

Article



Physicochemical and Electrochemical Characterization of Vanadium Electrolyte Prepared with Different Grades of V_2O_5 Raw Materials

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Abstract: The physicochemical and electrochemical performance of electrolytes prepared with different grades of V₂O₅ raw materials were investigated systematically for a vanadium redox flow battery. Physicochemical tests showed that the conductivity of electrolytes prepared with lower grades of V₂O₅ raw materials obviously decreased, while the viscosity increased. The results of electrochemical experiments showed that the electrochemical activity and reversibility of electrolytes decreased, and the solution resistance increased obviously, as the grade of V₂O₅ raw materials gradually decreased. In addition, the battery efficiency and charge-discharge capacity were negatively affected by impurities in the lower grade V_2O_5 raw materials, due to an increase of polarization on the charge-discharge voltage. Moreover, the performance of electrolytes was related to the total concentration of impurities in the electrolyte, and Na, K impurity ions were the main factors that adversely affected the electrochemical activity and reversibility, mass transfer, and capacity of the electrolytes. Based on the economic analysis, the impurities in V₂O₅ raw materials would not only reduce the performance of electrolytes, but also affect the production costs of electrolytes and the economic profits. Through this fundamental research, people can better understand the influence of V₂O₅ raw materials on electrolyte properties, and direct more attention to research how to effectively use lower grade V₂O₅ raw materials to reduce the costs of electrolyte preparation.

Keywords: vanadium redox flow battery; electrolyte preparation; impurity ions; grade of V_2O_5 raw materials; electrochemical performance

1. Introduction

In recent years, renewable energy has been rapidly developed to ease the exhaustion of fossil fuel reserves and the pressure of environmental protection [1,2]. However, the intermittent and unstable nature of this energy, such as solar and wind power, makes these valuable electrical energies difficult to apply [3,4]. In view of this problem, the application of large-scale energy storage systems combined with the clean energy can greatly improve the stability and utilization rate of these energy resources. The VRFB (vanadium redox flow battery) is widely attracting attention and application as green energy storage technology, owing to advantages such as its flexible application, safety, high energy conversion rate, and long operation life [5,6].

Compared with other secondary batteries such as lithium ion batteries, the higher initial installation cost of VRFB limits the large-scale development and application of this



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). technology [7,8]. In the VRFB system, the cell stack, ion exchange membrane (prevent vanadium ions crossover), and electrolyte are important components [9–11]. The electrolyte circulates to the surface of the electrodes in the cell stack, where the vanadium ion redox reactions take place. Based on cost analysis of the VRFB system, the cell stack and the electrolyte account for most of the cost. Moreover, the electrolyte can account for 30%–40% of the total VRFB system cost [12]. In addition, compared with other redox flow battery systems, the electrolyte cost of a VRFB system (\leq 87 kWh⁻¹) is higher than zinc-based systems (\leq 42 kWh⁻¹) and iron-based systems (\leq 20 kWh⁻¹) [13,14].

During the charge–discharge process, the VO²⁺/VO₂⁺ in the positive half-cell and the V³⁺/V²⁺ in the negative half-cell are the active materials that achieve energy storage and release [15,16]. Therefore, the electrolyte directly affects the performance of the VRFB. High purity (\geq 99.5%) vanadium pentoxide is a typical raw material used to prepare the high purity electrolyte to avoid possible negative influences on the performance of the electrolyte, and this results in a high cost for the electrolyte [17,18]. As discussed above, one economically efficient approach to significantly reduce electrolyte cost is to use lower purity vanadium pentoxide for preparing the electrolyte. However, there usually are various impurity ions in lower purity vanadium pentoxide during the production or recovery process of vanadium [19]. Therefore, the influence of trace impurity ions in lower grade vanadium pentoxide on the performance of electrolytes for VRFBs must be systematically researched.

Early researchers tried to focus on the influence of potential metal impurities or additives on the electrochemical properties for VRFBs [8]. Researchers found that lithium ions could increase the irreversibility of the negative electrode reaction, and large amounts of potassium ions could affect the diffusion of V³⁺ ions, as nickel and chromium ions decreased the electrochemical activity of negative electrolyte [8]. In addition, some researchers reported the influence of some impurities such as Mn²⁺ [20], Cr³⁺ [21], Mg²⁺ [22], Fe^{3+} [23], K^+ [24] and Na^+ [25] on the stability and electrochemical properties of electrolytes for VRFBs. These impurities would have negligible effects on the performance of a VRFB when their concentrations are below their ultimate concentration in the electrolyte. In order to determine the effects of impurities on a mixed-acid electrolyte, Chuanlin Fan prepared the electrolyte using the analytical pure vanadium oxytrichloride with 98.5% grade vanadium pentoxide, and the relatively lower impurity concentration and better electrochemical performance of the higher purity electrolyte were demonstrated [26]. Moreover, researchers compared the performance of electrolytes with 99%, 99.9% and 99.99% grade of $VOSO_4$, and they found that the increasing impurity concentration in the $VOSO_4$ materials could deteriorate the battery efficiency and capacity of VRFBs [27]. Given this research, the impurities in different grades of electrolyte preparation raw materials may have bad impacts on the characterization of the electrolyte, but the effects of different grades of typical raw material vanadium pentoxide on electrolyte properties are unclear. Therefore, further detailed studies about the effects of vanadium pentoxide purity on the physicochemical and electrochemical properties are required to establish a lower cost preparation of electrolyte from lower purity vanadium pentoxide for VRFB development.

In this paper, different grades (98–99.5%) of vanadium pentoxide were selected as raw materials for electrolyte preparation, and the high purity (99.9%) VOSO₄ was prepared as the standard electrolyte. The chemical composition, physicochemical, and electrochemical characterization of the different purity electrolyte samples were carefully investigated and compared with the standard electrolyte. In addition, the correlation between impurities in the V₂O₅ raw materials and the properties of the electrolytes were analyzed. The costs of electrolytes prepared with different grade of V₂O₅ raw materials and their economic benefits were also discussed.

2. Materials and Methods

2.1. Electrolyte Preparation

The low purity electrolytes (LPE) and high purity electrolytes (HPE) of V(IV) electrolytes with 1.6 mol/L vanadium concentration and 5.0 mol/L total sulfate concentration, were prepared by reductive dissolution of different grades of V_2O_5 (98%, 99% and 99.5%) by the reductant of $C_2H_2O_4 \cdot 2H_2O$ (because oxalic acid as a reduction agent has a good reduction rate and will not introduce impurity ions to electrolyte) [28] in concentrated sulfate acid (Figure 1). The SE sample (standard electrolyte) with same concentration of vanadium and sulfate was prepared by dissolving high purity VOSO₄ (99.9%) in a sulfate acid solution. In this paper, de-ionized water was used to prepare the solution, and the chemical agents were analytically pure. Table 1 showed the prepared electrolyte samples were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima-4300DV, PerkinElmer, Boston, MA, USA).



Figure 1. The process of preparing electrolytes with V_2O_5 raw materials.

Electrolyte	Material	Grade	Manufacturer
SE	VOSO ₄	99.9%	Chengdu Advanced Metal Material Co. Ltd., Chengdu, China
LPE1 HPE1	$\begin{array}{c} V_2O_5\\V_2O_5\end{array}$	98% 99.5%	Hubei Ping-Fan Mining Co. Ltd., Hubei, China
LPE2 HPE2	$\begin{array}{c} V_2O_5\\ V_2O_5\end{array}$	98% 99.5%	Panzhihua Iron & Steel Co. Ltd., Panzhihua, China
LPE3 HPE3 HPE4	$V_2O_5 V_2O_5 V_2O_5 V_2O_5$	98% 99.5% 99%	Shanghai Huiyan Chemical Products Co. Ltd., Shanghai, China

2.2. Physicochemical Characterization of Electrolytes

The viscosity of electrolyte was tested by a Ubbelohde viscometer at 25 $^{\circ}$ C. The conductivity of electrolyte samples were measured by Mettler Toledo AG (S230-K, Urdorf, Switzerland) at 25 $^{\circ}$ C. During this experiment, we conducted tests three times and calculated average values.

2.3. Electrochemical Measurements

The electrochemical measurements of V(IV) electrolytes incude Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS). The device was a CHI660 electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., Shanghai, China), and the three-electrode system [23–25] was used. Before the experiments, using SiC grit paper polished the graphite electrode and ultrasonically cleaned by ethanol and distilled water for 10 min, respectively. In the EIS tests, the voltage set as 5 mV and the frequency range was between 1 Hz to 100 kHz.

2.4. VRFB Single Cell Charge–Discharge Tests

The charge–discharge tests of the electrolyte samples were carried out using a CT2001B-5 V/10 A (Wuhan Land Co. Ltd., Wuhan, China) between 0.65 V to 1.65 V at 40 mA/cm² [24,25]. The VRFB single cell (Dongguan Zhisheng Chemical Co. Ltd., Dongguan, China) consisted of a Nafion 117 membrane (Dupont) (Nafion 117 membrane was selected to minimize the influence of vanadium crossover on the battery efficiencies), PAN-based graphite felts (8 cm × 8 cm × 3 mm), and conductive plastic plates. The photographs of VRFB systems and SEM-EDS of the graphite felt electrode were shown in Figure 2. Before tests, the electrodes were treated at 400 °C for 6 h, and the membrane was soaked in deionized water for 24 h. Then, 60 mL V(IV) electrolyte was installed into the positive electrolyte storage tank, and 30 mL V(IV) electrolyte into the negative electrolyte storage tank. After the initial charging, the positive electrolyte was the V(V) electrolyte, and the negative electrolyte was the V(II) electrolyte, and 30 mL V(V) electrolyte was poured from the positive electrolyte storage tank, then the circulating charge–discharge tests were conducted. So, the electrolyte volumes were 30 mL, and a peristaltic pump circulated the electrolyte with a flow rate of 40 mL/min.



Figure 2. The photographs of VRFB systems and SEM-EDS of the graphite felt electrode.

3. Results and Discussion

3.1. Composition Analysis of Electrolyte

The different grades of V_2O_5 usually contained different kinds and concentrations of impurities, such as K, Na, Mg, Fe, Al, Ca, Mn, Cr, resulting in prepared electrolytes of different purities. Impurities may have negative influences on the physicochemical and electrochemical properties of the electrolyte, and finally reduce the performance of the VRFB. Thus, the chemical composition of the electrolyte is important for the application of the VRFB.

As shown in Table 2, the chemical composition of the electrolytes prepared with different grades of V_2O_5 raw materials were checked by ICP-OES. The SE sample prepared

with 99.9% grade VOSO₄ contained a few impurities with concentrations of 5~40 mg L⁻¹, such as 25.5 mg L⁻¹ Ca, 31.1 mg L⁻¹ Fe and 5.1 mg L⁻¹ Ti, but the other impurity ions were mostly less than 1.0 mg L⁻¹. Compared with SE, the LPE1, LPE2 and LPE3 samples prepared with different manufacturers producing 98% grade V₂O₅, therefore these samples contained many impurity ions with higher concentrations, such as Ca, Cr, Fe, K, Mg and Na. While the impurity ions in the HPE1, HPE2, HPE3 and HPE4 samples were almost the same as the SE sample, only a few kinds of impurity ions exceeded the SE sample, such as 59.1 mg L⁻¹ K and 14.6 mg L⁻¹ Mg in the HPE1 sample; 30.9 mg L⁻¹ Cr, 40.3 mg L⁻¹ K and 16.2 mg L⁻¹ Mg in the HPE3 sample; 18.3 mg L⁻¹ Al, 58.7 mg L⁻¹ K, 20.1 mg L⁻¹ Mg and 135.4 mg L⁻¹ Na in the HPE4 sample.

Table 2. The chemical composition of electrolytes prepared with different grades of V₂O₅ raw material.

Impurities Concentration	Electrolyte Samples							
$(mg L^{-1})$	SE (99.9%)	HPE1 (99.5%)	HPE2 (99.5%)	HPE3 (99.5%)	HPE4 (99%)	LPE1 (98%)	LPE2 (98%)	LPE3 (98%)
Al	<1.0	<1.0	5.2	20.0	18.3	1.0	4.8	8.4
Ca	25.5	23.5	1.8	29.1	27.9	71.6	2.2	37.4
Cr	2.7	3.9	30.9	2.9	4.3	43.3	77.0	48.1
Fe	31.1	22.9	15.1	5.7	5.6	21.1	15.8	60.2
Κ	<1.0	59.1	40.3	58.7	62.2	326.7	87.7	60.6
Mg	1.1	14.6	16.2	20.1	20.5	26.9	17.8	18.0
Na	<1.0	7.2	13.5	135.4	141.3	30.1	264.9	371.5
Mn	1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.3	1.7
Ti	5.1	5.0	<1.0	<1.0	<1.0	4.5	<1.0	6.5
Мо	<1.0	<1.0	1.5	3.6	3.6	<1.0	2.0	1.5
Ni	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cu	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Au	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Pt	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
As	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Pd	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Si	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

The electrolyte may contain higher amounts of impurity ions, such as Cr and Fe, when the preparation material was V_2O_5 extracted from vanadium–titanium magnetite. Additionally, impurity ions such as Al, Ca, Fe, K, Mg and Na may have been produced by the hydrometallurgical vanadium extraction process. Polyvalent impurities, such as Cr and Fe in the electrolyte, could participate in electrochemical reactions, causing a redox side reaction and subsequent charge–discharge capacity reduction [21,23]. The alkali or alkaline earth metal impurities would be adsorbed by the membrane and electrode, resulting in increased polarization and decreased voltage efficiency [24,25]. Due to the complex physicochemical characteristics and electrochemical properties of the electrolyte, however, the influence of different grades of V_2O_5 raw material on the performance of the electrolyte should be further systematically investigated.

3.2. Physicochemical Characteristics of the Electrolyte

The variety of conductivity and viscosity can reflect the influence of the purity of V_2O_5 raw materials on the physicochemical characteristics of the electrolyte. As shown in Figure 3, among these samples, the SE sample had the highest conductivity and lowest viscosity. It is well known that the electrochemical kinetics and solution resistance could be impacted by the conductivity, and the diffusion of vanadium ions and energy consumption could be affected by the viscosity [29]. Accordingly, the SE sample had the best physicochemical properties and would have better electrochemical performance. Compared with SE sample, the conductivity of the LPE1, LPE2, LPE3 and HPE4 samples were reduced

by 7.41%, 8.61%, 8.48%, 6.44%, respectively, while the conductivity of HPE1, HPE2 and HPE3 only decreased by 5.16%, 3.80% and 4.19%. In addition, the viscosity of the LPE1, LPE2, LPE3 and HPE4 samples respectively increased by 8.19%, 11.29%, 10.73% and 6.78%, but the viscosity of HPE1, HPE2 and HPE3 only varied by 2.54%, 2.26% and 3.67%. This indicates that LPE1, LPE2, LPE3 and HPE4 had poor physicochemical performance, while HPE1, HPE2 and HPE3 had better physicochemical performance.



Figure 3. The conductivity and viscosity of electrolytes prepared with different grades of V₂O₅ raw material.

There are many factors that can affect conductivity and viscosity, such as vanadium, sulfate, hydrion, and impurity concentration. Based on the analysis of the chemical composition of the electrolyte samples as mentioned above (Section 3.1), the concentration of impurities such as Cr, Fe, Mg, K, Na in these electrolyte samples were higher than the SE sample. Therefore, the impurities maybe have important effects on the diffusion and electromigration velocity of VO²⁺/VO₂⁺ and H⁺, which resulted in changes of the physicochemical properties. On the basis of above analysis, it is thought that the grade of V₂O₅ raw material had a nonnegligible influence on the physicochemical properties of the electrolytes, and the physicochemical characterizations of these electrolyte samples followed the trend SE (99.9% VOSO₄) > HPE2 \approx HPE1 \approx HPE3 (99.5% V₂O₅) > HPE4 (99% V₂O₅) > LPE1 \approx LPE2 \approx LPE3 (98% V₂O₅).

3.3. Electrochemical Properties of Electrolytes

3.3.1. Cyclic Voltammetry Analysis

The electrochemical properties of the electrolyte samples were analyzed by CV measurements. According to the CV curves, the electrochemical parameters were obtained.

As presented in Figure 4, the shape of the CV curves of these electrolyte samples were basically the same, but the peak current and peak potential showed great differences. The J_{pa} (oxidation peak current) and J_{pc} (reduction peak current) of HPE1, HPE2, HPE3 and HPE4 were basically consistent with SE sample. However, the J_{pa} of LPE1, LPE2 and LPE3 decreased by 15.85%, 11.52% and 20.62%, respectively, from 55.72 mA cm⁻² (SE) to 46.89 mA cm⁻² (LPE1), 49.30 mA cm⁻² (LPE2) and 44.23 mA cm⁻² (LPE3). The J_{pc} of LPE1, LPE2 and LPE3 also decreased by 16.17%, 25.32% and 29.62%, from 41.19 mA cm⁻² (SE) to 34.53 mA cm⁻² (LPE1), 30.76 mA cm⁻² (LPE2) and 28.99 mA cm⁻² (LPE3). This indicates that the electrode reaction activity of the electrolyte samples prepared with 98% grade V₂O₅ was poor. In addition, the ΔE_p (peak potential separation) of HPE1, HPE2, HPE3 and HPE4 were slightly changed compared to the SE sample. However, the ΔE_p of LPE1, LPE2 and LPE3 increased dramatically, from 276 mV (SE) to 412 mV (LPE1), 440 mV (LPE2) and



520 mV (LPE3), respectively, which indicated that the electrochemical reversibility of these electrolyte samples significantly deteriorated.

Figure 4. CV curves of (**a**) low purity electrolytes and (**b**) high purity electrolytes, (**c**) the peak current, and (**d**) the peak potential of electrolytes prepared with different grades of V_2O_5 material.

From the above CV tests, the electrochemical performance of HPE1 and HPE2 samples were basically same as the SE sample, and were slightly better than the HPE3 and HPE4 samples, but significantly better than the electrolyte samples prepared with 98% grade vanadium pentoxide.

3.3.2. Electrochemical Impedance Spectroscopy

As shown in Figure 5, the Nyquist plots and Bode plots of electrolytes prepared with different grades of V_2O_5 raw material were measured by EIS tests and the equivalent electric circuit model was given. The Nyquist plots were consisted with a semicircle and a sloped line. The semicircle represents the charge transfer process in the high frequency region and the straight line represents the diffusion-limited process in the low frequency region [29]. The corresponding parameters were obtained by fitting the Nyquist plots with the equivalent circuit model, as displayed in Table 3.

Compared with the SE sample, the EIS curves of electrolytes prepared with different grades of V_2O_5 raw material had significant changes. This indicates that the impurities in the electrolytes had obvious effects on the electrode reaction processes. Table 3 shows that the C (capacitance of electrode/solution interface) and W (Warburg impedance) of these electrolyte samples changed little, while the R_1 (solution resistance) and R_2 (charge transfer resistance) had a significant difference. The R_1 and R_2 of the HPE2 sample were almost consistent with the SE sample. The R_1 of HPE1, HPE3 and HPE4 were slightly higher than the SE sample, and the R_2 of these samples were slightly decreased. As for the electrolyte samples prepared with 98% grade V_2O_5 raw materials, only the R_2 of the LPE1 sample increased by 9.24%, from 9.74 Ω cm⁻² to 10.64 Ω cm⁻², but the R1 of LPE1, LPE2

and LPE3 all sharply increased by 9.09%, 32.87% and 81.82%, respectively. As shown in Figure 5b, when the frequency (f) increased from 1 to 10⁵ Hz, the log (Z) values decreased sharply first and then flattened, while the phase angle (ψ) gradually increased. In the high frequency region (f tended to 10⁵ Hz), the log (Z) curves were almost parallel to the log (f) axis, at which region the log (Z) was equal to log (R_1). It was seen that the solution resistance (R_1) of LPE3 and LPE2 electrolyte samples were larger than the higher pure electrolyte samples, and the analysis was consistent with the fitting results in Table 3. It indicated that the solution resistance of those electrolyte samples was greatly increased, implying that the process of mass transfer was very difficult.

The results of the EIS tests were consistent with the CV and physicochemical tests, and further demonstrated that higher concentrations of impurity ions in the electrolyte resulted in an increase of solution resistance, which affected the mass transfer process and worsened electrolyte electrochemical performance.



Figure 5. The EIS curves and the equivalent electric circuit model of V(IV) electrolytes prepared with different grades of V_2O_5 raw materials; (a) Nyquist plots, (b) Bode plots.

Table 3. The	parameters resulting	g from fitting	the EIS tests v	vith the equ	uivalent electric	circuit model
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Sample	$ m R_1$ ($\Omega~cm^{-2}$)	R_2 (Ω cm ⁻²)	C (F cm ⁻²)	W,Y ₀ (S s ⁻⁵ cm ⁻²)
SE	1.43	9.74	0.058	0.24
HPE1	1.51	8.63	0.059	0.26
HPE2	1.48	9.75	0.061	0.20
HPE3	1.58	8.91	0.061	0.21
HPE4	1.58	9.01	0.062	0.21
LPE1	1.56	10.64	0.059	0.19
LPE2	1.90	9.75	0.057	0.19
LPE3	2.60	8.89	0.054	0.19

3.4. Charge–Discharge Tests

Although Sections 3.2 and 3.3 demonstrated that the physicochemical and electrochemical properties of the electrolytes prepared with different grades of V₂O₅ raw materials followed the order: SE > HPE1 \approx HPE2 > HPE3 > HPE4 > LPE1 > LPE2 > LPE3, it is necessary to analyze the performance of VRFBs with different electrolyte purities. The battery efficiency of various electrolyte purities are shown in Figure 6a–c.



Figure 6. (a) Coulombic efficiency, (b) voltage efficiency, (c) energy efficiency, (d) charge–discharge curves, and (e) discharge capacity of VRFBs with different electrolyte purities at a current density of 40 mA cm⁻² (σ represents the standard deviation).

Firstly, the CE (coulombic efficiency) increased with rising cycle numbers, while the VE (voltage efficiency) decreased gradually. The larger CE at the later test stage should be attributed to adsorption of impurity ions on the electrode surface [24,25], which led to a decrease of charge–discharge capacity (Figure 6e). In addition, the absorption of impurity ions in the membrane may also prevent vanadium crossover, since more impurity ions may permeate through the membrane instead of vanadium ions, resulting in vanadium ion crossover through the membrane being slowed down, with subsequent capacity loss decreases in the later cycles [30,31]. Moreover, the solution resistance and charge transfer resistance increased with increasing amounts of impurity ions in the electrolyte, which led to an increase of electrochemical polarization, and eventually the VE decreased.

Secondly, the CE of SE, HPE1, HPE2, HPE3 and HPE4 were stabilized at 90~92%, while that of LPE1, LPE2 and LPE3 were fluctuant in the range of 88~89%. The VE of LPE1,

LPE2 and LPE3 decreased obviously, and their average values were 92.98%, 92.92% and 93.15%, which were lower than that of SE, HPE1, HPE2, HPE3 and HPE4 (94.76%, 94.75%, 94.95%, 94.76% and 93.86%, respectively). As for EE (energy efficiency), the average EE of SE, HPE1, HPE2, HPE3 and HPE4 were both higher than 84.94%, while that of LPE1, LPE2 and LPE3 decreased to 80~82%, which should be attributed to their lower CE and VE. The tests illustrated that different grades of V_2O_5 raw materials greatly affected the efficiency of the VRFB, and especially decreased the VE when the impurity ions were increased in the electrolyte.

In addition, the charge-discharge curves (Figure 6d) showed that the average charge voltage increased with decreases of electrolyte purity, while the discharge voltage decreased. Compared to the discharge capacity of the SE sample (1.092 Ah), the discharge capacity of LPE1, LPE2 and LPE3 sharply decreased to 0.528 Ah, 0.488 Ah and 0.245 Ah, respectively. The theoretical capacity of the VRFB is 1.287 Ah with 30 mL of 1.6 M vanadium electrolyte. Therefore, the electrolyte utilization (EU) can be calculated (EU is defined as the ratio of actual discharge capacity to theoretical capacity [32]), as shown in Figure 7. The EU of SE could reach 84.84%, and the EU of electrolytes prepared with 99.5% grade V_2O_5 raw materials decreased to 75.76-82.05%, while the EU of electrolytes prepared with 98% grade V_2O_5 raw materials decreased to 19.04–41.03%. The lower EU means that the electrolytes prepared with lower grades of V₂O₅ raw materials have lower energy densities, and require greater volumes of electrolytes in the same VRFB system. The results indicate that the impurity ions could increase the overpotential of the electrode reaction process caused by the increase of polarization which impacted the VE. The higher charge voltage and lower discharge voltage also caused a decrease in capacity due to the charge-discharge time being shortened at the same cut-off voltages during the tests. This was consistent with the results in Figure 6a,b.



Figure 7. Electrolyte utilization of VRFBs with different electrolyte samples at a current density of 40 mA cm^{-2} .

3.5. Comprehensive Analysis

3.5.1. Correlation Analysis of Electrolyte Properties and Impurity Ions

The radar graph shown in Figure 8 reports the variation trend of electrolyte performances and the impurities concentration based on Sections 3.1–3.4; the relevant formulas are as follows:

$$\Delta P = \frac{|P_x - P_{SE}|}{P_{SE}} \times 100\% \tag{1}$$

$$\varepsilon = \frac{C_x}{C_{tx}} \times 100\% \tag{2}$$

$$\Delta \varepsilon = \frac{|C_x - C_{SE}|}{|C_{tx} - C_{tSE}|} \times 100\%$$
(3)

where the ΔP stands for the performance (Conductivity, Viscosity, J_{pa}, ΔE_p , R₁, EE and Capacity) change ratio of the test samples relative to the standard electrolyte; P_x is the performance of the electrolyte sample; P_{SE} is the performance of the *SE*; ε is the percentage of *x* ion (i.e., Al, Ca, Fe ...) concentration to total impurities concentration; C_x is the *x* ion (i.e., Al, Ca, Fe ...) concentration in the electrolyte sample; C_{tx} is the total impurities concentration; C_{SE} is the ion (i.e., Al, Ca, Fe ...) concentration in the electrolyte sample; $\Delta \varepsilon$ stands for the relative change percentage of impurity concentration; C_{SE} is the ion (i.e., Al, Ca, Fe ...) concentration in *SE*; and C_{tSE} is the total impurities concentration in *SE*.



Figure 8. The changing trends of performance and impurities concentration of the electrolyte samples. (**a**) The performance change ratio, (**b**) the total impurities concentration, (**c**) the impurity concentration, (**d**) the percentage of ion concentration to total impurities concentration, (**e**) the relative change percentage of impurity concentration.

Figure 8a (calculated from Equation (1)) shows that the performance of J_{pa} , ΔE_p , R_1 and the capacity of the electrolyte were greatly affected by the impurity ions, indicating that the electrode reaction activity, reversibility, mass transfer, and capacity of lower purity electrolyte samples were seriously deteriorated. Figure 8d (calculated from Equation (2)) and Figure 8e (calculated from Equation (3)) show the different changing trends with Figure 8a, indicating that the percentage concentration and relative change percentage concentration of impurities in electrolytes were not the reason for the performance variety in the electrolyte samples. However, the Figure 8b shows that the total impurity concentration in lower purity electrolyte samples was higher than other electrolyte samples. Moreover, the Figure 8c shows that the Na ion concentration in LPE3, LPE2, HPE4, HPE3, and K ion concentration in LPE1 were higher than the others. It illustrated that the performance of the electrolyte was related to the total concentration of impurity ions in the electrolyte, and Na, K impurity ions were the main factors that adversely affected electrode reaction activity, reversibility, mass transfer, and capacity of the electrolyte.

3.5.2. Economic Analysis

The preparation costs of electrolytes are an important factor affecting large-scale production and application of VRFBs. Therefore, it is necessary to analyze and compare the costs of electrolytes prepared with various grades of V_2O_5 raw materials. The following were the economic methods and formulas used for the analysis:

- (1) The electrolytes could work for at least 15 years, and the losses of cell stacks and circulation pumps are negligible.
- (2) The VRFB achieved profits based on the difference of the peak–valley period, and the selling price of the peak period is \$0.15/kWh, while the selling price of the valley period is \$0.042/kWh (originally from site research of the Hubei vanadium energy storage Co., Ltd., XiangYang City of Hubei Province in China) (\$1 = 6.49 RMB).
- (3) The investment cost of cell stacks is \$616.3/kW; the circulation pumps are \$924.5 (2 units); the control system cost is \$154.1; the inverter cost is \$77.0/kW [12].
- (4) The concentration of the electrolyte is 1.6 mol/L; the price of 98% grade V₂O₅ is \$16.18/kg, the price of 99% grade V₂O₅ is \$18.49/kg, the price of 99.5% grade V₂O₅ is \$37.75/kg (sourced from the China ferroalloy network in 2020).

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(5) The total costs of the system are calculated as Equation (4) [12]:

$$V = C_e + C_f \tag{4}$$

where *W* represents all costs of the VRFB system, C_e is electrolyte costs, C_f is fixed costs including the costs of cell stacks, pumps, the control system, and inverter.

The profit of the VRFB is calculated as Equation (5) [12]:

$$Profit = (R_{out} - \frac{R_{in}}{EE}) \times C_{VRFB}$$
(5)

where R_{out} and R_{in} are the peak–valley period and peak period prices of electricity; *EE* is the energy efficiency of the VRFB; C_{VRFB} is the capacity of the VRFB system.

The payback years of the VRFB are calculated as Equation (6) [12]:

$$Y = \frac{W}{ACF} = \frac{W}{\text{Profit} \times 365} \tag{6}$$

where Y is payback years of all costs; ACF means cash flow every year.

The economic analysis (based on the Section 3.4) of the electrolytes prepared with various grades of V_2O_5 raw materials are exhibited in Tables 4 and 5. The results show that the various grades of V_2O_5 raw materials not only affected the performance of the VRFB, but also greatly affected the electrolyte costs and the economic profits of the VRFB. Because the price of lower grade V_2O_5 raw materials was much lower than that of higher grade of V_2O_5 raw materials, the preparation costs of electrolytes were lower and the

payback years of total investments for the VRFB system were shorter at the same capacity scale. However, when the electrolyte properties were extremely poor, the electrolyte costs were higher, and the payback years were longer. The electrolyte costs and the payback years of the electrolyte samples prepared with different grades of V_2O_5 raw materials are as follows: HPE4 < LPE1 < LPE2 < HPE1 < HPE2 < HPE3 < LPE3. Based on the above analysis, impurities in V_2O_5 raw materials would not only reduce the performance of the electrolyte, but also affect the production costs of the electrolyte and the economic profits.

Table 4. The costs of electrolytes prepared with different grades of V_2O_5 raw materials for a 1 MW/4 MWh VRFB system.

Sample	Discharge Capacity (Ah)	Energy Density (Wh L ⁻¹)	Electrolyte Volume (L)	m(V ₂ O ₅) (Kg)	Electrolyte Costs (\$)
HPE1	1.056	24.47	163,466	23,784	897,863.6
HPE2	1.008	22.45	178,174	25,924	978,651.5
HPE3	0.975	22.04	181,488	26,407	996,856.9
HPE4	0.913	20.88	191,571	27,874	515,381.8
LPE1	0.528	12.11	330,306	48,059	777,541.3
LPE2	0.488	11.11	360,036	52,385	847,527.0
LPE3	0.245	5.39	742,115	107,978	1,746,943.0

Table 5. The economic profits of a 1MW/4MWh VRFB system with different purities of electrolytes.

Sample	EE (%)	Profit (\$/day)	W (\$)	Y (years)
HPE1	86.28	411.1	1,592,316.5	10.6
HPE2	85.58	409.6	1,673,104.4	11.1
HPE3	87.12	412.9	1,691,309.8	11.2
HPE4	84.97	408.2	1,209,834.7	8.1
LPE1	82.85	403.1	1,471,994.2	10.0
LPE2	82.32	401.8	1,541,979.9	10.5
LPE3	82.15	401.4	2,441,395.9	16.7

4. Conclusions

There were more kinds and higher concentrations of impurities such as Cr, Fe, K, Mg and Na in the electrolytes prepared with lower grade V_2O_5 raw materials. The conductivity of electrolytes increased with an increase of the grade of V_2O_5 raw materials, while the viscosity decreased. Electrochemical measurements showed that the electrolytes prepared with lower grade V_2O_5 raw materials had worse electrochemical activity and reversibility, and higher solution resistance. The charge–discharge performance of different purity electrolytes showed that energy efficiency decreased from 87.38% to 82.15%, and the discharge capacity also decreased from 1.092 Ah to 0.245 Ah, when the grade of V_2O_5 raw materials gradually decreased.

The performances of the electrolytes were related to the total concentration of impurities in the electrolytes; Na and K impurities were the main factors that adversely affected electrochemical activity, reversibility, mass transfer and capacity of the electrolytes. Based on the economic analysis, the impurities in V_2O_5 raw materials would not only reduce the performance of the electrolyte, but also affect the production costs of the electrolyte and the economic profits.

In view of the above results, we need to control the concentration of K and Na impurities during the electrolyte preparation process when using lower grade V_2O_5 raw materials. This fundamental investigation could provide a theoretical reference for the practical application of VRFBs using lower cost electrolyte preparation with lower grade V_2O_5 raw materials.

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