



Article Mitigating Capacity Decay by Adding Carbohydrate in the Negative Electrolyte of Vanadium Redox Flow Battery

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Abstract: Glucose, sucrose, D(+)-xylose and α -lactose monohydrate are selected as additives relative to the negative electrolyte of Vanadium Redox Flow Battery (VRFB), with the aim of reducing vanadium permeation and improving electrochemical performance to mitigate capacity decay. The results of a charge–discharge test show that the cell with α -Lactose monohydrate in the negative electrolyte exhibits the best capacity retention. The capacity retention of a single cell employing 1 wt% α -Lactose monohydrate in the negative electrolyte was 71% after 30 cycles, which is 41.5% higher than 29.5% of the control group. Correspondingly, adding α -Lactose monohydrate into the negative electrolyte also significantly inhibits vanadium crossover and water transfer. Furthermore, the effects of additives on the performance of the negative electrolyte are studied by thermal stability experiments, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The stability experiments indicate that the introduction of 1 wt% α -Lactose monohydrate can elevate the stability of the negative electrolyte at low temperatures. The electrochemical measurements indicate that V(III) electrolyte with 1 wt% α-Lactose monohydrate obtains superior electrochemical activity and reversibility, which can be ascribed to the fact that the hydroxyl group carried by the additive provides more active sites for the redox reaction. Herein, the study provides a meaningful reference for mitigating the capacity decay of VRFB.

Keywords: vanadium redox flow batteries; additive; capacity decay/retention; stability

1. Introduction

Natural renewable energy sources, such as solar and wind, have gained increasing attention and are being utilized to replace dwindling fossil fuels to alleviate the pressure to combat environmental pollution [1,2]. However, the instability and intermittency of renewable energy sources make it difficult to integrate them directly into grid applications. Therefore, researchers had developed large-scale energy storage systems as an intermediate bridge to convert them reciprocally with electrical energy [3]. Proposed by Skyllas-Kazacos [4] in the 1980s, VRFB has received widespread attention and systematic research due to its independent power and capacity, long cycle life and high safety performance [5,6]. In addition, VRFB, using the same element in both half-cells, thereby reduces the problem of cross-contamination as much as possible, which differs from the chemistry of first-generation iron-chromium flow batteries with heterogeneous elements [6]. However,



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Copyright: © 2022 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/). the significant capacity degradation of VRFB and its poor electrochemical performance during long-term operation shorten its cycle life and hinder its rapid commercialization [7,8].

Thus far, it has been found that the asymmetric transfer of vanadium ions on the cation/proton exchange membrane and its accompanying side reactions cause concentration imbalance and valence imbalance of active substances in the positive and negative electrolytes, resulting in a gradual decline of battery capacity [9]. Anion exchange membranes have a better ability to stop vanadium ions from crossing the membrane, but their poor electrical conductivity and stability still cause battery capacity loss [10]. In addition, electrolytes with poor electrochemical activity have a low vanadium ion utilization, which can bring about the loss of actual battery capacity [11]. Existing studies have reported that the capacity loss of VRFB can only be alleviated, but not completely eliminated. The strategies to deal with the capacity loss for VRFB are mainly based on the following three aspects: first, remixing the overly imbalanced positive and negative electrolytes directly [12,13] or rebalancing the valence state of vanadium in the electrolyte by reducing the oxidized active material [14,15] when the capacity loss reaches a certain level; second, inhibiting vanadium ions and water molecules through the ion exchange membrane to suppress the imbalanced of the positive and negative electrolytes [16,17]; third, improving the electrochemical activity and reversibility of the electrolyte and the electrode active specific surface to enhance the utilization of the active material and cell efficiency [18,19].

Zhang et al. [13] chose the appropriate current density and runtime to mix the electrolyte; thus, the cycle number of VRFB in this system increased from 145 to 598, but the problem of low capacity retention cannot be avoided by remixing the imbalanced electrolyte. In addition, the method of reducing the oxidized active material poses other problems, including the introduction of additional impurities and the hydrogen evolution in long-term operation [20]. Therefore, several researchers had attempted to modify membranes [21,22] and prepared membranes with high ion selectivity [23] to reduce vanadium ions transfer for mitigating capacity decay. On the basis of membrane modification, adding a soluble draw solute [17], which can narrow the osmotic pressure of the electrolyte on both sides during the cell operation into the negative electrolyte, also markedly reduced the crossover of vanadium ions. The charge capacity decay of the battery was suppressed from 60.7% to 27.5% within 55 h by adding the solute, but the solute seemed to have an adverse effect on the electrochemical performance of the electrolyte. However, the method provided a research idea to inhibit vanadium ions to cross the membrane to mitigate the capacity decay of VRFB.

To improve the electrochemical performance of the battery, the researchers treated graphite-felt electrodes by introducing oxygen-containing and nitrogen-containing functional groups on the electrode surface to enhance the kinetics of redox reactions in VFBR [24,25]. The modification of the electrodes improves vanadium ion utilization and then increases the actual charge and discharge capacity of the battery. However, the limitations of vanadium ion wettability on the electrode surface and vanadium ion diffusion ability lead to low interfacial activity between electrolyte and electrode, which still hinders the further increase in battery capacity. To increase the interfacial activity and contact area between electrolyte and electrode, hydrophilic functional groups such as $-NH_2/-SO_3H/-OH/-COOH/=O$ were introduced into the electrolyte [26–30]. The addition of these additives provided more active sites for electrode reactions to enhance battery capacity and the additives could complex with vanadium ions to enhance the solubility and stability of the electrolyte. Therefore, adding appropriate additives to increase the osmotic pressure of the negative electrolyte and introduce beneficial functional groups to the negative electrolyte is a meaningful approach to mitigate the capacity decay of VRFB.

Carbohydrates, have been proved to improve the electrochemical performance of electrolytes due to their large number of oxygen-containing hydroxyl functional groups [29]. Moreover, in the field of medicine and biology, the ability of carbohydrates to regulate osmotic pressure is often mentioned [31]. In order to mitigate the capacity decay of VRFB from the perspective of the electrochemical performance and vanadium permeation, four

carbohydrates including two kinds of monosaccharide (glucose and D(+)-xylose) and two types of disaccharide (sucrose and α -Lactose monohydrate) were selected for this study. The effects of the four additives on the electrochemical performance of negative electrolytes and vanadium ion permeation across membranes and battery capacity were comparatively investigated.

2. Experimental

2.1. Preparation of Electrolyte

The original V(IV) electrolytes containing 1.8 M V(IV) sulfate and 3.0 M H₂SO₄ were prepared by dissolving VOSO₄ (99.9% purity, Panzhihua Iron and Steel Research Institute Co., Ltd., Panzhihua, China) into sulfuric acid. The V(III) electrolyte was prepared by placing the same concentration and volume of the V(IV) electrolyte in a two-chamber electrolytic cell, and then obtaining the V(III) electrolyte on the negative side. The V(II) electrolyte was prepared by placing the same volume of V(IV) electrolyte on the positive side and V(III) electrolyte on the negative side in the two-compartment electrolysis cell, and then the V(II) electrolyte was obtained on the negative side. The termination of the electrolytic reaction and valence state of vanadium ions that existed in the electrolyte were determined by UV-Vis spectrometry analysis. The concentration of total vanadium ions in the electrolyte was measured by chemical titration, and ammonium ferrous sulfate solution was used as a standard titration solution. The electrolyte containing additives was obtained by adding glucose, sucrose, D(+)-xylose and α -Lactose monohydrate at a concentration of 1 wt% (mass percentage of the additive to V(III) electrolyte) into the V(III) electrolyte, respectively.

2.2. Thermal Stability Experiments of V(III) Electrolyte

The prepared V(III) electrolytes containing 1.8 M V(III) sulfate and 3 M H₂SO₄ without and with different additives were sealed, respectively, into two 10 mL silica glass battles and statically deposited in the thermostatic water bath at 25 °C and low-temperature refrigeration thermostat at -20 °C. The above electrolytes were examined periodically, and the time when visible precipitation occurred was recorded.

2.3. Electrochemical Measurements

To ascertain the effects of negative electrolytes with the additives on the electrochemical performance, the electrochemical measurements were conducted with a CHI660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., Shanghai, China) in a three-electrode system at room temperature. The three-electrode system included a graphite electrode (1 cm × 1cm) as a working electrode, a platinum sheet electrode (1.5 cm × 1.5 cm) as a counter electrode and a saturated calomel electrode (SCE) accompanied by a salt bridge filled with saturated KCl solution as the reference electrode. Cyclic voltammetry (CV) measurements of negative electrolytes were tested with a voltage range of $-0.2\sim-0.8$ V and a scan rate of 20 mV s⁻¹. Before the test, the graphite electrode needed to be polished carefully and then ultrasonically cleaned in ethanol and deionized water in sequence for 10 min to avoid the effect of ions attached to the electrode surface. Electrochemical impedance spectroscopy (EIS) was also measured on a CHI660E electrochemical workstation. The sinusoidal excitation voltage of 5 mV was exerted to the cells with a frequency range between 1 Hz and 10⁵ Hz, and the relevant parameters of EIS were obtained by fitting the test results using a simplified equivalent circuit model.

2.4. Charge–Discharge Test

The charge–discharge tests were conducted in a VRFB single dynamic cell with two liquid storage tanks, and the key material of the cell consisted of two graphite felt electrodes (Dongguan Zhisheng Chemical Co., Ltd., Dongguan, China) and a proton exchange membrane (Nafion 117, DuPont, Suzhou, China) sandwiched between two electrodes. The area of the electrode is 25 cm². The volume of the electrolyte on both sides was set to 30 mL and the prepared V(IV) and V(III) electrolyte served, respectively, as a positive

electrolyte and negative electrolyte initially, which were conserved in two glass containers and were pumped persistently into the anode and cathode side, respectively, by two peristaltic pumps (DlPump550, Kamoer Fluild Tech Co., Ltd., Shanghai, China) under the flow rate of 60 mL min⁻¹. The tests of cell performance were carried out on CT2001B-5V/10A battery test system (Wuhan Land Co. Ltd., Wuhan, China) at a constant current density of 40 mA cm⁻¹, and the voltage range from 0.65 to 1.65 V.

2.5. Vanadium Permeation Measurements

The amount of vanadium ions permeation was measured by using a two-compartment diffusion units separated by a proton exchange membrane (2.83 cm², Nafion 117, DuPont, Suzhou, China). Before the test, one side of the unit was filled with 1.8 M V(III) sulfate in 3 M H₂SO₄ solution with or without additives, while another side was filled with a mixed solution of 1.8 M MgSO₄ and 3 M H₂SO₄ for balancing the cation concentration, the volume of the solution on each side is 70 mL. The diffusion experiment was carried out by employing magnetic stirring apparatus stirring continuously both solutions of the unit to avoid concentration. A sample from the side containing MgSO₄ was taken periodically and the concentration of vanadium was determined by chemical titration, which employed ammonium ferrous sulfate solution as a standard titration solution. At the same time, aliquots of the solution were taken from both the vanadium-rich side and the receiving side at specified intervals to minimize osmotic effects.

2.6. Characterization

The UV-Vis spectrometry of the prepared V(III) electrolyte with and without additive was analyzed on a UNIC 4802S UV-Vis spectrophotometer (Shanghai, China) with the range of 190–1100 nm using 1.0 cm glass cells. H_2SO_4 measuring 3 M was selected as the referenced sample during the test. Furthermore, the V(IV) concentration of positive electrolyte after 30 cycles was worked out by the standard curve via absorbance measured by an ultraviolet spectrophotometer. The standard curve is shown in Figure 1.



Figure 1. The standard curve of (IV) concentration vs. absorbance.

The Raman spectroscopy of V(III) electrolytes with and without additives was conducted using a Labram-010 spectrophotometer, which was excited by using He-Ne Raman Renishaw image microscope (632.8 nm, 12798 cm⁻¹, red), which provides a powerful monochromatic beam.

FT-IR (Fourier transform infrared spectroscopy) spectra of the graphite felt electrodes were measured at room temperature with vertex 70X Fourier transform spectrometer, and the absorption frequency range was 400–4000 cm⁻¹. The potassium bromide tablet method was used to prepare samples.

The apparent morphology and elemental analysis of the graphite felt electrode obtained from charge–discharge tests were characterized with the scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) tests (JEOL, JSM-6610, Japan) at an acceleration voltage of 20 KV.

3. Results and Discussion

3.1. Thermal Stability of the Electrolyte

To verify whether the addition of four carbohydrates would affect the stability of the negative electrolyte, 1.8 M V(II) ions and 1.8 M V(III) ions in 3 M sulfuric acid with and without additives were, respectively, placed and sealed in a temperature-controlled container at 25 °C and -20 °C. The time of visible precipitation formation is displayed in Table 1.

V Species	A 11.0	Time for Precipitation/h		
	Additive	25 °C	−20 °C	
V(II)	Pristine	S	5 ± 0.75	
	D(+)-xylose	S	7 ± 0.5	
	Glucose	S	8 ± 0.5	
	Sucrose	S	12.5 ± 0.8	
	α-Lactose monohydrate	S	20 ± 0.4	
V(III)	Pristine	S	S	
	D(+)-xylose	S	S	
	Glucose	S	S	
	Sucrose	S	S	
	α -Lactose monohydrate	S	S	

Table 1. Effect of types of additives on the stability of 1.8 M vanadium electrolyte.

S means the electrolyte can remain stable for least 30 days.

As demonstrated, the V(II) electrolyte with and without additives formed crystallization in a short time, while the V(III) electrolyte remained stable at -20 °C for 30 days. That meant that V(II) electrolytes are relatively less stable at low temperatures, which was related to the fact that V(II) requires fewer ions to form polymeric precipitation compared with V(III) [32]. Moreover, the V(II) electrolyte and V(III) electrolyte could all keep stable at 25 °C for 30 days. It could be found that the stability of the V(II) electrolyte with four additives was improved compared to the original electrolyte. The prolongation of the stability time of V(II) electrolyte could be explained by the fact that the hydroxyl and carbonyl groups in carbohydrate additives adhere to the surface of the nuclei to disperse V(II) ions by electrostatic repulsion, which could retard the polymerization of V(II) ions and the formation of crystals [33]. In contrast, the stability of the V(II) electrolytes containing disaccharide was better than that of the V(II) electrolytes containing monosaccharide at -20 °C, which may be due to the larger spatial structure of the disaccharide molecules, which is easier to disperse the V(II) ions complexed with them. Among them, the stability time of the V(II) electrolyte with α -lactose monohydrate was 15 h longer than that of the pristine sample, which indicates the best microthermal stability.

3.2. Cyclic Voltammetry

To obtain a deeper insight into the effect of four carbohydrate additives in the V(III) electrolytes containing 1.8 M V(III) sulfate and 3 M H₂SO₄ on the electrochemical performance, some comparative experiments were performed. Cyclic voltammetry (CV) tests with and without 1 wt% four carbohydrate additives were conducted, and the result of CV tests are displayed in Figure 2. Table 2 presents the main related parameter results of CV for describing in detail the effects of different carbohydrate additives on the V(III) electrolyte. As demonstrated in Figure 2, anodic peaks and cathodic peaks related to the oxidation and reduction in V²⁺/V³⁺ were detected at approximately -0.3 V and -0.65 V.

0.08

0.06

0.04

0.02

-0.02

-0.04

-0.06

-0.08

-0.10

0.08

0.06

0.0

0.02

-0.02

-0.04

-0.06

-0.08

-0.10

-0.8

-0.7

-0.6

-0.5

Potential vs.SCE/V

-0.4

-0.3

Current/A cm² 0.00

Current/A cm² 0.00



-0.0

-0.08

-0.10

-0.8

Figure 2. CV curves of the negative electrolyte with and without four carbohydrate additives. (a) glucose; (b) D(+)-xylose; (c) sucrose; (d) α -Lactose monohydrate.

-0.7

-0.6

-0.5

Potential vs.SCE/V

-0.4

-0.2

-0.3

Table 2. Th	e parameters of C	V tests of 1.8 M V(III) electrol	yte with and without f	our carbohydrate additives.
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	Anodic Peak		Cathodic Peak			
Sample	i _{pa} (mA cm ²)	E _{pa} (mV)	i _{pc} (mA cm ²)	E _{pc} (mV)	ΔEp (mV)	i _{pc} /i _{pa}
Pristine	42.5	-317	58.3	-650	333	1.37
D(+)-xylose	47.0	-310	61.7	-615	305	1.31
Glucose	42.9	-274	57.7	-664	390	1.36
Sucrose	48.6	-308	63.6	-618	358	1.31
α -Lactose monohydrate	49.1	-311	63.7	-596	285	1.30

-0.2

The test results show that the addition of carbohydrates increased the peak current of V(III) electrolytes, implying that electrochemical activity improved, especially for V(III) electrolytes with sucrose and α -Lactose monohydrate. Apparently, the electrolyte with α -Lactose monohydrate performed the best electrochemical behavior, the oxidation peak current increased by 15.5%, and the reduction peak current increased by 9.3%. Meanwhile, the peak current ratio is closest to 1, and the peak potential separation (ΔEp) reaches a minimum of 288 mV. From Figure 2b and Table 2, the oxidation peak current of the V(III) electrolytes decreased after adding glucose, which indicated that the aldehyde groups had a negative effect on the electrochemical properties. By comparing Figure 2a,c,d, it was clear that the α -Lactose monohydrate and sucrose with disaccharide structure were more conducive than glucose with the monosaccharide structure relative to electron transfer. The result was probably due to the fact that the above disaccharide can accommodate more vanadium ions to complex with hydroxyl groups, and these hydroxyl groups could

be adsorbed on electrode surfaces to provide more active sites for the redox reaction of V^{2+}/V^{3+} under the same quality conditions, especially for α -Lactose monohydrate. The corresponding mechanism needs to be further investigated.

3.3. Electrochemical Impedance Spectroscopy

EIS was used to further analyze the effect of the α -Lactose monohydrate on the electrochemical performance of the V(III) electrolyte containing 1.8 M V(III) sulfate and 3 M H₂SO₄, and the corresponding Nyquist plots are exhibited in Figure 3.



Figure 3. Nyquist plots of the graphite electrode in negative electrolyte with and without α -Lactose monohydrate and the corresponding equivalent circuit.

As exhibited in Figure 3, each plot comprised a depressed semicircle in the highfrequency region and a straight line in the low-frequency region, indicating that the V^{2+}/V^{3+} redox reaction should be controlled by a mixture of electrochemical reaction and diffusion steps. The radius of the semicircle was relevant to the charge–transfer resistance, while the linear part corresponds to the diffusion of vanadium ions in the electrode [34,35]. A simplified equivalent circuit model was employed to investigate the impedance spectra, where R_1 stands for solution resistance, C means the constant phase element of the interface between the electrolyte and the electrode, R_{ct} represents the charge–transfer resistance during the electrochemical process and W represents the Warburg diffusion impedance, respectively [36].

The simulation results of impedance parameters obtained from Zsimpwin software are displayed in Table 3. The electrolyte with α -Lactose monohydrate exhibited slightly higher solution resistance (R_1) and diffusion impedance (W) compared with the pristine sample, which might be related to the slight increase in viscosity (with α -Lactose monohydrate 4.82 mm²/s VS the pristine 4.73 mm²/s). The reduced R_{ct} indicated a faster electron transfer process, which could be attributed to the catalytic property of hydroxyl groups adhered to the electrode [34–36]. Furthermore, the hydrophilic nature of hydroxyl groups was beneficial for the electrode to absorb more vanadium ions and promoted the diffusion of vanadium ions on the electrode's surface, which might account for the increase in the diffusion capacitance (C) of the ions and the electric double-layer capacitance at the electrode/electrolyte interface [34].

Table 3. Fitting results of EIS in electrolyte with and without α -Lactose monohydrate.

Sample	$R_1 (\Omega/\mathrm{cm}^2)$	$C imes 10^{-5}$ (F/cm²)	R_{ct} (Ω/cm^2)	$W, Y_0 \ ({\rm S}/{\rm s}^5 \ {\rm cm}^2)$
Pristine	1.19	3.404	4.956	0.1830
α-Lactose monohydrate	1.21	4.260	3.988	0.1775

3.4. Charge–Discharge Tests

The charge–discharge measurements were conducted in a dynamic single cell using different negative electrolytes with and without 1 wt% four carbohydrate additives to further investigate the effect of battery performance. The coulombic efficiency (CE) and energy efficiency (EE) of the cells in 30 cycles are compared, respectively, in Figure 4a,b.



Figure 4. The performance of VRFB single-cell employing the anolyte with and without four carbohydrate additives at 40 mA cm⁻² in 30 cycles: (**a**) Coloumbic efficiencies, (**b**) energy efficiencies and (**c**) the charge–discharge curves for the 1st cycle.

As observed, the introduction of the carbohydrates could improve the CE and EE of the cell, and the α -Lactose monohydrate sample exhibits the best results. The average coulombic efficiency of the cell with α -Lactose monohydrate in the negative electrolyte was 96.3%, which was a 2.8% increase over the pristine sample (93.5%), and the average energy efficiency increased from 78.5% to 82.0%. Figure 4c shows the typical charge–discharge curves of VRFB with and without carbohydrates in negative electrolyte at the current density of 40 mA cm⁻² at 25 °C. As exhibited, the cell with carbohydrates in the negative electrolyte had a lower charging voltage and higher discharging voltage plateau as well as higher capacities than the pristine one, implying that the ohmic polarization of the electrolyte weakened. The sample with α -Lactose monohydrate exhibited the best largest capacity and the lowest value of charge–discharge overpotential, which indicated the enhancement of electrochemical reaction reversibility [29]. The above result revealed that the number of active species involved in the electrochemical reaction increased, and the battery's capacity enhanced. It supports the results of CV and EIS.

The charge and discharge capacity changes for VRFB with and without carbohydrates at 25 °C in 30 cycles are presented in Figure 5. Obviously, the charge and discharge capacity

decay of the cell with carbohydrates was significantly reduced, which demonstrated a higher capacity retention ratio compared with the pristine sample. As exhibited in Figure 5a, the cell with 1 wt% α -Lactose monohydrate had the highest discharge capacity retention ratio of 71.1% after 30 cycles, while the pristine cell was merely 29.5%. Similarly, Figure 5b exhibits that the discharge capacity of the cell also decreased gradually during operation, 69.8% decay from 1.065 to 0.322 Ah for the pristine cell and 38.0% decay from 1.207 to 0.869 Ah for the cell with 1 wt% α -Lactose monohydrate, respectively. The results indicated that the cell with 1 wt% α -Lactose monohydrate could obtain the best cycle performance and the most effective improvement of the utilization of the active material in the electrolyte compared with others.



Figure 5. (a) Charge capacity degradation and (b) discharge capacity degradation of the VRFB employing negative electrolyte with and without four carbohydrate additives in 30 cycles.

The decay capacity of the cell is mainly due to the different diffusion rates of vanadium ions with different valences through the membrane, which eventually leads to the transfer of vanadium ions and water molecules from the negative side to the positive side [37]. The addition of α -Lactose monohydrate could increase the osmotic pressure of the negative electrolyte, and α -lactose monohydrate could more easily form coordination with vanadium ions, thus mitigating consequently the diffusion and migration of vanadium ions.

In order to verify that the addition of carbohydrates inhibited the diffusion of vanadium ions across the membrane, the amount of vanadium ions and the volume of the positive and negative electrolyte was tested and compared with the pristine sample, respectively, after 30 cycles, and the result is shown in Figure 6.

As observed in Figure 6, the imbalance of the vanadium amount and volume occurred between two half-cells after cycles finished, the specific phenomenon was that the negative electrolyte (NE) was diluted and the positive electrolyte (PE) became enriched. The osmotic pressure difference generated by the concentration gradient between the positive and negative electrolytes could further accelerate vanadium crossover (especially the migration of the negative electrolyte to the positive) and battery capacity decay [38,39]. The results shown that the introduction of the carbohydrates in the negative electrolyte effectively retarded the diffusion of vanadium ions and the imbalance of electrolyte volume, which was attributed to the decrease in osmotic pressure differences between the positive and negative electrolytes during the battery cycle. The α -lactose monohydrate sample exhibited the best cycle performance.



Figure 6. (a) Amount of vanadium and (b) volume of the electrolytes with and without four carbohydrate additives after 30 cycles.

3.5. Mechanism Analysis

In order to further explain that the addition of α -Lactose monohydrate in the negative electrolyte could mitigate the diffusion of vanadium ion cross membrane, the transfer of vanadium ions was studied, and the results are shown in Figure 7.





Figure 7. (a) Effect of the addition of α -Lactose monohydrate on the concentration of V³⁺ in the permeate side and (b) two-compartment diffusion unit.

As exhibited, the permeation of vanadium ion was obviously reduced when the α -Lactose monohydrate exists in the electrolyte, embodying the fact that the V³⁺ permeability of the group with added α -Lactose monohydrate (7.01 $\times 10^{-4}$ mol) was 37% less than that (1.12 $\times 10^{-3}$ mol) of the blank sample after 25 h. The addition of α -lactose monohydrate to the negative electrolyte could increase the number of particles per unit volume of electrolyte, thus increasing its osmotic pressure. From the above charge–discharge results, it could be seen that there was a decrease in the transfer number of vanadium ions from the negative to the positive electrolyte, which could be attributed to the increase in the osmotic pressure of the negative electrolyte. The corresponding change process is illustrated in Figure 8. The additional driving force of 95.94 KPa was provided by mixing 1 wt% α -Lactose monohydrate into the negative electrolyte, which can be obtained from the Van't Hoff formula [23]:

$$\pi = \beta CRT$$

where π means the osmotic pressure, β means the Van't Hoff factor, *C* means the concentration (mol·L⁻¹) and *R* means the universal gas constant (8.31 KPa L mol⁻¹·K⁻¹).





Figure 8. The effect of osmotic pressure in the negative electrolyte increased during the cycles process.

In order to confirm how the α -Lactose monohydrate played a role in the electrolyte, UV-Vis spectrometry with and without 1 wt% α -Lactose monohydrate was measured, and the result is shown in Figure 9a. As exhibited, the UV-Vis test curves of the V(III) electrolyte exhibited two characteristic absorption peaks, respectively, at 604 nm and 404 nm. In addition, neither a new absorption peak nor peak shift appeared after adding 1 wt% α -Lactose monohydrate into V(III) electrolyte, which indicated that the valence state and the concentration of vanadium had not been affected by the coexistence of the α -Lactose monohydrate and V(III) ions.

The electrolyte sample measured in the UV-Vis test was a 50-fold diluted solution of the original electrolyte; thus, it is not possible to state the specifics in the electrolyte at high concentrations, and it is unclear whether new forms of vanadium ion structural bonding are formed. To further investigate whether the α -lactose monohydrate forms a new vanadium ion bonding structure with the V(III) electrolyte, the electrolyte with and without α -Lactose monohydrate was characterized by Raman spectra. The test result in the range of 200–1500 cm⁻¹ is demonstrated in Figure 9b. Through the peak-differentiating and imitating the vibration peak at 400–500 cm⁻¹, 986 cm⁻¹ and 1047 cm⁻¹, the areas of HSO₄⁻, V-O and SO₄²⁻ in the Raman spectra were obtained, as exhibited in Figure 9c,d, and the corresponding result is displayed in Table 4. Based on the Raman spectra of vanadium oxide and the band frequencies of the electrolyte mentioned previously in the literature, the corresponding assignments of the main peaks [26,27] are displayed in Table 5.

Table 4. The results of peak-differentiating and imitating in Raman spectra for HSO_4^- , SO_4^{2-} and V-O bonds.

	400–500	cm ⁻¹	986 cm ⁻¹	$1047~\mathrm{cm}^{-1}$
Samples	Area (HSO ₄ ⁻)	Area (V-O)	Area (SO $_4^{2-}$)	Area (HSO_4^-)
Pristine	3021.99	4734.19	1264.27	1616.40
α -Lactose monohydrate	3351.39	5638.76	1487.29	1765.79

Table 5. Band frequencies and corresponding assignments of main peaks in Raman spectrometry.

Raman Shift (cm ⁻¹)	Assignment
400–500	$\mathrm{HSO_4}^-$ and V-O (V-O bridging mode)
603	HSO_4^- , symmetric stretch
660–680	V-O-S, bridging stretch
803	V-O, bridging stretch
899	V-O, terminal stretch
986	SO_4^{2-} , symmetrical stretch
1047	HSO_4^- , asymmetrical stretch



Figure 9. (a) UV-Vis spectra and (b) Raman spectrum of V(III) electrolyte with and without α -Lactose monohydrate. Peak-differentiating and imitation of (c) HSO₄⁻ and V-O bonds between 400 cm⁻¹ and 500 cm⁻¹ and (d) SO₄²⁻ and HSO₄⁻ at 986 cm⁻¹ and 1047 cm⁻¹ in the Raman spectra.

As seen from Figure 9b, no new peaks appeared and the original peak vanished in the Raman spectrum, which is consistent with the test results of UV-Vis spectrometry and indicates that a new valence state of vanadium ions had formed. Nevertheless, the intensity of peaks at 400–500, 603, 986 and 1047cm⁻¹ enhanced slightly since α -Lactose monohydrate existed in the V(III) electrolyte; more SO₄^{2–}, HSO₄[–] and V-O structures formed correspondingly. This indicated that the hydroxyl group in α -Lactose monohydrate could combine with vanadium ions to form a stable V-O bridge structure and that it replaced a part of the SO₄^{2–}/HSO₄[–] ligand from the coordinated vanadium ions, resulting in increased SO₄^{2–} and HSO₄[–] ions presented in the electrolyte. In addition, the complex of α -lactose monohydrate with vanadium ions could hinder vanadium ions across the membrane to some extent.

The related study [40,41] pointed out that the improvement of V²⁺/V³⁺ redox reactions by hydroxyl groups included the interfacial transfer of vanadium ions between the bulk solution and electrode surface, their ion-exchange with hydroxyl groups or hydrogen ions on the graphite felt and the subsequent electron transfer reaction. From the results of the charge–discharge test and electrochemical test, it could be observed that the introduction of α -Lactose monohydrate promoted the electrochemical reaction that occurred on the surface of the electrode. To prove that α -Lactose monohydrate could be adsorbed on the surface of the electrode, FT-IR, SEM and EDS tests were conducted, and the results are exhibited in Figure 9.

It can be observed from Figure 10a that the bands at 3525 cm^{-1} , which represents the stretching vibration of the hydroxyl group, and the bands at 1725 cm^{-1} , which belongs to α -Lactose monohydrate [42], appeared. Moreover, Figure 10b shows that increased

O elements were enriched on the surface of graphite–felt electrode, which was employed in the electrolyte with α -Lactose monohydrate compared with the pristine sample, implying that the hydroxyl functional groups in α -Lactose monohydrate could be adsorbed to the electrode during operation. The hydroxyl groups attached to the electrode surface did not change the structure of the electrode, but they supplied more available active sites for ion exchange and accelerated the process of V²⁺/V³⁺ redox reactions [43,44]. The hydroxyl functional groups provided more active specific surface area on the electrode's surface, allowing more vanadium ions to participate in the redox reaction. As a result, vanadium utilization increased, and the cell was more adequately charged and discharged. Furthermore, this was due to the increase in osmotic pressure caused by the α -Lactose monohydrate in the electrolyte, which inhibited the decrease in active material in the negative electrolyte. More vanadium ions, thus, could be involved in the electrochemical reaction, leading to high output current density.





Figure 10. (a) FT-IR spectra and (b) SEM images and EDS mappings of the graphite felt electrode after 30 cycles of the cell with and without α -Lactose monohydrate.

4. Conclusions

In this work, Glucose, sucrose, D(+)-xylose and α -Lactose monohydrate were applied as additives for the negative electrolyte of VRFB. Capacity decay was mitigated by adding additives in the negative electrolyte to enhance electrochemistry and inhibit vanadium ion diffusion. Moreover, the best performances were achieved by adding α -Lactose monohydrate among them.

According to the results of SEM, EDS and FT-IR, the enhancement on the electrochemical performance of V(III) electrolyte with α -Lactose monohydrate was attributed to the increased active sites for V²⁺/V³⁺ redox reactions by hydroxyl groups attached to the electrode and the enhanced hydrophilic property of the electrode. Meanwhile, the hydroxyl group in α -Lactose monohydrate easily formed coordination with vanadium ions, which is conducive to prolonging the low-temperature stability time of the negative electrolyte. More importantly, α -Lactose monohydrate can provide extra osmotic pressure to the negative electrolyte and form coordination with vanadium ions to reduce vanadium ions across the membrane.

Consequently, VRFB with α -Lactose monohydrate in the negative electrolyte performed excellent discharge capacity retention of 72.0% (29.5%) after 30 cycles, while the average coulombic efficiency is 96.3% (93.5%), and the average energy efficiency is 82.0% (78.5%).

Therefore, the α -Lactose monohydrate can be regarded as a promising additive for the negative electrolyte of VFRB.

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