Equivalent Circuit Model Considering Self-discharge for SOC Estimation of Vanadium Redox Flow Battery

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Abstract—The vanadium redox flow battery (VRFB) consists of the electrodes, pump, and membrane, but the pump is causative of self-discharge because it continuously operated the ions diffusion through membrane. Thus, the equivalent circuit of VRFB should consider the self-discharge to enhance the accuracy of the state of charge (SOC) estimation. This paper proposes the equivalent circuit model of VRFB, which is comprised of the basic RC ladder. In addition, to consider the self-discharge of VRFB the proposed equivalent circuit takes into account that the capacitance of the vanadium redox flow battery is changed by the charging and discharging cycles. The self-discharge test profile was proposed by applying the decreased capacity depending on cycles, and the derived amount of self-discharge was applied to the RC ladder based equivalent circuit model based on resistance. The parameters for the equivalent circuit model is extracted by the actual experimental data. The equivalent circuit model with the basic RC ladder is modeled by using MATLAB/Simulink. Based on the equivalent circuit model considering self-discharge, EKF (Extended Kalman filter) suitable for nonlinear system of vanadium redox flow battery was used for SOC estimation.

I. Introduction

Energy storage systems have carried out a key role in diversifying energy sources and replacing renewable energy sources in global markets. In addition to popularized lithium-ion batteries, various energy storage devices have been developed, vanadium redox flow battery (VRFB) are also used in variety of applications as mass storage devices.

Vanadium redox flow batteries are attracted as next generation batteries that replace lithium-ion batteries with a long life cycle and high energy efficiency. Vanadium redox flow battery is a secondary battery that charge and discharge based on circulating the electrolyte when energy storing. Therefore, the cost maintenance can be remarkably decreased, and the power and energy capacity can be adjusted easily according to the requirements of the user. However, in order to apply the vanadium redox flow battery to various applications, various factors must be taken into account in operation of vanadium redox flow battery.

Many researches have reported the equivalent circuit models for adaptability and accuracy considering the dynamic characteristics of the vanadium redox battery. The properties of the open circuit voltage (OCV) and state of rest in the vanadium redox flow battery are the major consideration to apply various applications.

The general equivalent circuit for the lithium ion battery do not consider the self-discharge in the vanadium redox flow battery. In addition, many researches based on the material of the membrane improve the performance of the vanadium redox flow battery. However, the self-discharge is negligible.

This paper proposes the model of the vanadium redox flow battery considering the self-discharge; the model consists of the basic RC ladder. To do this, the proposed model differentiates the charging, discharging, and rest parts. Moreover, to enhance the accuracy, the proposed model is investigated under the various current densities and charge/discharge profiles.

II. Operation of VRFB

A. Pinciple of vanadium redox flow battery

A vanadium battery basically consists of an electrolytic tank for storing electrolytes and a pump and a cell for supplying an electrolyte, and a reaction occurs depending on various conditions such as temperature and flow rate. Equation (1) shows the process of oxidation of V^{4+} ion to V^{5+} ion in positive electrode and (2) shows the process in which V^{3+} ion is reduced to V^{2+} ion in negative electrode. As a result, as shown in (3), charge and discharging process occur with redox reaction is repeatedly performed at the anode and the cathode [1].

$$\text{Positive electrode}: V^{4+} + H_2 0 \leftrightarrow V^{5+} + e^- \tag{1}$$

$$\text{Negative electrode}: V^{3+} + e^- \leftrightarrow V^{2+} \tag{2}$$

$$V^{4+} + V^{3+} + H_2 0 \leftrightarrow V^{5+} + V^{2+}\ 2\mathrm{H} \tag{3}$$

B. Self-discharge

Self-discharge in a vanadium redox flow battery is caused by a side effect on the membrane in which ions move in addition to the normal reaction that occurs between the positive electrode and the negative electrode and between the membrane. Side effect on the membrane is the main factor of self-discharge at the state of rest of vanadium redox flow battery. Ideally, as shown in (1)–(3), the ion reaction must occur on at the time when the current is applied[2]. However, in general, the ion exchange between the membrane by operating of pump and circulating of electrolytes when the state of rest in the during the experimental voltage and current profile.

Self-discharge due to ions exchange between membrane is serious factor that makes it difficult to estimate the accurate state of charge(SOC) according to OCV. Therefore, self-discharge must be reflected in the R-C based equivalent circuit model [3].

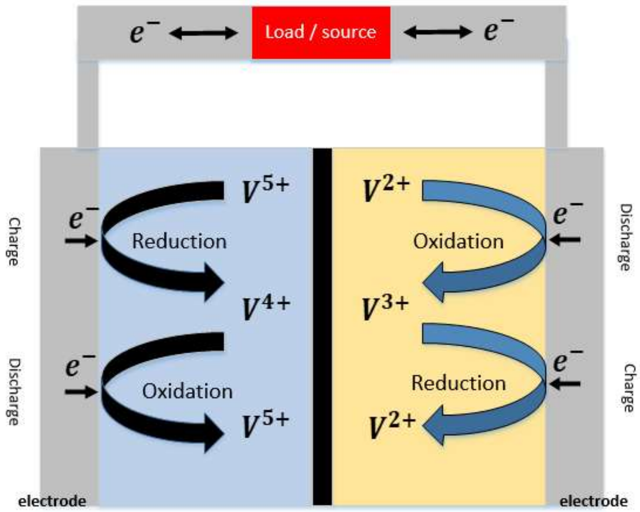

Fig. 1. Principle of VRFB

C. Cross Over

The capacity loss during charging and discharging cycles of vanadium redox flow battery is caused by the cross over phenomenon in which the ions move in addition to the normal ionic reaction occurring between the anode and cathode in the membrane. Cross over phenomenon is main factor of capacity decrease during the charging and discharging cycles of vanadium redox flow battery. Even if charging and discharging are started with the same amount of electrolyte, the amount of electrolyte at the anode and cathode is changed as repeated cycles by cross over phenomenon [4].

In the cross over phenomenon, in addition to the ideal oxidation-reduction reactions, other side reaction occur between membrane.

$$2VO^{2+} + V^{2+} + 2H^{+} \leftrightarrow 3VO^{2+} + H_2O \tag{4}$$

$$VO_2^{+} + V^{3+} \leftrightarrow 2VO^{2+} \tag{5}$$

$$VO^{2+} + V^{2+} + 2H^{+} \leftrightarrow 2V^{3+} + H_2O \tag{6}$$

$$V^{2+} + VO^{2+} + 2H^{+} \leftrightarrow 2V^{3+} + H_2O \tag{7}$$

$$2V^{2+} + VO^{2+} + 4H^{+} \leftrightarrow 3V^{3+} + 2H_2O \tag{8}$$

$$V^{3+} + VO_2^{+} \leftrightarrow 2VO^{2+} \tag{9}$$

In addition to the ideal ion reaction shown in (1)–(3), side reaction between membrane are shown in (4– (9). Abnormal ion redox reactions are showed in (4)–(6) are occur in the positive electrode and (7)–(9) are occur in the negative electrode.

$$\Delta VO^{2+} = (-(-J_{VO_2^+}(t) + 2J_{V^{3+}}(t) + 3J_{V^{2+}}(t))\ \Delta tA \tag{10}$$

$$\Delta VO_2^{+} = (-J_{VO_2^+}(t) - J_{V^{3+}}(t) - 2J_{V^{2+}}(t))\ \Delta tA \tag{11}$$

$$\Delta V^{2+} = (-J_{V^{2+}}(t) - J_{VO^{2+}}(t) - 2J_{VO_2^+}(t))\ \Delta tA \tag{12}$$

$$\Delta V^{3+} = (-J_{V^{3+}}(t) + 2J_{VO^{2+}}(t) + 3J_{VO_2^+}(t))\ \Delta tA \tag{13}$$

Equation (10)–(12) represent the abnormal diffusion over time of the ions moving in anode and cathode through the membrane. In (10)–(12), J means the amount of ions diffused during charging and discharging cycles and A is the size of membrane in which the ions move as the electrolyte circulate [5].

III. Experimental Setup

Fig. 2. Experimental setup of VRFB

In this paper, 6×5 carbon felt (Graphite) and Nafion -115 membrane were used. The charging and discharging cycle was progressed at a 50ml / min flow rate using 2.6mol of sulfuric acid and 1.7 mol of vanadium.

The operation for separating the ions (V^{2+}, V^{3+}, V^{4+}, V^{5+}) in the initial state was conducted at a current density of 10Ma /cm^2 (300Ma: Current density×Area of membrane), and all experiments related to capacity and self-discharge after the operation were performed at current density of 20mA /cm^2(600Ma)

A. Reduced capacity by number of cycle

The cross over phenomenon, which is a chemical reaction other than the normal ion transfer according to the above-mentioned charge and discharge cycles, is the biggest factor that the capacity is continuously decreased according to the number of charge and discharge charge and discharge. In this paper, estimated the SOC of the vanadium redox flow battery by repeated charging and discharging based on discharge capacity. Since the self-discharge characteristics were analyzed in a specific SOC, it was predicted that the capacity to be applied would decrease according to the number of times of charging and discharging.

As can be seen in Fig.3, when the charge and discharge are repeated 10times, the capacity decreases as the cycles are progressed. Table 1 shows the capacities according to the number of cycles. In order to analyze the self-discharge characteristics according to the specific SOC, each time a self-discharge in one specific SOC is derived, different capacities were assigned to each cycle.

TABLE I. CAPACITY LOSS ACCORDING TO THE NUMBER OF CYCLE

Number of cycle	*Capacity[Ah]*	*Rate of loss*
1	1.3369	1
2	1.2859	0.9618
3	1.2304	0.9203
4	1.1792	0.882
5	1.1268	0.8428
6	1.0753	0.8043
7	1.0232	0.7653
8	0.9751	0.7293.
9	0.9265	0.6930

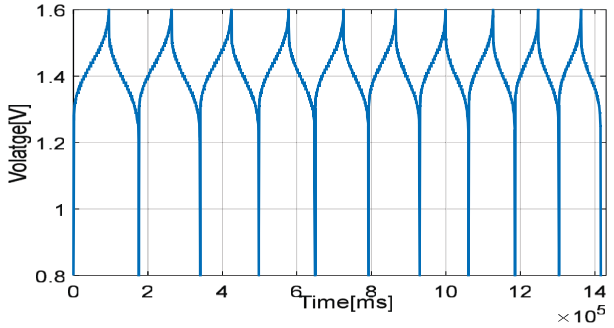

Fig. 3. Voltage profile of cycle test

B. *Self-discharge characteristics analysis*

In this paper, the characteristic analysis is performed at a specific SOC during the pump is operating. Then, as shown in (14), for accurate calculation according to the Ampere-Counting method, the charge and discharge were performed at room temperature(25℃) at 600mA. Figure 4 shows the capacity test voltage profile for deriving the discharge capacity at room temperature. As a result of the capacity test, 1.7341[A/h] was derived. The capacity of VRFB varies with external conditions such as temperature and current density, but is basically determined by the amount of electrolyte contained in the tank. In this paper, experiments were conducted with 50 ml of electrolyte in both tanks. The maximum and minimum voltages were tested at 1.6V and 0.8V, respectively.

$$SOC = SOC_0 + \frac{1}{Q}\int i\,dt \tag{14}$$

Table 2 shows the capacities derived from the discharge capacity test and the capacities predicted according to the cycle reflecting the capacity reduction rate obtained in Table 1. As shown in Figure 5, The predicted capacity according to the cycle was assigned differentially during the 9 cycles. Figure 5 shows the voltage profile for deriving the self-discharge at the state of rest and derives amount of self-discharge at the state of rest by subtracting the end voltage from the starting voltage in the state of rest for 2 hours. Table 3 shows the self-discharge at each SOC derived from the voltage profile from Figure 5. As a result, the amount of self-discharge at high SOC and low SOC is much higher than the amount of self-discharge at region of middle SOC.

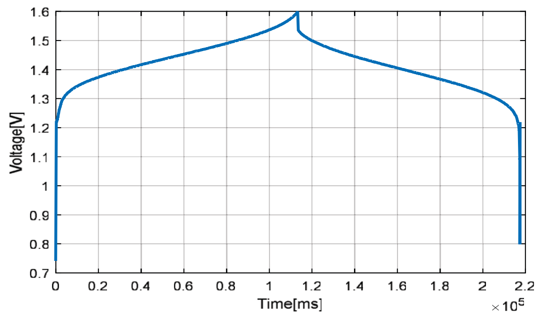

Fig. 4. Voltage profile of capacity test

TABLE II. PREDICTED CAPACITY LOSS ACCORDING TO THE NUMBER OF CYCLE

Number of cycle	*Capacity[Ah]*
1	1.7341
2	1.6678
3	1.5958
4	1.5294
5	1.4614
6	1.3947
7	1.3571
8	1.2646
9	1.2017

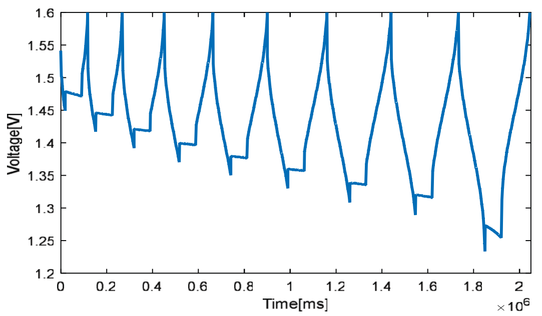

Fig. 5. Voltage profile of self-discharge test

TABLE III. SELF-DISCHARGE AT SPECIFIC SOC

SOC[%]	*Self-discharge[V]*	$R_{self-discharge}$*[Ω]*
90	0.00672	0.0112
80	0.00366	0.0061
70	0.0029	0.0048
60	0.00153	0.0025
50	0.00229	0.0038
40	0.00259	0.0043
30	0.00275	0.0045
20	0.00412	0.0068
10	0.01877	0.0312

IV. EQUIVALENT CIRCUIT MODEL OF VRFB

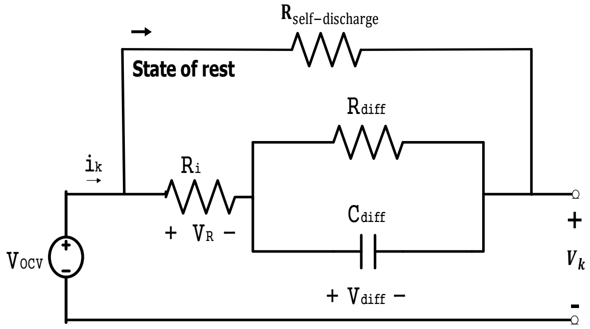

Fig. 6. Proposed Equivalent circuit of VRFB

Fig. 5 is equivalent circuit model consists of SOC dependent voltage in series with RC ladder. The SOC is estimated using the Ampere-counting method based on actual capacity as shown in (14). An expression for the resistor current following discrete time is shown in (15). In the model, the state of charge equation remains same as Ampere-counting method and the terminal voltage equation is determined by (16) [6].

$$iR_{diff}[k+1] = \exp(-\frac{\Delta t}{R_{diff}\,C_{diff}})\ iR_{diff}[k] + (1 - \exp(-\frac{\Delta t}{R_{diff}\,C_{diff}}))i[k] \qquad (15)$$

$$V[k] = OCV(SOC[k]) - iR_{diff}[k] - R_i i[k] \qquad (16)$$

Unlike widely used lithium ion batteries, vanadium redox flow battery shows self-discharge at state of rest. Therefore, the equivalent circuit model of the vanadium redox flow battery requires additional self-discharge characteristics when current is not applied. Therefore, as shown in Table 3, when the current is applied, it follows the general dynamic characteristic based on the RC circuit of vanadium redox flow battery, However, in the state of rest, the voltage decreases according to the resistance converted based on the self-discharge at the specific SOC [7]. $R_{self-discharg}$ shows a characteristic that the self-discharge is remarkable at high and low SOC than middle SOC, and the voltage is linearly decreased at the state of rest according to the $R_{self-discharg}$ which is differentially assigned to the specific SOC.

A. Extended Kalman filter(EKF)

The EKF method is a technique that can estimate the SOC by reflecting the nonlinear battery condition. As stated as before, SOC is usually detected by the Ampere-counting method. EKF is a quadratic state estimator for battery system and uses the observed data u(k) and y(k) to find the minimum mean squared error making the estimated state $\overline{x}$(k) close to the true state x(k). The state-space model of EKF is formulated as equation (17)–(20).

$$x_{k+1} = F(x_k, x_k) + w_k \qquad (17)$$

$$y_k = G(x_k, u_k) + v_k \qquad (18)$$

$$w_k \sim (0, \textstyle\sum w) \qquad (19)$$

$$v_k \sim (0, \textstyle\sum v) \qquad (20)$$

$$\text{state vector } x = \begin{pmatrix} soc \\ V_{diff} \end{pmatrix} \qquad (21)$$

$$\text{input signal vector } u = [i_k] \qquad (22)$$

$$A = \begin{pmatrix} 1 & 0 \\ 0 & 1 - \exp(\frac{-\Delta t}{R_{diff}\,C_{diff}}) \end{pmatrix} \qquad (23)$$

$$B = \begin{pmatrix} \frac{dt}{Q} \\ 1 - \exp(\frac{-\Delta dt}{R_{diff}\,C_{diff}}) \end{pmatrix} \qquad (24)$$

x[k] is the system state vector, u[k] and y[k] are the system input and measurement, respectively, w[k] and v[k] are the process noise and measurement noise. The detailed procedures for implementing EKF are shown in Figure.7. where the state vector is shown as [8].

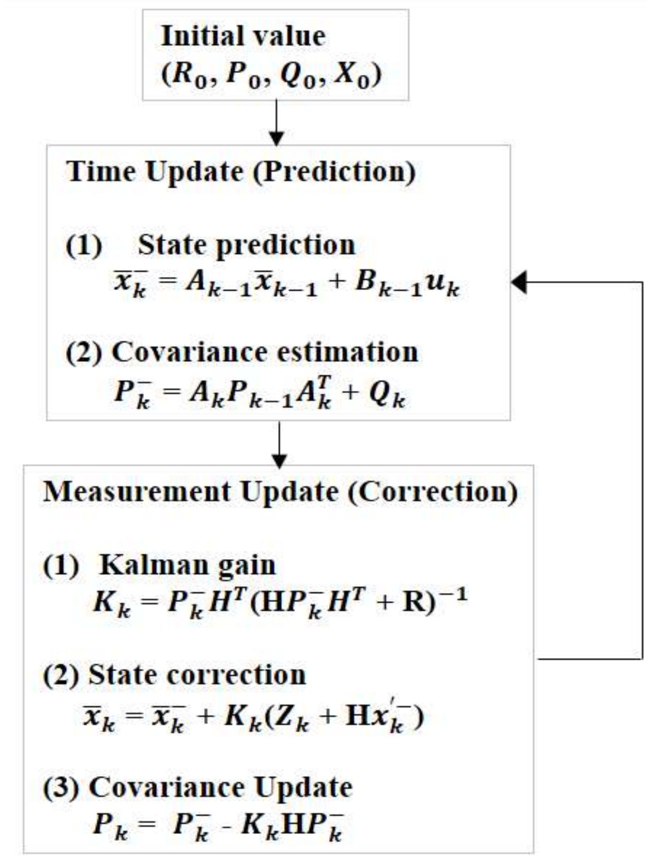

Fig. 7. Principle of EKF

B. Simulation

The proposed method is verified by an extended Kalman filter suitable for nonlinear systems. As a result, it is proved that the proposed self-discharge model based on SOC is appropriate for estimation performance of terminal voltage and SOC in vanadium redox flow battery. The parameter used in simulation were extracted from actual experiments and performed using MATLAB / Simulink.

Figure 8 and Figure 9 show the terminal voltage estimation using EKF with and without the proposed method, respectively. In contrast to Figure 8, Figure 9 shows that the self-discharge table based on resistance is applied to model at the state of rest.

Figure 10 and Figure 11 show the error of terminal voltage between model and experimental data using EKF with and without the proposed method, respectively. Comparing the two case, it can be seen that the error rate when using the proposed method is 0.8025 and the error rate and the error rate at the other case is 0.8597. It was confirmed that the error rate when using the proposed method was reduced by 0.572.

Figure 12 and Figure 13 show the SOC estimation using EKF with and without the proposed method, respectively. Since the vanadium redox flow battery have characteristic of capacity reduction due to cross over phenomenon during the cycle, simulation was carried out with emphasis on the actual data based on Ampere-counting method rather than model.

Figure 14 and Figure 15 show the error of SOC between model and experimental data using EKF with and without the proposed method, respectively. The error of SOC is compared with the maximum value of error because the estimation model focuses on the Ampere-counting method which have characteristics of error accumulation.

As shown in Figure, When the proposed method is applied, the maximum error is 9.288×10^{-5} and the maximum error when not applied is $1.5761 \text{ x } 10^{-6}$.

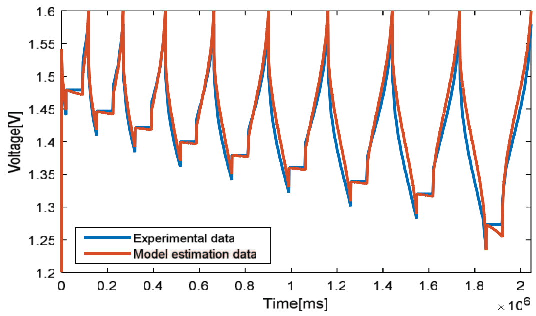

Fig. 8. Terminal voltage estimation without proposed method by EKF

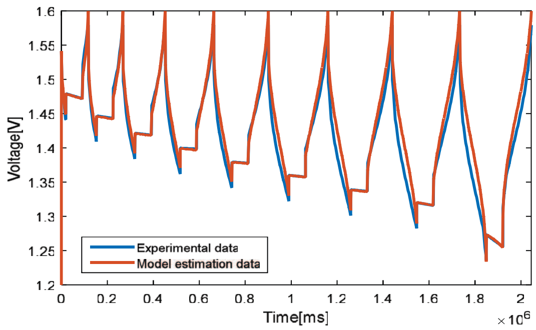

Fig. 9. Terminal voltage estimation with proposed method by EKF

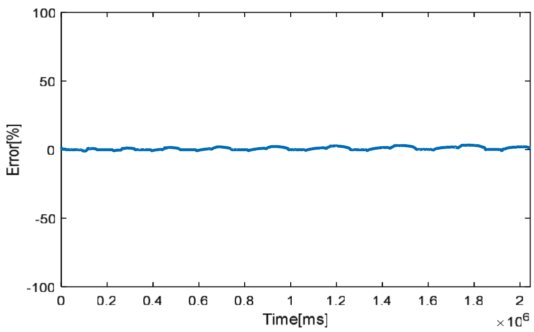

Fig. 10. The error of terminal voltage between model and EKF without proposed method

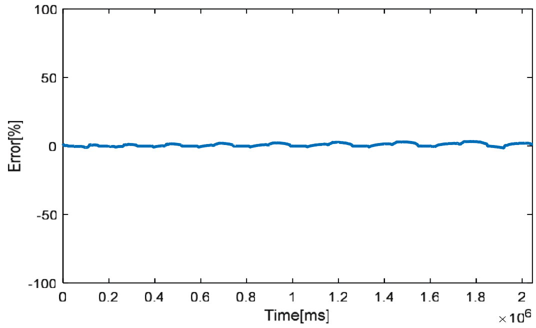

Fig. 11. The error of terminal voltage between model and EKF with proposed method

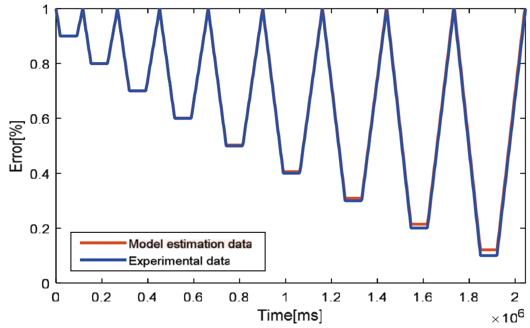

Fig. 12. SOC estimation without proposed method by EKF

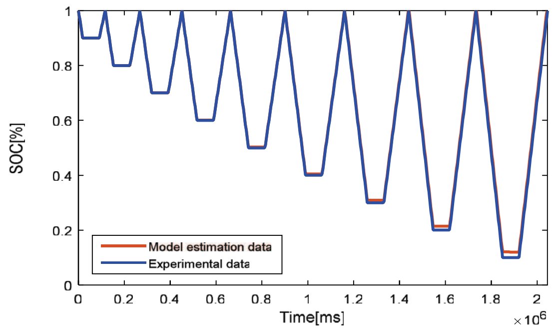

Fig. 13. SOC estimation with proposed method by EKF

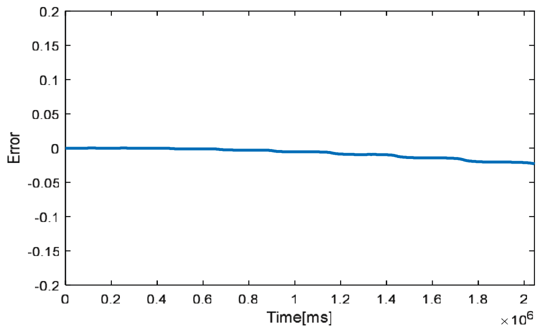

Fig. 14. The error of SOC between model and EKF without proposed method

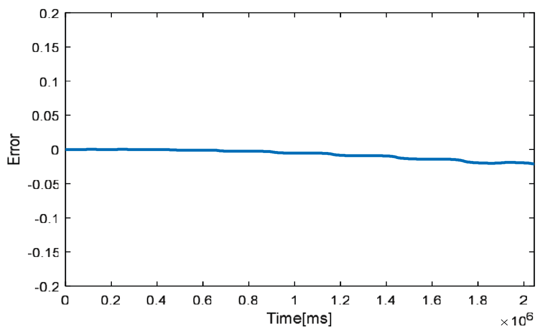

Fig. 15. The error of SOC between model and EKF with proposed method

V. Conclusion

In this paper, the proposed modeling method of VRFB has been proposed. An equivalent circuit model based on RC ladder has been proposed to take in to account not only general dynamic characteristics but also self-discharge characteristics when pumps continue operating in state of rest based on exact parameters derived from actual experimental data. In order to propose a new method of modeling, the rate of capacity reduction during charge and discharge is derived. The rate of capacity reduction rate was substituted differently for the self-discharge test for analyze the amount of self-discharge at specific SOC. The proposed method is verified by an extended Kalman filter suitable for nonlinear system of vanadium redox flow battery. As a result, it is proved that the model considering self-discharge based on specific SOC is more accurate in estimation performance of terminal voltage and SOC.

Acknowledgment

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government (MSIT) (No. NRF-2018R1C1B6004482)

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