

Characteristics of the all-vanadium redox flow battery using ammonium metavanadate electrolyte

Bo-Young Jung, Cheol-Hwi Ryu, and Gab-Jin Hwang[†]

Grad. School, Dept. Green Energy Eng., Hoseo University, Asan City, Chungnam 31499, Korea

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Abstract—An electrolyte was prepared using ammonium metavanadate (AMV) to apply in the all-vanadium redox flow battery (VRFB). The component and composition of the prepared electrolyte by AMV were analyzed by X-ray diffraction (XRD) and inductively coupled plasma (ICP). It was confirmed from the analysis results that the component was almost the same as that of vanadyl sulfate and the composition was almost the same as that of prepared by 2.1 mol of the vanadyl sulfate dissolved in 3 M H₂SO₄. The cell performance of VRFB using the prepared electrolyte by AMV was measured at current density of 60 mA cm⁻². The efficiency of VRFB using the prepared electrolyte by AMV was 97.66%, 86.31%, 84.30% for an average current efficiency, average voltage efficiency and average energy efficiency, respectively. It was expected that the prepared electrolyte by AMV was usable as the electrolyte of VRFB from the viewpoint of the cell performance.

Keywords: Energy Storage, Redox Flow Battery, Vanadium, Electrolyte, Cell Performance

INTRODUCTION

The redox flow battery, particularly, the all-vanadium redox flow battery (VRFB) for an emergency uninterruptable power supply, is being investigated as an energy storage system for load leveling and frequency regulation to solve the low energy density and intermittent nature of renewable energy, such as a solar and wind power [1-3]. The VRFB stores electrical energy in a chemical energy form at charge, and converts that energy into electricity at discharge [4-6]. An advantage of the VRFB is that the power and energy storage capacity can be scaled easily.

The VRFB is being investigated for an ion exchange membrane (IEM) as a separator having good chemical stability and low cost with low permeation rates of the vanadium ions (V²⁺, V³⁺, VO²⁺, VO₂⁺) [2,3,7-13]. And the modification of graphite felt as an electrode material having a good stability in highly acidic solutions and providing a large reactive surface area and a sufficient number of redox reaction sites is being researched [14-18]. Moreover, the improvement of electrolyte by adding materials (stabilizing agents, and organic and inorganic additives) to improve stability over the temperature of 40 °C and to prevent the precipitate formation in pentavalent vanadium electrolyte solution is also being researched [19-23].

The energy storage capacity of the VRFB, which was using the VO²⁺/VO₂⁺ and V³⁺/V²⁺ redox couples, dissolved in H₂SO₄ aqueous solution as a positive and negative electrolyte, respectively, are dependent on the concentration and volume of the electrolytes. The cost of electrolyte in the VRFB is very high and the proportion of electrolyte solution in the VRFB system price takes up over 40%

[24]. Therefore, it needs the investigation for the electrolyte to decrease the cost of the VRFB system.

Ammonium metavanadate (AMV, NH₄VO₃) is a material initially generated when vanadium recovered from vanadium ore, ash after burning coal and waste catalyst. The vanadyl sulfate (VS, VOSO₄) and vanadium oxide (V₂O₅) generally used in the VRFB as an electrolyte are made from AMV through some process [25,26]. So, if it is possible to make an electrolyte solution using AMV, the cost of electrolyte would be reduced. The electrochemical preparation method to prepare an electrolyte solution for the VRFB from AMV has been studied [27]. However, more research for the electrolyte preparation method from AMV did not proceed.

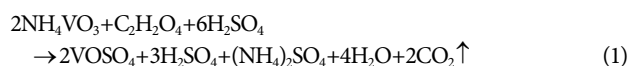
In this study, an electrolyte was prepared by the chemical reaction using ammonium metavanadate (AMV) to use in VRFB. The electrochemical characteristic of VRFB using the prepared electrolyte was evaluated, and then it was evaluated for the usability of the prepared electrolyte by AMV in VRFB.

EXPERIMENTAL

1. Preparation of an Electrolyte

The electrolyte using AMV was prepared as follows; 6 M (mol L⁻¹) H₂SO₄ was added in 1,000 cm³ flask, and 2 mol of ammonium metavanadate (AMV, 98%, EG metal Co.) and 1 mol of oxalic acid (C₂H₂O₄, Junsei Chemical Co.) were added in the flask. Then the reaction was carried out at 25 °C until no bubbles showed with stirring. When the bubbles did not show, the reaction was stopped and the reacted solution was filtered.

The reaction proceeded as follows.



The CO₂ gas was removed as a bubble during the reaction. The

[†]To whom correspondence should be addressed.

E-mail: gjhwang@hoseo.edu

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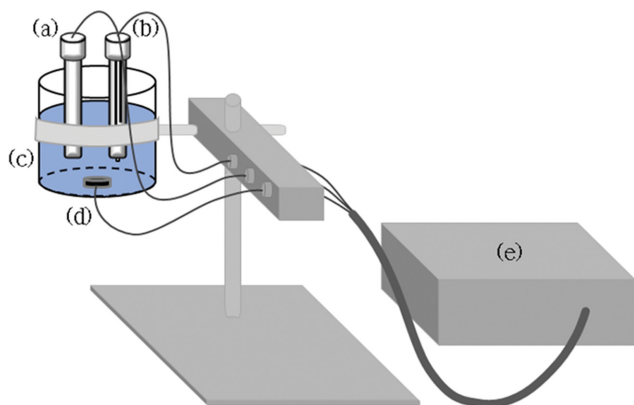


Fig. 1. Experimental apparatus for cyclic voltammetry test. (a) Counter electrode, (b) Reference electrode, (c) Electrolyte solution, (d) Working electrode, (e) Potentio/Galvanostat.

filtered solution was analyzed by XRD (X-ray diffraction). To analyze by XRD, the filtered solution was dried in the oven at 110 °C and the powder was obtained. The powder was used in XRD analysis. XRD pattern was obtained by means of a SmartLab (Rigaku Co.) using Cu-K α radiation with a nickel filter operated at 34 kV and 20 mA. The average wavelength of the radiation was given as 1.5418 Å. Angle of diffraction was taken between 10 [2 θ] and 90 [2 θ]. The mol concentration of vanadium was analyzed by inductively coupled plasma (ICP).

The electrolyte using vanadyl sulfate (VS, VOSO₄) prepared by 2.1 mol of the vanadyl sulfate (VOSO₄·nH₂O, Shinko Chemical Co.) was dissolved in 3 M (mol L⁻¹) H₂SO₄.

2. Cyclic Voltammetry Test of an Electrolyte

Cyclic voltammetry (CA) tests of the prepared electrolyte were performed using a potentio/galvanostat (Wanatech Co., WMPG1000) in a room temperature.

Fig. 1 shows the experimental apparatus for cyclic voltammetry test.

In CV test, a conventional 3-electrode electrochemical cell was used. A carbon felt (9 cm², XF30A, Toyobo Co.), platinum mesh (3×3 cm) and saturated calomel electrode were used as a working electrode, counter-electrode and reference electrode, respectively. The curves of current versus potential were recorded with the scan rate of 5 mV s⁻¹ in the range of -0.5 V~2.0 V.

3. Electrochemical Characteristic Test of VRFB

3-1. Experimental Apparatus

As shown in Fig. 2, the experimental apparatus consisted of one unit cell with an effective electrode area of 410×614 mm (252 cm²); two 500 cm³ Erlenmeyer flasks (one was used as a reservoir for VO²⁺ aqueous solution and the other as a reservoir for the electrochemically reduced V³⁺ aqueous solution from VO²⁺ aqueous solution); and one micro tube pump. A Tygon tube was used to connect the components.

The solution (350 cm³) in anolyte reservoir was filled with slightly more than that (320 cm³) in catholyte reservoir to avoid overcharging. The flow rate of electrolyte was 1.0 ml cm⁻² min⁻¹.

An HPCS2 (Wonatech Co.) was used to charge and discharge in the unit cell, and to measure the electrical potential in the unit

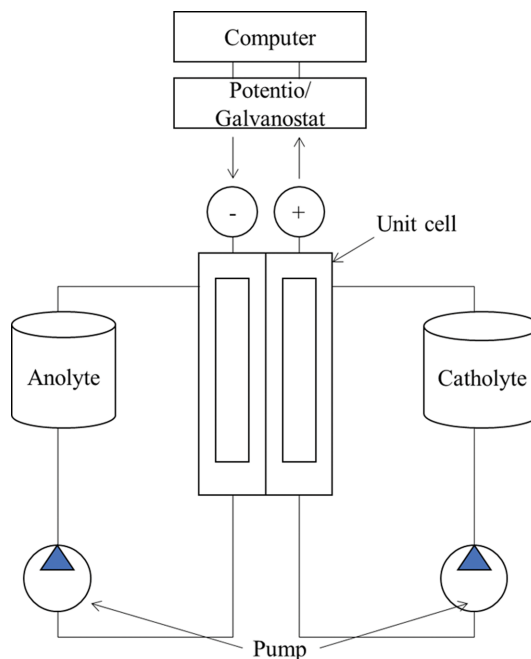
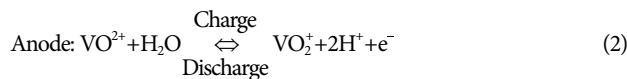


Fig. 2. Experimental apparatus for the test of VRFB performance.

cell. All charge and discharge operations progressed in the unit cell. A computer was connected to an HPCS2 to record the electrical potential distribution. The temperatures of the two flasks were maintained at room temperature.

The charge and discharge reactions of VRFB are as follows.



A unit cell as shown in Fig. 3 was used to measure the battery

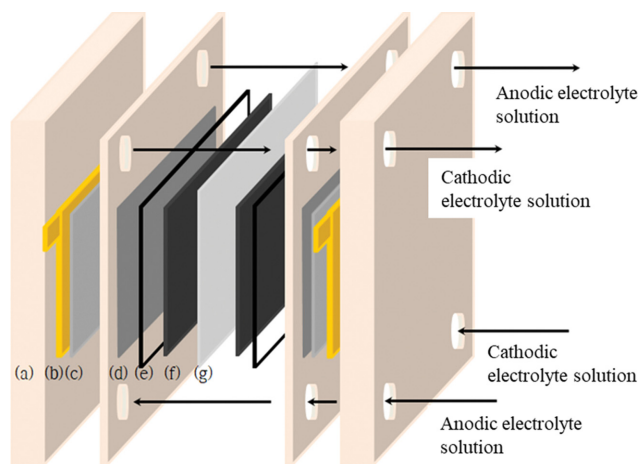


Fig. 3. Schematic diagram of unit cell. (a) PVC plate, (b) Current collector (Au coated Cu plate), (c) Current collector (graphite foil), (d) Flow frame with graphite plate, (e) O-ring, (f) Electrode (carbon felt), (g) Ion exchange membrane.

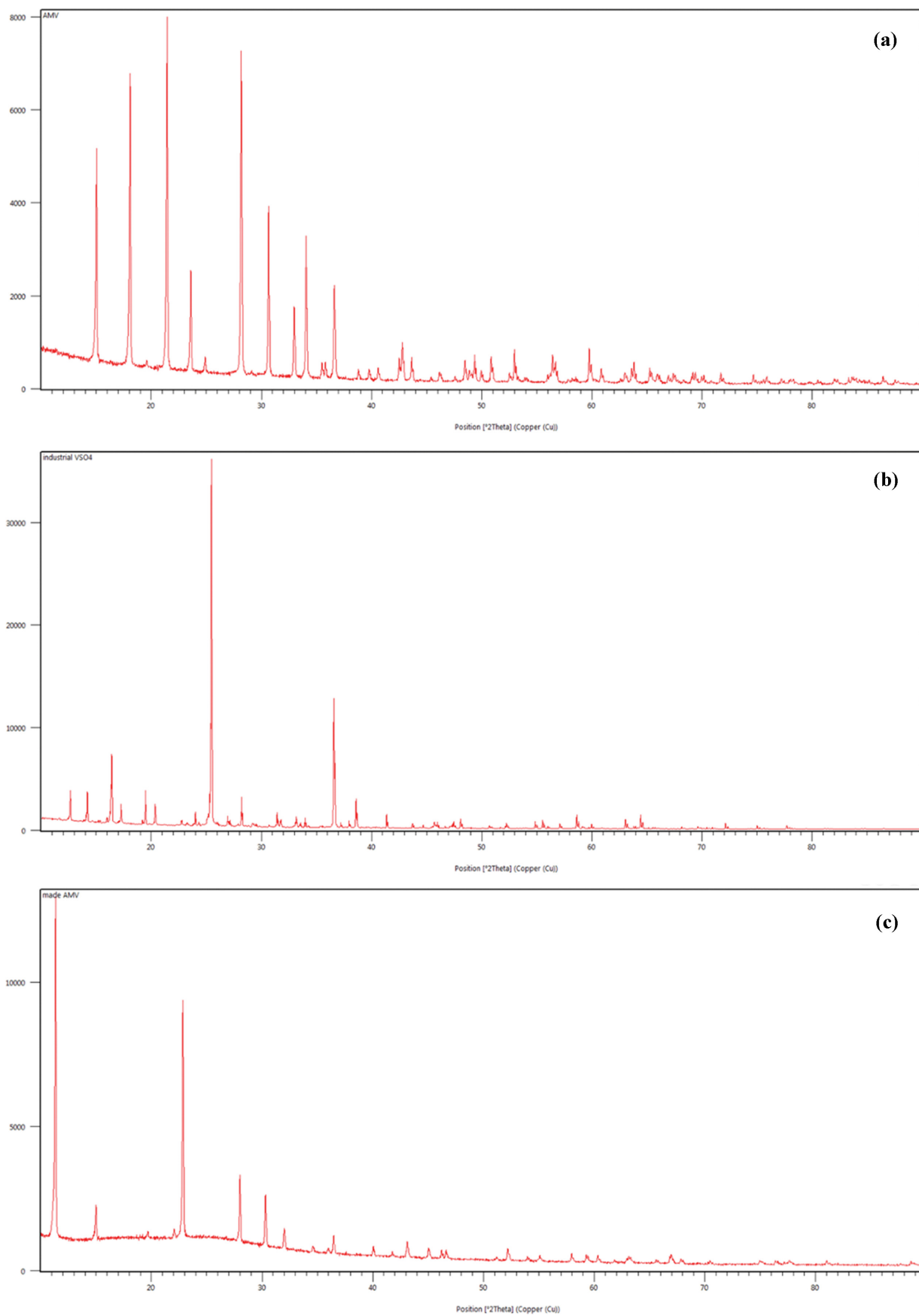


Fig. 4. XRD patterns of the (a) AMV powder, (b) VOSO₄ powder, and the (c) prepared electrolyte powder by AMV.

performance. The unit cell consisted of PVC (polyvinyl chloride) plate; the current collector (Au coated Cu plate and graphite foil); the flow frame with phenol resin impregnated graphite plate (CO-134, Ildo F&C Co.); the electrode (carbon felt, GF051BH, JNTG Co.); and an ion exchange membrane (APS, ASTOM Co., anion exchange membrane).

3-2. Cell Performance Test of VRFB

The cell performance of VRFB using the prepared electrolyte by VS and AMV was measured using the experimental apparatus as shown in Fig. 2. The current density of unit cell in the charge and discharge was 60 mA cm^{-2} . A performance test of the VRFB was carried out using the cut-off method, which was 1.6 V for charge and 1.0 V for discharge [3]. The charge-discharge test of VRFB was repeatedly carried out five times.

The cell properties, such as a current efficiency (η_C), voltage efficiency (η_V), and energy efficiency (η_E), were calculated by Eqs. (4)–(6), respectively.

$$\eta_C = Q_D / Q_C \quad (4)$$

$$\eta_V = E_{AD} / E_{AC} \quad (5)$$

$$\eta_E = \eta_C \times \eta_V \quad (6)$$

where Q_C and Q_D (C) are the quantity of the coulomb for charge and discharge, respectively, and E_{AC} and E_{AD} (V) are the average cell voltage for charge and discharge, respectively.

The charge-discharge test of VRFB using the prepared electrolyte by AMV was repeatedly carried out 20 times for the usability evaluation in VRFB.

RESULTS AND DISCUSSION

1. XRD and ICP Analysis of the Electrolyte

Fig. 4 shows the XRD patterns of the AMV powder, VOSO_4 powder, and the prepared electrolyte powder by AMV. The peaks of the obtained XRD analysis were analyzed by the joint committee on powder diffraction standards (JCPDS) card. XRD analysis confirmed that the AMV powder had the XRD pattern of ammonium vanadium oxide (NH_4VO_3), the VOSO_4 powder had that of vanadyl sulfate hydrate ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$), and the prepared electrolyte powder by AMV had that of vanadyl hydrogen sulfate ($(\text{VOSO}_4)_2 \cdot \text{H}_2\text{SO}_4$).

The XRD pattern of the prepared electrolyte powder by AMV showed the compound contained H_2SO_4 . For the reason the prepared electrolyte powder contained H_2SO_4 , it seems that H_2SO_4 was not clearly removed in the dry process to obtain the powder.

It was confirmed from the result of XRD pattern that the electrolyte prepared by AMV (NH_4VO_3) is transferred to the electrolyte form of vanadyl sulfate by the chemical reaction as shown in Eq. (1).

Additionally, the ion chromatographic analysis (ICA) for ammonium ion (NH_4^+) proceeded. It was confirmed from the result of ICA analysis that the ammonium ion existed in the prepared electrolyte powder using AMV. This means that the ammonium ion in the prepared electrolyte powder by AMV existed as the $(\text{NH}_4)_2\text{SO}_4$ form by the chemical reaction as shown in Eq. (1).

Table 1 shows the vanadium content analyzed by ICP in the prepared electrolyte by AMV.

Table 1. Vanadium content analyzed by ICP in the prepared electrolyte by AMV

Sample	Volume (mL)	Weight (g)	Vanadium content (%)
No. 1	10	14.8831	7.569
No. 2	10	14.7728	7.234

The mol concentration of vanadium from the data of Table 1 was calculated as follows:

$$\text{Sample 1: } 14.8831 \text{ g} \times \frac{7.569}{100} \times \frac{1 \text{ mol}}{50.9415 \text{ g/mol}} \times \frac{1,000 \text{ mL/L}}{10 \text{ mL}} = 2.21 \text{ mol/L} \quad (7)$$

$$\text{Sample 2: } 14.7728 \text{ g} \times \frac{7.234}{100} \times \frac{1 \text{ mol}}{50.9415 \text{ g/mol}} \times \frac{1,000 \text{ mL/L}}{10 \text{ mL}} = 2.097 \text{ mol/L} \quad (8)$$

$$\text{Average value: } \frac{2.21 + 2.097}{2} = 2.15 \text{ mol/L} \quad (9)$$

It was confirmed from the data of ICP analysis that the mol concentration of vanadium in the prepared electrolyte by AMV was about 2.15 mol L^{-1} . This means that the mol concentration of VOSO_4 was 2.15 mol L^{-1} because the vanadium existed as the VOSO_4 form, as shown in Eq. (1). This also means that the mol composition of

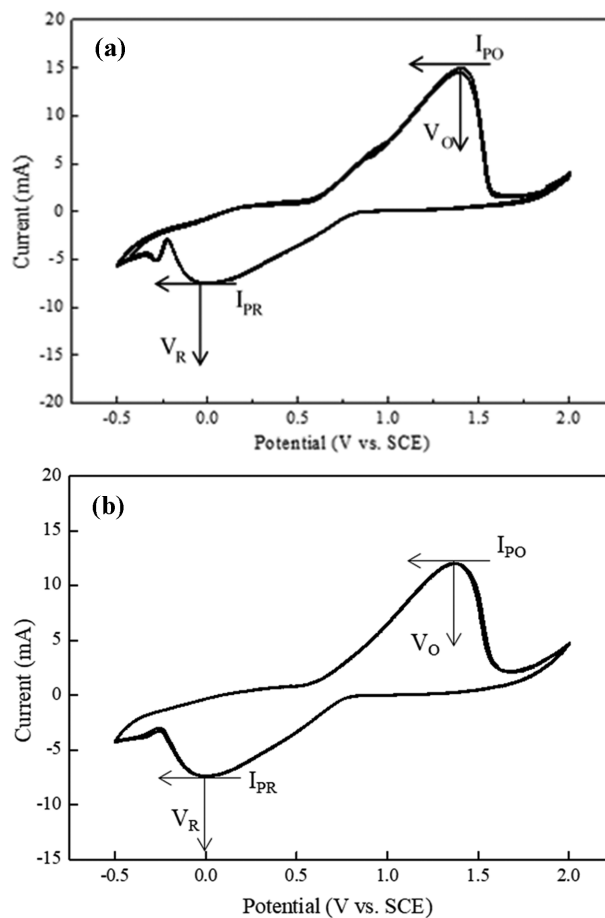


Fig. 5. CV curves of prepared electrolyte by VS and AMV on the carbon felt electrode at 25°C and a scan rate of 5 mV s^{-1} . (a) VS (2.1 M VOSO_4 in $3 \text{ M H}_2\text{SO}_4$), (b) AMV (2.15 M VOSO_4 in $3 \text{ M H}_2\text{SO}_4$).

Table 2. Oxidation-reduction peak potential difference (ΔV_p) and the ratio of oxidation-reduction peak current (I_{PO}/I_{PR}) calculated from the data of Fig. 5

Electrolyte	ΔV_p (V)	I_{PO} (mA)	I_{PR} (mA)	I_{PO}/I_{PR}
VS (2.1 M VOSO_4 in 3 M H_2SO_4)	1.398	14.514	7.523	1.93
AMV (2.15 M VOSO_4 in 3 M H_2SO_4)	1.369	12.06	7.39	1.63

VO^{2+} electrolyte prepared by AMV was almost the same as that of prepared by 2.1 mol of the vanadyl sulfate dissolved in 3 M H_2SO_4 .

2. Cyclic Voltammetry Test of the Prepared Electrolyte by AS and AMV

Fig. 5 shows CV curves of prepared electrolyte by VS and AMV on the carbon felt electrode at 25 °C and a scan rate of 5 mV s^{-1} . As shown in Fig. 5, CV curves of prepared electrolyte by VS and AMV showed the identical peak position and patterns, and were similar to each other in the peak shape and exhibited only a pair redox peaks. The upper right peak presents the oxidation reaction of $\text{VO}^{2+}/\text{VO}_2^+$ and the lower left presents the reduction reaction of $\text{VO}_2^+/\text{VO}^{2+}$.

Table 2 shows the oxidation-reduction peak potential difference (ΔV_p) and the ratio of oxidation-reduction peak current (I_{PO}/I_{PR}) calculated from the data of Fig. 5. The oxidation-reduction peak potential difference ($\Delta V_p = V_O - V_R$) was calculated by the subtraction of the reduction peak potential (V_R) from the oxidation peak potential (V_O). ΔV_p in the prepared electrolyte by VS (2.1 M VOSO_4 in 3 M H_2SO_4) was 1.398 V, and that in the prepared electrolyte by AMV was 1.369 V. The ratio of oxidation-reduction peak current (I_{PO}/I_{PR}) in the prepared electrolyte by VS was 1.93 and that in the prepared electrolyte by AMV was 1.63.

In general, it is well known that if the ratio of oxidation-reduction peak current (I_{PO}/I_{PR}) approaches a value of 1, the reaction mechanism reversibly proceeds. As shown in Table 2, the value of I_{PO}/I_{PR} in the prepared electrolyte by AMV had a little low value compared to that in the prepared electrolyte by VS. This means that the prepared electrolyte by AMV had a little higher reversible reaction than the prepared electrolyte by vanadyl sulfate.

From the results of CV test, the prepared electrolyte by AMV showed no significant change in peak position and pattern compared to the prepared electrolyte by VS generally used in VRFB. Therefore, it seems that the prepared electrolyte by AMV can be used as the electrolyte for VRFB.

3. Cell Performance of VRFB Using the Prepared Electrolyte by VS and AMV

Fig. 6 shows the relationship between the cell voltage and the charge-discharge operation time of VRFB using the prepared electrolyte by VS and AMV. In Fig. 6, the unit of x-axis (A.U.) is time, and 1 A.U. is 100 seconds. Fig. 6 shows a tendency that the cell voltage increased with the charging time and decreased with the discharging time. The charge-discharge times tended to decrease a little with the increase in the number of charge-discharging cycles. This seems caused by the vanadium ions (V^{2+} , V^{3+} , VO^{2+} , VO_2^+) being moved to the opposite solution through the membrane, and the potential of solution was changed by self-discharge in there, and then the capacity and cell voltage was decreased. Therefore, the change width of the potential would be increased with an increase of charge-discharge cycle, and the charge-discharge time would

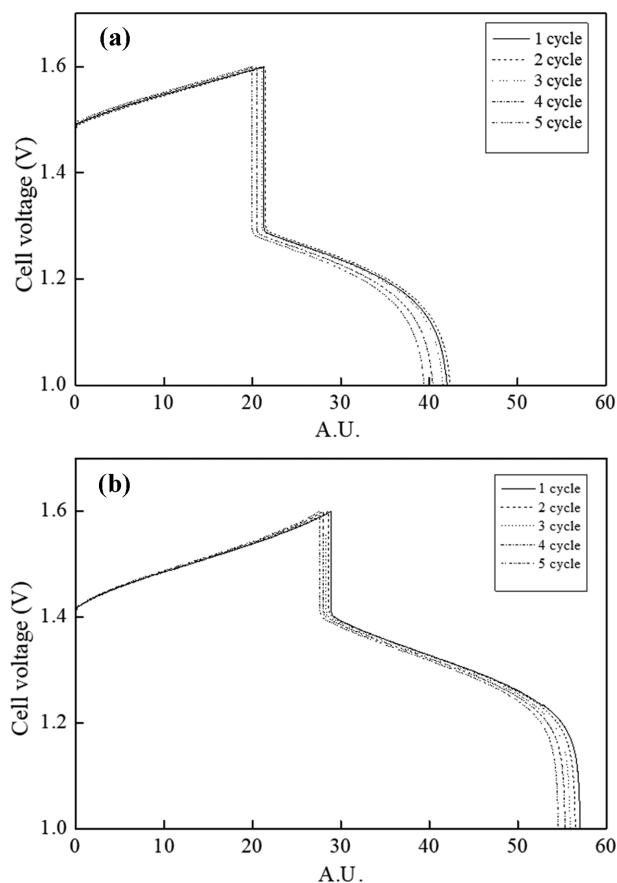


Fig. 6. Relationship between the cell voltage and the charge-discharge operation time of VRFB using the prepared electrolyte by (a) VS and (b) AMV.

be decreased with an increase of change width of the potential.

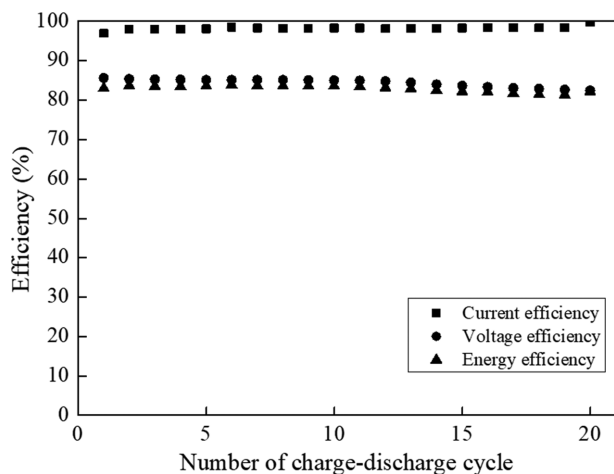
The result of Fig. 6 showed that the charge-discharge time in VRFB using the prepared electrolyte by AMV was longer than that in VRFB using the prepared electrolyte by VS. This means that the capacity of prepared electrolyte by AMV was higher than that of prepared electrolyte by VS. It was reported [28] that the additive of NH_4^+ function group in the electrolyte led to significantly improving the electrochemical activity and reversibility for the redox reaction of $\text{VO}^{2+}/\text{VO}_2^+$ couple, and improving the stability and electrochemical performance of the VRFB. It seems that the higher capacity of prepared electrolyte by AMV than VS was caused by the existent NH_4^+ function group in the prepared electrolyte by AMV, which improved the electrochemical activity and reversibility for the redox reaction of $\text{VO}^{2+}/\text{VO}_2^+$ and $\text{V}^{3+}/\text{V}^{2+}$.

Table 3 shows the average efficiencies calculated from the data of Fig. 6.

The efficiency of VRFB using the prepared electrolyte by VS

Table 3. Average efficiencies calculated from the data of Fig. 6

Electrolyte	Average current efficiency (%)	Average voltage efficiency (%)	Average energy efficiency (%)
VS (2.1 M VOSO ₄ in 3 M H ₂ SO ₄)	97.57	78.15	76.25
AMV (2.15 M VOSO ₄ in 3 M H ₂ SO ₄)	97.66	86.31	84.30

**Fig. 7. Efficiency change of VRFB using the prepared electrolyte by AMV during 20 charge-discharge cycles.**

was 97.57%, 78.15%, 76.25% for the average current efficiency, the average voltage efficiency and the average energy efficiency, respectively. And that of VRFB using the prepared electrolyte by AMV was 97.66%, 86.31%, 84.30% for the average current efficiency, the average voltage efficiency and the average energy efficiency, respectively. The average energy efficiency of VRFB using the prepared electrolyte by AMV had a higher value than that of VRFB using the prepared electrolyte by VS.

Fig. 7 shows the efficiency change of VRFB using the prepared electrolyte by AMV during 20 charge-discharge cycles.

As shown in Fig. 7, the efficiencies such as current efficiency, voltage efficiency and energy efficiency of VRFB using the prepared electrolyte by AMV did not largely change during 20 charge-discharge cycles, and showed almost the same values. From the result of Fig. 7, it was expected that the VRFB using the prepared electrolyte by AMV was usable as the electrolyte in VRFB with a non-change of efficiency.

The efficiency of VRFB using the prepared electrolyte by AMV during 20 charge-discharge cycles was 98.23%, 84.41%, 82.92% for the average current efficiency, the average voltage efficiency and the average energy efficiency, respectively. The above results indicate that the prepared electrolyte by AMV can be used as the electrolyte of VRFB with good cell performance.

CONCLUSIONS

The electrolyte using AMV (ammonium metavanadate, NH₄-VO₃) to apply in VRFB was prepared by AMV chemically reacted with oxalic acid and sulfuric acid. XRD analysis confirmed that the prepared electrolyte powder by AMV had an XRD pattern of vanadyl hydrogen sulfate ((VOSO₄)₂-H₂SO₄). ICP analysis confirmed

that the mol concentration of vanadium in the prepared electrolyte by AMV was about 2.15 mol L⁻¹, and the electrolyte composition was almost the same as that prepared by 2.1 mol of the vanadyl sulfate dissolved in 3 M H₂SO₄. From the results of CV (cyclic voltammetry) test, it was confirmed that the prepared electrolyte by AMV had no significant change in peak position and pattern compared to the prepared electrolyte by vanadyl sulfate (VS, VOSO₄) generally used in VRFB. The efficiency of VRFB using the prepared electrolyte by AMV was 97.66%, 86.31%, 84.30% for the average current efficiency, the average voltage efficiency and the average energy efficiency, respectively. The average energy efficiency of VRFB using the prepared electrolyte by AMV had a higher value than that of VRFB using the prepared electrolyte by VS. The energy efficiency of VRFB using the prepared electrolyte by AMV did not largely change during 20 charge-discharge cycles and showed the almost same values. From the obtained results in this study, it was expected that the prepared electrolyte by AMV is usable as the electrolyte of VRFB from the view point of the cell performance.

NOMENCLATURE

- η_C : current efficiency [%]
 η_V : voltage efficiency [%]
 η_E : energy efficiency [%]
 Q_C Q_D : quantity of the coulomb for charge and discharge, respectively (C)
 E_{AC} E_{AD} : average cell voltage for charge and discharge, respectively (V)

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