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Perfluorinated polymer for vanadium flow battery

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ABSTRACT

The perfluorinated polymers (Nafion) that have different thickness were evaluated for vanadium flow battery at different current density. The charge/discharge capacities depend on the start voltage of charge/discharge at each cycle. The cell with low vanadium permeability and low area resistance may improve vanadium flow battery performance. The performance, such as energy efficiency, coulombic efficiency, and voltage efficiency of the Nafion membranes, shows the large difference at low current density than at high current density. This suggests that the area resistances and ion crossover are more sensitive at low current density than at high current density.

Keywords: Vanadium flow battery; Ion crossover; Charge/discharge; Capacity; Nafion

1. Introduction

Electricity generation from renewable source, such as solar and wind, is being deployed in larger numbers because of growing environmental concerns about fossil fuels and limited hydrocarbon reserves. The storage of electrical energy generated in wind and solar energy plants has become a key technology and one of the greatest challenges faced by the energy technology sector. Innovative solutions are required to compensate the imbalances between generation and demand of electrical energy. One of the promising technologies for energy storage is redox flow batteries [1]. Redox flow batteries have many technical benefits over other energy storage systems as well as an excellent combination of energy efficiency, capital cost, and life cycle costs compared with other technologies [1].

Redox flow cell storage systems use two soluble redox couple as electroactive species that are oxidized or reduced to store or deliver energy. The electrodes are separated by an ion-exchange membrane, while the reactants contained in separate storage tanks are re-circulated through the redox flow cells where the electrochemical reactions take place [2]. Fig. 1 shows the basic concept of a vanadium flow battery cell.

The major components of the vanadium battery are the electrodes made up of highly porous carbon felt, the electrolyte, and the ion-exchange membranes. The electrolyte is prepared by dissolving vanadium oxide or sulfate in sulfuric acid solutions in vanadium flow battery. It is important to develop the membrane that has a pathway allowing conduction of ion.

The concentration and volume of the electrolytes determines the capacity of the battery. Increasing the

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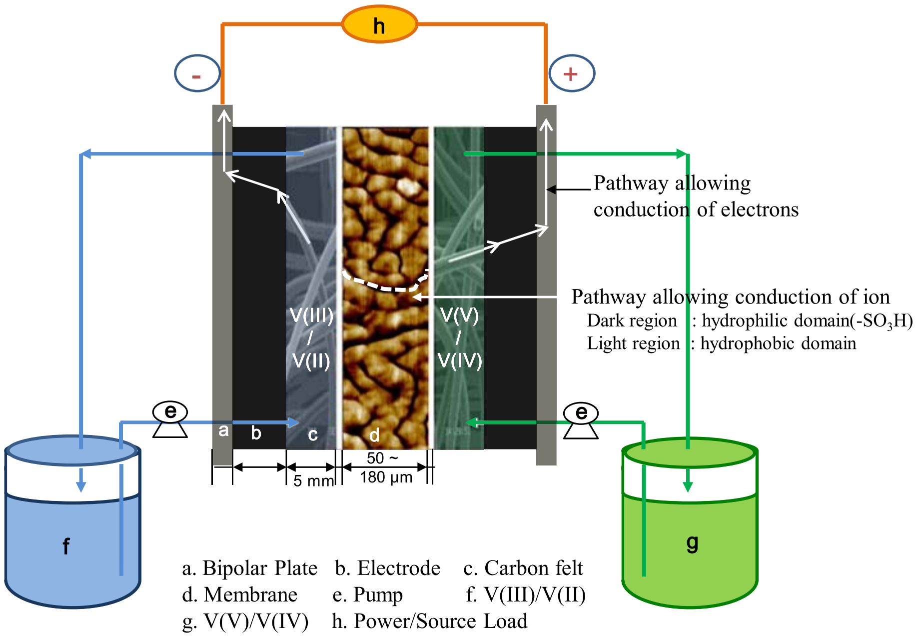

Fig. 1. Schematic of vanadium flow battery.

concentration of the electrolyte such as vanadium will increase the energy density of the battery. The power of the flow battery is determined by the size of electrodes and the number of cells [3].

An ideal membrane for vanadium flow battery should have low permeability of water and vanadium ions to minimize self-discharge, high ion conductivity, good chemical stability during operation, and low cost [3]. Although many research groups reported the synthesized hydrocarbon or composite membrane designed for vanadium applications, it is still need to study of chemical stability as well as more scientific behavior of the membrane during cell operation. In relation to the membrane, there are many factors to effect on the cell performance, such as membrane thickness, morphology, ion exchange capacity (IEC), conductivity, and ion crossover, but a few articles only reported these effects on vanadium flow cell performance.

We consider the effect of membrane thickness on the vanadium flow battery performance. To minimize the effect caused by other factors such as ion conductivity, membrane morphology, and IEC, we selected the perfluorinated polymers (Nafion) that have only different thickness.

2. Experimental

2.1. Materials

Commercial Nafion PFSA membranes (Nafion 112, 115, 117) were purchased from DuPont. The properties of these PFSA type membranes were listed in Table 1.

Table 1
Experimental conditions

Specification description		
Electrode	Materials	Carbon felt (treatment: 10 h at 500 ℃, air)
	Area and thickness	35 cm^2/5 mm
Operating temperature	Room temp.	
Current density @ charge and discharge	20, 35, 50 (mA/cm^2)	
Cycle	10 @ each current density	
Flow rate (ml/min)	40	

2.2. Pre-treatment of membrane samples

All membrane samples were immersed into H_2SO_4 (0.5 M) solution at boiling temperature for 1 h and washed with boiling water for 1 h.

2.3. Membrane characterization

The water content was measured by soaking the samples in distilled water for more than 24 h. After this period, they were wiped with a filter paper and then weighed immediately. The samples were then dried under vacuum until a constant weight was obtained. The water content (%) was determined using the following equation:

$$\text{Water content }(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{1}$$

where W_{wet} and W_{dry} are the wet and dry membrane weights, respectively. The values of the water content reported are the mean of at least five measurements, and the average estimated error was ±8%.

The IEC value was measured using the classical titration technique. The IEC value (in meq/g) was calculated by following equation described by Kim et al. [4]:

$$\text{IEC} = \frac{M_{\text{O,NaOH}} - M_{\text{E,NaOH}}}{W_{\text{dry}}} \tag{2}$$

where $M_{\text{O,NaOH}}$ is the milli-equivalent (meq) of NaOH in the flask at the beginning of the titration, $M_{\text{E,NaOH}}$ is the meq of NaOH after equilibrium, and W_{dry} is the weight of the dry membrane (g).

Proton conductivity of the membrane was determined according to the previous methods [4]. The impedance of the membranes was measured with an impedance analyzer using a Zahner Impedance spectrometer (ZENNIUM PP211) over a frequency range from 1 to 100 kHz at room temperature and 100% RH. The proton conductivity was obtained from

$$\sigma = \frac{L}{R \times S} \tag{3}$$

where σ is proton conductivity (in S/cm). L is the distance between the counter electrodes and the working electrode used to measure the potential (1 cm). R is the impedance of membrane (in Ω). S is the surface area required for proton to penetrate the membrane (in cm^2).

The ion permeability of the membranes was determined using a diaphragm diffusion cell [4]. This cell consisted of two reservoirs, each with a capacity of approximately 100 ml, separated by a vertical membrane. The membrane was clamped between the two reservoirs, the contents of which were stirred during the experiments. Initially, one reservoir (V_A) contained the solution of 1.5 M $VOSO_4$ in 3 M H_2SO_4, and the other reservoir (V_B) was filled with the solution of 1.5 M $MgSO_4$ in 3 M H_2SO_4. $MgSO_4$ was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effects. In the permeability tests, the temperature was conducted at room temperature. Accordingly, pseudo-steady-state condition was used and the vanadium ion concentration in the V_B reservoir as a function of time is given by the following equation: An UV–vis spectrometer was used to measure the vanadium concentration.

$$P = \frac{1}{A} \times \frac{C_B(t)}{C_A(t - t_0)} \times V_B L \tag{4}$$

where C_B and C_A are the two vanadium ion concentrations, A and L the membrane area and thickness, and P is permeability of the vanadium ion. The assumptions made in this study were that the value of P did not depend upon the vanadium ion concentration. The value of C_B was measured several times during the experiments, and the permeability was calculated from the gradient of the straight lines obtained from plots of the data.

For the vanadium redox battery (VRB) single cell used in the charge/discharge tests, 100 ml of 1.8 M V^{3+} in 2.5 M H_2SO_4 solution was pumped into the negative half-cell and 100 ml of 2.0 M V^{4+} in 2.5 M H_2SO_4

Table 2
Properties of the membranes (water uptake and conductivity measured at 20℃)

Copolymer	Density[a] (g/cm^3)	Thickness (μm)	IEC$_w$[b] (meq./g)	IEC$_v$[c] (meq./cm^3)		Water uptake		Proton conductivity (mS/cm)	Ion permeability (10^{-6} cm^2/min)
				Dry	Wet	wt%[d]	vol%[e]		
Nafion 112	1.97	50	0.91	1.79	1.11	31	61	97.5	2.09
Nafion 115	1.92	130	0.91	1.75	1.17	25	49	83.1	1.82
Nafion 117	1.97	183	0.91	1.79	1.20	25	48	99.6	2.33

[a] Based on dry state.

[b] Based on weigh of dry membrane.

[c] Based on volume of dry and/or wet membranes (IEC$_v$ (wet) = IEC$_v$ (dry)/(1 + 0.01 WU)).

[d] WU (mass%) = $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100$.

[e] WU (vol%) = $((W_{\text{wet}} - W_{\text{dry}})/\delta_w)/(W_{\text{dry}}/\delta_m) \times 100$, ($W_{\text{wet}}$ and W_{dry} are the weights of the wet and dry membranes, respectively; δ_w is the density of water (l g/cm^3), and δ_m is the membrane density in the dry state).

solution was pumped into the positive half-cell. The VRB single-cell cycling was performed at a charge/discharge current density of 20–50 mA/cm^2. The lower voltage limit for discharge and the upper voltage limit for charge were controlled to 1.0 and 1.6 V, respectively. Other properties were listed in Table 2.

3. Results and discussion

3.1. Membrane properties

The density, IEC and water uptake of the Nafion 112, 115 and 117 were listed in Table 2. Volume-based quantities under operating conditions (hydrated membranes) have been reported to be the most appropriate comparison basis, because electrochemical properties such as ion conductivity and ion permeability occur over length scales under operating conditions independent of mass [5].

The ion permeability was measured using the free-standing membranes and listed in Table 2. Although the Nafion 117 shows lower ion permeability than Nafion 112 and 115, it is not depend on the membrane thickness. However, the effect of membrane thickness was observed in open circuit voltage (OCV) test (Fig. 2). The voltage drop time related to ion crossover depends on the membrane thickness. Different ionic species (V^{3+}/V^{2+}, V^{5+}/V^{4+}) tend to diffuse across the membrane due to the concentration gradient across the cell, resulting in coulombic efficiency (CE) loss derived from self-discharge [6]. It is reported that in the fully charged cell, the concentration of V^{5+} and V^{2+} decreased with time because of ion crossover, and the self-discharge reactions can further decrease the concentration of the charged ions [6]. In this study, the OCV test was performed in the fully discharged cell using V^{3+} on the negative side and V^{4+} on the positive side. The start voltages are 1.22 V. As time increases, the OCV decreased. Voltage drop ratio with time was calculated (from 0 to 200 min) and shown in Fig. 2. Voltage drop ratio for Nafion 117 was 7.67 mV/h, while Nafion 112 and 115 showed a voltage drop ratio of 10.74 and 10.68 mV/h, respectively. The decrease in OCV in fully charge cell and/or discharge depends on the ion crossover. In the same conditions, the ion crossover depends on the membrane thickness as shown in Fig. 2.

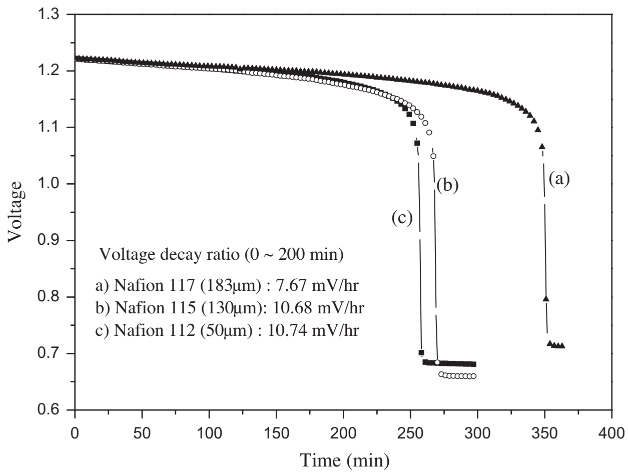

Fig. 2. OCV decay of the vanadium flow battery cell with Nafion 112, 115 and 117.

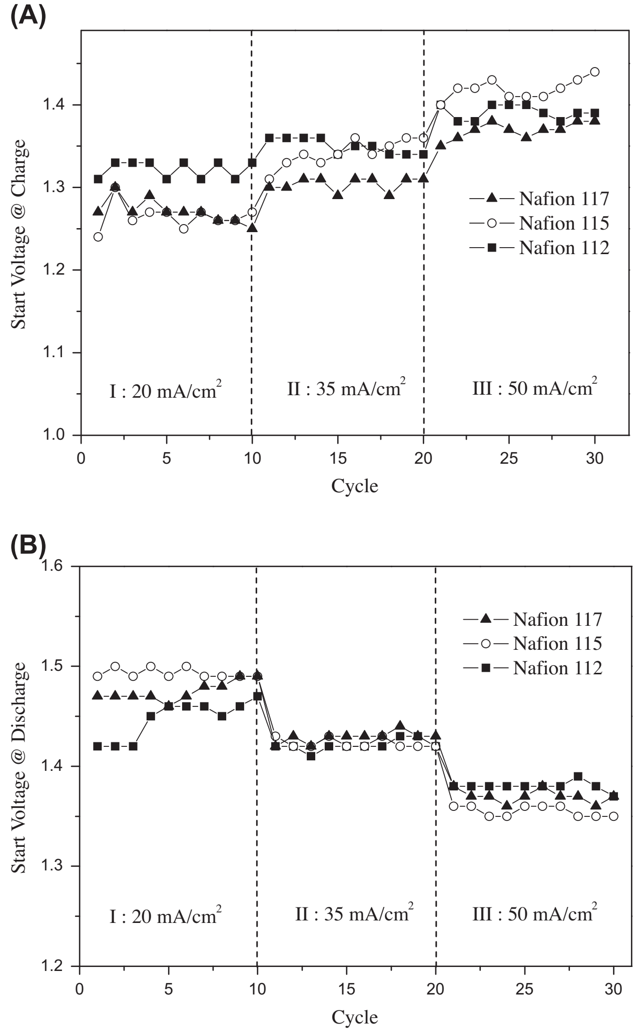

Fig. 3. Start voltage variation at (A) charge and (B) discharge with current density.

3.2. Cell performance

The change of the cell resistance during cell operation affects the cell performance. Fig. 3 shows the start voltage of charge and discharge at each cycle. The start voltage of charge increased with increasing the current density. The Nafion 117 shows the low variation of voltage with increasing current density. For examples, the variation of voltage of Nafion 117 between 20 and 50 mA/cm^2 is 0.06 V (from 1.33 V at 20 mA/cm^2 to 1.39 V at 50 mA/cm^2) while that of Nafion 115 is 0.16 V (from 1.26 V at 20 mA/cm^2 to 1.42 V at 50 mA/cm^2). This behavior affects the capacity as shown in Fig. 4. As shown in Fig. 4(B), the discharge capacities of Nafion 117 at 20 and 50 mA/cm^2 are 4.7 and 3.9 Ahr, respectively (Decrease in 17%). However, the discharge capacities of Nafion 115 decreased from 4.9 to 3.4 Ahr (decrease in 30.6%) with increasing the current density. Although the charge/discharge capacity decreased with increasing the current density, the

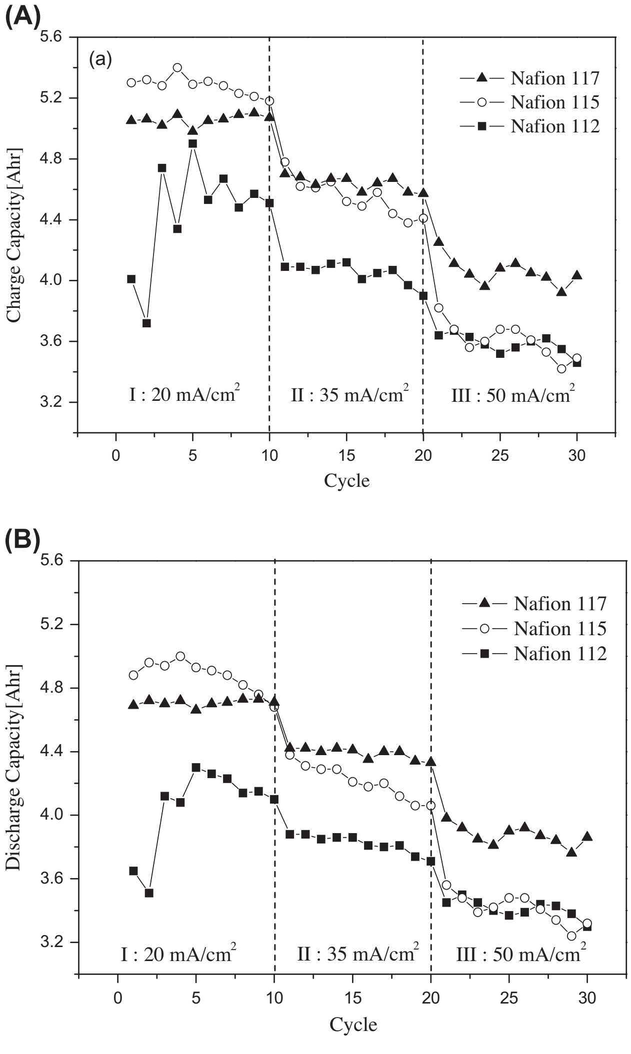

Fig. 4. Capacity variation at (A) charge and (B) discharge with current density.

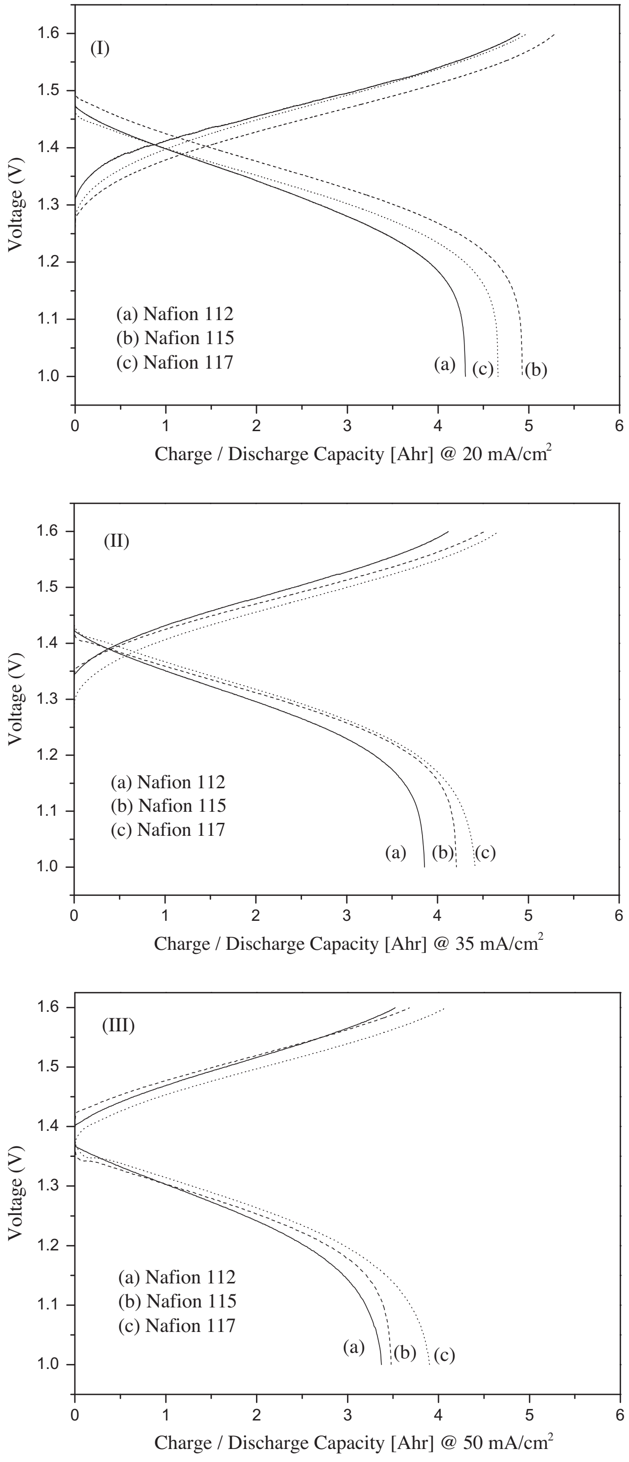

Fig. 5. Charge–discharge curves of single cell at different current density.

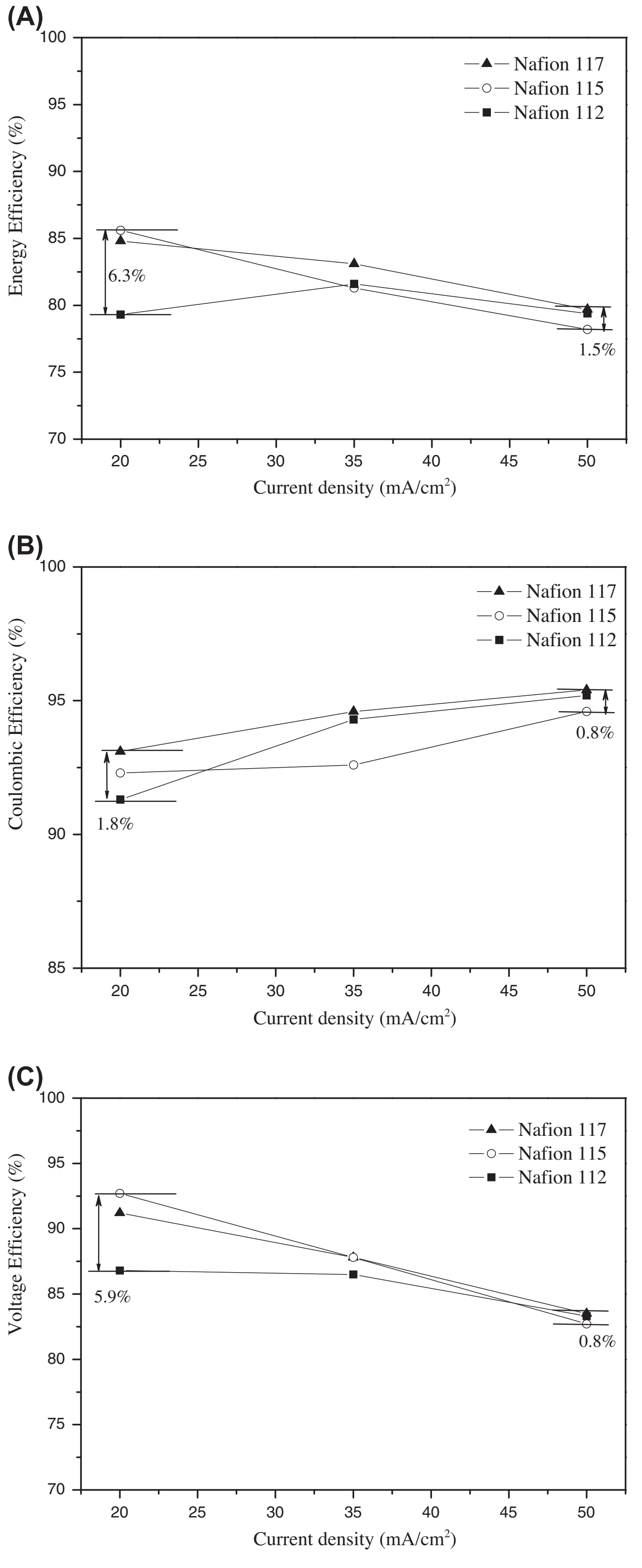

Fig. 6. (A) Energy efficiency, (B) CE and (C) VE at different current density.

charge/discharge capacities are maintained at the same current density.

The typical charge/discharge curves of single cell were presented in Fig. 5. As shown in Figs. 3(a) and 5 (I), the average charge voltage based on Nafion 115 at current density of 20 mA/cm^2 is a little bit lower than that of based on Nafion 112. However, at high current density (50 mA/cm^2), the average charge voltage based on Nafion 115 is higher than that of based on Nafion 112. The variation of charge voltage depends on the IR drop (Ohmic drop) caused by the area resistance of the membrane. The large IR drop was shown in Nafion 115 with increasing current density.

The discharge time of Nafion 117 at 35, 50 mA/cm^2 is a little longer than that of Nafion 112, 115. The reason for this behavior may be the reduction in self-discharge of the single cell due to low ion crossover. As shown in Fig. 4(B), the Nafion 117 shows the high discharge capacity compared with Nafion 112, and 115 at current density of 35, and 50 mA/cm^2. The Nafion 115 that have high discharge capacity at 20 mA/cm^2 shows the longer discharge time (Fig. 5 (I)). The discharge capacity and discharge time of Nafion 115 decrease with increasing the current density. The ion crossover of Nafion 115 may be more sensitive to the current density compared with Nafion 117.

Fig. 6 shows the efficiency of single cell. In general, the low area resistances of membrane lead to the high-voltage efficiency (VE). The high crossover of vanadium ions through the membrane results in a loss of electrochemical energy during the cell operation [7]. The VE decreases with increasing the current density. However, the CE increased with increasing current density. The difference of efficiency is a little bigger at low current density than at high current density. As shown in Fig. 6, the difference of energy efficiency between Nafion 112 and 115 at 20 mA/cm^2 is 6.3%. However, the difference of efficiency decreased to 1.5% at 50 mA/cm^2. This suggests that the area resistances and ion crossover is more sensitive at low current density.

4. Conclusions

The alternative membrane materials are being developed to replace the perfluorinated polymer (Nafion) for vanadium flow battery. To do that, many research groups use the Nafion membrane (such as Nafion 112, 115, and 117) as reference materials to compare the cell performance. However, it is rarely reported to directly compare the performance of these Nafion materials that have different thickness. Although there are many factors to effect on cell performance, minimize the effect caused by other factors, such as ion conductivity, membrane morphology, and IEC, we selected the perfluorinated polymers (Nafion 112 (50 μm), 115 (130 μm), 117 (183 μm)) that have only different thickness. The Nafion 117 showed the lower ion crossover compared with Nafion 112 and 115. The Nafion 117 showed the better performance related with the variation of start voltage and capacity at charge/discharge with increasing the current density compared with Nafion 112 and 115. The efficiency of cell is more sensitive at low current density than high current density. In this study, we did not consider the flow rate at each current density. The cell performance considered other effects such as flow rate will be reported in another publication.

Acknowledgments

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