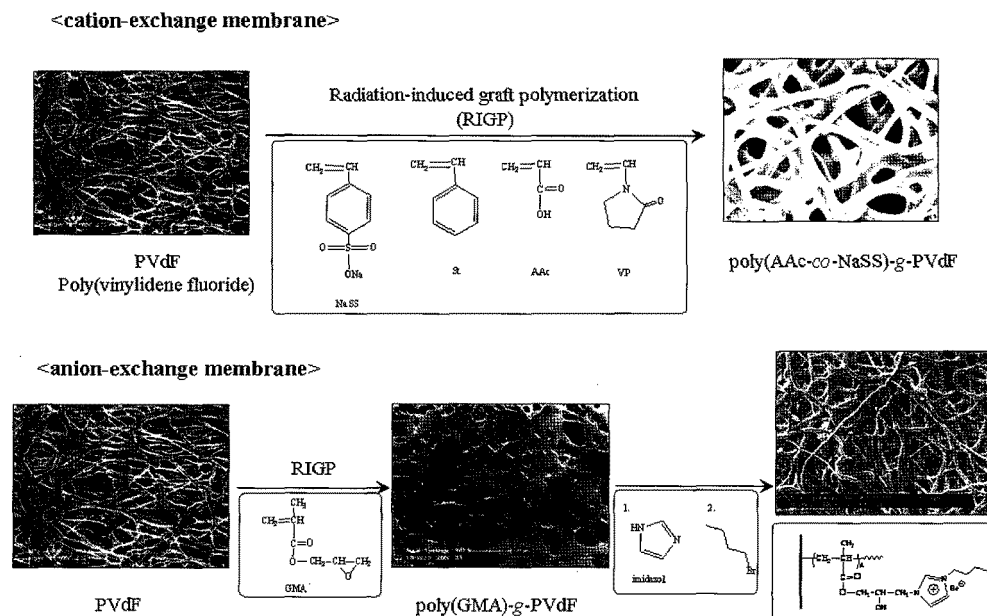
Battery separators for use in electrochemical cell systems desirably possess the following characteristics:<sup>1–3</sup> (i) it should have spontaneous, uniform and permanent wettable surface in order to accommodate and fully retain the aqueous electrolytic solution<sup>4,5</sup> and (ii) it should be dimensionally stable, and should not swell or shrink significantly upon introduction of the electrolytic solution. The additional desirable feature

of such battery separator is that it presents a minimal electrolytic resistance, preferably a resistance about 100–350  $\Omega/\text{cm}^2$  measured in 30% KOH at 1000 Hz at 23 °C or resistance even as low as 60  $\Omega/\text{cm}^2$  determined by the requirements of a given battery cell.<sup>1</sup>

Various battery separators have been designed throughout the years in an attempt to achieve one or more of this desirable advantages.<sup>6–9</sup> However, the battery separators have not compromised a number of desirable features.

Radiation-induced graft polymerization has been considered as a general method for the modification of the physical and

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**Scheme 1.** Preparation procedure of the cation- and anionic-exchange membranes by the radiation-induced graft polymerization.

chemical properties of polymer materials, and is of particular interest for synthesis of the hydrophilic membrane. Polymers such as polyethylene, polypropylene and their copolymer for battery separator require a large electrolyte retention volume, excellent chemical and thermal stability in electrolyte and high electrical conductivity. However, a little has been reported that the radiation-induced graft polymerization of the nano-fiber-type membrane using sodium styrene sulfate because sodium is acted as a strong radical scavenger.

In this study, we prepared cation-exchange nanofiber PVdF membranes by RIGP of NaSS in the presence of the polymerizable access agents in methanol solution. Secondly, the anion-exchange nanofiber PVdF membrane was also prepared by RIGP of GMA and its subsequent chemical modification. The prepared ion-exchange membranes were characterized by SEM, XPS, thermal analysis, water content, and ion-exchange group content, respectively. Furthermore, the proton conductivity was examined by Impedance instrument as a function of temperature in order to compare to the commercial Nafion membrane.

## Experimental

**Reagents.** The PVdF with the thickness of the 13.0  $\mu\text{m}$  and density of cal. 1.30  $\text{mg}/\text{m}^2$  was washed with methanol and dried in a vacuum oven at 50  $^{\circ}\text{C}$  for 12 h. Reagent-grade, sodium styrene sulfate (NaSS), styrene (St), acrylic acid (AAc, 99%), vinyl pyrrolidone (VP), and glycidyl methacrylate (GMA), imidazole, and 1-bromobutane were obtained

from Sigma-Aldrich (Korea), and used as received. The other chemicals were reagent grade.

**Synthesis of Cation- and Anion-Exchange Nanofiber PVdF Membrane.** Scheme 1 shows the preparation of cation- and anion-exchange nanofiber PVdF membrane by radiation-induced graft polymerization. In detail, the purified PVdF nanofibers were used as the supporting materials for grafting with NaSS including sulfonate group. The PVdF nanofiber (0.5 g), NaSS (0.25 g), and AAc (0.25 g) as polymerizable access agent were mixed in methanol (50 mL). Nitrogen gas was then bubbled through the solution for 30 min to remove oxygen, and the solution was irradiated by  $\gamma$ -rays of Co-60 source under atmospheric pressure and ambient temperature. A total irradiation dose of 30 kGy (a dose rate =  $1.0 \times 10^4$  Gy/h) was used. The obtained poly(AAc-co-NaSS)-g-PVdF membrane was dried in a vacuum oven at 50  $^{\circ}\text{C}$ , respectively. Other cation-exchange membranes such as poly(St-co-NaSS)-g-PVdF membrane and poly(VP-co-NaSS)-g-PVdF membrane were also prepared as similar method. In this study, the degree of grafting is defined as:

$$\text{Degree of grafting (\%)} = [(W_g - W_0) / W_0] \times 100 \quad (1)$$

where  $W_g$  and  $W_0$  denote the weights of the grafted and the ungrafted PVdF nanofiber, respectively.

Secondly, the anion-exchange nanofiber PVdF membrane was prepared as follows: the PVdF nanofiber (0.5 g) and GMA (0.5 g) were mixed in deionized water (50 mL). Nitrogen gas was bubbled through the solution for 30 min to

remove oxygen, and then the reaction solution was irradiated by  $\gamma$ -ray of Co-60 source under atmospheric pressure and ambient temperature. A total irradiation dose of 30 kGy (a dose rate =  $1.0 \times 10^4$  Gy/h) was used. The obtained poly (GMA)-*g*-PVdF nanofiber was dried in a vacuum oven. Finally, the anion-exchange PVdF membrane was prepared by the reaction of imidazole-modified nanofiber (0.5 g) and 1-bromobutane (0.5 g) in toluene at 70 °C for 12 h. Prior to the preparation of the membrane, the imidazole-modified PVdF nanofiber was prepared by the reaction of poly (GMA)-*g*-PVdF with epoxy group (0.5 g) and imidazole (0.5 g) in toluene at 70 °C for 12 h.

**Evaluation of Ion-Exchange Capacity (mmol/g) and Water Uptake(%).** In cation-exchange PVdF membrane, the content of ion-exchange group was determined from the measurement of total ion-exchange capacity by titration method. Priority, the poly (AAc-*co*-NaSS)-*g*-PVdF and poly (St-*co*-NaSS)-*g*-PVdF was soaked in 1.0 M NaCl solution for 24 h before measuring ion-exchange capacity. The Na-modified cation-exchange PVdF membrane was immersed in 1.0 M HCl aqueous solution at room temperature for 24 h, and then the hydroxyl ion remained in the solution was titrated with 0.01 M NaOH aqueous solution using phenolphthalein indicator.

$$\text{Ion-exchange capacity (mmol/g)} = \frac{(\text{X mmol of NaOH}) / (\text{weight of PVdF})}{\quad} \quad (2)$$

In anion-exchange PVdF membrane, the bromated-modified PVdF membrane was soaked in 0.5 M AgNO<sub>3</sub> solution at room temperature for 12 h. The precipitated AgBr salts were filtered through filter paper, and then dried in a vacuum oven at 60 °C. The weight of AgBr salts was measured.

Water uptake was calculated as the ratio of the weight of sorbed water in a given membrane sample to the vacuum dried sample weight as seen in eq. (3). When the sample was fully equilibrated with water, the surface of the membrane sample was quickly wiped using an absorbent paper to remove the excess of water adhering to it and the sample was then weighed.

$$\text{Water uptake (wt\%)} = [(W_w - W_d) / W_d] \times 100 \quad (3)$$

Where  $W_w$  and  $W_d$  are the weights of wet and dried membranes, respectively. The reported values were the mean of at least five measurements.

**Proton Conductivity.** A four-point probe method was used to measure the proton conductivity of the membranes using

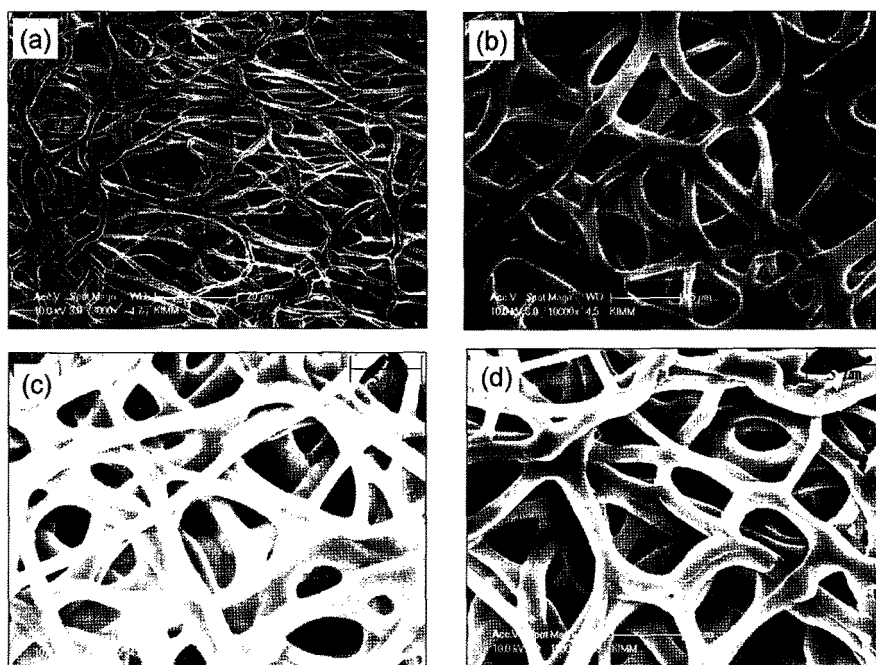
home made conductivity cell. The salt-form membranes were converted into acid form by submersing in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution for 16 h, followed by washing with deionized water. Before the measurement of proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range 1–8 MHz at 20 °C, using a ZAHNER IM-6 impedance analyzer. The impedance spectra of membranes can be used to generate Nyquist plots, and the proton conductivity was calculated from the plots. The impedance of each sample was measured five-times to ensure good data reproducibility. The average estimated error was  $\pm 5\%$ .

**Characterization.** For field emission scanning electron microscopy (FE-SEM), a sample of  $0.5 \times 0.5$  cm<sup>2</sup> was coated with gold-palladium alloy prior to the measurement. The sputtered sample was then scanned by the electron beam in scanning electron microscope (XL 30SFEG) and thermogravimetric analysis (TGA) of the cation- and anion-exchange membrane were made on the TA instruments of the TGA S-1000 model with a heating rate of 10 °C/min in the temperature range of 50–700 °C. The complex impedance measurements were carried out in the frequency range 1–8 MHz at 20 °C, using a ZAHNER IM-6 impedance analyzer.

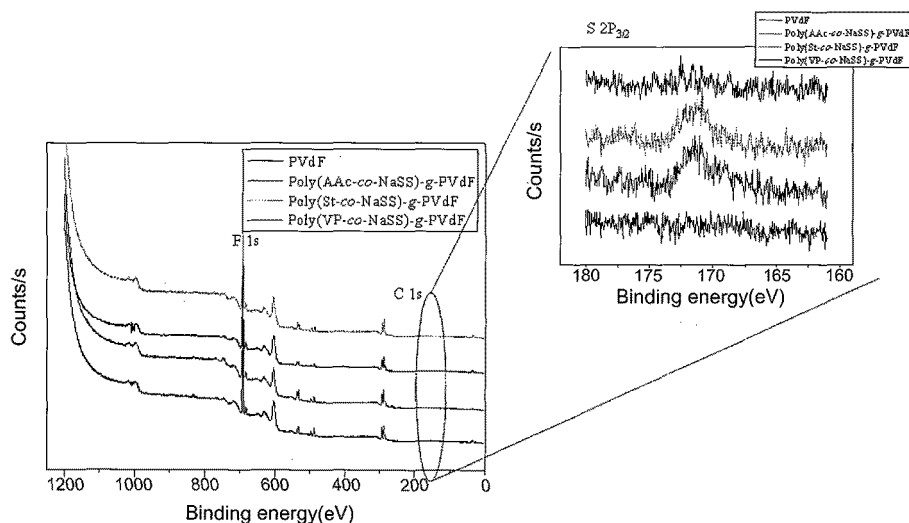
## Results and Discussion

In a previous paper,<sup>10</sup> cation-exchange hollow fiber membrane was prepared by radiation-induced grafting of styrene onto polyethylene hollow fiber membrane (PHFM) and its subsequent chemical modification. In order to introduce a sulfonic acid group (–SO<sub>3</sub>H), the chlorosulfonic acid (ClSO<sub>3</sub>H) in dichloroethane was reacted with polystyrene-grafted PHFM in the presence of H<sub>2</sub>SO<sub>4</sub> as a catalyst. During the sulfonation of PHFM, the toxic gas and large amounts of waste solution was produced. The introduction of sulfonate group of polymer subtracts may be successfully performed by RIGP when sodium styrene sulfate (NaSS) with a sulfonate group was used. However, when the NaSS without a sulfonate group was used, the RIGP was not actually occurred due to the sodium in NaSS used as a radical scavenger. The RIGP of NaSS can be successfully performed using polymerizable access agents such as styrene, acrylic acid and vinyl pyrrolidone as shown in Scheme 1.

Figure 1 shows the FE-SEM images of cation-exchange PVdF membrane prepared by RIGP: (a) Base PVdF, (b) poly (St-*co*-NaSS)-*g*-PVdF, (c) poly (AAc-*co*-NaSS)-*g*-PVdF and (d) poly (VP-*co*-NaSS)-*g*-PVdF. The morphology of PVdF was smooth fibers with diameter of 0.8  $\mu$ m as shown



**Figure 1.** SEM images of cation-exchange PVdF membranes prepared by RIGP: (a) base PVdF; (b) poly(St-co-NaSS)-g-PVdF; (c) poly(AAc-co-NaSS)-g-PVdF; (d) poly(VP-co-NaSS)-g-PVdF.



**Figure 2.** XPS data of cation-exchange PVdF membrane prepared by RIGP.

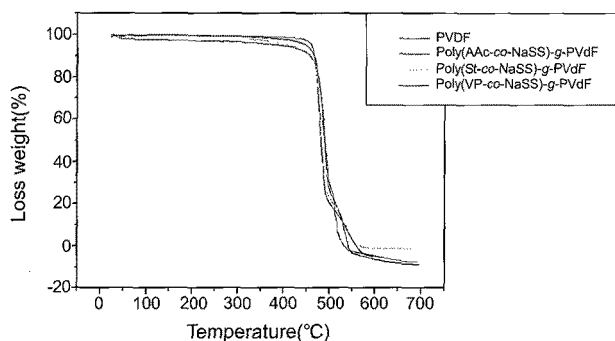
in Figure 1(a), whereas the morphology of poly(St-co-NaSS)-g-PVdF was an irregular shape of fibers with a 3.2  $\mu\text{m}$  diameter. In Figure 1(c), the poly(AAc-co-NaSS)-g-PVdF was dramatically changed from independent nanofibers (Figure 1(a)) to the form of connect neighboring nanofibers. In Figure 1(d), the poly(VP-co-NaSS)-g-PVdF was shown as irregular connect morphology form. As these results, the cation-exchange PVdF nanofiber membranes were successfully prepared with the sulfonate group using polymerizable access agents, by one-step reaction.

The XPS analysis was performed to confirm the binding of sulfonate group on the membrane. Figure 2 represents the XPS data of the cation-exchange PVdF membrane. The C1s peaks of the poly(vinylidene fluoride) appear at 291 eV and 286 eV, respectively, as shown in Figure 2(a). The predominant F1s peak is at 688 eV in the cation-exchange PVdF membrane. After radiation grafting of the co-monomer of NaSS and polymerizable access agents on the PVdF nanofiber, the S 2P<sub>3/2</sub> peak appears about 170 eV except for the poly(VP-co-NaSS)-g-PVdF membrane as shown in Figure

2(d). As a result, the sulfonate group was successfully introduced on to PVdF membrane by radiolytic copolymerization using polymerizable access agents.

Figure 3 shows the TGA curve of the cation-exchange PVdF membrane prepared by RIGP. A considerable change in the thermal behavior of PVdF membrane has occurred upon grafting. In Figure 3(b), the 1st loss in weight at 111 °C can be interpreted as the moisture content on the surface. The grafted (AAc-co-NaSS) weigh loss appears around 300 °C.

Glycidyl methacrylate (GMA) is one of the monomers which are easily modified into various functional groups. As GMA is polymerized, the epoxy group assists GMA becoming useful for the introduction of various functional groups, such as amines,<sup>11,12</sup> amino acid,<sup>13</sup> phosphoric acid,<sup>14</sup> and so on.<sup>15</sup>



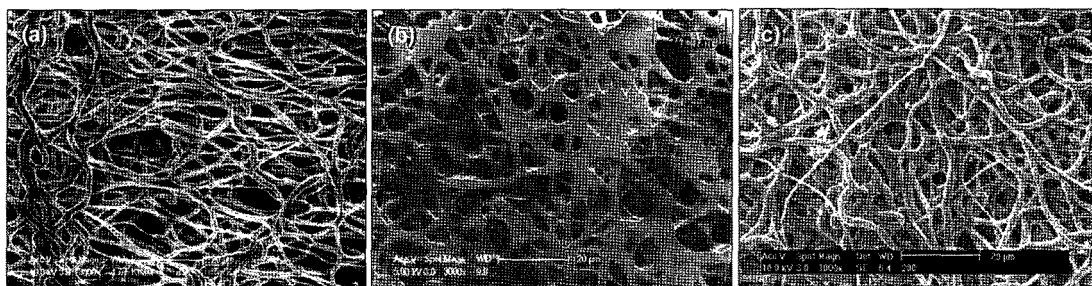
**Figure 3.** TGA curves of the cation-exchange PVdF membranes prepared by RIGP.

However, the amine with ion-liquid properties has not been reported until now.

Figure 4 shows the FE-SEM images of the anion-exchange PVdF membrane and its subsequent chemical modification: (a) original PVdF, (b) poly(GMA)-g-PVdF and (c) anion-exchange PVdF membrane (see, No. 3 in Table 1). After radiation grafting of GMA onto PVdF nanofiber, the amorphous poly(GMA)-g-PVdF nanofiber was observed as shown in Figure 4(b). After the introduction of ion liquid group onto the poly(GMA)-g-PVdF nanofiber, the morphology was changed the primary texture as shown in Figure 4(c). This is considered that the homopolymer was dissolved in toluene during chemical modification of imidazole salts as shown in Scheme 1. The diameter of the anion-exchange PVdF membrane, Figure 4(c), was in the range of 3–4.5 μm. From these results, it was confirmed that the anion-exchange PVdF membrane was successfully prepared by RIGP and conventional chemical reaction.

Figure 5 shows the XPS spectra of the anion-exchange PVdF membrane prepared by RIGP. The N1s peak of the anion-exchange PVdF membrane appears at about 400 eV due to imidazole molecule. However, the bromide signal does not present due to the removal of bromide ion under high vacuum during XPS analysis.

Figure 6 exhibits the TGA curve of the anion-exchange PVdF membrane prepared by RIGP. A remarkable change in the thermal behavior of PVdF membrane has occurred upon grafting. In Figure 6(b), the 1st weight loss at 250 °C



**Figure 4.** SEM images of the anion-exchange PVdF membranes prepared by RIGP: (a) original PVdF; (b) poly(GMA)-g-PVdF; (c) anion-exchange PVdF membrane, No. 3 in Table 1.

**Table 1. Properties of Cation- and Anion-exchange PVdF Membranes Prepared by RIGP**

No	Ion-exchange membrane	Yield (%) <sup>a</sup>	Ion-exchange content (mmol/g) <sup>b</sup>	Water uptake (%) <sup>c</sup>	Proton conductivity (S/cm) <sup>d</sup>		
					20 °C	30 °C	50 °C
1	Poly(St-co-NaSS)-g-PVdF	30.0	2.85	74.5	0.024	0.020	0.019
2	Poly(AAc-co-NaSS)-g-PVdF	31.2	2.94	147	0.020	0.019	0.010
3	Anion-exchange PVdF	32.3	3.01	66.6	0.053	0.015	0.010
4	Nafion 117 <sup>e</sup>	—	—	41.0	0.082		

<sup>a</sup>Degree of grafting (%) =  $[(W_g - W_0)/W_0] \times 100$ . <sup>b</sup>Ion-exchange content (mmol/g) was measured by titration method. <sup>c</sup>Water uptake (wt%) =  $[(W_w - W_0)/W_0] \times 100$ . <sup>d</sup>Proton conductivity was measured by impedance analyzer (IM6ex). <sup>e</sup>Nafion 117 was used as model membrane.

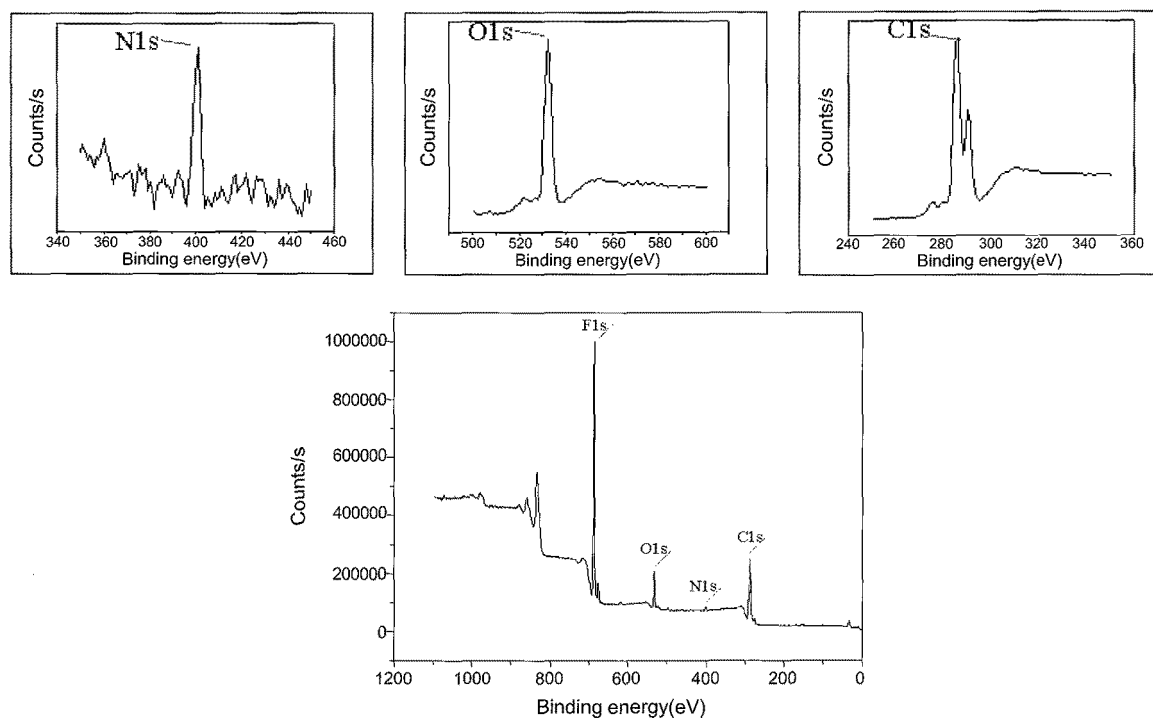


Figure 5. XPS data of the anion-exchange PVdF membrane prepared by RIGP.

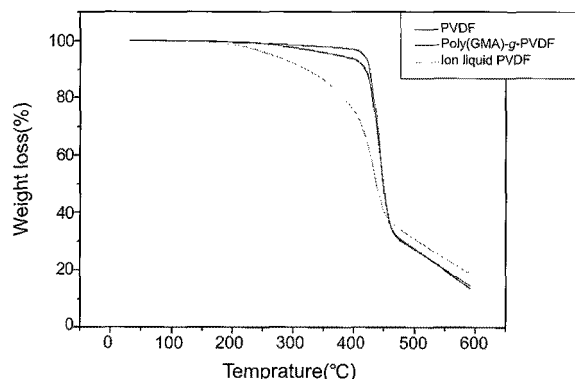


Figure 6. TGA curves of anion-exchange PVdF membranes prepared by RIGP (No. 3 in Table 1).

can be interpreted as the loss of the grafted poly (GMA) on the surface of PVdF nanofiber. The weight loss of the anion-exchange PVdF membrane appears at 150 °C due to the ion liquid properties of bromobutyl imidazole salts.

Table 1 presents the properties of cation- and anion-exchange PVdF membrane prepared by RIGP. In order to compare proton conductivity, the Nafion 117 membrane is also listed. The anion-exchange PVdF membrane shows higher proton conductivity than that of other membranes at 20 °C. However, its proton conductivity is still lower than that of commercial Nafion 117 membrane. The proton conductivity of as-prepared membrane is decreased with

increasing test temperature. On the other hand, there is one problem about the high swelling effects for prepared anion-exchange PVdF membrane.

## Conclusions

Cation- and anion-exchange PVdF membrane for the secondary battery separator were prepared by radiation-induced graft polymerization and its subsequent chemical modification. The following conclusions are based on the results:

- (1) The cation-exchange PVdF membrane having sulfonate group was successfully prepared using polymerizable access agents by RIGP.
- (2) The anion-exchange PVdF membrane with ion liquid was prepared by RIGP and its subsequent chemical modification.
- (3) The ion-exchange PVdF membrane was characterized by grafting yield, water uptake, ion-exchange content, and proton conductivity. As a result, the anion-exchange PVdF membrane among the ion-exchange PVdF membranes has good proton conductivity.
- (4) The prepared ion-exchange PVdF membrane by RIGP appears to be good candidates for a battery separator.

**Acknowledgment:** This study was supported by the Hannam

University Research Fund (2009).

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