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ARTICLE

Effect of Polyacrylic Acid on the Thermal Stability and Electrochemical Performance of the Positive Electrolyte for All-Vanadium Redox Flow Battery

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Abstract: Effects of poly acrylic acid (PAA) addition on the thermal stability and electrochemical performance of the V(V) positive electrolyte for all-vanadium redox flow battery (VRFB) were investigated by ex-situ stability tests, UV-Vis spectrometry, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and charge-discharge test. The results indicate that PAA additives can improve the thermal stability of V(V) electrolyte. A small amount of PAA additives have little effect on the electrochemical properties of electrolyte, which only slightly improve electrochemical performance of the positive electrolyte and the energy efficiency of the VRFB at room temperature. Besides, the cell employing the positive electrolyte solution with 3% PAA shows good cycling performance at 50 °C, the charge capacity retention of which is higher than that of the cell without PAA during the cycling.

Key words: vanadium redox flow battery; poly acrylic acid; additive, thermal stability; capacity retention

Since 1985, all vanadium redox flow battery (VRFB) was proposed by Skyllas-Kazacos et al because of its long cycle life, flexible design, fast response time, deep-discharge capability, low cost and environmental friendship in energy storage [1-3]. Vanadium redox couples V(II)/V(III) and V(V)/V(IV) couples in sulfuric acid solution were used as negative and positive electrolytes in the VRFB [4]. The electrolyte solution does not only act as the conductor of the ion but also as the energy-storage medium, which is one of the most important components for VRFB[5].

However, the low solubility and stability of the electrolyte, especially the V(V) electrolyte suffering from thermal precipitation above 40 °C, significantly affect the energy density of VRFB[6,7]. At elevated temperature, V(V) in electrolyte solution forms irreversible V_2O_5 precipitates, which may block the pump, leading to energy loss and the final failure of the battery[6,8,9].

In the past years, several effective methods have been reported on preventing and delaying the precipitate formation in the positive electrolyte solution of VRFB. For example, increasing the concentration of the aqueous sulfuric acid can enhance the thermal stability of V(V)[8]. However, it favors the precipitation of V(II),V(III) and V(IV) ions due to the common ion effect[10,11] and may result in the increasing risk of materials corrosion. The mixed acid as electrolyte solution for VRFB system has also been reported. The electrolyte solution has higher vanadium concentration and wider operating temperature range. However, it requires a high concentration of the mixed acid, which increases the cost of VRFB or may increase the risk of materials corrosion[12,13]. Adding stabilizing agent into electrolyte solution is one of the most economic and effective methods to improve the thermal stability of V(V). Some inorganic and organic materials have been used as stabilizer for VRFB electrolytes[4,14,15]. Several organic additives, such as surfactants, dispersants, or other organic chemicals containing one or more oxygen-containing functional groups. $-NH_2$ or -SH groups can increase the thermal stability of V(V)[16-19], as well as enhance the

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electrochemical properties of the VRFB at normal temperature. But few works about the capacity retention of the VRFB with additives at higher temperature have been reported.

Poly acrylic acid (PAA) containing (–COOH) groups is a commonly used dispersant. In this paper, effect of poly acrylic acid as additive for VRFB positive electrolyte solution was reported, including its effect on the thermal stability, electrochemical performance and battery performance evaluation at higher temperature.

1 Experiment

1.1 Thermal stability experiment of V(V)

The V(IV) electrolyte solutions were prepared by dissolving $VOSO_4$ in 3.0 mol/L H_2SO_4 supporting electrolyte solution. The V(V) electrolyte was prepared by charging the prepared V(IV) electrolyte solutions in a flow cell. The concentration of vanadium ion was analyzed by a redox titration method.

During the thermal stability of V(V) electrolyte tests, V(V) electrolyte solutions with different molar ratios of PAA additives to V(V) were statically stored in a temperature-controlled bath at 50 °C for 20 h. The electrolyte solutions were taken and centrifuged for analyzing the change of the vanadium concentration by redox titration.

1.2 Electrochemical measurements

Cyclic voltammetry (CV) were performed on CHI660 electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) at 10 $mV \cdot s^{-1}$ scan rates in a potential range of 0~1.6 V at room temperature. A three-electrode cell was used with Pt electrode as a counter electrode, a saturated calomel electrode (SCE) as a reference electrode, and a freshly-polished graphite plate with a surface area of 1.0 cm^2 as a working electrode.

The charge-discharge tests were carried out by a lab-scale flow VRFB on a battery test system BTS-5V3A (Shenzhen Neware Electronics Co., China) at room temperature. The cell consisted of two graphite felt electrodes, a nafion 117 ion exchange membrane (DuPont, USA) and conductive plastic parts served as the current collector. The effective reaction area of electrode was about 100 cm^2. 1.8 mol/L V(III)/V(IV) in 3.0 mol/L H_2SO_4 solutions served as negative and positive electrolytes. 70 mL negative and 70 mL positive electrolytes were cyclically pumped into the each half-cell. The single cell was charged and discharged between 0.7 and 1.7 V at a constant current density of 50 $mA \cdot cm^{-2}$. Then the lab-scale static single cells with and without additives were also tested at higher temperature (50 °C) to investigate the capacity decay of the cell.

1.3 Characterizations

UV-Vis spectrometry of V(IV) electrolyte was measured on UV-1200 UV/Vis spectrophotometer (Shanghai, China) in the range of 400~900 nm using 1.0 cm quartz cell. The measured solutions are 0.015 mol/L V(IV) and 3.0 mol/L H_2SO_4 without and with additives, and 3.0 mol/L H_2SO_4 used as the blank solution.

Raman spectroscopy experiments of vanadium species with and without additives were carried out on Renishaw in Via Raman spectrometer system.

X-ray photoelectron spectroscopy (XPS) test was conducted on Escalab 250XI (USA Thermo) to investigate the effect of the additive on the surface of electrode after 50 charging-discharging cycles.

2 Results and Discussion

2.1 Thermal stability of V(V)

Table 1 shows the time of precipitate formation for the 1.89 mol/L V(V) ion in 3 mol/L H_2SO_4 solution with different amounts of PAA additives at 50 °C. It can be found that the formation of precipitation is delayed after adding the additives. Fig.1 displays the results of the thermal stability of sealed the some concentration V(V) ion solution with and without PAA, which was placed in a water bath at 50 °C for 20 h. It can be seen that the concentration of V(V) electrolyte with PAA is higher than that of the electrolyte without PAA after being kept in bath at 50 °C for 20 h, where the precipitation of V_2O_5 is obviously alleviated. The concentration of V(V) ion remains 0.92, 1.04, 1.08, 1.12, 1.15 and 1.23 mol/L with increasing the additive amount of PAA from 0%, 1%, 2%,3%, 4% to 8%, respectively. It indicates that the V(V) electrolyte with the addition of PAA can improve the thermal stability of V(V) solutions. On the whole, although the PAA cannot persistently prevent V_2O_5 precipitation in the positive electrolyte at higher temperature, it can still delay the precipitation. This may be ascribed to the –COOH anionic functional groups in poly acrylic acid which ionise in aqueous system to release negatively charged functional groups and counterions[20-22].

Table 1 Time of precipitate formation for V(V) electrolyte solutions with different additive amounts of PAA at 50 °C

PAA amount/%	0	1	2	3	4	8
Time of precipitate formation/h	<5	<7.5	<8	<9	<9.5	<11

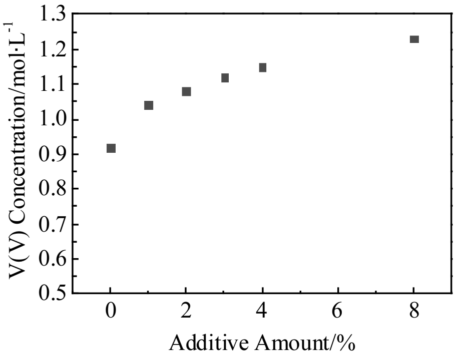
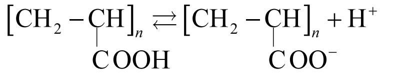
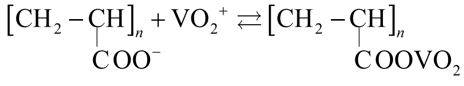


Fig.1 Effect of different amounts of PAA additives on thermal stability of V(V) electrolyte at 50 °C for 20 h

These negatively charged groups and positively charged V(V) ions are attracted by static electricity, which delays and inhibits the formation of precipitation[22]. A plausible thermal stability mechanism is purposed in Eq.(1) and (2).



$$\underset{\text{COOH}}{[\text{CH}_2-\text{CH}]_n} \rightleftarrows \underset{\text{COO}^-}{[\text{CH}_2-\text{CH}]_n} + \text{H}^+ \tag{1}$$



$$\underset{\text{COO}^-}{[\text{CH}_2-\text{CH}]_n} + \text{VO}_2^+ \rightleftarrows \underset{\text{COOVO}_2}{[\text{CH}_2-\text{CH}]_n} \tag{2}$$

2.2 Cyclic voltammetry

Fig.2 shows the cyclic voltammogram behavior of positive electrolyte with different amounts of PAA at a scan rate of 10 mV·s^{-1}. It can be seen that after introduction of PAA (1%~4%), there is no significant change, which indicates that the small amount of PAA (1%~4%) would not too largely change the electrochemical activity and reversibility of V(IV)/V(V). In order to choose a suitable amount of additives, the relevant data of peak current and potential interval of anodic peak and cathodic peak are listed in Table 2. As can be seen, the additive amount increases from 1% to 3%, the peak current increases slightly, which can improve the electro- chemical activity of V(IV)/V(V)[19,23]. The potential gap between oxidization and reduction peaks (ΔE_p) decreases slightly, indicating better electrochemical reversibility[24,25]. This may be ascribed to more oxygen-containing functional groups (-COOH) in the molecules, which are adsorbed on the surface of electrode as active sites for electron transfer[5]; meanwhile, the COOH group plays a more important role on catalyzing the V(IV)/V(V) reaction than –OH[26]. But as the additive amount of PAA further increases, the peak current shows a slight decrease. When PAA amount further increases to 8%, the anodic current drops and ΔE_p increases compared with the blank one. This may be attributed to that the higher dose of additive may damage the hydrated layer of vanadium ion and the adsorption of more molecules of PAA on the surface of vanadium ions, and enlarges their sizes which thus hinders the mass transport[22]. Therefore, combining with the previous thermal stability of V(V) experiment, 3% is a suitable additive amount for the positive electrolyte.

Table 2 Relevant data obtained from CV of 1.2 mol/L V(IV) electrolyte with different amounts of PAA additives at the scan rate of 10 mV·s^{-1}

PAA amount/%	Anodic peak, $I_{pa}/\times10^{-2}$ A	Cathodic peak, $I_{pc}/\times10^{-2}$ A	ΔE_p/V	I_{pa}/I_{pc}
Blank	3.84	2.42	0.39	1.59
1	3.97	2.50	0.32	1.58
2	4.07	2.56	0.27	1.58
3	4.20	2.68	0.26	1.56
4	4.10	2.56	0.30	1.60
8	3.76	2.49	0.46	1.51

2.3 UV-vis spectra of V(IV) electrolyte

Fig.3 shows the UV-vis spectra for V(IV) electrolyte with and without 3% PAA. The V(IV) electrolyte with and without additives are 0.015 mol/L V(IV) in 3 mol/L H_2SO_4. It is reported that the highest absorption peak of UV-Vis for pristine V(IV) appears at about 770 nm [27,28]. As can be seen, compared with the blank one, there is no new absorption peak and wavelength shift appears in electrolyte samples with the 3% PAA, where the two curves are almost coincident. The results show that PAA could not form new substances with the vanadium ions in the electrolyte and change the effective concentration of V(IV).

2.4 Raman spectrometry

Fig.4 shows the Raman spectra for V(V) electrolyte with and without 3% PAA. All the peaks fit well with previous literature reported on the Raman spectra of vanadium oxides in sulfate solution system[29], band frequencies and assignments of V(V)-sulfate species. Besides, it can be seen that the Raman spectra of electrolyte with PAA show similar features to that of the blank one, indicating that there is no new chemical bonds. Therefore the chemical bonding state of

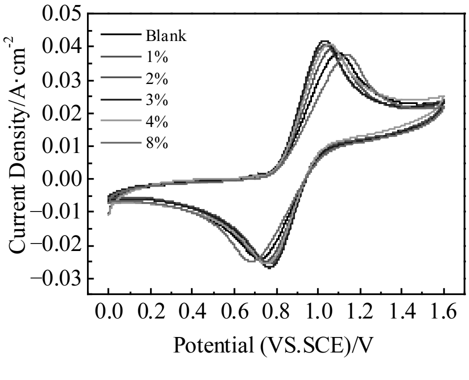


Fig.2 CV curves of 1.2 mol/L V(IV) electrolyte with different amounts of PAA additives at the scan rate of 10 mV·s^{-1}

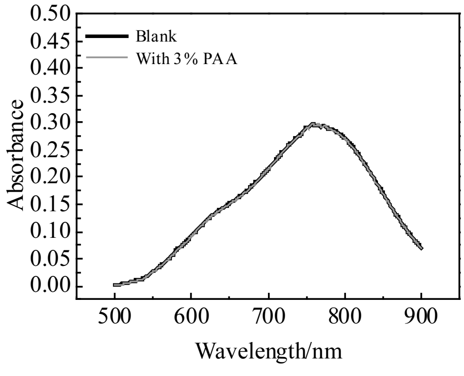


Fig.3 UV-vis spectra of V(IV) electrolyte solution with and without PAA

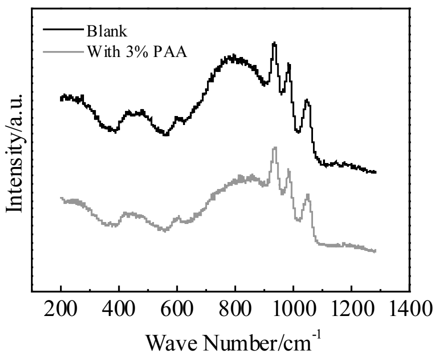


Fig.4 Raman spectra of V(V) electrolyte with and without PAA

the V(V) ion remain unchanged after introduction of a small amount of PAA.

2.5 Cell tests

The charge-discharge experiments were performed in a single dynamic cell at the current density of 50 mA·cm^{-2}. Fig.5 shows the discharging capacity of the cells in 50 cycles. As observed, the discharging capacity of two cells shows a decreasing trend with the increase of cycle number, but the discharging capacity decay rate of the cell with adding 3% PAA in electrolytes is slower and the capacity is nearly always slightly higher than that of blank cell. After 50 cycles, the discharge capacity retention of the cell with 3% PAA is 77.87%, 3.72% higher than that of blank cell, implying a better cycling stability of cell with PAA. During the charge/discharge cycling, one of the main reasons for the capacity fading of the cell is the imbalanced vanadium active species caused by cross-contamination through the membrane. The higher discharge capacity of the cell with PAA may be ascribed to the adsorption of PAA on the electrode, providing more active sites.

The efficiency of the cells in 50 cycles are compared in Fig.6. It can be known from Fig.6 that the coulombic efficiency of both the cells is almost the same with increasing of cycle number, which is as high as over 94%. The average energy efficiency of the cell with PAA is 69.91%, 1.35% higher than that of the blank cell.

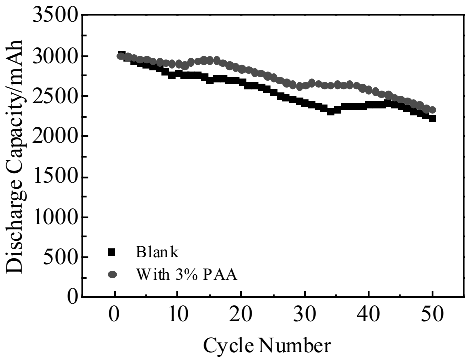


Fig.5 Discharge capacity of the cells using positive electrolyte with and without 3% PAA at a current density of 50 mA·cm^{-2}

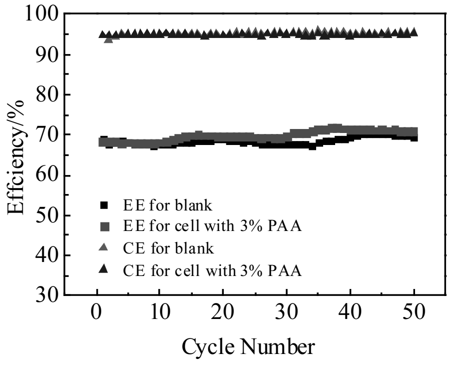


Fig.6 Efficiency of the cells using positive electrolyte with and without 3% PAA at a current density of 50 mA·cm^{-2}

Moreover, Fig.7 shows the 50th charge-discharge curves of cells using positive electrolyte with and without 3% PAA. The cell with 3% PAA exhibits a smaller charge–discharge plateau interval than the cell without PAA, suggesting better electrochemical activity and kinetic reversibility, which is consistent with the CV results.

2.6 X-ray photoelectron spectroscopy

Fig.8 shows the XPS spectra of the graphite felt used in cells after 50 charge-discharge cycles to investigate the effect of PAA on the surface of electrode. It can be seen that the O1s signal in 3% PAA cell is much stronger than that in the pristine cell. XPS measurements show that the binding energy for carbon and oxygen are centered on 285, 532 eV, the content of oxygen increases from 12.57% to 22.61%. It indicates that using the electrolyte with PAA can increase oxygen-containing functional groups on the surface of graphite felt.

2.7 Capacity decay test at higher temperature

In order to investigate the cycling stability of the positive

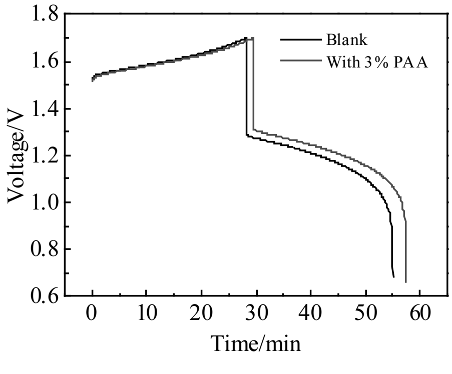


Fig.7 50th charge-discharge curves of the cells using positive electrolyte with and without 3% PAA at a current density of 50 mA·cm^{-2}

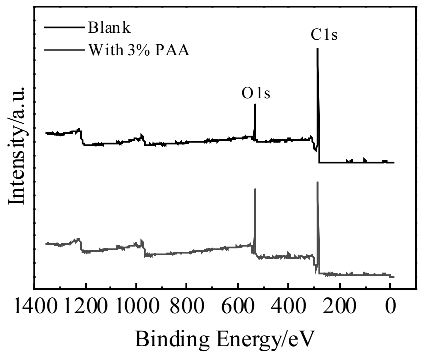


Fig.8 XPS spectra of graphite felt in blank and 3% PAA cells tests after 50 charge-discharge cycles

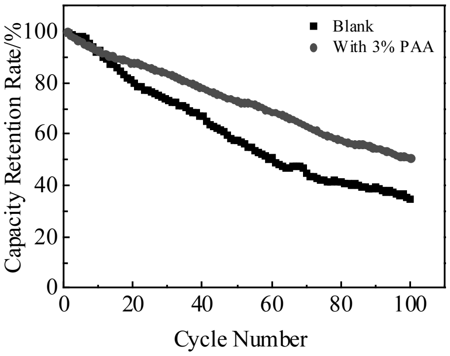


Fig.10 Charge capacity retention rate of the cells using positive electrolyte with and without 3% PAA at 50 °C

electrolyte at a higher temperature, the charge-discharge experiments were performed in the lab-scale static single cells at the current density of 30 mA·cm^{-2}. The charge-discharge curves of single cell at the different cycles are shown in Fig.9. It can be seen that a single charge and discharge time of the two cells is reduced with the increase of cycle number, because of capacity fading during charge/discharge cycling, but the VRFB with 3% PAA has a lower charge voltage plateau and a higher discharge voltage plateau than the blank cell, and this phenomenon is more and more obvious with the increase of cycle number, suggesting better electrochemical activity and cycling stability at higher temperature.

Fig.10 shows the charge capacity losses of the cells operating at 50 °C. In addition to the crossover of vanadium ions across the membrane[4], the precipitation of vanadium active species at relatively higher temperature is also the main reason for capacity fading during charge/discharge cycling. It can be seen that both of cells show a decreasing trend in charge capacity with the increase of cycle number, but charge capacity retention of the cell with 3% PAA is higher than that of the blank cell. The charge capacity retention of the cell with 3% PAA after 100 cycles is 58.81%, 23.76% higher than that of the blank cell. The result of thermal stability experiments indicate that PAA can improve the thermal stability of V(V) electrolyte. Therefore, this is also the reason for the improvement of charge capacity retention of the cell with PAA at 50 °C. On the whole, the cell with 3% PAA exhibits better performance compared with the blank one, especially at higher temperatures.

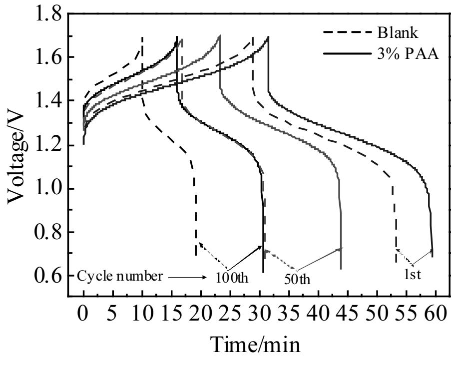


Fig.9 Charge-discharge curves of the cells with and without 3% PAA at 50 °C at different cycle number

3 Conclusions

1) A small amount of PAA can delay the precipitating time of V(V) electrolyte without altering the chemical bonding state of V(V) species.

2) A small amount of PAA has little effect on the electrochemical properties of electrolyte, which only slightly improve the electrochemical performance of the positive electrolyte, and 3% is a suitable addition amount.

3) The long-term cycling stability of the V(V) electrolyte with 3% PAA is demonstrated by the charge capacity retention of the cell, which is 58.81% after 100 cycles, 23.76% higher than that of the blank cell at 50 °C.

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聚丙烯酸对钒电池正极热稳定性和电化学性能的影响

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摘　要：通过原位热稳定性试验、紫外-可见光谱、拉曼光谱、X 射线光电子能谱(XPS)、循环伏安法和充/放电试验，研究了聚丙烯酸(PAA)对全钒氧化还原流电池(VRFB)正极电解液的热稳定性和电化学性能的影响。结果表明，PAA 添加剂可以提高 V(V)电解液的热稳定性。在室温条件下，少量的 PAA 添加剂对电解液电化学性能影响不大，仅能轻微地提高正极电解液的电化学性能和 VRFB 的能量效率。此外，以 PAA 添加量为 3%的正极电解液组装电池，该电池在 50 ℃时表现出良好的充/放电循环性能，其充电容量保持率高于没有添加 PAA 的电池。

关键词：钒氧化还原流电池；聚丙烯酸；添加剂；热稳定性；容量保持率

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