



Coulter dispersant as positive electrolyte additive for the vanadium redox flow battery

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ABSTRACT

Coulter dispersants were investigated as the additive into the positive electrolyte (more than 1.8 M vanadium ions) of vanadium redox flow battery (VRB). The electrolyte stability tests showed that, at 45, 50 and 60 °C, the addition of 0.050–0.10 w/w Coulter dispersant IIIA (mainly containing coconut oil amine adduct with 15 ethylene oxide groups) into the positive electrolyte of VRB could significantly delay the time of precipitate formation from 1.8–12.3 h to 30.3 h ~ 19.3 days. Moreover, the trace amount of Coulter dispersant IIIA as the additive can enhance the electrolyte stability without changing the valence state of vanadium ions, reducing the reversibility of the redox reactions and incurring other side reactions at the electrode. Using the Coulter IIIA dispersant as the additive also improved the energy efficiency of the VRB. The UV–vis spectra confirmed that the trace amount of Coulter IIIA dispersant did not chemically react with V(V) to form new substances. The synergy of Coulombic repulsion and steric hindrance between the macromolecular cationic surfactant additive and the solution reduced the aggregation of vanadium ions into V₂O₅ and increased the supersaturation of V₂O₅ crystal in the solution.

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1. Introduction

Vanadium redox flow battery (VRB) is a promising technology that provides independent tunable power and storage capacity, which makes it suitable for large-scale, renewable and grid energy storage [1–5]. However, to date the vanadium battery has not achieved widespread application [6] because several limitations have restricted its industrialization. For example, the electrode materials can get etched in the strongly acidic and oxidizing electrolyte [7–9], the Nafion membrane used as the battery separator is highly expensive [10,11], and the stability and the match between cathode and anode solutions are inadequate [12], etc. Particularly, after recharging the vanadium battery, the positive electrolyte tends to generate red precipitate, which deposits on the carbon felt and blocks the porous electrode surface. This cripples the pump circulation and severely reduces the charge/discharge efficiency of the battery, and may even cause battery dysfunction [13].

Several works have been reported on preventing and delaying the precipitate formation in the positive electrolyte of VRB [14–18]. Adding stabilizing agent into electrolyte is one of the most economic and effective methods to improve the performance of VRB

[19–23]. The stabilizers (1–3%) are usually alcohols that have ring or chain structures and can increase the solubility of V(II)–V(V) ions in the solution, stabilize the electrolyte and reduce vanadium precipitation in the electrolyte.

Recently, we found that the additives can somewhat improve the stability of V(V) in the positive electrolyte and, however, they also have negative impacts on the cell. For instance, the addition of trace amount (0.10 w/w) of glycerol can keep 2.0 M V(V) solution free from precipitation at 60 °C for at least 20 days. However, it changes the valence of V(V) in the solution, consequently making the VRB self-discharge during operation. The other example is that the addition of CTAB leads to the formation of lots of gas bubbles in the vanadium electrolyte. Since VRB usually uses pump as the power source to transfer the fluids, the presence of gas may affect the operation of the pump.

Coulter dispersant (Beckman Coulter Company, USA) is an aqueous dispersant. Currently no literature reports on the effect of Coulter dispersant on vanadium electrolyte. We found in our recent study that the addition of trace amount (0.050–0.10 w/w) of Coulter dispersant into the VRB positive electrolyte can effectively delay the precipitation in the VRB positive electrolyte at elevated temperature. In this work, we report in detail the effect of the Coulter dispersant as an additive into VRB positive electrolyte on the stability and the electrochemical properties of the electrolyte.

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2. Experimental

2.1. Preparation of test solution

The solution of 1.8–2.2 M vanadium sulfate concentrations was prepared by electrolytic dissolution of the appropriate weight of V_2O_5 (>99.95%, Dadi Vanadium Research Institute, Chongyang, Hubei, China) in 5.0 M H_2SO_4 supporting electrolyte [20]. The resulted solution was then placed in the vanadium redox cell and charged with a current density of 40 mA/cm² until a bright yellow solution of V(V) was produced in the positive half cell containing 1.87 M V(V) and 0.01 M V(IV), and the total acidity concentration was adjusted to 3.2 M using 60% H_2SO_4 . The valence and concentration of the vanadium ions in the electrolyte were measured by T50 (Mettler TOLEDO) potentiometric titrator. The total acidity concentration was determined based on acid-base titration using HANNA HI9024 pH meter (Beijing Hanna Company).

2.2. Introduction of additives

Dispersants, IA, IB, IC, IIA and IIIA (Beckman Coulter, USA), consisted of deionized water and surfactant. Dispersants IA, IB and IC contain non-ionic surfactants with different carbon atoms. Dispersant IIA contains anionic surfactant, and dispersant IIIA contains cationic surfactant.

The test solutions were placed in sealed glass jars with different types and amounts of additives in water baths set at 45, 50 and 60 °C for 30 days. Each solution was examined visually every day, and the time taken for a slight precipitate of V_2O_5 to appear was recorded. At the end of the 30-day test period the solutions were filtered and the 'equilibrium' vanadium ion concentration determined by potentiometric titrator analysis.

The tested solutions containing additives with different types and amounts were placed in sealed glass jars in water baths set at 45, 50 and 60 °C for 30 days. All solutions were examined visually every day, and the time was recorded when a slight precipitation of V_2O_5 appeared visually. At the end of the 30-day test period, all tested solutions were filtered and the concentration of 'equilibrium' vanadium ion was determined by potentiometric titrator analysis.

2.3. Electrochemical measurements

2.3.1. Cyclic voltammetry

Solution I consisted of 50 mL test solution without any additive, and it was used as the blank solution. Into 50 mL test solution was added 0.050–0.10 w/w (mass percentage of the additive to the solution) IA, IB, IC, IIA, IIIA and glycerol (solutions II–VII), respectively. Cyclic voltammetry was carried out in a 3-electrode electrochemical cell using saturated mercurous sulfate electrode as the reference electrode, graphite electrode as the working electrode (surface area 4.9 mm²), and platinum electrode as the counter electrode. The graphite electrode was soaked in the test solution for at least 0.5 h before the scan. The scans were carried out at room temperature at 30 mV/s over 0.0–0.9 V on a Solartron SI1287A electrochemical workstation (UK). The viscosity and conductivity of solutions I–VII were measured, respectively, using an NDJ-5S digital viscometer (Shanghai, China) and a Leici DDS-307 conductivity meter (Shanghai, China).

2.3.2. Charging and discharging tests

The flow cells consisted of two graphite felt electrodes, two copper current collectors and a Nafion 117 membrane. The active area of both electrode and membrane was about 50 cm². The test solution with and without Coulter dispersants was tested. The cathode was sealed to prevent oxidation. A balanced flow cell contained 20 L anolyte and 20 L catholyte. The flow rate was controlled by a drive

pump at 3.0 L/min. An Arbin battery tester (BT-2000) was used to evaluate the performance of flow cells and to control the charging and discharging of the electrolytes. An environmental chamber was used to control the temperatures during flow cell tests.

For cell performance evaluation and electrolyte solution preparation, the cell was normally charged at a current density of 40 mA/cm² to 1.72 V and discharged to 0.8 V with a current density of 40 mA/cm². Cell cycling tests were performed at 90% state-of-charge and state-of-discharge at a fixed charging and discharging current density of 40 mA/cm².

2.4. UV-vis spectrometry

UV/visible spectroscopy was measured on a Cary 100 UV/Vis spectrophotometer (USA) in the range of 190–900 nm using 2.0 cm quartz cell. 3.2 M H_2SO_4 was used as the blank solution. The measured solutions are as follows: solution I, 1.25×10^{-5} M Coulter IIIA dispersant in 3.2 M H_2SO_4 (colorless); solution II, 1.09×10^{-5} M test solution (slightly yellow); solution III, 0.050 w/w Coulter IIIA dispersant in solution II (slightly yellow); solution IV, 0.070 w/w Coulter IIIA dispersant in solution II (slightly yellow).

3. Results and discussion

3.1. Selection of additives

Table 1 shows the time of precipitation for the electrolyte under different temperatures after adding trace amount (0.05–0.10 w of the total mass of test solution) of additive to the test solution.

According to Table 1, at 45–60 °C, except for the Coulter IIA dispersant which contains anionic surfactant, all other additives could delay precipitation at various degrees in the positive electrolyte, and stabilize the vanadium battery positive electrolyte. Among the Coulter dispersants, the cationic IIIA type showed best stabilizing ability, followed by the non-ionic IC and IB, IA Coulter dispersants, and the anionic IIA type had the poorest stabilization effect. The addition of alcohols (e.g., glycerol and hexanehexol), thiols and other compounds with chain or ring structure into the positive electrolyte have been found to effectively inhibit precipitation. However, we found that such organic compounds are easily oxidized in the strongly oxidative V(V) solution. During charging and discharging, they could participate in the electrochemical reaction of the vanadium battery and release CO₂. By analyzing the positive electrolyte in the absence and presence of additive, we found that, at room temperature, after adding 0.10 w/w glycerol into the test solution, allowing for sufficient stirring and then standing for 15 min, 5.5% V(V) was reduced to V(IV). Furthermore, 25.7% V(V) was reduced if the mixture was allowed to stand for 10 days.

In contrast, although the Coulter dispersant cannot persistently prevent V_2O_5 precipitation in the positive electrolyte under high temperature as glycerol could, it can still delay the precipitation. In practice, the continuous use of the vanadium battery electrolyte at above 45 °C generally does not exceed 8 h. Besides, as measured by the T50 automatic potentiometric titrator, the addition of trace amount of Coulter IIIA dispersant does not alter the concentration or valence of vanadium ions in the positive electrolyte. Compared with CTAB, using the same amount of Coulter IIIA dispersant as the additive generated much less gas bubbles in the vanadium electrolyte and eliminated the operating issue of gas formation.

3.2. Amount of additives

In order to study the effect of additive dose on inhibiting precipitation, we added various amounts of Coulter IIIA dispersant to the test solution and measured the inhibition effect. The experimental results are shown in Table 2.

Table 1

Time of precipitate formation for test solutions with different additives at different temperatures.

		Time of precipitate formation						
Additive		None	IA	IB	IC	IIA	IIIA	Glycerol
Testing temperature	45 °C	12.3 h	26.0 h	56.0 h	63.0 h	12.2 h	19.3 days	>30 days
	50 °C	5.2 h	18.0 h	35.0 h	39.0 h	4.8 h	4.8 days	>30 days
	60 °C	1.8 h	3.5 h	5.8 h	6.0 h	1.0 h	30.0 h	>20 days

Table 2

Effect of additive dose on precipitate formation (viscosity and conductivity are measured at 25 °C).

Additive	IIIA								
Additive dose (w/w)	0	0.01	0.02	0.05	0.07	0.1	0.30	0.50	1.00
Precipitation time at 60 °C (h)	1.8	14.3	19.5	27.9	30.0	29.0	39.5	48.5	50.0
Viscosity (mPa s)	6.19	6.47	6.69	7.16	7.24	7.27	7.28	7.35	7.36
Conductivity (ms/cm)	109.4	108.5	108.1	107.2	107.0	106.3	106.0	105.8	105.5

According to Table 2, the precipitation was delayed further when a larger dose of additive was applied. However increasing the additive dose resulted in other problems. Foams were readily generated in the solution when the amount of Coulter IIIA dispersant exceeded 0.3 w/w. Because vanadium battery usually use vacuum pump to transfer solution, the presence of large amounts of foam will stop the pump from working properly. Besides, Table 2 shows that the higher dose of the IIIA dispersant increased the viscosity and reduced the conductivity of the solution. The higher viscosity increases the mass transfer resistance and the kinetic energy loss of the electrolyte circulation pump, and the lower conductivity reduces the charging and discharging capacity of the vanadium battery. After thoroughly considering the effect of IIIA dispersant dose on the electrolyte viscosity, conductivity and inhibition of precipitation, we selected 0.050–0.10 w/w Coulter IIIA dispersant as the additive to the vanadium battery positive electrolyte to prevent or delay the precipitation at high temperatures.

3.3. Cyclic voltammetry of the solution

3.3.1. Effect of the additive on the reversibility of the positive electrolyte

The cyclic voltammetry of the test solution with 0.070 w/w additive was examined to investigate the effect of the additive on the electrochemical properties of the electrolyte.

According to Fig. 1, the cyclic voltammogram of the test solution with IIIA dispersant had identical peak positions and patterns compared with that of the blank solution. The ΔV_p (the difference between the oxidation and reduction peak potential) of the solutions with IA, IB, IC, IIA Coulter dispersant were all larger than that of the blank solution, and the ΔV_p of the solution with glycerol was the largest. It was indicated that the addition of the IIIA dispersant did not appear to affect the reversibility of the electrode process, whereas the other additives reduced the reversibility of the electrode process.

3.3.2. Effect of the additive on the electrolyte cycle stability

Considering its overall impact on inhibition of precipitation, electrolyte conductivity, viscosity, valence, etc., IIIA dispersant is deemed to have superior property than the other additives. We added 0.070 w/w IIIA dispersant to the test solution and carried out 20 cycles of continuous voltammetric scans to investigate the electrolyte cycle stability during multiple cycles. Fig. 2 shows that the peak shape and difference of the oxidation and reduction peak potential remained unchanged as the scans proceeded, indicating that the positive electrolyte with Coulter IIIA dispersant has good cycle stability.

Fig. 3 shows the cyclic voltammograms of 5 continuous scans of the vanadium electrolyte after it had been heated at 50 °C for

50 min. It can be clearly seen that the electrochemical stability of the V(V) solution deteriorated at elevated temperature. Compared with the blank solution, the test solution having 0.070 w/w Coulter IIIA additive showed better cycle stability and basically identical ΔV_p and ΔI_p .

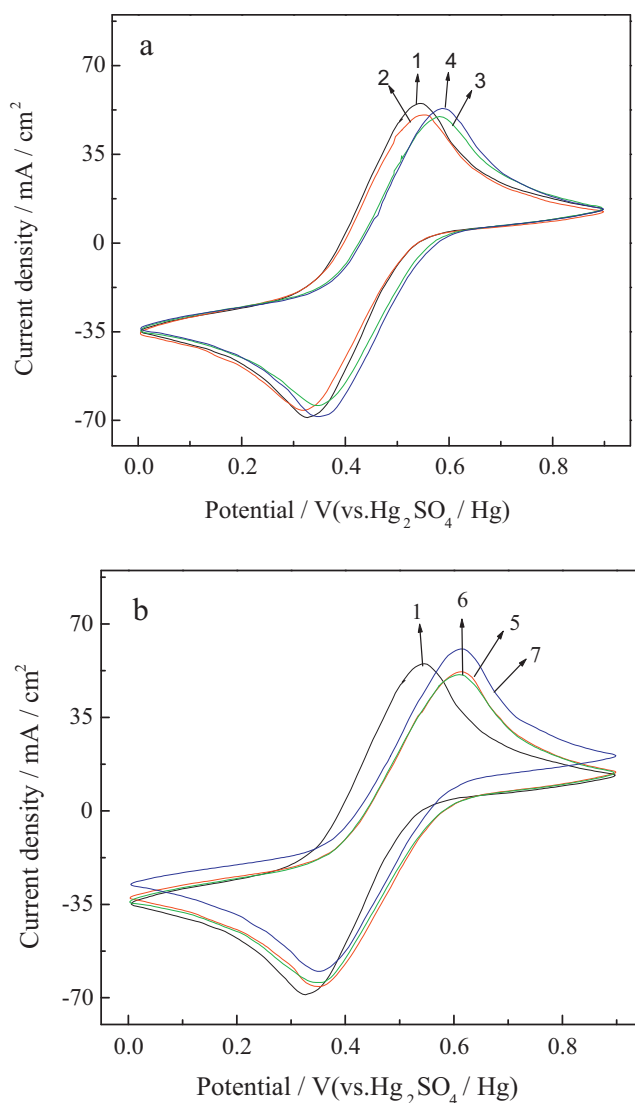


Fig. 1. Cyclic voltammograms of the test solutions with different additives. (1) no additive; (2) IIIA additive; (3) IB additive; (4) IC additive; (5) IA additive; (6) IIA additive and (7) glycerol additive.

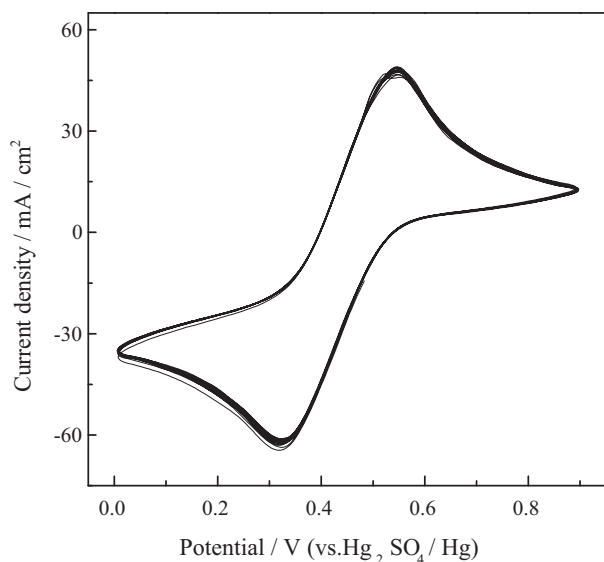


Fig. 2. Cyclic voltammograms (20 scans) of the test solution with 0.070 w/w IIIA.

3.4. Charging and discharging tests

Fig. 4 shows the Coulombic efficiency and the energy efficiency of VRB as a function of cycling number and also compares the VRB cell performance with and without 0.070 w/w Coulter IIIA dispersant in the electrolyte. At room temperature, VRB with additive had somewhat fluctuations in the Coulombic efficiency and the energy efficiency compared with the blank test solution. As the cycles proceeded, VRB with additive showed the same Coulombic efficiency, and the energy efficiency of the VRB with additive was higher. We postulate that it takes some time for the interaction between the additive and the vanadium ions in the test solution to equilibrate, therefore the initial cycles of the VRB with additive showed fluctuations in the Coulombic and energy efficiency. As the cycles proceeded, the vanadium ions and the additive reached dynamic equilibrium and the Coulombic efficiency stayed constant. On the other hand, the additive reduced the possible aggregation of the vanadium ions during cell operation and thus

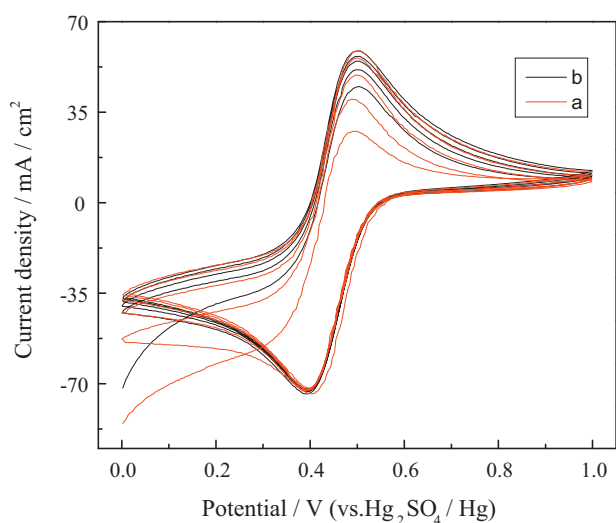


Fig. 3. Cyclic voltammograms of the electrolyte at 50 °C. (a) test solution and (b) test solution with 0.070 w/w Coulter IIIA dispersant. (For interpretation of the references to color in the artwork, the reader is referred to the web version of the article.)

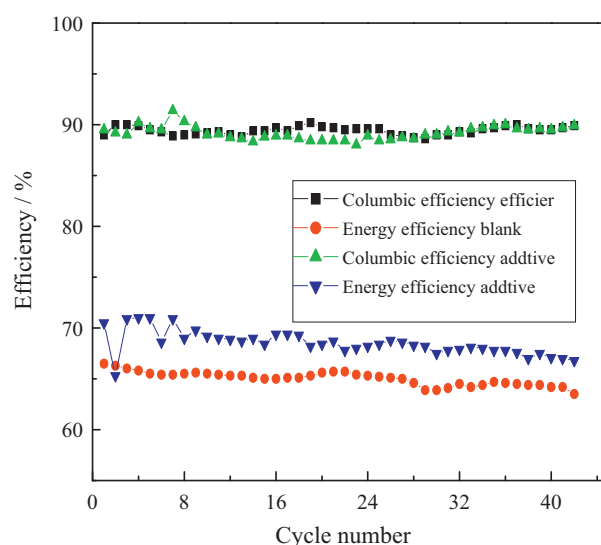


Fig. 4. Charging and discharging tests at 25 °C of the test solution (blank) and the vanadium electrolyte with 0.070 w/w Coulter IIIA dispersant.

increased the energy efficiency. Overall, the cells containing 0.070 w/w Coulter IIIA electrolyte clearly exhibited higher energy efficiency and equal Coulombic efficiency compared with the blank test solution.

3.5. UV-vis spectrometry

Fig. 5 shows the UV-vis spectra of the solutions listed in Section 2.4. According to Fig. 5a, the UV absorbance of the Coulter IIIA dispersant is at $\lambda_{\max} = 200$ nm, and the UV absorbance of solution II is at $\lambda_{\max} = 198$ nm. Upon the addition of the Coulter IIIA dispersant into solution II, no new absorption peak formed and λ_{\max} increased only 1 nm. Further addition of the IIIA dispersant (within 0.05–0.1 w/w) only slightly increased the A_{\max} , but the λ_{\max} remained the same, as can be seen by comparing the spectra of solutions III and IV. The results prove that the Coulter IIIA dispersant interacted with V(V) in a different way compared with the cationic surfactant CTAB micelles. The Coulter IIIA dispersant did not chemically react with the vanadium ions in the electrolyte to form new substances, therefore the addition of trace amount of Coulter IIIA dispersant would not change the electrochemical properties of the VRB positive electrolyte. This agrees with the cyclic voltammetry results in Section 3.3. Furthermore, the UV spectra of solution III at four different times (Fig. 5b) confirm that the Coulter IIIA dispersant and the vanadium electrolyte formed a very stable system. Because no new substance is generated after the addition of the Coulter IIIA dispersant, the concentration of the vanadium ion in the electrolyte remains unchanged and no side reaction is incurred on the electrode.

The stabilization effect of the trace amount of Coulter IIIA dispersant on the VRB positive electrolyte could be due to the intercalation of the macromolecular cyclic compounds in the dispersant in the layered structure of V_2O_5 , which increases the basal distance between the V_2O_5 layers. On the other hand, the cationic surfactant keeps apart the positively charged V(V) ions and their aggregates in the electrolyte. The synergy of Coulombic repulsion and steric hindrance reduces the aggregation of vanadium ions into V_2O_5 and increases the supersaturation of V_2O_5 crystal in the electrolyte. Therefore, the presence of the Coulter IIIA dispersant in the electrolyte may significantly delay the formation of the red precipitate.

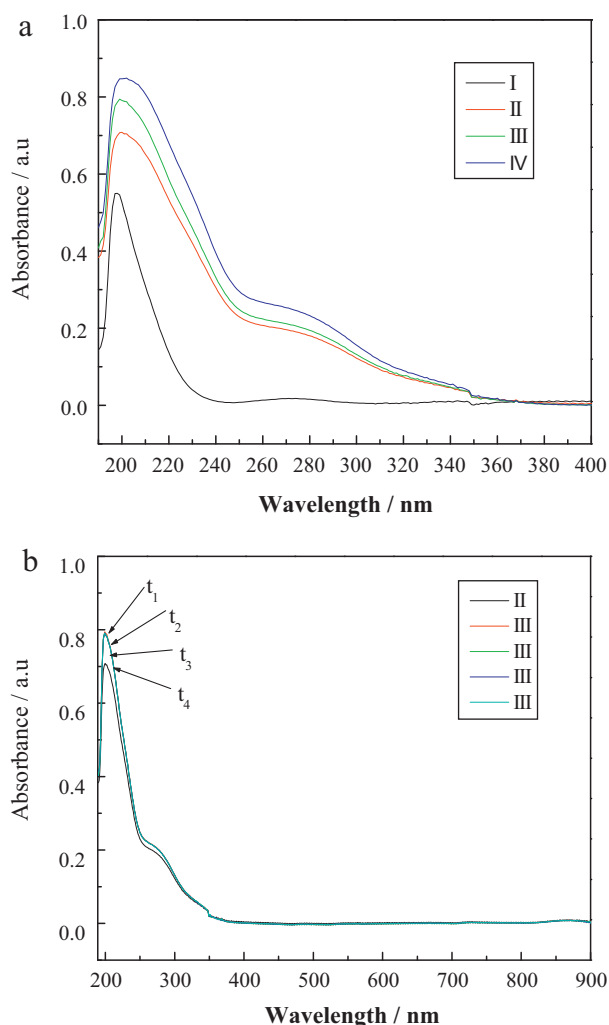


Fig. 5. UV-vis spectra of electrolyte solutions. (a) Spectra of solution I, solution II, solution III and solution IV. (b) Spectra of solution III tested at different times. (For interpretation of the references to color in the artwork, the reader is referred to the web version of the article.)

4. Conclusion

It was found that the addition of 0.05–0.1 w/w Coulter IIIA dispersant can greatly delay the occurrence of precipitation in the VRB

positive electrolyte at 45–60 °C after recharge. The addition of trace amount of the IIIA dispersant does not change the valence and concentration of vanadium, and also does not alter the electrochemical properties of the positive electrolyte. Furthermore, charge and discharge data clearly exhibited higher energy efficiency and equal coulombic efficiency compared with the blank test solution. The Coulter dispersant IIIA can increase the stability of the vanadium battery positive electrolyte because of its cationic surfactant component containing coconut oil amine adduct with 15 ethylene oxide groups. The synergy of coulombic repulsion and steric hindrance reduces the aggregation of vanadium ions into V_2O_5 and increases the supersaturation of V_2O_5 crystal in the electrolyte. Therefore, adding the Coulter IIIA dispersant in the electrolyte can significantly delay the precipitate formation.

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