Macromolecular Research, Vol. 20, No. 2, pp 205-211 (2012)
DOI 10.1007/s13233-012-0032-3
www.springer.com/13233

Synthesis and Characterization of EFFE-*g*-(VBTAC-*co*-HEMA) Anion Exchange Membranes Prepared by a ^{60}Co Radiation-Induced Graft Copolymerization for Redox-Flow Battery Applications

Noh-Seok Kwak, Jin Sun Koo, and Taek Sung Hwang*

Department of Applied Chemistry and Biological Engineering, Chungnam National University, Daejeon 305-764, Korea

Received June 22, 2011; Revised August 25, 2011; Accepted September 2, 2011

Abstract: Vinyl benzyl trimethyl ammonium chloride (VBTAC) was grafted onto poly(ethylene-*co*-tetrafluoroethylene) (ETFE) film by γ-ray using simultaneous irradiation graft copolymerization in the presence of 2-hydroxyl ethyl methacrylate (HEMA). The structure of the ETFE-*g*-(VBTAC-*co*-HEMA) anion membrane was confirmed by Fourier transform infrared spectroscopy and thermogravimetric analysis. The degree of grafting (DG) of the membrane increased with total irradiation dose and VBTAC monomer concentration. The highest DG of an ETFE-*g*-(VBTAC-*co*-HEMA) membrane was 92%, which was synthesized by the treating of an ETFE film with a 0.8 M solution of VBTAC monomer in the presence of 50 kGy irradiation. Different properties of the anion membrane, such as water uptake and ion exchange capacity, increased as DG increased. The permeability and vanadium redox-flow battery performance were measured for a membrane with a DG of 92%. The average voltage efficiency, coulombic efficiency, and energy efficiency were 0.79, 0.88, and 0.70, respectively, all of which remained stable as the number of cycles increased.

Keywords: radiation-induced graft copolymerization, ethylene tetrafluoroethylene, vinyl benzyl trimethyl ammonium chloride, 2-hydroxy ethyl methacrylate, vanadium redox battery (VRB).

Introduction

Since the vanadium redox flow battery was proposed by Skyllas-Kazacos, it has attracted attention as a promising energy storage system.[1,2] In particular, the vanadium redox battery (VRB) has the advantage of a higher electromotive force and a higher energy density compared to other redox flow batteries (RFBs). Furthermore, the VRB has a long cycle life, fast response time, design flexibility, deep-discharge capability and low pollution emission.[3,4]

The RFB system is composed of two electrolyte solutions, two electrodes and an ion exchange membrane. Ion exchange membrane is the key component in a VRB system because the RFB cell requires a separator to avoid mixing and direct chemical reaction of reductant and oxidant electrolytes.[3,4] Moreover, Ion exchange membrane employed in RFB system requires chemical resistance because the electrolyte solutions are strong acid. On the other hand, it is possible to apply cation exchange membrane or anion exchange membrane as a separator. Anion exchange membrane has an advantage of lower permeability of vanadium ions since its positive charge prevent vanadium ion from transporting across the membrane. However, most of anion exchange membranes have low chemical resistance.[3,5]

Ion exchange membranes in RFB system should possess the following properties to achieve a high energy efficiency and a long life cycle: high ionic conductivity, low permeability of vanadium ions, good chemical stability and low cost. Therefore, improving the properties of the ion exchange membranes is of great importance for satisfying the demands of a large scale application of VRBs.[5]

Radiation graft polymerization has been widely used as an effective method for polymer modification. The advantage of radiation graft polymerization is that it can be conducted without chemical initiators or catalysts and can provide control over the degree of grafting. Radiation graft polymerization is initiated by the formation of active sites on the polymer backbone using a radiation source such as ã-rays and an electron-beam. The active sites may be ionic chemical groups or free radicals.[6-10]

There has been a growing interest in fluoropolymers because of their thermal, chemical and mechanical stabilities.[11-17] Qiu *et al*. reported on the preparation of amphoteric ion exchange membranes by graft copolymerization of styrene and dimethyl amino ethyl methacrylate onto a PVDF film[11] and Rohani *et al*. reported on the kinetics of graft

---

*Corresponding Author. E-mail: tshwang@cnu.ac.kr copolymerization of styrene onto a poly(ethylene-*co*-tetrafluoroethylene) (ETFE) film.[12]

Moreover, as an anion exchange membrane monomer, VBTAC has several advantages. The synthesis of an anion exchange membrane using VBTAC does not require an additional amination reaction because the VBTAC has an anion functional group $-NH^{4+}$, which improves the homogeneity of the reaction.

However, it is difficult to graft VBTAC onto a hydrophobic fluoropolymer because VBTAC can be easily ionized and VBTAC is incompatible with hydrophobic polymer as a result, hence a few reports using 2-hydroxyl ethyl methacrylate (HEMA) have been reported in order to overcome this difficulty. Kolhe *et al.* reported on the grafting of VBTAC onto nylon-6 fabric in the presence of HEMA[18] and Tsuneda *et al.* have attempted to graft VBTAC onto polyethylene in the presence of HEMA;[19] however, these works did not elaborate on the ion exchange properties (such as IEC) and only discussed the structural analysis of the products.

In this work, VBTAC which prevents vanadium ion from cross-over due to its anion functional group was grafted onto ETFE filme which has a high durability in the presence of HEMA by using ^{60}Co γ-irradiation and its characterization was investigated. The degree of grafting was modulated by varying the reaction conditions, such as the monomer concentration and radiation time. The structure of the graft copolymers was confirmed by FTIR, DSC and TGA characterization methods. In addition, the important properties of ion exchange membranes, such as the water uptake, ion exchange capacity, ion conductivity, permeability of vanadium ions and VRB performance, were evaluated.

Experimental

Materials. An ETFE film of 100 μm thickness, supplied by Asahi Glass Co., Ltd. (Tokyo, Japan), was used as a substrate. VBTAC and HEMA were purchased from Sigma-Aldrich Co. (New York, USA). The solvents dimethyl formamide (DMF) and methanol were obtained from Samchun Chemical Company (Seoul, Korea). $VOSO_4 \cdot 3H_2O$ as an analytical reagent was supplied by Shanghai Luyan Fine Chemical Industry. Nafion 117 membrane was purchased from Du Pont and immersed in deionized water for 24 h prior to use.

Graft Copolymerization. Figure 1 shows the synthetic route for the preparation of the ETFE-*g*-(VBTAC-*co*-HEMA) anion exchange membrane by radiation-induced graft copolymerization of HEMA and VBTAC onto an ETFE film. The ETFE film (6 cm×7 cm) was washed with acetone and dried to a constant weight. Subsequently, the ETFE film was immersed in an aqueous solution of HEMA and VBTAC monomer in a sealed test tube. After degassing with nitrogen for approximately 30 min, the sealed test tube was subjected to γ-ray irradiation from a ^{60}Co source. The monomer concentration and grafting conditions are described in Table I. The irradiation induces a scission in the π bonds of the vinyl group in HEMA and VBTAC, leading to the formation of HEMA and VBTAC radicals. It is possible that HEMA and VBTAC are grafted onto active sites in the ETFE film and the reaction is finally terminated by hydrogen radicals.

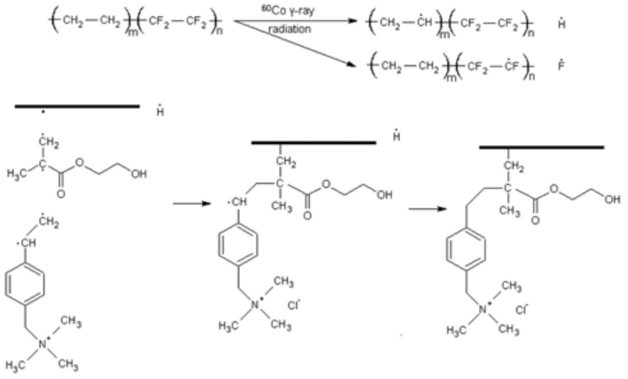

Figure 1. Schematic mechanism of irradiation-induced grafting of HEMA and VBTAC onto an ETFE film.

Table I. Monomer Concentration and Grafting Conditions for the Synthesis of ETFE-*g*-(VBTAC-*co*-HEMA)

Matrix	Concentration		Radiation Conditions	
	VBTAC (M)	HEMA (M)	Dose Rate (kGy/h)	Total Dose (kGy)
ETFE Film	0.10	1.5	1	10-50
	0.20			
	0.40			
	0.80			

The radiation dose rate was 1 kGy/h and the degree of grafting was measured with respect to the dose time. After the irradiation, the samples were washed with methanol for 24 h and then dried in the oven for 12 h. The DG was calculated using the following eq. (1):

$$DG\ (\%) = (W_g - W_0)/W_0 \times 100 \tag{1}$$

where W_g and W_0 are the weight of irradiated and un-irradiated ETFE film, respectively.

FTIR Spectroscopy and Thermal Analysis. The original ETFE film and the ETFE-*g*-(VBTAC-*co*-HEMA) membranes were characterized by using FTIR spectroscopy (Model IR Prestige-21, Shimadzu, Kyoto, Japan), thermogravimetric analysis (TGA Q500, USA) and differential scanning calorimetry (DSC Q20, TA instruments, USA). The FTIR spectra were collected in the transmission method using 20 scans with a resolution of 4 cm^{-1} at room temperature. For TGA and DSC analyses, the sample was heated to 600 °C at a heating rate of 10 °C/min using a nitrogen gas flow rate of 100 mL/min.

Scanning Electron Microscopy (SEM). Surface images of the original ETFE film and the ETFE-*g*-(VBTAC-*co*-HEMA) membranes were obtained by using an SEM (JEOL JSM-840A, USA). Incident electron beam energies of 0.5 to 30 keV were used. In all cases, the beam was at normal incidence with respect to the sample's surface and a measurement time of 100 s was used. All surfaces of the sample were covered with osmium using the ion sputtering method.

IEC. The method for measuring the IEC was developed from procedures described in the literature.[20] The ETFE-*g*-(VBTAC-*co*-HEMA) anion exchange membrane was equilibrated in a 1.0 N Na_2CO_3 solution for 24 h. Subsequently, the equilibrated solution was titrated with a 0.1 N $AgNO_3$ solution. A K_2CrO_4 standard solution was used as an indicator. The ion exchange capacity was calculated using the following eq. (2):

$$\text{IEC (meq/g)} = (N \times V)/W \times 100 \tag{2}$$

where N and V are the concentration (meq/mL) and the volume (mL) of $AgNO_3$, respectively.

Water Uptake and Swelling Ratio. The ETFE-*g*-(VBTAC-*co*-HEMA) anion exchange membrane was immersed in deionized water for 24 h. The membrane was then removed from water and the surface was patted dry with an absorbent paper to remove the excess water adhering to the surface. The membrane was weighed and the water uptake was calculated using the following eq. (3):[21]

$$\text{Water uptake (\%)} = (W_w - W_g)/W_g \times 100 \tag{3}$$

where W_w and W_g are the weight of the sample under wet and dry conditions, respectively.

A dried membrane sample (3×3 cm) was also immersed in water for 24 h to measure the swelling ratio. After removal from the water, the length of the samples was measured. The swelling ratio was calculated using eq. (4).

$$\text{Swelling ratio (\%)} = (l_w - l_d)/l_d \times 100 \tag{4}$$

Here, l_w and l_d are the length of the samples in wet and dry conditions, respectively.

Permeability of Vanadium Ions. The permeability of vanadium ions through the ETFE-*g*-(VBTAC-*co*-HEMA) anion exchange membrane was investigated. A Vanadium (IV) solution was prepared by dissolving 1 M $VOSO_4 \cdot 5H_2O$ in a 2 M H_2SO_4 solution. The left reservoir was filled with a vanadium ion solution and the right reservoir was filled with a 1 M $MgSO_4$ solution in 2 M H_2SO_4. $MgSO_4$ was used to balance the ionic strength and reduce the osmotic pressure. The area of the membrane exposed to the solution was 1.77 cm^2 and the volume of the solutions on both sides was 25 mL. An aliquot of the $MgSO_4$ solution was removed and analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, Leeman, Profile) at regular time intervals to determine the concentration of vanadium ions in the solution. For comparison, the permeability of vanadium ions through a Nafion 117 membrane was also tested using the same method.

VRB Performance. The VRB was fabricated by sandwiching the membrane between two pieces of graphite of carbon electrodes. Solutions of 1.5 M V(II)/V(III) and V(IV)/V(V) in 2.5 M H_2SO_4 were used as the electrolyte in the positive and negative half-cell, respectively. The area of the membrane was 5 cm^2 and the volume of the electrolyte solution in each half-cell was 40 mL. The battery was first charged to 1.6 V at a current density 20-60 $mA \cdot cm^{-2}$. Subsequently, the open circuit voltage (OCV) was measured at room temperature.[22]

Results and Discussion

Synthesis of ETFE-*g*-(VBTAC-*co*-HEMA) Anion Exchange Membranes. The effect of the total irradiation dose and the monomer concentration on the degree of grafting are shown in Figure 2. An increase in total dose from 0 to 30 kGy affected the degree of grafting. Above 30 kGy, a further increase in the total dose has little or no effect on the DG. In addition, the degree of grafting increases with increasing monomer concentration. The maximum degree of grafting of 91.7% was obtained at a total dose of 50 kGy and a VBTAC monomer concentration of 0.80 M.

FTIR Spectroscopy. The structures of the original ETFE film and the ETFE-*g*-(VBTAC-*co*-HEMA) membrane were

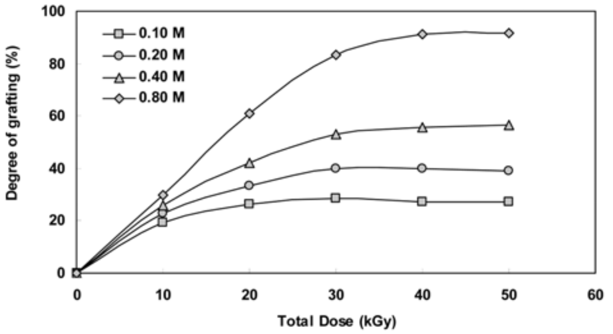

Figure 2. Effects of the total total dose on the degree of grafting at different monomer concentrations.

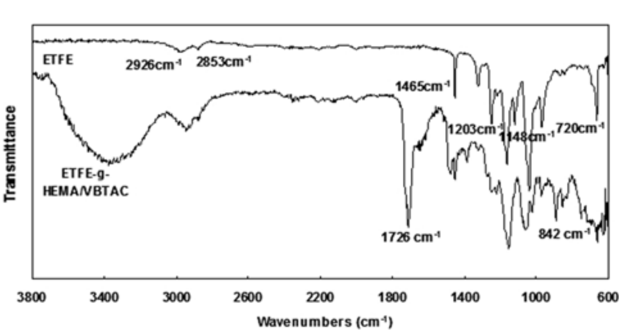

Figure 3. FTIR spectra of original ETFE film and ETFE-*g*-(VBTAC-*co*-HEMA) membrane, with a degree of grafting of 91.74%.

confirmed using FTIR spectroscopy[23,24] (Figure 3). The peaks at 2926 and 2853 cm^{-1} are assigned to the -CH$_2$- asymmetric and symmetric stretching vibration in ETFE (Figure 3(a)), respectively. Moreover, the peaks at 1465 and 720 cm^{-1} are attributed to the -CH$_2$- scissoring and rocking deformation, respectively. Upon grafting, the intensity of the peaks at 1203 and 1148 cm^{-1}, assigned to the -CF$_2$- asymmetric and symmetric peaks, shows a decrease (Figure 3(b)). A new peak appears at 1726 cm^{-1} due to the presence of a -COO- group, as well as a broad peak in the region of 3600-3000 cm^{-1}, attributed to the -OH group of HEMA. Furthermore, the appearance of a peak at 842 cm^{-1} is attributed to *p*-disubstituted benzene. This peak confirms the presence of the aromatic ring of VBTAC. In this manner, the structure of the ETFE-*g*-(VBTAC-*co*-HEMA) membrane is confirmed.

Thermal Analysis. Figure 4 shows the TGA and DSC curves of the original ETFE film and ETFE-*g*-(VBTAC-*co*-HEMA) membranes with a degree of grafting of 19.10%, 52.96%, and 91.74%. The original ETFE film shows high thermal stability above 480 °C and exhibits a rapid decomposition above this temperature. However, the TGA curve of ETFE-*g*-(VBTAC-*co*-HEMA) shows a two-step weight loss: one in the range of 260-400 °C and another above 480 °C due to the degradation of the graft chain and that of the ETFE matrix, respectively. In the case of ETFE-*g*-(VBTAC-*co*-HEMA) with a degree of grafting of 91.74%, approximately 41% of grafted VBTAC and HEMA were found to be decomposed in the first step.[25] As shown in Figure 4(b), the melting points of the original ETFE film and various ETFE-*g*-(VBTAC-*co*-HEMA) membranes are observed at approximately 260 °C. This similarity indicates that the intrinsic crystallinity of the ETFE parent film and the ETFE-*g*-(VBTAC-*co*-HEMA) membranes is similar, which suggests that the grafting occurs in the amorphous region.[26]

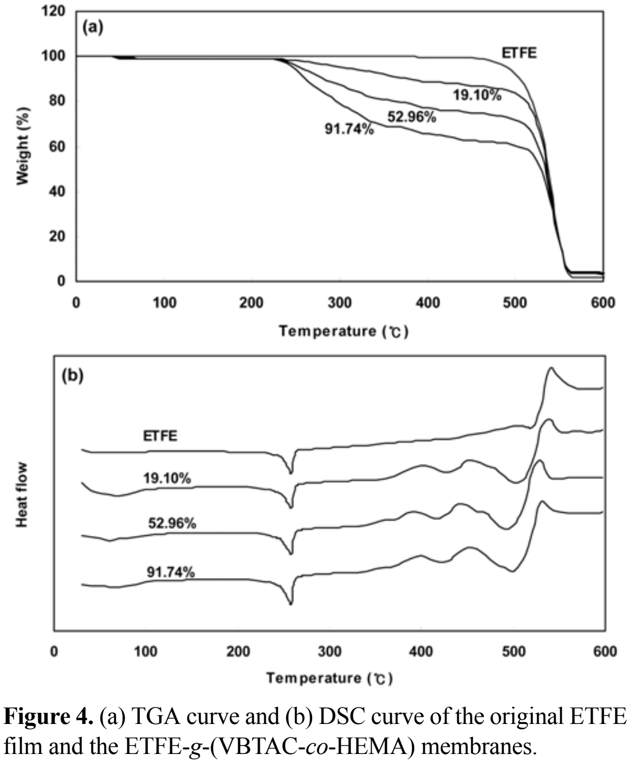

Figure 4. (a) TGA curve and (b) DSC curve of the original ETFE film and the ETFE-*g*-(VBTAC-*co*-HEMA) membranes.

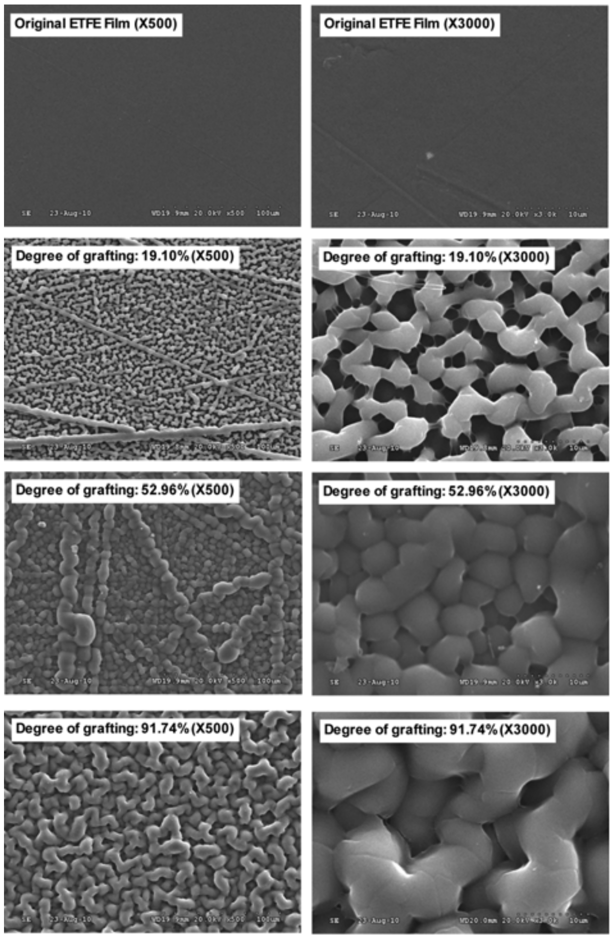

Figure 5. SEM images of the original ETFE film and the ETFE-*g*-(VBTAC-*co*-HEMA) membranes.

SEM Images. SEM images with a 500x and 3,000x magnification of the original ETFE film and the ETFE-*g*-(VBTAC-*co*-HEMA) membranes with a degree of grafting of 19.1%, 52.9%, and 91.7% are shown in Figure 5. The original ETFE film has a smooth surface in all of the images at a magnification of 500x and 3,000x; however, in the case of ETFE-*g*-(VBTAC-*co*-HEMA), a number of grains appear in the SEM image. Furthermore, as the grafting reaction proceeds, the size of the grain increases. This trend is clearly observed in the images at a 3,000x magnification. The ETFE-*g*-(VBTAC-*co*-HEMA) membrane with a degree of grafting of 19.1% has smaller grains relative to the other membranes in the series, but the graines of the ETFE-*g*-(VBTAC-*co*-HEMA) anion exchange membranes becomes larger as the grafting reaction proceeds.

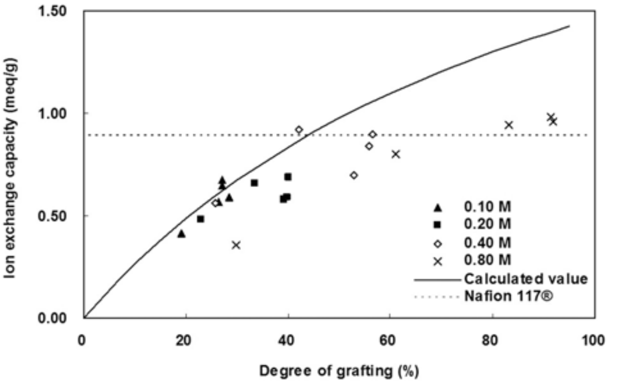

Figure 6. Effects of the degree of grafting on the ion exchange capacity.

Effect of Degree of Grafting on the IEC. IEC measures the content of the ammonium ion in the ETFE-*g*-(VBTAC-*co*-HEMA) membranes. The relationship between the degree of grafting, the IEC and the calculated ion exchange capacity is shown in Figure 6. The calculated value was obtained based on the assumption that the reaction was conducted using the same mole ratio of VBTAC to HEMA. The IEC increased with an increasing degree of grafting and the values were similar with Nafion 117® when the degree of grafting was 40% or more. This result is likely due to factors such as steric hindrance within the polymer. In the images with a 3,000x magnification, it is shown that, as the grafting reaction proceeds, the pore size decreased so that the number of adsorption sites decreases due to a reduction in the surface area, even though the degree of grafting increases. Moreover, the observed IEC values are somewhat lower than the calculated values, which may occur because the mole ratio of VBTAC to HEMA is not the same in the reaction.

Water Uptake and Swelling Ratio. The influence of water uptake of the membranes on the degree of grafting is shown in Figure 7(a). This figure indicates that the water uptake reaches 34.98% for a degree of grafting of 91.74%. The increase in swelling corresponds to the higher content of ammonium groups with an increasing degree of grafting, which in turn increases the hydrophilicity in the membrane. This result is also confirmed in Figure 7(b), which shows the relationship between the water uptake and the IEC. The data in Figure 7(a) can be fit by a linear function, whereas that of Figure 7(b) can be fit by a quadratic function. The swelling ratio is also given in Figure 7(a) to investigate dimensional stability because water uptake affect swelling ratio. As shown in Figure 7(a), the swelling ratio increased dramatically at the degree of grafting of 83% or more and the value was more than 10%. Thus, the optimum degree of grafting is considered to be below 63%.

The hydration number, defined as the amount of water molecules per quaternary ammonium (nH$_2$O/NR$_4^+$), calculated from Figure 7(a) and (b), is approximately 7.6 for all of the samples. On the other hand, the water uptatke of Nafion 117® was approximately 20% and the value was similar with the synthesized anion exchange membrane at a degree of grafting of 40%-60%.

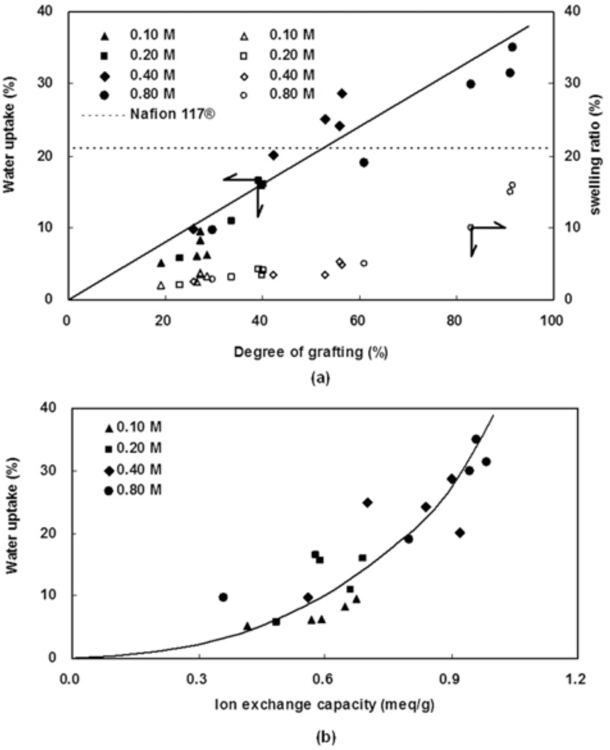

Figure 7. Effects of the degree of grafting (a) and the ion exchange capacity: (▲■◆●) water uptake, (△□◇○) swelling ratio and (b) on the water uptake properties.

Permeability of Vanadium Ions through the ETFE-*g*-(VBTAC-*co*-HEMA) Anion Exchange Membrane. Although ion exchange membrane is the key component in a VRB system, crossover of vanadium ion result in serious self-discharge of the battery and low energy efficiency. Anion exchange membrane avoids this problem because its positive charge prevent crossover of vanadium ion. The crossover of vanadium ion through the anion exchange membrane synthesized in this study and commercial cation exchange membrane, Nafion 117® is given in Figure 8. As time increases, the vanadium concentration increases gradually; however, the change in the concentration is smaller than that of Nafion 117®. According to Luo *et al.*, the concentration of vanadium ions in right reservoir is given as below:[27]

$$V\frac{dc_t}{dt} = A\frac{P}{T}(c_0 - c_t) \tag{5}$$

where V is the volume of the solution, A is the area of the membrane, P is the permeability of vanadium and T is the thickness of the membrane; c_0 and c_t are initial concentration of the vanadium solution and the concentration of right reservoir at time (t).

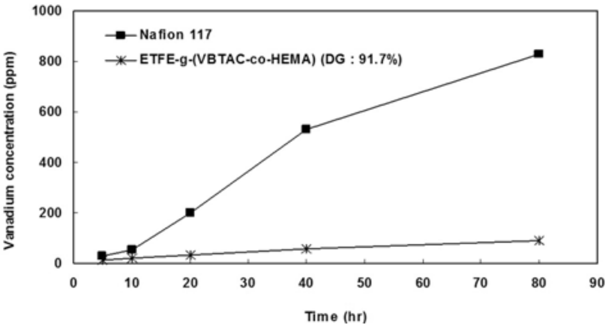

Figure 8. The change in the concentration of vanadium ions in the right reservoir with time.

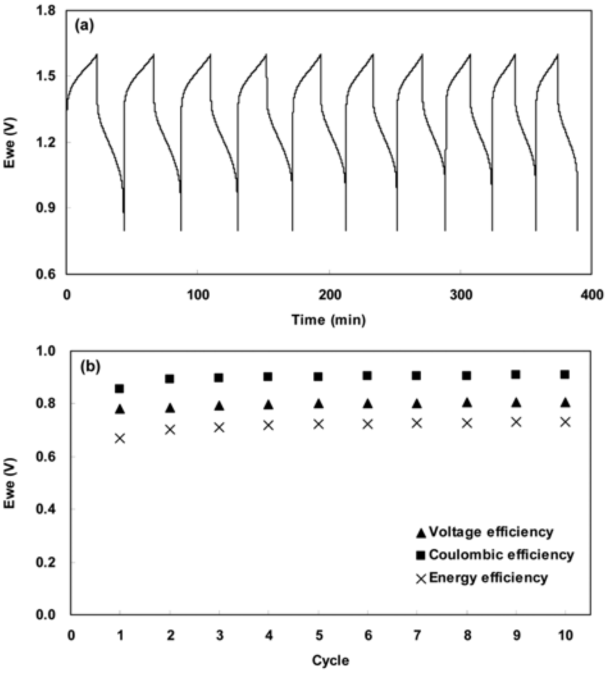

Figure 9. (a) Ten charge-discharge cycles curves and (b) their efficiencies (at the DG of 92%).

The permeability obtained from Figure 8 was calculated from the eq. (4). The values of Nafion 117® and anion exchange membrane were 8.42×10^{-7} and 0.49×10^{-7} cm^2/min, respectively.

VRB Performance of the ETFE-*g*-(VBTAC-*co*-HEMA) Anion Exchange Membrane. The charge-discharge performance of the ETFE-*g*-(VBTAC-*co*-HEMA) anion exchange membrane (DG of 91.7%) at a current density of 20 mA·cm^{-2} is presented in Figure 9(a) and (b). The average voltage efficiency and coulombic efficiency are 0.79 and 0.88 V, respectively. Accordingly, the whole energy efficiency ranges from 0.66 to 0.73 V. Furthermore, the efficiencies are stable as the number of cycles increases, indicating that the ETFE-*g*-(VBTAC-*co*-HEMA) anion exchange membrane is suitable for VRB.

Table II. The Voltage, Coulombic and Energy Efficiencies at 20-60 mA·cm^{-2}

Current Density (mA·cm^{-2})	Cycle Number	Cell Efficiency (%)		
		η_V	η_C	η_E
20	1	78.0	85.7	66.9
	5	80.0	90.2	72.1
	10	80.5	90.8	73.1
30	1	76.7	85.1	65.3
	5	77.2	87.3	67.4
	10	78.3	89.2	69.8
40	1	75.3	83.5	62.9
	5	76.1	83.9	63.8
	10	76.9	84.1	64.7
50	1	73.1	81.1	59.3
	5	73.2	81.7	59.8
	10	72.8	82.2	59.8
60	1	72.3	79.8	57.7
	5	72.1	79.2	57.1
	10	70.6	78.5	55.4

The voltage, coulombic and energy efficiency values at a current density of 20-60 mA·cm^{-2} are summarized in Table II. The highest energy efficiency was obtained at a current density of 20 mA·cm^{-2}. As the current density increases, the efficiencies of the membrane are gradually reduced, but the difference is not large.

Conclusions

ETFE-*g*-(VBTAC-*co*-HEMA) membranes were prepared using ^{60}Co γ-ray irradiation in the presence of HEMA and VBTAC and their properties were evaluated. The effect of grafting was confirmed by FTIR, TGA, DSC, and SEM analyses and the membrane properties, such as degree of grafting, water uptake and IEC, were investigated. The increases in the total dose and the monomer concentration have been shown to exert influences over the degree of grafting. The maximum degree of grafting was 91.74% and was achieved at a total dose of 50 kGy and a VBTAC monomer concentration of 0.80 M. The IEC and water uptake of ETFE-*g*-(VBTAC-*co*-HEMA) increased with an increasing degree of grafting because of the increase in the amount of functional groups and hydrophilicity, respectively. In this study, the optimum IEC and water uptake were 0.80 meq/g and 19.01%, respectively, at a 61.02% degree of grafting. The permeability of vanadium ions was lower than that of Nafion 117. The average voltage efficiency, coulombic efficiency and energy efficiency were stable as the number of cycle times increased. The highest energy efficiency was obtained at a current density of 20 mA·cm^{-2}.

Acknowledgements. This research was supported by the Ministry of Education, Science Technology (MEST) and the National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation (No. I0087) and by the Small & Medium Business Administration (SMBA) (No. S1073137). We gratefully appreciate the generous help that was provided.

References

(1) E. Sum and M. Skyllas-Kazacos, *J. Power Sources*, **15**, 179 (1985).

(2) E. Sum, M. Rychcik, and M. Skyllas-Kazacos, *J. Power Sources*, **16**, 85 (1985).

(3) S. Zhang, C. Yin, D. Xing, D. Yang, and X. Jian, *J. Memb. Sci*., **363**, 243 (2010).

(4) G.-J. Hwang and H. Ohya, *J. Memb. Sci*., **55**, 132 (1997).

(5) J. Qiu, M. Li, J. Ni, M. Zhai, J. Peng, L. Xu, H. Zhou, J. Li, and G. Wei, *J. Memb. Sci*., **297**, 174 (2007).

(6) M. M. Nasef and E. A. Hegazy, *Prog. Polym. Sci.,* **29**, 499 (2004).

(7) D. S. Wavhal and E. R. Fisher, *J. Memb. Sci*., **209**, 255 (2002).

(8) Y. Wang, J. Kim, K. Choo, Y. Lee, and C. Lee, *J. Memb. Sci*., **169**, 269 (2000).

(9) Y. Kimura, M. Asano, J. Chen, Y. Maekawa, R. Katakai, and M. Yoshida, *Radiat. Phys. Chem*., **77**, 864 (2008).

(10)A. Vahdat, H. Bahrami, N. Ansari, and F. Ziaie, *Radiat. Phys. Chem.,* **76**, 787 (2007).

(11) J. Qiu, J. Zhang, J. Chen, J. Peng, L. Xu, M. Zhai, J. Li, and G. Wei, *J. Memb. Sci*., **334**, 9 (2009).

(12) R. Rohani, M. M. Nasef, H. Saidi, and K. Z. M. Dahlan, *Chem. Eng. J.,* **132**, 27 (2007).

(13) Y. Su, Y. Liu, D. Wang, J. Lai, Y. Sun, S. Chyou, and W. Lee, *J. Memb. Sci*., **349**, 244 (2010).

(14) S. D. Flint and R. C. T. Slade, *Solid State Ion.,* **97**, 299 (1997).

(15) G. Y. Moon and J. W. Rhim, *Macromol. Res.,* **16**, 524 (2008)

(16) M. M. Naseff, N. A. Zubir, A. F. Ismail, M. Khayet, K. Z. M. Dahlan, H. Saidi, R. Rohani, T. I. S. Ngah, and N. A. Sulaiman, *J. Memb. Sci*., **268**, 96 (2006).

(17) S. Takahashi, H. Okonogi, T. Hagiwara, and Y. Maekawa, *J. Memb. Sci*., **324**, 173 (2008).

(18) S. M. Kolhe and A. Kumar, *Radiat. Phys. Chem.,* **76**, 901 (2007).

(19) S. Tsuneda and K. Saito, *J. Electrochem. Soc*., **142**, 3659 (1995).

(20) T. Xu, Z. Liu, and W. Yang, *J. Memb. Sci*., **249**, 183 (2005).

(21) W. M. Lee, S. C. Gil, H. J. Lee, and H. Y. Kim, *Macromol. Res.,* **17**, 451 (2009).

(22) D. K. Lee, J. T. Park, J. K. Choi, D. K. Roh, J. H. Lee, Y. G. Shul, and J. H. Kim, *Macromol. Res.,* **16**, 549 (2008).

(23) R. M. Silverstein, F. X. Webster, and D. J. Kiemle, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, Inc., USA, 2005.

(24) Z. Liang, W. Chen, J. Liu, S. Wang, Z. Zhou, W. Li, G. Sun, and Q. Xin, *J. Memb. Sci*., **233**, 39 (2004).

(25) S. M. Kolhe and A. Kumar, *Radiat. Phys. Chem*., **77**, 384 (2005).

(26) J. Chen, M. Asano, T. Yamaki, and M. Yoshida, *J. Memb. Sci*., **269**, 194 (2006).

(27) X. Luo, Z. Lu, J. Xi, Z. Wu, W. Zhu, L. Chen, and X. Qiu, *J. Phys. Chem. B*, **109**, 20310 (2005).