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Journal of Energy Chemistry 23(2014)73–81

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journal-of-energy-chemistry/2095-4956
www.elsevier.com/locate/jngc

Study on stabilities and electrochemical behavior of V(V) electrolyte with acid additives for vanadium redox flow battery

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[Manuscript received July 18, 2013; revised September 17, 2013]

Abstract

Several acid compounds have been employed as additives of the V(V) electrolyte for vanadium redox flow battery (VRB) to improve its stability and electrochemical activity. Stability of the V(V) electrolyte with and without additives was investigated with ex-situ heating/cooling treatment at a wide temperature range of −5 °C to 60 °C. It was observed that methanesulfonic acid, boric acid, hydrochloric acid, trifluoroacetic acid, polyacrylic acid, oxalic acid, methacrylic acid and phosphotungstic acid could improve the stability of the V(V) electrolyte at a certain range of temperature. Their electrochemical behaviors in the V(V) electrolyte were further studied by cyclic voltammetry (CV), steady state polarization and electrochemical impedance spectroscopy (EIS). The results showed that the electrochemical activity, including the reversibility of electrode reaction, the diffusivity of V(V) species, the polarization resistance and the flexibility of charge transfer for the V(V) electrolyte with these additives were all improved compared with the pristine solution.

Key words

vanadium redox flow battery; V(V) electrolyte; acid additives; stability; electrochemical behavior

1. Introduction

A redox flow battery system, which has been paid much attention in recent years, is an efficient large-scale Electrical Energy Storage (EES) approach that was originally conceived by NASA during the energy crises of the 1970s [1]. All-vanadium redox flow battery (VRB), pioneered by M. Skyllas-Kazacos group at UNSW in Australia [2], has been considered as one of the most promising redox flow battery technologies for large-scale EES. The VRB overcomes inherent problem of cross contamination by diffusion of different redox ions across the membrane faced by all other redox flow batteries. By employing the V(V)/V(IV) and V(III)/V(II) redox couples in H_2SO_4 as the positive and negative half-cell electrolytes respectively, the capacity and power output of VRB are dependent on the volume and concentration of the electrolytes [3,4]. However, the low energy density of the vanadium sulphate electrolyte due to the low solubility and stability of the active vanadium species at elevated temperature, especially for V(V) species in the electrolyte of the VRB limits its use to stationary systems [5]. V(V) species exist in a relatively stable hydrated penta co-ordinated structure of $[VO_2(H_2O)_3]^+$ in H_2SO_4 at low temperatures. When the temperature increases, the structure will deprotonate and produce a neutral structure of $VO(OH)_3$ (1), which will ultimately lead to the formation of the crystallization of V_2O_5 (2) [6].

$$2[VO_2(H_2O)_3]^+ - 2H^+ \longrightarrow 2VO(OH)_3 + 2H_2O \tag{1}$$

$$2VO(OH)_3 \longrightarrow V_2O_5 + 3H_2O \tag{2}$$

The rate and extent of the precipitation in V(V) solutions were found to be mainly controlled by the solution temperature, the vanadium concentration, the sulfuric acid concentration, and the state of charge (SOC) of the electrolytes [7,8]. In the past years, great effort has been made to increase the stability of V(V) species in H_2SO_4, aimed at developing high concentration, stable vanadium electrolytes for VRB systems [9−22]. It was found that the stability of V(V)

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This work was supported by the Doctoral Program of Higher Education (No. 20110181110003), the Collaborative innovation fund by China Academy of Engineering Physics and Sichuan University (No. XTCX2011001) and the Sichuan Provincial Department of Science and Technology R&D Program (No. 2013FZ0034).

doi: 10.1016/S2095-4956(14)60120-0

electrolyte can be improved by increasing the concentration of H_2SO_4, decreasing the concentration of V(V) species to below 1.8 M and adjusting the temperature from 10 °C to 40 °C. But high concentration of H_2SO_4 favors the precipitation of V(II), V(III) and V(IV) species [23], the concentration below 1.8 mol/L would greatly decrease the energy density of VRB [3], and the temperature controlled from 10 °C to 40 °C would limit the practical applications of VRB [24]. Adding stabilizing agents into electrolyte is thought to be one of the most economic and effective methods for preventing and delaying the precipitate formation [25]. Compounds containing –OH groups with ring or chain structures [16−18,21,22], surfactants such as Coulter dispersants [19] and cetyltrimethylammonium bromide (CTAB) [20], acid compounds such as polyacrylic acid and its mixture with methanesulfonic acid [15,26], were reported as potential stabilizing agents for V(V) electrolyte, which could encapsulate the hydrated penta coordinated vanadate ion and inhibit the precipitation formation [10]. Recently, researchers of Pacific Northwest National Laboratories in the USA reported [27,28] a high energy density electrolyte for VRB using a 2.7 M vanadium electrolyte in a mixture of sulphuric acid and hydrochloric acid, which had not only shown energy efficiency as high as 87%, but also no precipitation was observed at 0 °C and 50 °C over 20 days, indicating that acid compounds as supported electrolytes can significantly improve the stability of vanadium electrolyte. However, there has been very little research on acid compounds as additives of vanadium electrolyte with much less amount than the supported one [15].

Based on this fact, several acid compounds were chosen and added into the V(V) electrolyte in order to find a potential acid stabilizing agent. Corresponding effects on stability at different temperature and electrochemical behavior were studied and compared with the pristine solution.

2. Experimental

2.1. Preparation of V(V)

V(IV) electrolyte solutions were prepared by electrolytic dissolution of V_2O_5 (AR grade) in 3.0 mol/L H_2SO_4 supporting electrolyte and then the V(V) electrolyte solutions were obtained by charging the prepared V(IV) electrolyte solutions both in a two-compartment electrolysis cell [16,17,19]. The total acidity concentration was adjusted to 5.0 mol/L using appropriate amounts of 98 wt% H_2SO_4 and deionized water. The resulting solution was analyzed by redox titration to determine the valence and concentration of vanadium ions. In order to ensure the error of the above redox titration less than 3%, preliminary experiments were started from a V(V) solution of reagent V_2O_5.

2.2. Thermal stability experiment of V(V)

The tests were carried out in sealed glass tubes at a temperature range of −5 °C to 60 °C in a temperature-controlled bath for 30 days. To investigate the additive effect on high concentration V(V) anolyte (3.0 mol/L V(V)/5.0 mol/L H_2SO_4), a certain amount of additives were added into the glass tubes with electrolyte solutions before starting the stability tests. All the stability tests were carried out statically (i.e., without any agitation). During the test, each sample was visually monitored and recorded more than twice a day for slight precipitation of V_2O_5 and solution color change. At the end of the 30-day test period, the solutions were filtered and the 'equilibrium' vanadium ion concentration was determined by redox titrator analysis again.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) tests and steady polarization study of 3.0 mol/L V(V)/5.0 mol/L H_2SO_4 electrolyte solutions with and without additives were performed using CHI 600B electrochemical workstation (Shanghai Chenhua Instrument, China) in a temperature-controlled bath at −5 °C, 25 °C and 45 °C. The curves of current versus potential were recorded in a 3-electrode electrochemical cell using graphite electrode as the working electrode (surface area of 3.14 mm^2), saturated mercurous sulfate electrode as the reference electrode, and platinum electrode as the counter electrode. Prior to test, the working electrode was manually polished with 0.3 and 0.5 μm α-Al_2O_3 power and then washed by ultrasonic cleaning in ethanol and distilled water for 5 min, respectively. Electrochemical impedance spectroscopy (EIS) was conducted by a Solartron 1287 electrochemical workstation (Solartron Metrology, UK) at room temperature. The sinusoidal excitation voltage applied to the cells was 5 mV with a frequency range between 0.01 Hz and 100 kHz.

3. Results and discussion

3.1. Effect of additives on stability of V(V)

Additive plays an important role in the thermal stability of vanadium electrolyte solutions. Several acid additives (0.5 wt%) were selected to investigate the additive effect on thermal stability of 3.0 mol/L V(V)/5.0 mol/L H_2SO_4 solution at a wide temperature range of −5 °C to 60 °C. As shown in Table 1, the stability of V(V) solution without additives decreased greatly when the temperature increased from −5 °C to 60 °C due to the endothermic nature of the precipitation reaction of V(V) ions (3) [7]:

$$2VO_2^+ + H_2O \longrightarrow V_2O_5 + 2H^+ \quad \Delta H > 0 \tag{3}$$

The change of the stability with temperature could be related to the formation of different V(V) ions-containing species at different temperatures [15]. Compared with the results of the pristine test, most of the studied acid additives improved the stability of V(V) solution at a wide temperature from −5 °C to 45 °C. For example, the pristine sample (without additives) suffered from precipitation within less than 20 days from −5 °C to 30 °C. After methanesulfonic acid (CH_3SO_3H) or boric acid (H_3BO_3) addition, V(V) solution was stable without any precipitation in 30 days from $-5\,^\circ C$ to $30\,^\circ C$, indicating that CH_3SO_3H and H_3BO_3 could improve the stability of V(V) solution significantly. Other additives, such as hydrochloric acid (HCl), trifluoroacetic acid (CF_3SO_3H), polyacrylic acid (PAA), oxalic acid(($(COOH)_2$), methacrylic acid (MAA), phosphotungstic acid (PTA), tungstosilicic acid (TSA), 5-sulfosalicylic acid dehydrate (SHA) could also improve the stability of V(V) solution significantly from $-5\,^\circ C$ to $45\,^\circ C$ compared with the pristine solution.

At the same time, the concentrations of V(V) solution with and without acid additives were monitored after 30 days at $-5\,^\circ C$, $10\,^\circ C$ and $30\,^\circ C$, respectively. As listed in Table 1, the concentrations of all the V(V) solution were observed decreasing with the increasing temperature, which was consistent with the stability tests above. The concentration of V(V) solution could be remained at a certain degree through adding acid additives. For example, the concentration of test sample with H_3BO_3 remained 2.8 mol/L, which was 0.4 mol/L higher than the pristine one at $30\,^\circ C$. It was found that the concentration of V(V) solution with most of the studied additives remained more than 2.0 M, which would be helpful to increase the energy capacity over current sulfate system of VRB [3]. However, poor stability and the precipitation reaction suffered in a short time for most of the V(V) solution were observed at a high temperature ($60\,^\circ C$), probably due to the acceleration of endothermic process for a high concentration of V(V) solution in Equation (3).

Table 1. Effect of different acid additives (0.5 wt%) on the stability of 3.0 mol/L V(V)/5 mol/L H_2SO_4 electrolyte solution at different temperatures

Additives	−5 °C		10 °C		30 °C		*t* (h)	
	t (d)[a]	*c* (mol/L)[b]	*t* (d)[a]	*c* (mol/L)[b]	*t* (d)[a]	*c* (mol/L)[b]	45 °C	60 °C
HCl	>30	3.0	>30	2.9	>30	2.8	23	1
HBr	>30	2.3	>30	2.2	>30	1.9	24	1
HF	10	2.9	9	2.6	8	2.5	14	1
H_3PO_4	precipitation at once							
HNO_3	18	2.9	15	2.7	13	2.5	8	1
H_3BO_3	>30	3.0	>30	2.9	>30	2.8	33	2
HCOOH	18	2.9	16	2.8	15	2.7	8	1
CH_3COOH	20	3.0	14	2.8	13	2.7	7	1
$(COOH)_2$	>30	2.9	>30	2.7	>30	2.6	30	20
CH_3SO_3H	>30	3.0	>30	2.9	>30	2.8	23	2
CF_3SO_3H	>30	3.0	>30	2.9	>30	2.8	24	1
Methacrylic acid (MAA)	>30	2.9	>30	2.6	>30	2.4	18	2
Citric acid	>30	2.2	>30	1.9	>30	1.7	>30 d	>30 d
5-Sulfosalicylic acidehydrate (SHA)	>30	2.8	>30	2.6	>30	2.5	34	15
Ethylenediaminetetraacetic acid (EDTA)	>30	2.3	>30	1.9	>30	1.8	4 d	24
Polyacrylic acid (PAA)	>30	2.9	>30	2.8	>30	2.7	25	1
Phosphotungstic acid (PTA)	>30	3.0	>30	2.8	>30	2.7	22	1
Tungstosilicic acid (TSA)	>30	3.0	>30	2.9	>30	2.8	24	1
Pristine	17	2.8	13	2.6	9	2.4	6	1

[a] Time to precipitation; [b] Concentration of V(V) after 30 days

The improved stability and remained higher concentration of V(V) solution through adding additives at a certain temperature may be interpreted from that the additives could facilitate dispersion of the hydrated form of V(V) ions for the synergy of coulombic repulsion and steric hindrance [6,19,21,22]. Herein, the increased stability was probably due to the presence of more H^+ ions (increased ratio of H^+ ions to V(V) ions) which favors the following reaction in the forward direction (4) [7]:

$$V_2O_5(c) + 2H^+ \longrightarrow 2VO_2^+ + H_2O \tag{4}$$

The formation of soluble neutral species with hydrated co-ordinated vanadate ion and anion groups of acid compounds, such as $VO_2Cl(H_2O)_2$ [28] could also improve the stability of V(V) solution (5).

$$[VO_2(H_2O)_3]^+ + HCl \rightarrow VO_2Cl(H_2O)_2 + [H_3O]^+ \quad \Delta H > 0 \tag{5}$$

Moreover, the strong oxidation V(V) solution is likely to be reduced to V(IV) due to the slight reduction of some additives, thus becoming V(V)/V(IV) mixed solution, which would change SOC of the electrolyte and finally improve the stability of V(V) solution [7,15,19]. But the stability of V(V) solution is improved at the cost of energy capacity in this case. For example, citric acid, ethylenediaminetetraacetic acid (EDTA) and hydrobromic acid (HBr) as additives could improve the stability of V(V) solution at a high temperature but maintain a low concentration of V(V) solution (less than 2.0 mol/L) due to their strong reduction. Furthermore, V(V) solution with phosphoric acid (H_3PO_4) at different temperatures suffered precipitation at once due to the formation of $VOPO_4{\cdot}H_2O$, which was consistent with early report [15]. Hydrofluoric acid (HF), nitric acid (HNO_3), formic acid (HCOOH), acetic acid (CH_3COOH) were found could not significantly improve the stability of V(V) solution, which may be due to the formation of insoluble neutral species between their anion groups and hydrated co-ordinated vanadate ion.

So more factors such as anion species, quantity, structure, reduction, solubility, safety and price of acid compounds should be considered and controlled when acid additives are selected to improve the stability of V(V) solution in practical application.

3.2. Cyclic voltammetry

As seen in Figure 1, CV curves of the test solutions with and without additives had identical peak positions and patterns, which were similar to each other in peak shape at 25 °C and exhibited evidently only one couple of redox peaks. However, the reversibility of V(V)/V(IV) redox couple with acid additives was changed in three aspects. Firstly, the separation between the oxidation and reduction peak potentials (ΔV_p), and the ratios of oxidation peak current to reduction peak current (I_{pO}/I_{pR}) of the solutions with acid additives were both changed compared with those of the pristine solution. Most of the acid additives could decrease ΔV_p and make I_{pO}/I_{pR} close to one, which improved the reversibility of V(V)/V(IV) redox couple at a certain extent. Secondly, the increasing oxidation and reduction peak currents were observed when most of the acid additives were added into the test solution, which indicated the improvement of electrode reaction kinetics [17,29].

Finally, further study on the reversibility of V(V)/V(IV) redox couple with additives was carried out through monitoring ΔV_p, I_{pO}/I_{pR} and peak currents at a lower (−5 °C) and higher temperature (45 °C), respectively. As shown in Table 2, the CV tests of ΔV_p, I_{pO}/I_{pR} and peak currents at −5 °C and 45 °C showed similar results with 25 °C.

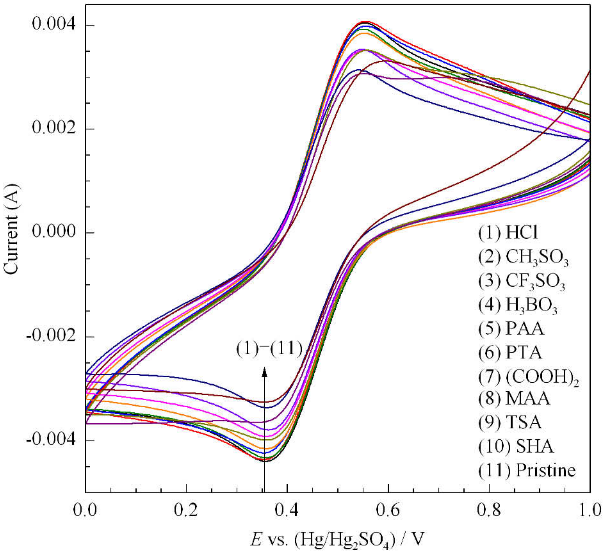

Figure 1. CV curves of the electrolyte (3.0 mol/L V (V) /5.0 mol/L H_2SO_4) with 0.5 wt% different acid additives on graphite electrode at 25 °C at a scan rate of 50 mV·s^{-1}

Table 2. CV curves data of the electrolyte (3.0 mol/L V(V)/5.0 mol/L H_2SO_4) with 0.5 wt% various additives at different temperatures on graphite electrode

Additives	−5 °C		20 °C		45 °C	
	ΔV_p (V)	I_{pO}/I_{pR}	ΔV_p (V)	I_{pO}/I_{pR}	ΔV_p (V)	I_{pO}/I_{pR}
TSA	0.53	0.96	0.23	0.85	0.23	0.96
SHA	0.41	0.95	0.23	0.93	0.23	1.04
MAA	0.27	0.97	0.19	0.94	0.20	1.00
PTA	0.24	0.97	0.20	0.94	0.20	0.98
$(COOH)_2$	0.23	0.99	0.20	0.95	0.20	1.01
PAA	0.20	0.97	0.21	0.95	0.20	1.01
H_3BO_3	0.26	0.97	0.20	0.94	0.20	0.98
CF_3SO_3H	0.24	0.98	0.19	0.94	0.20	0.98
CH_3SO_3H	0.28	1.00	0.20	0.93	0.20	0.97
HCl	0.28	0.98	0.19	0.96	0.20	1.01
Pristine	0.28	0.97	0.20	0.93	0.22	0.97

Compared with the results of the pristine test, most of the studied acid additives could improve the electrode reaction kinetics and the reversibility of V(V)/V(IV) redox couple at different temperatures. Taking the test solutions with 0.5 wt% CH_3SO_3H and H_3BO_3 for example, ΔV_p values were reduced, I_{pO}/I_{pR} values were closer to one and the peak currents were increased at a certain temperature comparing with the pristine test solution. Their peak currents were also found to increase with the increase of temperature due to the improvement of electrode reaction kinetics (Figure 2).

In addition, the cyclic stability of V(V) solutions with different acid additives was tested by continuous CV scans for 50 cycles at a scan of 50 mV·s^{-1} at a graphite electrode at −5 °C and 45 °C, respectively. It was found that almost no variation was observed on the peak shape and peak potential separation, suggesting that V(V) electrolyte with 0.5 wt% CH_3SO_3H (Figure 3a) and H_3BO_3 (Figure 3b) at −5 °C and 45 °C both had good cycling stability. The results indicated that the reversibility and cyclic stability of the test solutions with CH_3SO_3H and H_3BO_3 addition was improved. Similar results were also found in the test solutions with HCl, CF_3SO_3H, $(COOH)_2$, PAA, MAA and PTA addition. Each of these acid additives above (except HCl) contains more stable –OH groups, which are not easily oxidized by V(V) species, so they can complex with V(V)/V(IV) ions in the solution and provide available –OH groups for the ion-exchange between

V(V)/V(IV) ions and –OH groups on electrode surface, leading to high oxidation and reduction peak currents and the improvement of the electrochemical reversibility and cyclic stability of V(V)/V(IV) redox couple [16−18]. HCl could improve the electrochemical activity of V(V)/V(IV) redox couple as other acid additives, probably due to the formation of soluble neutral species $VO_2Cl(H_2O)_2$ in Equation (5). While SHA and TSA decreased the electrochemical activity of V(V)/V(IV) redox couple and brought a worse outcome of ΔV_p, I_{pO}/I_{pR} and peak currents compared with the pristine sample. This unsatisfactory result may be due to that SHA and TSA would produce new stable neutral complexes after interacting with V(V) species, which would decrease the activity of V(V) species and hinder the transfer of charge, causing a higher electrolyte resistance and charge transfer resistance of V(V) solution.

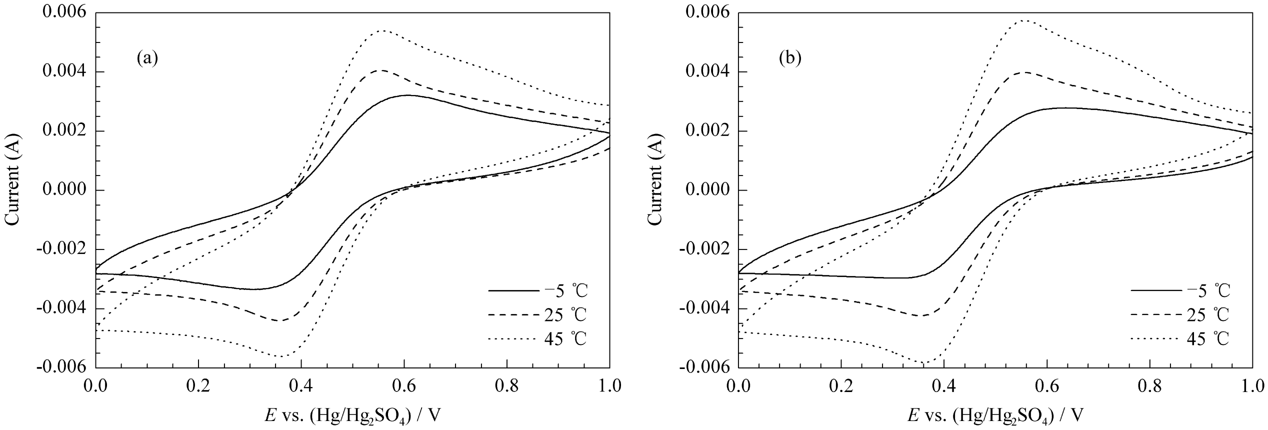

Figure 2. CV curves of the electrolyte (3.0 mol/L V(V) /5.0 mol/L H_2SO_4) with 0.5 wt% CH_3SO_3H (a) and 0.5 wt% H_3BO_3 (b) on graphite electrode at different temperatures at a scan rates of 50 mV·s^{-1}

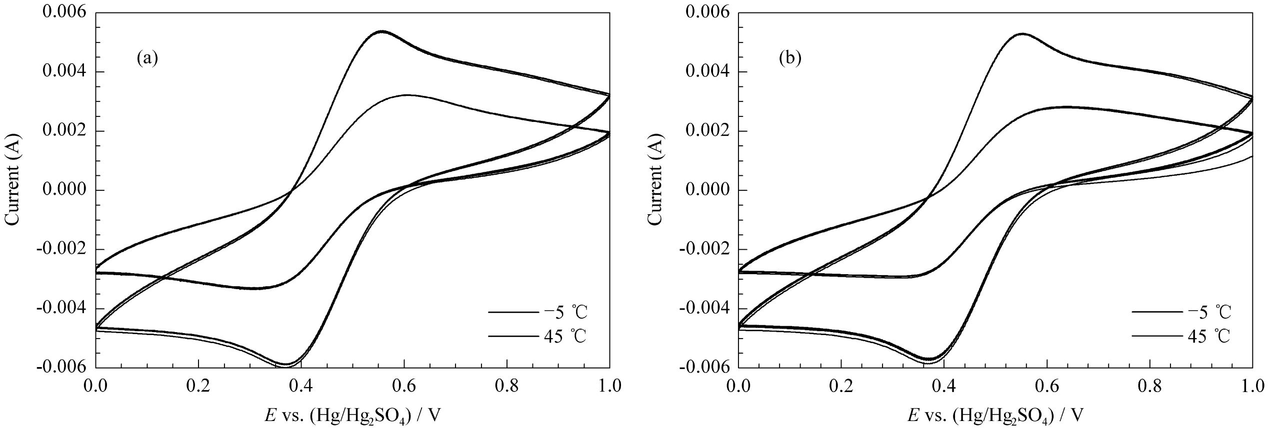

Figure 3. CV curves (50 cycles) of the electrolyte (3.0 mol/L V(V) /5.0 mol/L H_2SO_4) with 0.5 wt% CH_3SO_3H (a) and 0.5 wt% H_3BO_3 (b) on graphite electrode at −5 °C and 45 °C at a scan rate of 50 mV·s^{-1}

In order to further investigate the effect of additives on the kinetics of electrode reaction, a series of CV curves for test solutions containing (3.0 mol/L V(V)/5.0 mol/L H_2SO_4) with 0.5 wt% CH_3SO_3H and H_3BO_3 on the graphite electrode at various scan rates were shown in Figure 4(a) and 4(c). It presented the typical characteristics of a quasi-reversible one-electron process for the oxidation and reduction peak potentials change gradually with the scanning rates. A plot of redox peak currents as a linear function of the square root of scan rates with 0.5 wt% CH_3SO_3H and H_3BO_3 addition (Figure 4b and 4d) further verified the quasi-reversible process for V(V)/V(IV) redox reaction.

Theoretically, the value of diffusion coefficient for a quasi-reversible reaction (D) is between that for a reversible (D_1) one and an irreversible (D_2) one [29]. For a reversible and irreversible one-step and one-electron reaction, the peak current i_p is given in Equations (6) and (7), respectively [30]: For a reversible reaction:

$$i_p = 0.4463(F^3/RT)^{1/2}ACD_1^{1/2}u^{1/2} \tag{6}$$

For an irreversible reaction:

$$i_p = 0.4958(F^3/RT)^{1/2}\alpha^{1/2}ACD_2^{1/2}u^{1/2} \tag{7}$$

where, F is the Faraday constant, R is the universal gas constant, T is the Kelvin temperature, A is the surface area of

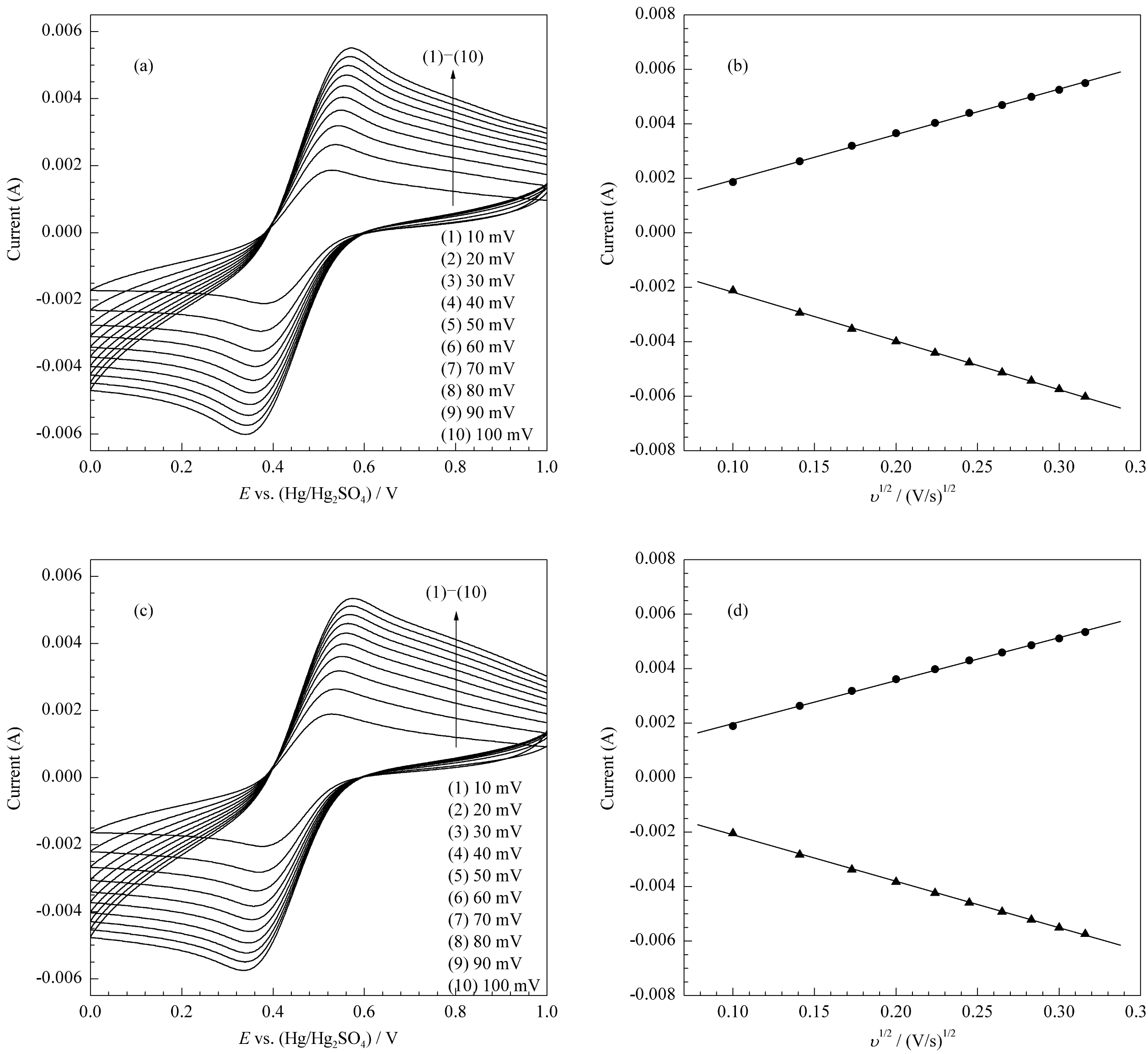

Figure 4. CV curves of the electrolyte (3.0 mol/L V(V) /5.0 mol/L H_2SO_4) with 0.5 wt% CH_3SO_3H (a) and 0.5 wt% H_3BO_3 (c) on graphite electrode at room temperature at different scan rates. (b) and (d) Corresponding relationship of oxidation and reduction peak current as a function of the square root of scan rate

working electrode, C is the bulk concentration of primary reactant, D_1 and D_2 refer to the diffusion coefficient for a reversible reaction and an irreversible reaction, respectively. u is the scanning rate, α refers to the transfer coefficient for a reversible reaction.

For a one-step and one-electron reaction at different temperatures, similar Equations of the peak current $i_{\rm p}$ can be deduced base on Equations (6) and (7). For example, when $T = 25$ °C, Equations (6) and (7) can be transformed as follows:

$$i_{\rm p} = 2.69 \times 10^5 ACD_1^{1/2} u^{1/2} \tag{8}$$

$$i_{\rm p} = 2.99 \times 10^5 \alpha^{1/2} ACD_2^{1/2} u^{1/2} \tag{9}$$

Based on the known experimental conditions, Equations (8) and (9) can be further transformed as follows:

$$i_{\rm p} = 25.34 D_1^{1/2} u^{1/2} = ku^{1/2} \tag{10}$$

$$i_{\rm p} = 28.17 D_2^{1/2} u^{1/2} = ku^{1/2} \tag{11}$$

It is found that k refers to the slope of the line in point of the linear Equations (9) and (10), where the variables are the current peak $i_{\rm p}$ and the square root of scan rate $u^{1/2}$. k can be determined by the linear regression. D_1 and D_2 can be calculated by the following Equations:

$$D_1 = 1.56 \times 10^{-3} k^2 \tag{12}$$

$$D_2 = 1.26 \times 10^{-3} k^2 \tag{13}$$

According to Equations (12) and (13), it is observed that the diffusion coefficient D increases with the increasing slope k, which refers to the enhanced diffusivity of primary reactant. For a reversible redox couple, such as V(V)/V(IV), similar process of derivation and calculation above about the diffusion coefficient D at different temperatures can be reused.

Herein, the slope k was fitted and obtained according to the oxidation peak current i_p. The diffusion coefficient D_1 and D_2 of V(V) species with different additives at different temperatures were listed in Table 3. It was observed that the diffusion coefficient D (D_1 to D_2) increased with the increase of temperature, affected the electrode reaction diffusion kinetics of V(V) specie and intensified the processes of mass transfer and charge transfer for V(V)/V(IV) redox couple. Moreover, the diffusion coefficients of the test solutions with most of additives were increased at a certain temperature compared with the pristine test solution, indicating that additives could improve the diffusion of V(V) species on the electrode. As a result, corresponding reaction activity was improved. For example, the diffusion coefficient of V(V) species with 0.5 wt% CH_3SO_3H and H_3BO_3 addition was increased from 2.30×10^{-7}–2.85×10^{-7} $cm^2\cdot s^{-1}$(pristine) to 3.51×10^{-7}–4.34×10^{-7} $cm^2\cdot s^{-1}$ and 3.27×10^{-7}–4.06×10^{-7} $cm^2\cdot s^{-1}$ at 25 °C, respectively. Similar results were also observed for V(V) species with additives of 0.5 wt% HCl, CF_3SO_3H, PAA and $(COOH)_2$, PTA and MAA. While V(V) species with additives of 0.5 wt% SHA and TSA had a lower diffusion coefficient at a certain temperature compared with the pristine solution. The results were consistent with the studies of stability and CV.

Table 3. Effect of several additives (0.5 wt%) on the diffusion coefficient D_1 ($\times10^{-7}cm^2\cdot s^{-1}$) and D_2 ($\times10^{-7}cm^2\cdot s^{-1}$) of V(V) species at different temperatures

Additives	−5 °C		25 °C		45 °C	
	D_1	D_2	D_1	D_2	D_1	D_2
TSA	1.17	1.08	1.90	1.53	7.25	5.86
SHA	1.38	1.11	2.82	2.28	7.78	6.30
MAA	1.51	1.22	2.89	2.34	8.08	6.53
PTA	1.65	1.34	3.20	2.58	8.19	6.62
$(COOH)_2$	1.70	1.37	3.89	3.11	9.44	7.63
PAA	1.80	1.46	3.99	3.23	9.56	7.73
H_3BO_3	2.10	1.70	4.06	3.27	9.62	7.78
CF_3SO_3	2.22	1.80	4.20	3.39	9.68	7.83
CH_3SO_3	2.78	2.25	4.34	3.51	9.72	7.86
HCl	2.98	2.40	4.59	3.70	10.4	8.44
Pristine	1.42	1.15	2.85	2.30	7.83	6.31

3.3. Steady state polarization

The steady polarization curves for V(V) solution with different acid additives were employed to determine the polarization resistance, exchange current density and electrochemical reaction rate constant. In relatively low overvoltage area, current density and overvoltage should yield an approximate straight line. Polarization resistance could be calculated by the slope of the line and other parameters such as exchange current density and electrochemical reaction rate constant could be calculated as follows [17]:

$$R_p = \frac{\eta}{i_0},\ i_0 = \frac{RT}{nFR_p},\ k_0 = \frac{i_0}{nFC_0} \tag{14}$$

where, i_0 is the exchange current density, R is the universal gas constant, T is the Kelvin temperature, n is the number of electrons transferred in the reaction, F is the Faraday constant, R_p is the polarization resistance, k_0 is rate constant, and C_0 is the solution concentration. The steady polarization curves for 3.0 mol/L V(V)/5.0 mol/L H_2SO_4 with different acid additives on the graphite electrode were shown in Figure 5 and corresponding parameters containing polarization resistance, exchange current density and electrochemical reaction rate constant obtained from Equation (14) were summarized in Table 4. It was found that the polarization resistance decreased and the exchange current density and electrochemical reaction rate constant increased for V(V) solution with most of the selected acid additives except SHA and TSA compared with the pristine solution. For example, the polarization resistance of V(V) solution with additives of 0.5 wt% CH_3SO_3H and H_3BO_3 decreased from 6.535 $\Omega\cdot cm^2$ (pristine) to 5.281 $\Omega\cdot cm^2$ and 5.431 $\Omega\cdot cm^2$ at 25 °C, respectively. Meantime, the exchange current density of V(V) solution with additives of 0.5 wt% CH_3SO_3H and H_3BO_3 increased from 3.931 $mA\cdot cm^{-2}$ (pristine) to 4.864 $mA\cdot cm^{-2}$ and 4.730 $mA\cdot cm^{-2}$, and electrochemical reaction rate constant increased from 1.358×10^{-5} $cm\cdot s^{-1}$ (pristine) to 1.680×10^{-5} $cm\cdot s^{-1}$ and 1.634×10^{-5} $cm\cdot s^{-1}$ at 25 °C, respectively. Similar results were also found for V(V) species with additives of 0.5 wt% HCl, CF_3SO_3H, PAA, $(COOH)_2$, PTA and MAA, which were consistent with the study of stability, CV and diffusion coefficient. The V(V) solution with these acid additives had a faster kinetic process on the graphite electrode probably due to the improved diffusion and oxidation ability of V(V) species [17].

Table 4. Kinetic parameters by way of steady polarization for 3.0 mol/L V(V)/5.0 mol/L H_2SO_4 solution with different acid additives (0.5 wt%) on graphite electrode at different temperatures

Additives	−5 °C			25 °C			45 °C		
	R_p ($\Omega\cdot cm^2$)	i_0 ($mA\cdot cm^{-2}$)	k_0 ($10^{-5}cm\cdot s^{-1}$)	R_p ($\Omega\cdot cm^2$)	i_0 ($mA\cdot cm^{-2}$)	k_0 ($10^{-5}cm\cdot s^{-1}$)	R_p ($\Omega\cdot cm^2$)	i_0 ($mA\cdot cm^{-2}$)	k_0 ($10^{-5}cm\cdot s^{-1}$)
TSA	8.402	2.750	0.9499	6.925	3.709	1.281	4.248	6.453	2.229
SHA	8.139	2.839	0.9807	6.636	3.871	1.337	4.128	6.640	2.294
MAA	7.642	3.023	1.044	6.343	4.050	1.399	3.831	7.155	2.472
PTA	7.559	3.056	1.056	6.228	4.124	1.425	3.747	7.315	2.527
$(COOH)_2$	7.035	3.284	1.134	5.624	4.567	1.578	3.420	8.015	2.769
PAA	6.887	3.355	1.159	5.579	4.604	1.590	3.335	8.219	2.839
H_3BO_3	6.792	3.401	1.175	5.431	4.730	1.634	3.249	8.437	2.914
CF_3SO_3	6.650	3.474	1.200	5.349	4.802	1.659	3.194	8.582	2.964
CH_3SO_3	6.537	3.534	1.221	5.281	4.864	1.680	3.120	8.785	3.035
HCl	6.446	3.584	1.209	5.190	4.949	1.709	3.003	9.128	3.153
Pristine	8.082	2.859	0.9876	6.535	3.931	1.358	3.912	7.007	2.420

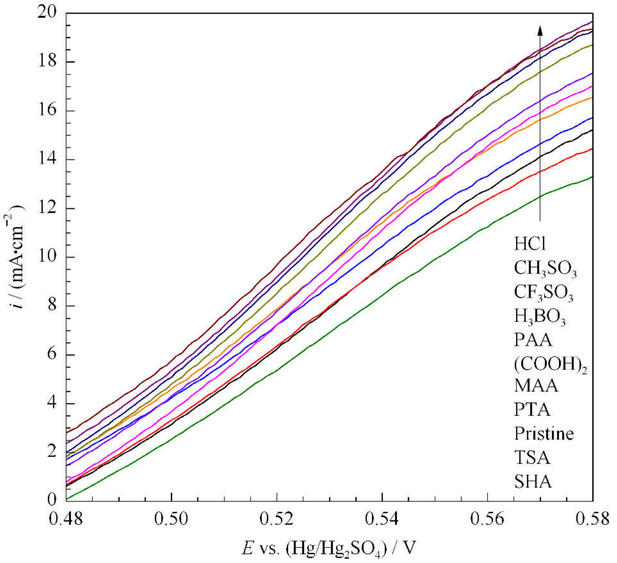

Figure 5. Steady polarization curves for 3.0 mol/L V(V) /5.0 mol/L H_2SO_4 solution with 0.5 wt% different acid additives on graphite electrode at a scan rate of 1 mV·s^{-1}

3.4. Electrochemical impedance spectroscopy

In order to analyze the electrode reaction diffusion kinetics of V(V) specie and the processes of mass transfer and charge transfer for V(V)/V(IV) redox couple, electrochemical impedance spectra were used to record Nyquist plots of the electrolytes with and without additives at 25 °C. As shown in Figure 6, each plot consisted of a semicircle in the high frequency region and a sloped line in the low frequency region, indicating that the redox reaction of V(V)/V(IV) couple was simultaneously controlled by the charge transfer process at high frequency and the diffusion process at low frequency. Consequently, the Nyquist plots could be fitted with the equivalent circuit of Figure 6. In the equivalent circuit, R_1 stands for the resistance composed of solution resistance, electrode resistance and the contact resistance. R_2 and W represent the charge transfer resistance and Warburg diffusion impedance in the electrochemical process, respectively. CPE is the constant phase element, which represents the electric double-layer capacitance of the electrode/solution interface [16,17].

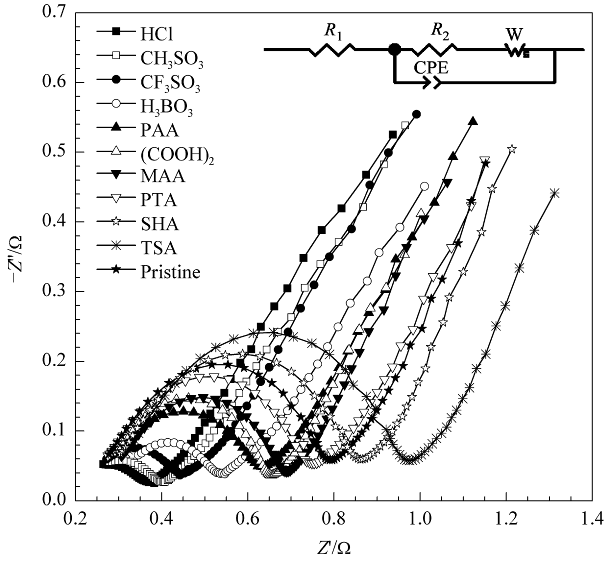

Figure 6. Nyquist spectra of electrochemical impedance spectra of the electrolytes with and without acid additives at 25 °C

The simulation results obtained by Zsimpwin software from fitting the impedance plots with the equivalent circuit model in Figure 6 were shown in Table 5. It was observed that there were significant differences in R_1 and R_2 for each sample and the electrolytes with most of acid additives exhibited a lower electrolyte resistance and charge transfer resistance than the pristine one, which indicated that the transfer of V(V) species and electron was more feasible after adding additives [16,17]. Taking V(V) solution with 0.5 wt% H_3BO_3 for example, R_1 and R_2 of V(V) species were decreased from 0.2772 Ω·cm^2 (pristine) to 0.2492 Ω·cm^2 and 0.5324 Ω·cm^2 (pristine) to 0.3240 Ω·cm^2, respectively. Moreover, the parameter $Y_{0,1}$ for the electrolyte was increased from 1.852×10^{-3} S·s^{-n}·cm^{-2} (pristine) to 2.605×10^{-3} S·s^{-n}·cm^{-2}, indicating the enhancement of electric double-layer capacitance of the electrode/electrolyte interface [16−18]. Meantime, the admittance of Warburg diffusion impedance $Y_{0,2}$ was increased from 1.691 S·s^{-5}·cm^{-2} (pristine) to 2.092 S·s^{-n}·cm^{-2} and exhibited a lower diffusion impedance. Similar results were also observed for V(V) species with additives of 0.5 wt% HCl, CF_3SO_3H, PAA, $(COOH)_2$, PTA and MAA. But higher electrolyte

Table 5. Parameters resulting from fitting the impedance plots with the equivalent circuit model in Figure 6

Additives (0.5 wt%)	R_1 (Ω·cm^2)	CPE (S·s^{-n}·cm^{-2})		R_2 (Ω·cm^2)	$W, Y_{0,2}$ (S·s^{-5}·cm^{-2})
		$Y_{0,1}$	n		
TSA	0.2910	8.453×10^{-4}	0.8579	0.6659	1.396
SHA	0.2797	1.641×10^{-3}	0.9488	0.5624	1.562
MAA	0.2726	1.949×10^{-3}	0.9666	0.5012	1.960
PTA	0.2676	2.171×10^{-3}	0.9669	0.3971	1.974
$(COOH)_2$	0.2583	2.179×10^{-3}	0.9774	0.3948	2.027
PAA	0.2497	2.397×10^{-3}	0.9879	0.3810	2.077
H_3BO_3	0.2492	2.605×10^{-3}	0.9910	0.3240	2.092
CF_3SO_3	0.2487	2.695×10^{-3}	0.9956	0.1731	2.162
CH_3SO_3	0.2450	2.876×10^{-3}	1	0.1299	2.358
HCl	0.2385	3.005×10^{-3}	1	0.1133	2.418
Pristine	0.2772	1.852×10^{-3}	0.9597	0.5324	1.691

resistance R_1 and charge transfer resistance R_2 for V(V) solution with 0.5 wt% SHA were found increased from 0.2772 $\Omega\cdot\text{cm}^2$ (pristine) to 2.797 $\Omega\cdot\text{cm}^2$ of R_1 and from 0.5324 $\Omega\cdot\text{cm}^2$ (pristine) to 0.5624 $\Omega\cdot\text{cm}^2$ of R_2, while for V(V) solution with 0.5 wt% TSA it was increased from 0.2772 $\Omega\cdot\text{cm}^2$ (pristine) to 2.910 $\Omega\cdot\text{cm}^2$ of R_1 and from 0.5324 $\Omega\cdot\text{cm}^2$ (pristine) to 0.6659 $\Omega\cdot\text{cm}^2$ of R_2, respectively. These results were consistent with the studies of stability, CV, diffusion coefficient and steady polarization.

4. Conclusions

The stability and electrochemical behavior of V(V) electrolyte with and without acid additives were studied and compared. The results showed that methanesulfonic acid, boric acid hydrochloric acid, trifluoroacetic acid, polyacrylic acid, oxalic acid, methacrylic acid and phosphotungstic acid could improve the thermal stability of V(V) electrolyte from −5 °C to 45 °C. And the concentration of V(V) solution with these acid additives remained more than 2.0 mol/L after 30 days, which would be helpful to increase the energy capacity of VRB. In addition, the electrochemical activities, including the reversibility of electrode reaction, the diffusivity, the polarization resistance and the flexibility of charge transfer for V(V) electrolyte with these acid additives were improved compared with the pristine solution. Through further optimizing the quantity of addition and the range of temperature, these acid additives can be used as promising stabilizing agents for V(V) electrolyte in practical application.

Acknowledgements

This work was financially supported by the Specialized Research Fund for the Doctoral Program of Higher Education (20110181110003), the Chengdu Natural Science Foundation (10GGYB380GX-023, 10GGYB828GX-023) and the Collaborative Innovation Funding by China Academy of Engineering Physics and Sichuan University (XTCX2011001).

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