



Article

Preparation of Vanadium (3.5⁺) Electrolyte by Hydrothermal Reduction Process Using Citric Acid for Vanadium Redox Flow Battery

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Abstract: In this study, vanadium (3.5⁺) electrolyte was prepared for vanadium redox flow batteries (VRFBs) through a reduction reaction using a batch-type hydrothermal reactor, differing from conventional production methods that utilize VOSO₄ and V₂O₅. The starting material, V₂O₅, was mixed with various concentrations (0.8 M, 1.2 M, 1.6 M, 2.0 M) of citric acid (CA) as the reducing agent and stirred for 60 min at 90 °C using a hot plate to ensure complete dispersion in the solution. The resulting solution was subsequently subjected to a hydrothermal reduction reaction (HRR) furnace at 150 °C for 24 h to generate vanadium (3.5⁺). The mixed states of the produced vanadium (3⁺) and vanadium (4⁺) were confirmed using UV-vis spectroscopy. The electrochemical properties of the electrolyte were investigated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), revealing that the optimal concentration of the CA was 1.6 M. The current efficiency, energy efficiency, and voltage efficiency of the electrolyte produced via the HRR process was compared with that prepared using VOSO₄ in charge and discharge experiments. The results demonstrate that the HRR process yields an enhanced electrolyte across all efficiency metrics produced through the given improved performance in all efficiencies. These findings indicate that the HRR process using citric acid can facilitate the straightforward preparation of vanadium (3.5⁺) electrolyte, making it suitable for large-scale production.

Keywords: vanadium sulfate (VOSO₄); vanadium pentoxide (V₂O₅); electrolyte; citric acid (CA); hydrothermal reduction reaction (HRR); vanadium redox flow battery (VRFB)



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1. Introduction

With the market acceleration for energy storage devices worldwide, the related market is growing continuously to meet the demand of increasing energy transformation devices. In particular, energy storage devices are one of the critical systems for strengthening the power grid stability, as it uses energy mix and distributed power [1,2]. Therefore, energy storage devices are receiving increased attention from researchers as various new renewable power sources enter the grid. Energy storage systems can be divided into physical storage and chemical storage. Physical storage methods include flywheels, supercapacitors, and compressed air energy storage systems [3–5]. One of the conventional chemical storage methods is the redox flow battery (RFB). The conditions for energy storage devices in power storage should be reviewed for their stability, long lifespan, and reusability. Of the different energy storage devices, the RFB is most generally used, as it is safe and can be reused, and the capacity can be increased easily. Moreover, using RFB the output and capacity can be controlled independently. Unlike conventional secondary batteries, RFB operates on the principle that the active material in the electrolyte is charged and discharged through oxidation and reduction reactions. It is an electrochemical power storage system that stores the chemical energy of electrolytes as electrical energy [6]. Research on RFB began in 1974 at NASA in the United States, and active research is being conducted on redox couples, electrochemical mechanisms, etc. The basic structure of RFB is shown in Figure 1 [7].

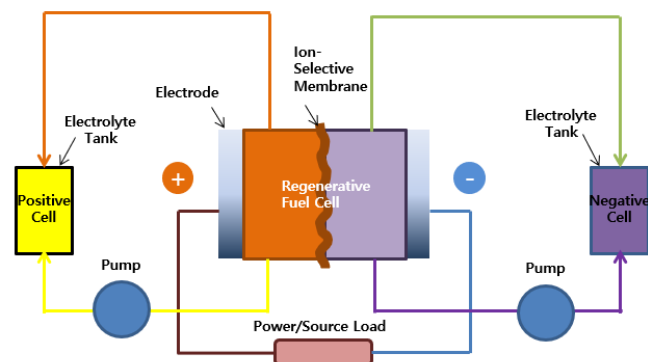


Figure 1. A schematic illustration of the structure of a redox flow battery.

The structure comprises electrolyte tanks that store active materials with different oxidation states, a pump that circulates the active materials during charging and discharging, an ion exchange membrane that exchanges hydrogen ions, and electrodes that convert the chemical energy of the electrolyte into electrical energy. Most of all, an all-vanadium redox flow battery (VRFB) is recognized as one of the most promising candidates for commercialization from the industrial field. With regard to these, numerous research is focused on the development of compartments in batteries, which comprise electrodes, membranes, and electrolytes. However, despite the various advantages of VRFBs, their commercialization is still hindered by the high cost of cell components. Especially, vanadium electrolytes account for a significant portion of the overall cost due to expensive vanadium precursor materials and the high production cost of the electrolyte. For example, in a 10 kW/120 kWh system, the cost for vanadium and electrolyte production represents 40% and 41% of the total energy cost, respectively. Furthermore, as the energy capacity of the system increases, the portion of the electrolyte cost in the total VRFB cost also rises. Therefore, to enable the broader adoption of VRFBs, it is essential to develop cost-effective methods for producing the electrolytes [8]. The vanadium active material is an important component that determines the performance of VRFBs. The energy density of a cell depends on the solubility of the active material, and the voltage of the cell is determined by the equilibrium potential of the active material that makes up the electrolyte of both cells [9–11]. Several studies have been conducted on different organic and inorganic active materials. Many researchers have made efforts to examine and characterize the representative active materials, such as iron/chromium, vanadium/bromine, zinc/bromine, and vanadium [7,12,13]. Among them, the most common active material is vanadium. Because it is composed of four different oxidation states in two electrolyte solutions, contamination of both electrolytes due to the crossover inside the cell does not occur [14,15]. Therefore, it has the advantage of being reusable. However, there are disadvantages as well; for example, a large amount of vanadium precursor is not completely soluble in aqueous solution, and vanadium (5^+) is precipitated when the battery is operated at a high temperature. In addition, in the case of the pure vanadium (4^+) precursor, the high manufacturing cost makes it difficult to mass-produce the electrolyte, which is an obstacle to commercialization. Recently, manufacturing vanadium (3.5^+), which is a mixture of vanadium (3^+) and vanadium (4^+), has attracted considerable attention. The electrochemical method used for production by Oxchem, which has already been commercialized, is the most commonly used method. It is currently manufactured by mixing vanadium (3^+) and vanadium (4^+) produced from a vanadium (5^+) solution obtained through electrochemical cell method. In addition, Heo et al. reported the successful production of vanadium (3.5^+) from vanadium (4^+) using a Pt/Ru catalyst layer and formic acid [8,16]. However, such a process may require sophisticated process control and incur an extremely high initial cost for mass production. The vanadium (3.5^+) electrolyte is an equimolar mixture of vanadium (4^+) and vanadium (3^+) electrolyte, which can be used simultaneously as both the positive and negative electrolytes in VRFBs. This allows VRFBs to operate without the need for the initial rebalancing of the positive and negative capacities, making it highly useful in industry. Upon the full charging of VRFBs, the vanadium (5^+)

electrolyte is produced at the positive electrode, while vanadium (2^+) electrolyte is generated at the negative electrode. In most cases, V_2O_5 is widely used as a vanadium precursor for preparing vanadium (3.5^+) electrolyte due to its lower cost compared with other vanadium precursors. The conventional method for preparing vanadium (3.5^+) electrolyte from V_2O_5 involves chemically reducing vanadium (5^+) to vanadium (4^+) using a reducing agent, followed by the electrolysis of vanadium (4^+) electrolyte to produce vanadium (3^+) electrolyte. The reduction in vanadium (5^+) to vanadium (4^+) can be easily achieved with an organic reducing agent like oxalic acid, which leaves no residues [8]. However, the reduction in vanadium (4^+) to vanadium (3^+) using oxalic acid is considerably slow, presenting a significant difficulty in the practical chemical production of vanadium (3.5^+) electrolyte.

To the best of the author's knowledge, no one has reported a production method via a hydrothermal reduction process utilizing citric acid. Therefore, this study confirmed the possibility of the mass production of the vanadium (3.5^+) electrolyte using a simple batch type process in a hydrothermal reactor.

2. Experimental

2.1. Chemicals

Vanadium sulfate ($VOSO_4 \cdot xH_2O$, 97%, Japan) and vanadium pentoxide V_2O_5 (99.5%, Sigma-Aldrich, Osaka, Japan) were purchased to manufacture the vanadium electrolyte. Also, sulfuric acid (H_2SO_4 , 98%, Daejung, Republic of Korea) was purchased. Ultrapure water was used to prepare a sulfuric acid solution. Additionally, citric acid anhydrous and oxalic acid dehydrate used as a reducing agent were purchased from Alfa Aesar (Lancashire, UK) and Duksan reagents (98%, Republic of Korea). All chemicals were utilized in their original, unpurified state. $VOSO_4$ and V_2O_5 precursors were stored separately in a storage container to avoid contact with moisture, and the temperature was maintained at 20 °C.

2.2. Preparation of Vanadium (3.5^+) Electrolyte from $VOSO_4$ as a Precursor

Figure 2 shows the manufacturing process of vanadium (3.5^+) electrolyte from $VOSO_4$. The manufacturing process for 1 L of 1.6 M vanadium (4^+) solution is as follows: mixing 268.86 g of $VOSO_4 \cdot xH_2O$ powder in 163.2 mL of sulfuric acid, then add water until the total volume reaches 1 L. The solutions are stirred for 24 h to prepare homogeneous electrolyte, which is 1.6 M $VOSO_4$ + 3 M H_2SO_4 . The prepared vanadium (4^+) electrolyte solution is charged to produce vanadium (3^+) in the negative solution and vanadium (5^+) in the positive solution. Then, 201.71 g (1.6 M) of reducing agent, oxalic acid, is added to vanadium (5^+) solution to produce vanadium (4^+) and stirred at 70 °C for 24 h. Finally, the equal amounts of both vanadium (3^+) and vanadium (4^+) are mixed to prepare vanadium (3.5^+) electrolyte.

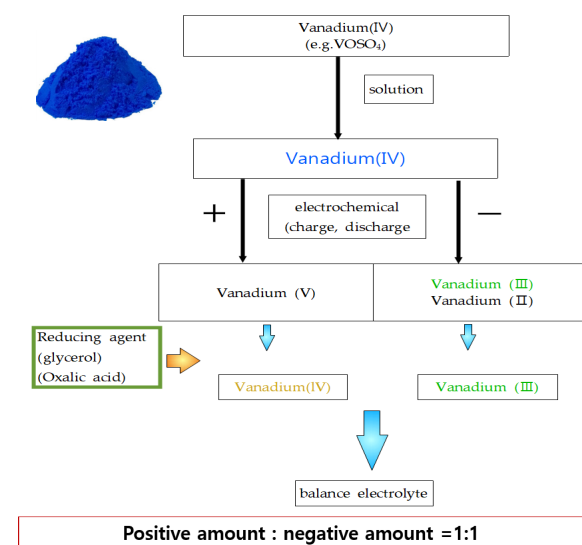


Figure 2. Manufacturing process of vanadium (3.5^+) electrolyte from $VOSO_4$ as a precursor.

2.3. Preparation of Vanadium (3.5^+) from V_2O_5 as a Precursor

The detailed process for preparation from V_2O_5 is shown in Figure 3. To prepare 1 L of 0.8 M vanadium (5^+) solution, mix 146.24 g of V_2O_5 powder in 163.2 mL of sulfuric acid, and then, add 100.86 g (0.8 M) of oxalic acid as a reducing agent to produce the vanadium (4^+) electrolyte solution. At this time, the amount of oxalic acid is equal to V_2O_5 and reacts to obtain vanadium (4^+). Through charging the vanadium (4^+) solution, vanadium (3^+) electrolyte in the negative solution and vanadium (5^+) electrolyte in the positive solution are produced. The vanadium (5^+) electrolyte in the positive solution is reduced using a reducing agent again to produce vanadium (4^+) electrolyte, which is mixed with the vanadium (3^+) from the cathode to produce the vanadium (3.5^+) electrolyte solution.

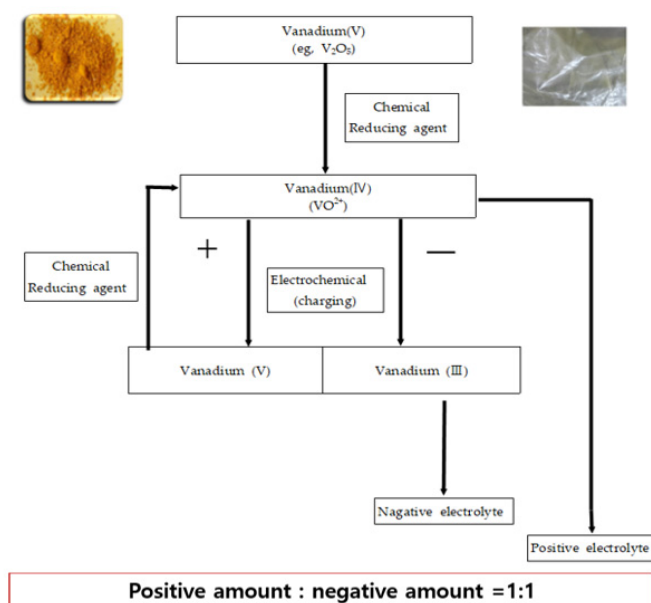


Figure 3. Manufacturing process of vanadium (3.5^+) electrolyte from V_2O_5 as a precursor.

2.4. Preparation of Vanadium (3.5^+) with $VOSO_4$ and V_2O_5 as a Precursor by Hydrothermal Reduction Reaction (HRR)

Figure 4 shows the preparation process of vanadium (3.5^+) electrolyte with $VOSO_4$ and V_2O_5 by means of HRR. A 20 L hydrothermal reactor was manufactured by us and used in the HRR process for the production of vanadium (3.5^+) electrolytes. First (a), when $VOSO_4$ is used as the precursor, the different concentrations 1.6 M, 3.2 M, and 6.4 M of oxalic acid are added to the vanadium (4^+) electrolyte solutions. In this process, the first step involves dissolving oxalic acid powder by stirring at around 90°C until it is no longer visible. In the second step, transfer the mixture to a hydrothermal reactor, heat it at a rate of $5^\circ\text{C}/\text{min}$ up to 150°C , and remove the CO_2 generated during this heating process. Secondly (b), when V_2O_5 is used as the precursor, the different concentrations 0.8 M, 1.2 M, 1.6 M, and 2.0 M of citric acid are added to the vanadium (5^+) electrolyte solutions. This process is carried out using the same method, followed by stirring at 90°C for 60 min on a hot plate to completely disperse citric acid in the solutions, while heating at a rate of $5^\circ\text{C}/\text{min}$ up to 150°C in a hydrothermal reactor. When placing the reactor containing solution into the furnace, fill the reactor with only 60% of the solution, and the reaction is permitted to continue. To prevent overflow of the solution upon opening the reactor after completion of the reaction, the reactor is filled to a level of only 60% of its maximum capacity. Because oxalic acid and citric acid are decomposed to release CO_2 , this increases the pressure inside the reactor.

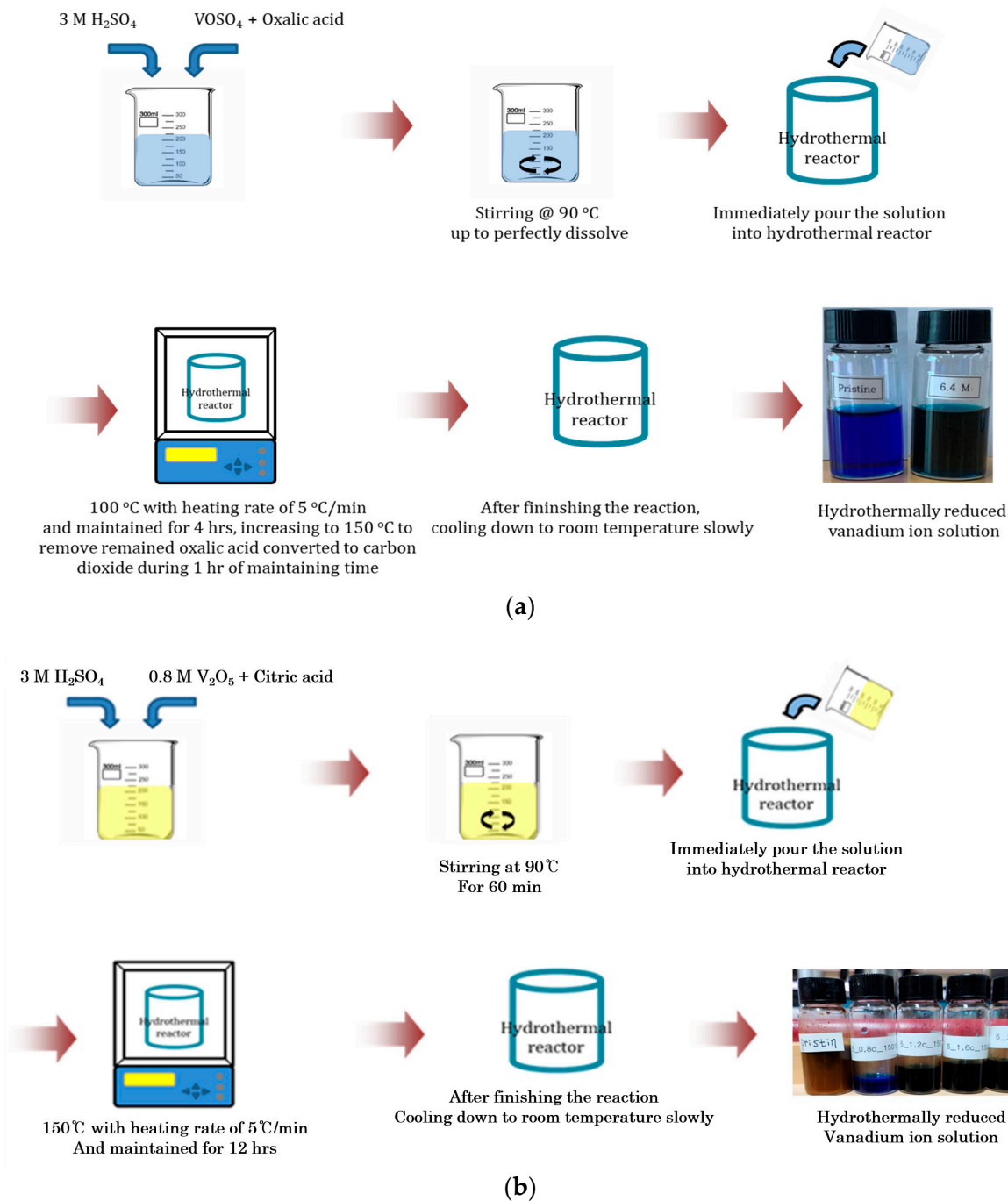


Figure 4. Preparation process of vanadium (3.5^+) through hydrothermal reduction process. (a) VOSO_4 + oxalic acid solution (b) V_2O_5 + citric acid solution.

The temperature and reaction time were determined based on the presence or absence of residual weak acid, such as oxalic acid and citric acid after reaction. After completing the reaction, the temperature of the reactor was slowly lowered. Once the temperature was completely lowered, the status of the sample was checked after opening the reactor. The mixed state (vanadium (3^+) and vanadium (4^+)) of the prepared sample was confirmed by UV-vis spectroscopy (Shimadzu, Japan). In Figure 5, (a) shows the electrolyte produced by reducing the precursor V_2O_5 to vanadium (4^+) using citric acid, while (b) depicts the production of vanadium (3.5^+) electrolyte HRR of the electrolyte from (a). By visually inspecting the color of the electrolyte in the reactor, it was confirmed to have vanadium (3.5^+).



Figure 5. The manufactured vanadium electrolyte (3.5^+) in 20 L hydrothermal reactor. (a): vanadium (4^+) electrolyte reduced using citric acid. (b): manufactured vanadium (3.5^+) electrolyte by HRR.

2.5. Electrochemical Analyses

Cyclic voltammetry (CV) was used to analyze the electrochemical properties of the samples prepared with different citric acid concentrations. The potentiostat/galvanostat (PGSTAT 302) was used for CV measurement. A three-electrode system was used: a carbon rod as the working electrode, Ag/AgCl (3 M KCl) as the reference electrode, and a Pt wire as the counter electrode. The scan was performed at room temperature with a scan rate of 20 mV/s. An electrochemical impedance spectroscopy (EIS) analysis was conducted following a cycling process within the potential range of 0.01~3.0 V at a current density of 1.5 A/g. The frequency range employed was 100 kHz to 10 mHz at room temperature. All three samples exhibited a semicircular shape in the middle-frequency range, accompanied by an inclined line at lower frequencies.

2.6. VRFB Cell Test

The vanadium RFB single cell was assembled by sandwiching a Nafion 212 membrane (5 cm × 5 cm, Dupont, Seoul, Republic of Korea) between two pieces of carbon felts (5 cm × 5 cm, 5 mm, Daedong carbon, Seoul, Republic of Korea), which were used as current collectors and were fixed by two conductive plastic plates. The corresponding charge and discharge tests were conducted using the battery test system (5 V/6 A, FamTech, Gyeongnam, Republic of Korea) at the current density to 80 mA cm⁻². In order to prevent the corrosion of carbon felts and the electrode side reaction, the upper and lower limits of the charge and discharge voltage were set at 1.7 V and 0.8 V, respectively. Charging and discharging were conducted for 50 cycles, and the current efficiency, voltage efficiency, and energy efficiency of the battery were calculated using the following equation:

$$CE(\%) = \frac{\text{Discharge Capacity (Ah)}}{\text{Charge Capacity (Ah)}} \times 100$$

$$VE(\%) = \frac{\text{Average Discharge Voltage (Wh)}}{\text{Average Charge Voltage (Wh)}} \times 100$$

$$EE(\%) = \frac{\text{Discharge energy (Wh)}}{\text{Charge energy (Wh)}} \times 100$$

3. Result and Discussion

3.1. UV Characteristics and Concentration Analysis of Vanadium Electrolyte

Figure 6a depicts the UV spectra characteristics of vanadium electrolytes for vanadium (3^+) electrolyte produced in Section 2.2. Figure 6b,d shows a linearized graph of vanadium (3^+ , 4^+) concentration against absorbance values. In the vanadium (3^+) electrolyte solution, peaks are observed at 400 nm and 620 nm. Figure 6c shows the peaks where vanadium (4^+) electrolyte is reduced from vanadium (5^+), observed at 770 nm.

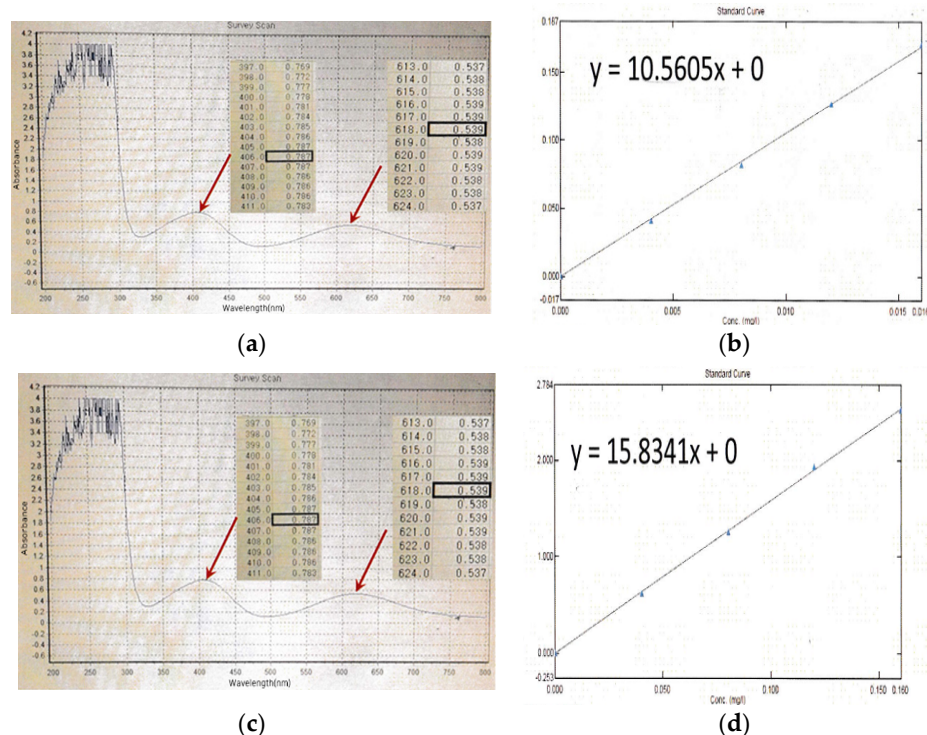


Figure 6. UV spectrum characteristic and correlation corresponding to the concentration of vanadium electrolyte solution. (a): vanadium (3^+) derived from VOSO_4 solution through charging. (b): vanadium (3^+) concentration versus UV absorbance. (c): vanadium (4^+) produced with oxalic acid reducing vanadium (5^+) produced after charging. (d): vanadium (4^+) concentration versus UV absorbance.

Typically, vanadium (3^+) electrolyte is produced by reducing it from the VOSO_4 electrolyte during charging processes; therefore, vanadium (3^+) electrolyte contains vanadium (4^+) electrolyte. This means that when analyzing vanadium (3^+) electrolyte, the characteristics of the UV spectrum of the vanadium (4^+) must be considered. Since the two components are mixed, it is possible to analyze vanadium (3^+) at 400 nm, where the peak spectrum of vanadium (4^+) electrolyte does not appear. Figure 7 shows the UV spectrum characteristics of vanadium (3.5^+) electrolyte derived from VOSO_4 and V_2O_5 by HRR. Figure 7a shows the results of UV when the concentration ratio of oxalic acid of 1.6 M VOSO_4 was changed to 0.5 (0.8 M), 1.0 (1.6 M), 1.5 (2.4 M), 2.0 (3.2 M), and 4.0 (6.4 M). It can be observed that, as the concentration of oxalic acid increases, the absorbance decreases. This indicates that with a higher amount of oxalic acid, the concentration of vanadium (4^+) in the electrolyte decreases, while the concentration of vanadium (3^+) increases. When examining absorbance according to the concentration of oxalic acid, a curve was found where the absorbance of vanadium (4^+) decreases at 750 nm, and the absorbance of vanadium (3^+) increases at 610 nm. This curve was observed at a concentration of 6.4 M. Therefore, this concentration was determined to be the optimal concentration. Figure 7b shows the results of the UV spectrum when the concentration ratio of citric acid at 0.8 M V_2O_5 was varied to 1.0 (0.8 M), 1.25 (1 M), 2.0 (1.6 M), 2.5 (2 M), 4.0 (3.2 M), and 6.0 (4.8 M). Figure 7c illustrates the UV characteristics of the citric acid concentration selected from Figure 7b. In the UV spectrum of Figure 7c, the change in vanadium (3^+) and vanadium (4^+) with varying concentrations of citric acid are measured.

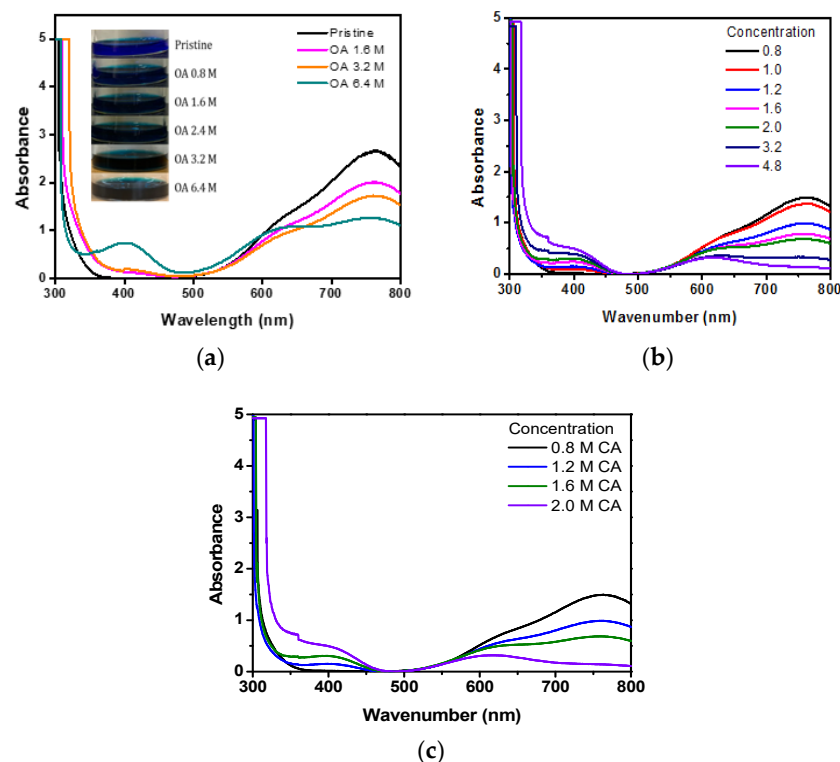


Figure 7. UV-vis spectra of the vanadium (3.5^+) electrolyte solution with different concentrations of reducing agent. (a): oxalic acid concentration (1.6 M, 3.2 M, 6.4 M), (b): citric acid concentration (0.8 M~4.8 M), (c): selected citric acid concentration (0.8 M, 1.2 M, 1.6 M, 2.0 M).

After adding citric acid to the V_2O_5 precursor and producing vanadium (3.5^+) by HRR, the UV spectrum shows a decrease in the peak value of vanadium (4^+) near 750 nm, while the peak value of vanadium (3^+) near 400 nm increases. This observation result indicated that it was reduced to vanadium (4^+) and vanadium (3^+). Also, when the concentration ratio of citric acid to V_2O_5 was 2.5 (2 M), it was observed that vanadium was completely converted to vanadium (3^+), and most of the vanadium (4^+) peak appearing at 750 nm disappeared. When the ratio of citric acid to V_2O_5 was 2.0 (1.6 M), complete conversion to vanadium (3^+) was achieved, as indicated by the almost complete disappearance of the peak at 750 nm. Therefore, to fully convert the V_2O_5 precursor to vanadium (3^+), citric acid should be added at a ratio of 2.0 (1.6 M) relative to the V_2O_5 precursor.

3.2. Electrochemical Properties of the Vanadium (3.5^+) Electrolytes Manufactured by HRR

To find the optimal concentrations of citric acid and oxalic acid, the concentrations of citric acid and oxalic acid were dispersed in the system, and electrochemical properties were conducted by CV analysis. As shown in Figure 8a,b, we varied the concentrations of citric acid and oxalic acid to find the concentration that provides the best electrochemical performance. From these results, we found that the electrolyte with 1.6 M citric acid and 6.4 M oxalic acid produced the highest current peak. Figure 8c depicts the two prepared electrolytes that were analyzed for their electrochemical properties in $V(2^+)/V(3^+)$ in the negative region and $V(4^+)/V(5^+)$ in the positive region. Table 1 illustrates the current and potential peaks at the oxidation and reduction reaction for the electrolyte prepared via the conventional method and the electrolyte produced through the hydrothermal reduction process with the addition of citric acid. The electrolyte produced by the hydrothermal reduction process has a smaller ΔE value compared with the one prepared by the conventional method, indicating faster electron transfer. A smaller ΔE value indicates a more reversible reaction between the electrode and the electrolyte. Additionally, an IP_A/IP_C ratio, which determines the reversibility of the electrolyte, indicates that the closer this

value is to 1, the more reversible the reaction at the electrode. Figure 8d shows the results of analyzing interfacial resistance through impedance spectroscopy. The electrolyte with added citric acid (CA) shows the smallest semicircle size corresponding to charge transfer resistance. So, it can be inferred that the electrochemical performance is improved, and the charge transfer resistance is reduced.

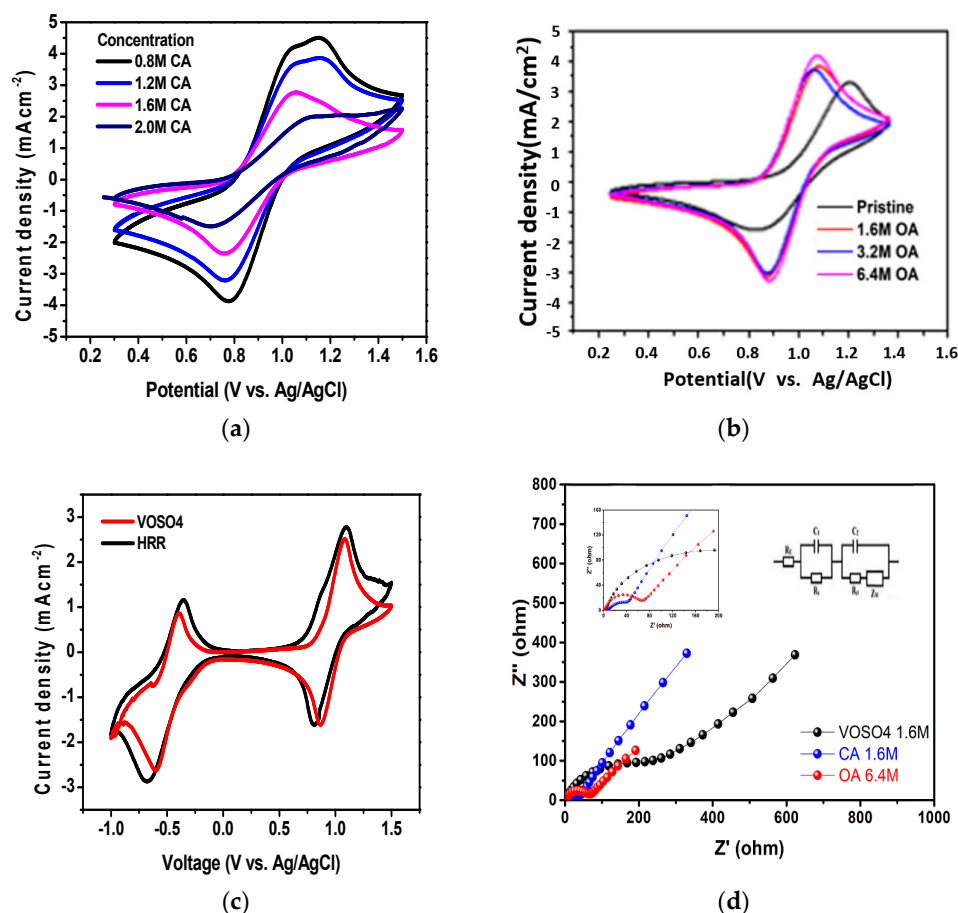


Figure 8. The cyclic voltammograms and impedance of the electrolyte with a different concentration of reducing agents. (a) Using citric acid (by HRR). (b) Using oxalic acid (by HRR). (c) Electrolyte manufactured by the HRR process (black) and by the conventional method (red). (d) Electrochemical impedance spectroscopy for electrolytes with a different manufacture process.

Table 1. Comparison of electrochemical parameters determined by CV.

Electrolyte	Redox Couple V^{2+}/V^{3+}				Redox Couple V^{4+}/V^{5+}			
	Ipa (mA)	Ipc (mA)	Ipa/Ipc	ΔE (V)	Ipa (mA)	Ipc (mA)	Ipa/Ipc	ΔE (V)
1.6 M $VOSO_4$ + 3 M H_2SO_4 (by conventional method)	2.28	1.10	2.07	0.36	1.62	2.81	0.57	0.45
0.8 M V_2O_5 + 3 M H_2SO_4 + CA (by HRR)	2.00	0.85	2.35	0.20	1.60	1.90	0.84	0.39

3.3. Performance of VRFBs Using Vanadium (3.5^+) Electrolytes by Electricity Reduction and HRR

To evaluate the performance of each electrolyte, VRFB tests were conducted over 50 cycles at a current density of 80 mA/cm^2 . The results of these tests, including energy efficiency (EE), voltage efficiency (VE), and current efficiency (CE), are shown in Figure 9. The performance evaluation of the battery showed that, while the increase in current efficiency was not significant, the overall performance of the battery improved due to the

enhancement in voltage efficiency. However, when comparing the three electrolytes, the voltage of the electrolyte prepared with oxalic acid via sequential synthesis was slightly lower than the others. This is believed to be due to the high chemical potential barrier associated with reducing vanadium (4^+) to vanadium (3^+) using oxalic acid. The current efficiency of the electrolytes prepared by the three different methods was almost identical, while the energy efficiency and voltage efficiency were highest in the electrolyte with added citric acid (CA). The increase in voltage efficiency is attributed to the reduction in polarization at the electrode surface, which results from an increased diffusion rate at the interface between the electrode and the electrolyte. This reduction in polarization likely decreases the voltage losses that occur during the charging and discharging of the battery. The results of the unit cell VRFB tests using the three different electrolytes are presented in Table 2. For the prepared vanadium (3.5^+) electrolyte from 1.6 M $\text{VO}_2\text{SO}_4 + 3 \text{ M H}_2\text{SO}_4 + \text{OA}$ (by conventional method) electrolyte, the current, energy, and voltage efficiency values were 94.82%, 77.48%, and 81.69%, respectively. For the prepared vanadium (3.5^+) electrolyte from 1.6 M $\text{VO}_2\text{SO}_4 + 3 \text{ M H}_2\text{SO}_4 + \text{OA}$ (by HRR), the current, energy, and voltage efficiency values were 96.52%, 78.38%, and 84.96%. Also, for the prepared vanadium (3.5^+) electrolyte from 0.8 M $\text{V}_2\text{O}_5 + 3 \text{ M H}_2\text{SO}_4 + \text{CA}$ (by HRR), the current, energy, and voltage efficiency values were 95.38%, 81.03%, and 84.96%, which shows improved performance compared with the commercialized electrolyte. It can be assumed that the protons in the citric acid in 0.8 M $\text{V}_2\text{O}_5 + 3 \text{ M H}_2\text{SO}_4$ were retained in the electrolyte, which not only facilitated charging and discharging, but also prevented the deterioration of electrolyte performance. After conducting a battery performance evaluation, it was observed that there was not a significant increase in the current efficiency; the overall performance of the battery improved due to enhanced voltage efficiency.

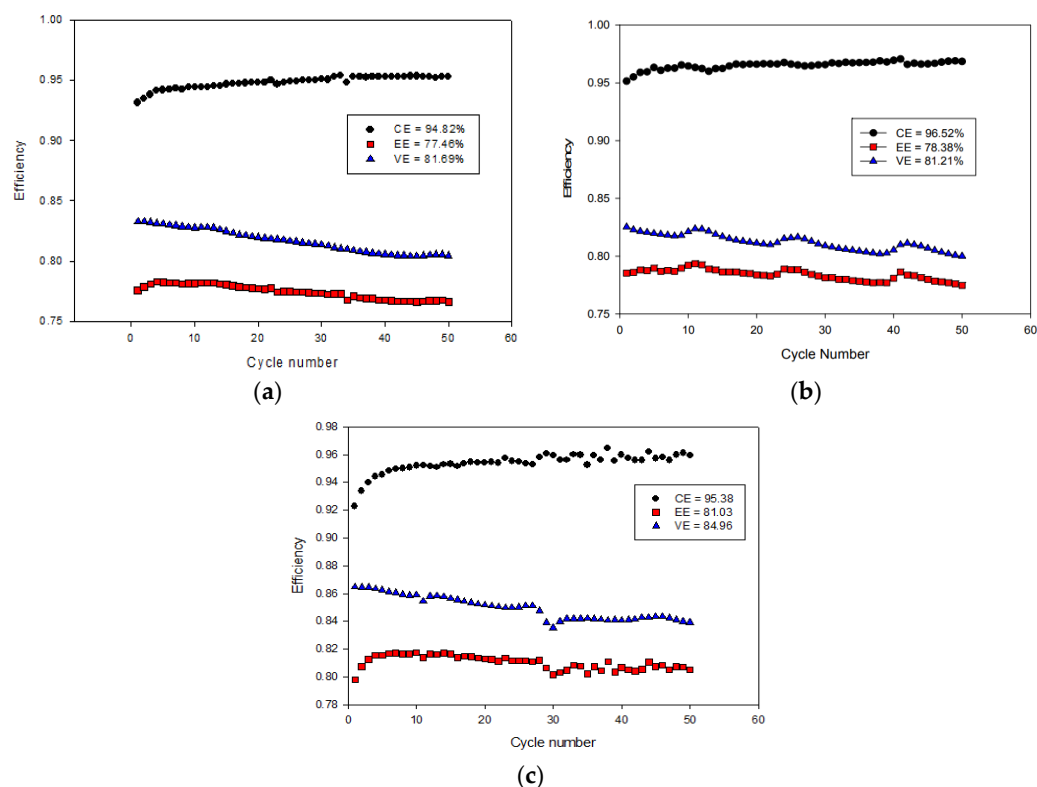


Figure 9. Comparison of charge/discharge performance of VRFB cell using the prepared electrolyte: (a) 1.6 M $\text{VO}_2\text{SO}_4 + 3 \text{ M H}_2\text{SO}_4 + \text{OA}$ (by conventional). (b) 1.6 M $\text{VO}_2\text{SO}_4 + 3 \text{ M H}_2\text{SO}_4 + \text{OA}$ (by HRR). (c) 0.8 M $\text{V}_2\text{O}_5 + 3 \text{ M H}_2\text{SO}_4 + \text{CA}$ (by HRR).

Table 2. The efficiencies of single-cell VRFBs with different electrolytes.

Electrolyte	CE	EE	VE
1.6 M VOSO ₄ + 3 M H ₂ SO ₄ + OA (by conventional method)	94.82	77.48	81.69
1.6 M VOSO ₄ + 3 M H ₂ SO ₄ + OA (by HRR)	96.52	78.38	81.21
0.8 M V ₂ O ₅ + 3 M H ₂ SO ₄ + CA (by HRR)	95.38	81.03	84.96

4. Conclusions

In this study, electrolytes were prepared using three methods: 1.6 M VOSO₄ + 3 M H₂SO₄ + OA (by the conventional method), 1.6 M VOSO₄ + 3 M H₂SO₄ + OA (by HRR), and 0.8 M V₂O₅ + 3 M H₂SO₄ + CA (by HRR). To find the optimal concentration of the electrolyte, CV analysis indicated that the highest peak was achieved with a solution comprising 6.4 M oxalic acid and 1.6 M citric acid. Electrochemical experiments using EIS were conducted to analyze mass transport and charge transfer. The results demonstrated that at a 1.6 M citric acid concentration, the reduction in charge transfer resistance resulted in the most significant enhancement in electrochemical performance. Furthermore, when charging and discharging experiments were performed with the prepared electrolytes, citric acid exhibited the highest voltage efficiency and energy efficiency. This is because, while oxalic acid can reduce vanadium (5⁺) to vanadium (4⁺), it faces a high chemical potential barrier to reduce vanadium (4⁺) to vanadium (3⁺). Therefore, citric acid, which has a higher reduction potential and can transfer four electrons to external substances due to its molecular structure, was used. The hydrothermal reduction process was employed to overcome the activation energy barrier by supplying external energy. Vanadium (3.5⁺) electrolyte was easily prepared using citric acid through the HRR process, and it showed comparable performance to commercial vanadium (3.5⁺) electrolytes, while demonstrating superior battery efficiency compared with existing electrolytes. This makes it suitable for industrial use and likely facilitates easy mass production. Additionally, it was confirmed that no residual citric acid remained in the electrolyte, and the process is expected to enable easy mass production. In addition, it was determined that no residual citric acid was left in the electrolyte.

In the future, we intend to investigate the use of an organic reductant to produce accurate vanadium (3.5⁺) and apply it in our experiments.

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Conflicts of Interest: The author declares no conflict of interest.

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