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ORIGINAL PAPER

Effects of additives on the stability of electrolytes for all-vanadium redox flow batteries

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Abstract The stability of the electrolytes for all-vanadium redox flow battery was investigated with ex-situ heating/cooling treatment and in situ flow-battery testing methods. The effects of inorganic and organic additives have been studied. The additives containing the ions of potassium, phosphate, and polyphosphate are not suitable stabilizing agents because of their reactions with V(V) ions, forming precipitates of $KVSO_6$ or $VOPO_4$. Of the chemicals studied, polyacrylic acid and its mixture with CH_3SO_3H are the most promising stabilizing candidates which can stabilize all the four vanadium ions (V^{2+}, V^{3+}, VO^{2+}, and VO_2^{+}) in electrolyte solutions up to 1.8 M. However, further effort is needed to obtain a stable electrolyte solution with >1.8 M V^{5+} at temperatures higher than 40 °C.

Keywords All vanadium redox flow batteries · Electrolyte stability · Stabilizing agent · Vanadium ions · Energy storage

1 Introduction

All-vanadium redox flow batteries (VRBs) employ the redox couples of V(II)/V(III) and V(IV)/V(V) in sulfuric acid solutions as anolyte and catholyte, eliminating the cross contamination effect of different electrolyte solutions. In recent years, VRBs have been widely studied for large-scale energy storage because of their significant advantages over other energy storage systems, such as high energy efficiency (>75%), deep discharge ability, fast response, low self-discharge, long cycle life and most importantly, independent power and energy ratings [1–4]. Systems up to multi-MW/MWh have been demonstrated [5]. However, VRBs still face some challenges in meeting performance and cost requirements for broad market penetration. The current electrolytes demonstrate a low energy density ($\sim$25 Wh kg^{-1}), which is mainly limited by the low solubility (<2 M) of vanadium species in sulfuric acid. While the energy density may not be critically required for the stationary applications, increasing the concentration of vanadium can reduce the initial capital investment and the operation cost.

The limited vanadium solubility is due to precipitation of solid vanadium oxides at above 40 °C in V(V) solutions or below 10 °C in V(II), V(III), and V(IV) solutions [6–8]. At the elevated temperatures, $[VO_2(H_2O)_3]^+$ cations lose H_2O and H^+ to form $V_2O_5{\cdot}xH_2O$ precipitation through the following inter-cation condensation reaction [9].

$$[VO_2(H_2O)_3]_2SO_4 \rightarrow V_2O_5 + H_2SO_4 + 5H_2O \quad (1)$$

In the past years, there has been great effort to increase the stability of vanadium species in sulfuric acid solutions, aimed at developing high concentration, stable vanadium electrolytes for VRB systems [6–8, 10–12]. The rate and extent of precipitation in the V(V) solutions were found to

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be largely controlled by the solution temperature, the vanadium concentration, the sulfuric acid concentration, and the state-of-charge (SOC) of the electrolytes [6, 11]. For example, the V(V) concentration could be increased up to 3 M without any precipitation at 40 °C when a sulfuric acid concentration higher than 5 M [8]. A solution of 5.4 M V(V)/7.0 M SO_4^{2-} was achieved without any precipitation at 50 °C over the 2-month test period [8]. However, increasing the sulfuric acid causes a decrease in the solubility of vanadyl sulfate ($VOSO_4$) [13], resulting in the precipitation of V(IV) solution at low temperatures (<10 °C). Nonetheless the stability of V(IV) solution at low temperatures can be improved by adding stabilizing agents [7, 10, 12]. Up to 4 M $VOSO_4$ were dissolved and stable in 3 M H_2SO_4 at 4 °C by adding 3 wt% sodium hexametaphosphate (SHMP), 2–5 wt% K_2SO_4, or 5 wt% urea [7]. This is a significant improvement over the 1.6 M solubility in 3 M H_2SO4 at 10 °C. These additives behaved as stabilizing agents and retarded the process of precipitation of V(IV) solution by being adsorbed on the surface of the nuclei and reducing the rate of crystal growth [7]. However, the effects of stabilizing agents on the stabilities of V(IV) and V(V) must be considered together as the redox couples co-exist in the positive electrolyte during flow cell operations. Furthermore, the stabilizing agents must meet the requirements for all the V(II), V(III), V(IV), and V(V) species at the same time because of the inevitable transport of the additives across the membrane.

To date, most of the work reported in the literature focused on the stability of the positive electrolyte (V^{4+} and V^{5+}-containing solutions), there has been limited study on the stability of negative electrolyte (V^{2+} and V^{3+}-containing solutions). As thus we have investigated the stability of V(II), V(III), V(IV), and V(V) solutions in the temperature range of −5 to 50 °C. The effects of some inorganic and organic stabilizing agents on the stabilities of vanadium ions in sulfuric acid solutions were also evaluated. This paper reports details of the work.

2 Experimental

The V(IV) electrolyte solutions were prepared by dissolving $VOSO_4 \cdot xH_2O$ in sulfuric acid solutions. The electrolyte solutions containing V(II), V(III), and V(V) cations were prepared electrochemically by charging the V(IV) solutions in a flow cell. The stability tests were carried out at a temperature range of −5 to 50 °C in a temperature-controlled bath. For the additive effect study, a certain amount of additives was added into the 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 monitored twice a day for precipitation and for solution color change. After filtration and dryness in air, some precipitation samples were analyzed using X-ray diffraction (XRD) for phase identification.

Flow cell cyclic performance of stabilized electrolytes was evaluated at ambient temperature using an in-house designed flow cell system. The system included a single cell, two peristaltic pumps, and two electrolyte reservoirs. The anolyte and catholyte flow rates were 20 mL min^{-1}. Two graphite felts (10 cm^2 each) were employed as the positive and the negative electrodes. A Nafion® 117 membrane was used as the electrolyte separator. The flow cell was cycled between 1.7 and 0.8 V at 50 mA cm^{-2} using a multichannel potentiostat (BT2000, Arbin instruments, TX, USA). The details of the single cell are described in a previous publication [14].

3 Results and discussion

3.1 Stabilities of vanadium ions in sulfuric acid solutions

The concentration of vanadium ions plays an important role on the stability of vanadium electrolyte solutions [6, 7, 11, 13]. In this work, the effects of vanadium concentration on the stability of an electrolyte were studied at −5 °C for the solutions of V(II), V(III), and V(IV) and at 40 °C for the solution of V(V). This is because the solutions of V(II), V(III), and V(IV) are not stable at low temperatures, and the V(V) solution is not stable at high temperatures (≥40 °C) [6, 7]. As listed in Table 1, for all the vanadium species, the stability of solutions decreased as the vanadium concentration increased. For example, the solution with

Table 1 Effect of vanadium concentration on the stabilities of electrolyte solutions

V species	Temperature (°C)	Concentration (M)		Time to precipitation
		V	SO_4^{2-}	
V(II)	−5	1.5	5.0	Stable (>90 days)
		2.0	5.0	419 h
V(III)	−5	1.5	5.0	Stable (>90 days)
		1.8	5.1	1608 h
		2.0	5.0	634 h
V(IV)	−5	1.5	5.0	Stable (>90 days)
		1.8	5.1	288 h
		2.0	5.0	18 h
V(V)	40	1.5	5.1	Stable (>90 days)
		1.8	5.1	357 h
		2.0	5.0	<95 h
		2.3	6.0	34 h

1.5 M V(V) ions was stable over 3 months, but precipitates were observed within 357 h when the V(V) concentration increased to 1.8 M. 2.0 and 2.3 M V(V) solutions suffered from precipitation in 95 and 34 h, respectively. A higher V(V) (exists in the form of a $[VO_2(H_2O)_3]^+$) concentration moves reaction (1) forward, leading to the formation of V_2O_5, whose solubility is very low in sulfuric acid solution. The same trend was also observed for the solutions of V(II), V(III), and V(IV) at −5 °C. Table 1 also shows that the vanadium electrolytes are stable (without any precipitation in 3 months) with a vanadium concentration of 1.5 M for all the V(II), V(III), V(IV), and V(V) species in the temperature range of −5 to 40 °C. This is consistent with the reported results for the positive electrolyte [7, 11].

The temperature influences the stability of vanadium electrolyte solutions significantly. As listed in Table 2, the stability of the V(IV) solution was improved by increasing the temperature, but the stability of the V(V) solution decreased with the temperature increase. For example, with the concentrations of 2 M V(IV)/5 M SO_4^{2-}, the V(IV) solution suffered from precipitation within 18 and 95 h at −5 and 23 °C, respectively. The V(IV) solution was stable at 40 °C without any precipitation in 33 days, indicating that the increasing temperature improves the stability of the V(IV) solution. The improved stability could be attributed to an increase in the solubility of $VOSO_4$ at higher temperatures [13]. The same trend was found for the V(II) and V(III) solutions (not shown here). On the contrary, with the same concentrations of V(V) and SO_4^{2-}, the stability of the V(V) solution decreased greatly when the temperature increased from −5 to 50 °C. For example, the solutions were stable, and no precipitates were found in the tests over 30 days at −5 and 23 °C. Precipitation occurred after 95 h at 40 °C. And precipitates were formed in even less than 18 h at 50 °C. The results indicate that the stability of the V(V) solution decreases with the increase of temperature. This trend is in accordance with an early report. [6] The change of the stability with temperature could be related to the formation of different V^{5+}-containing species at different temperatures. The mechanism of stability change and the transformation between different V^{5+}-containing species with temperature were studied using ^{51}V Nuclear Magnetic Resonance (NMR) and Density Functional Theory (DFT) modeling in our previous work [9]. The ^{51}V NMR results showed that the chemical shift of ^{51}V moves toward the positive direction with a temperature increase, and this change was not recoverable by cooling the electrolyte solution, indicating the irreversible change in molecular structure of V(V) in H_2SO_4 solution. DFT modeling results indicated that V(V) exists in a relatively stable structure of $[VO_2(H_2O)_3]^+$ at low temperatures, which will deprotonate with a temperature increase and produce a neutral structure of $VO(OH)_3$. Then the $VO(OH)_3$ will ultimately lead to the formation of the crystallization of V_2O_5 according to reaction (2) [9]:

Table 2 Temperature effect on the stability of V(IV) and V(V) solution with 2 M V/5 M total sulfate

V species	Temperature (°C)	Time to precipitation
V^{4+}	−5	18 h
	23	95 h
	40	Stable (>33 days)
V^{5+}	−5	Stable (>33 days)
	23	Stable (>33 days)
	40	<95 h
	50	<18 h

$$2VO(OH)_3 \rightarrow V_2O_5 + 3H_2O \qquad (2)$$

To improve the stability of vanadium electrolyte solutions with a high vanadium concentration and to increase the energy density of VRBs, some additives have been employed to stabilize the vanadium solutions [7, 10, 12, 15, 16]. In this work, a number of inorganic and organic chemicals were selected as stabilizing agents, and their effects on the stability of solutions were investigated.

3.2 Effects of inorganic additives on the stability of electrolyte solutions

Table 3 lists effects of the selected additives on the stability of the vanadium sulfate electrolyte solutions. The stability of 2 M V(IV)/5 M SO_4^{2-} was improved by adding 3 wt% K_2SO_4 at −5 °C. This positive effect of K_2SO_4 on the stability of V(IV) solution is consistent with an early

Table 3 Effect of inorganic additives on the stability of 2 M V/5 M total sulfate solution

V species	Temperature (°C)	Additives	Time to precipitation
V^{3+}	−5	Blank	634 h
		3 wt% Na_3PO_4	30 days
V^{4+}	−5	Blank	18 h
		3 wt% K_2SO_4	11 days
		3 wt% Na_2SO_4	42 h
		3 wt% Na_3PO_4	30 days
V^{5+}	−5 to 23	Blank	Stable (>12 days)
	40	Blank	<95 h
	−5 to 40	3 wt% K_2SO_4	18 h
	−5	3 wt% Na_2SO_4	11 days
	23	3 wt% Na_2SO_4	Stable (>12 days)
	40	3 wt% Na_2SO_4	70 h
	40	3 wt% $Al_2(SO_4)_3$	120 h
	−5 to 40	3 wt% Na_3PO_4	Stable (>33 days)

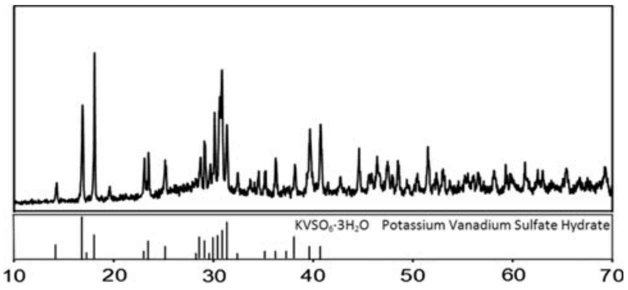


Fig. 1 XRD patterns of precipitates formed in the electrolyte solutions of 2 M V(V)/5 M SO_4^{2-}/3 wt% K_2SO_4 at the temperature of −5 °C

study [7]. However, addition of K_2SO_4 promoted precipitation of V(V) solution (18 h with 3 wt% K_2SO_4) vs. 95 h without additive). The same phenomena were observed in the whole temperature window from −5 to 40 °C, indicating that the precipitation reaction of the V(V) solution is insensitive to temperature. The precipitates formed in the solutions of 2 M V(V)/5 M SO_4^{2-} with 3 wt% K_2SO_4 additives were identified as potassium vanadium sulfate hydrate ($KVSO_6{\cdot}3H_2O$) by XRD (Fig. 1). Thus, the negative effect can be interpreted that the K^+ reacted with V(V) and SO_4^{2-}, producing the solid particles of $KVSO_6{\cdot}3H_2O$, whose solubility is very low in sulfuric acid solution. The results suggest that the solutions of V(V)/SO_4^{2-} are sensitive to K^+. Any additives containing K^+ are not suitable as stabilizing agents in the electrolytes for all-vanadium flow batteries.

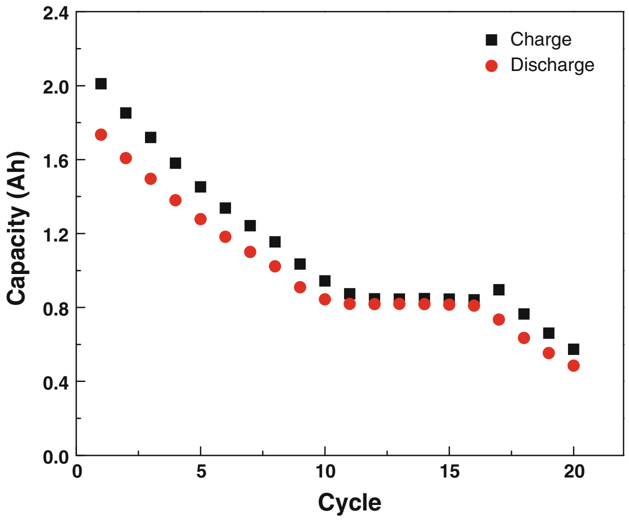


Fig. 2 Charge and discharge capacities as a function of cycles in a flow cell test at room temperature with 3 wt% Na_3PO_4 as additives in the electrolyte solution of 2 M V/5 M SO_4^{2-}

Table 3 also shows that Na_3PO_4 significantly improved the stabilities of V(III), V(IV), and V(V) cations in sulfuric acid solutions. For the blank test (without an additive), the precipitation was observed at 634 and 18 h at −5 °C for the solutions of 2 M V(III)/5 M SO_4^{2-} and 2 M V(IV)/5 M SO_4^{2-}, respectively, and 95 h at 40 °C for the solution of 2 M V(V)/5 M SO_4^{2-}. By adding 3 wt% Na_3PO_4, the solutions with the same vanadium and total sulfate concentrations exhibited excellent stability (without precipitation in 30 days) under all the studied temperatures. The same trend was found for the solution of 2 M V(II)/5 M SO_4^{2-} at −5 °C (not shown here). The ex situ heating/cooling testing results suggested that the stability of all vanadium cations can be improved by adding 3 wt% Na_3PO_4 as a stabilizing agent. The stability of vanadium electrolyte with 3 wt% Na_3PO_4 was further evaluated in a flow cell. A solution of 2 M V(IV)/5 M SO_4^{2-} with 3 wt% Na_3PO_4 was used as the starting positive and negative electrolytes. The charge and discharge cycles were conducted at a current density of 50 mA cm^{-2} during the flow cell test. As shown in Fig. 2, the charge and discharge capacities decreased significantly with cycling number, and the flow cell did not function any more after 20 cycles. The disassembled cell showed that there were a large number of precipitation particles on the graphite plate and the graphite felt on the positive pole. The graphite felt became more rigid because the pores were blocked by the precipitation particles. No precipitation was observed on the negative electrode. The precipitate was identified as $VOPO_4{\cdot}2H_2O(s)$ by XRD analysis (see Fig. 3), which is insoluble in sulfuric acid. It is believed that the VO_2^+ ions react with PO_4^{3-} in sulfuric acid solutions, producing $VOPO_4{\cdot}2H_2O$. This reaction may be catalyzed by graphite. It can be deduced that all the chemicals containing the anions of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and polyphosphate may form $VOPO_4{\cdot}2H_2O$ with VO_2^+ ions in a flow cell, and should be avoided. The results also suggest that the ex situ stability tests might be quite different from the in situ flow cell experiments. The flow cell test is still needed to determine the effects of additives on the stability of solutions, even though the ex situ test showed a promising effect.

3.3 Effects of organic additives on the stability of vanadium electrolyte solutions

Besides inorganic chemicals, organic chemicals can also be used as potential stabilizing agents. Accordingly, some organic chemicals were selected and their effects on the stability of vanadium electrolyte solutions were investigated. Table 4 lists some typical organic chemicals used in this study, which include some widely used solvents, polymers, and surfactants.

As shown in Table 5, some of the organic chemicals improved the stability of the 2 M V(II)/5 M SO_4^{2-} solution. The 2 M V(II)/5 M SO_4^{2-} solution underwent precipitation after 419 h without additives, but the additives of 0.2–1.0 wt% polyacrylic acid (PA) or 0.3 wt% Darvan® 821 A (DA) dramatically improved the stability: no

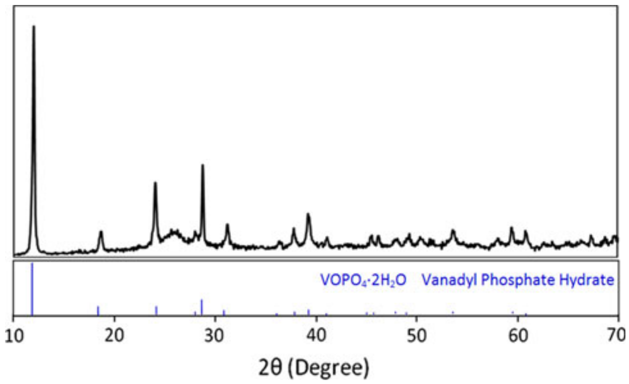


Fig. 3 XRD pattern of graphite felt after flow cell testing with 3 wt% Na_3PO_4 as additives in the electrolyte solution of 2 M V/5 M SO_4^{2-}

precipitation in 1200 h for 1.0 wt% PA and no precipitation even in 90 days for 0.2 wt% PA or 0.3 wt% DA. However, the Darvan® C(DC) additives deteriorated the stability of a V(II) solution, which might be a consequence of NH_4^+ ion which only exists in DC, not in PA and DA. Other chemicals, such as 10 wt% dimethyl sulfoxide (DMSO), 10 wt% ethanol glycol (EG), and 3–20 wt% CH_3SO_3H, all decreased the stability of the 2 M V(II)/5 M SO_4^{2-} solution at −5 °C. So the chemicals of PA and DA could be potential stabilizing agents for the solution of V(II) in sulfuric acid.

Table 6 lists the effects of some organic additives on the stability of 2 M V(III)/5 M SO_4^{2-} solutions at −5 °C. Most of the studied chemicals improved the stability of the V(III) solution, except that 0.3–1.0 wt% Darvan® C deteriorated the solution stability. Because CH_3SO_3H and DMSO improved the stability of the V(III) solution, but decreased that of the V(II) solution, these additives are not suitable for VRB. Thus, PA can be a potential candidate as a stabilizing agent for the negative electrolyte.

Table 7 shows the effects of some organic additives on the stability of V(IV) solutions. Compared to the results in the blank test (precipitation observed in 18 h) in Table 1, most of the studied chemicals improved the stability of V(IV) solutions. The solutions of 2 M V(IV)/5 M SO_4^{2-} with 10 wt% DMSO, 7 wt% CH_3SO_3H, 18 wt% CH_3SO_3H, 46 wt% CF_3SO_3H, and the solution of 2.5 M V(IV)/9.5 M SO_4^{2-} with 44 wt% CF_3SO_3H exhibited excellent stability at −5 °C. Although 0.5–5 wt% *p*-toluenesulfonic acid (PTSA) and 0.3 wt% boric acid was promising to some extent, the stability of the V(IV) solution with the vanadium

Table 4 Molecular structures of some studied organic chemicals as stabilizing agents

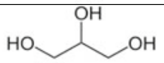
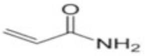
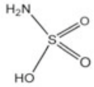
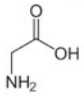
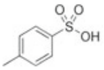
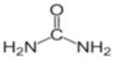
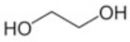
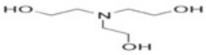
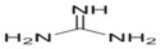
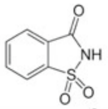
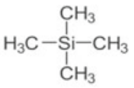
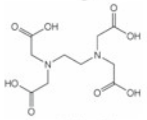
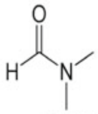
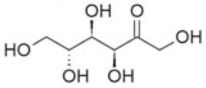
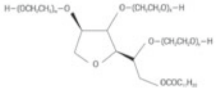
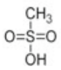
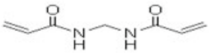
Chemical	MolecularStructure	Chemical	MolecularStructure
Glycerol		Acrylamide	
Sulfamic acid		Glycine	
p-Toluenesulfonic acid (PTSA)		Urea	
Ethylene glycol		Triethanol-amine	
Sodium stearate ($CH_3(CH_2)_{16}COONa$)		Guanidine carbonate	
Saccharin		Tetramethyl-silane (TMS)	
Ethylenediaminetetra-acetic acid (EDTA)		Dimethyl-formamide	
Fructose		Tween 20	
Poly acrylic acid (PA)	$[\text{-}CH_2CH(COOH)\text{-}]_n$	G-Aminohexanic Acid	
Methanesulfonic acid		N, N'-methylene-bis-acrylamide	

Table 5 Effect of organic additives on the stability of 2 M V(II)/5 M SO_4^{2-} solutions at −5 °C

Additive	Time to precipitation
0.2 wt% PA	Stable (>90 days)
0.3 wt% DA	Stable (>90 days)
1.0 wt% PA	1200 h
1.0 wt% Darvan® C	120 h
3 wt% CH_3SO_3H	70 h
7 wt% CH_3SO_3H	92 h
14 wt% CH_3SO_3H	120 h
20 wt% CH_3SO_3H	216 h
10 wt% DMSO	10 h
10 wt% EG	120 h

PA polyacrylic acid, *DA* Darvan® 821 A, *DMSO* dimethyl sulfoxide, *EG* ethanol glycol

Table 6 Effect of organic additives on the stability of 2 M V(III)/5 M SO_4^{2-} solutions at −5 °C

Additive	Time to precipitation
3 wt% CH_3SO_3H	63 days
7 wt% CH_3SO_3H	Stable (>75 days)
0.3 wt% PA	108 days
1.0 wt% PA	82 days
10 wt% DMSO	Stable (>60 days)
20 wt% CH_3SO_3H	Stable (>49 days)
0.3 wt% Darvan® C	168 h
1.0 wt% Darvan® C	144 h

PA polyacrylic acid, *DMSO* dimethyl sulfoxide

Table 7 Effect of organic additives on the stability of V(IV)/SO_4^{2-} solutions at −5 °C

Concentration (M)		Additive	Time to precipitation
V(IV)	SO_4^{2-}		
1.8	6.0	1.0 wt% PA	285 h
2.3	6.0	0.1 wt% PA	214 h
2.0	6.0	0.1 wt% PA + 3 wt% Na_2SO_4	482 h
2.0	5.0	10 wt% DMSO	Stable (>60 days)
2.0	5.0	3 wt% CH_3SO_3H	70 h
2.0	5.0	7 wt% CH_3SO_3H	1099 h
2.0	5.0	18 wt% CH_3SO_3H	935 h
2.0	5.0	3 wt% CF_3SO_3H	46 h
2.5	9.5	44 wt% CF_3SO_3H	Stable (>56 days)
2.0	9.0	46 wt% CF_3SO_3H	Stable (>56 days)
2.5	5.0	0.5–5 wt% PTSA	20–74 h
2.0	5.0	0.3 wt% Boric acid	120 h

PA polyacrylic acid, *DMSO* dimethyl sulfoxide, *PTSA* *p*-toluenesulfonic acid

concentration over 2 M is still not good enough at −5 °C. Thus, they do not work as stabilizing agents for the V(IV) solution.

As shown in Table 8, the stability of 2 M V(V)/5 M SO_4^{2-} solution at 40 °C was slightly improved by adding 0.1–1 wt% polyacrylic acid (PA) or 2.1–7 wt% CH_3SO_3H or 0.3 wt% Darvan® C. There was no precipitation found over 30 days at 40 °C in the solutions of 2 M V(V)/5 M SO_4^{2-} with the additives of 10 wt% iso-propanol, 1.0 wt% Glucose, 0.3 wt% PEG, 10 wt% DMSO, and 0.01 mL Tween 20; however, the color of the solutions changed from yellow to dark blue during the stability test. This indicated that part of the V(V) ions were reduced into V(IV) ions by the additives. In fact, due to the strong oxidative property of V(V) ions, most of additives were not stable and were oxidized by the V(V) ions, such as glycerol, fructose, thio-urea, oxalates, ethylenediaminetetraacetic acid (EDTA), formic acid, and etc. Most of the organic chemicals with the functional groups of C=C, OH, CHO, and C=O, especially for the chemicals with relative small molecular structures, are not stable in V(V) solutions. Thus, these chemicals are not suitable for V(V) as stabilizing agents. Table 8 also shows that 1.0 wt% boric acid, 0.3–1.0 wt% sulfamic acid, 0.3 wt% $CH_3(CH_2)_{11}SO_3Na$, and 0.1–2 wt% saccharin had negative effects on the stability of V(V) solutions. By adding 0.1–1.0 wt% PA or 7 wt% CH_3SO_3H and 0.4 wt% PA as stabilizing agents, a solutions with a 1.8 M V(V) remains stable at 40 °C for an extended period of time. As shown in Table 8, there was no precipitation observed at 40 °C during the 860 h of the test in the solutions of 1.8 M V/5 M SO_4^{2-} with the additive of 7 wt% CH_3SO_3H and 0.4 wt% PA. Combing the experimental results of V(IV) solutions, PA and its mixture with CH_3SO_3H appeared the most promising candidates as stabilizing agents for the positive electrolyte. However, these results still need to be verified with a flow cell test.

4 Conclusions

The stabilities of vanadium ions in sulfuric acid solution are controlled by the solution temperature, the concentration of vanadium, and the stabilizing agent. The stability of vanadium solutions decreases as the vanadium concentration increases because of the supersaturation effect. With the temperature increase, the stability of the V(V) solution decreases significantly, due to the formation of V_2O_5 precipitates. The stabilities of vanadium ions in sulfuric acid solution can be improved marginally by adding some additives as stabilizing agents. The K^+ cation and phosphate and polyphosphate anions have negative effects on the stability of vanadium solutions because of the formation of insoluble $KVSO_6$ or $VOPO_4$ with V(V) ions.

Table 8 Effects of organic additives on the stability of V(V)/SO_4^{2-} solutions at 40 °C

Concentration (M)		Additive	Time to precipitation	Other phenomena
V(V)	SO_4^{2-}			
1.8	5.1		357 h	
2.0	5.0		<95 h	
2.0	6.0		118 h	
1.8	5.0	10 wt% iso-propanol	Stable	Color change
1.8	5.0	1.0 wt% Glucose	Stable	Color change
2.0	5.0	0.3 wt% Darvan® C	120 h	
2.0	5.0	0.3 wt% PEG	Stable	Color change
2.0	5.0	0.3 wt% $CH_3(CH_2)_{11}SO_3Na$	65 h	
1.8	5.1	0.1–1.0 wt% Polyacrylic acid	526 h	
2.0	6.0	0.1–1.0 wt% Polyacrylic acid	147–166 h	
2.0	5.0	10 wt% DMSO	Stable	Color change
2.0	5.0	0.01 mL Tween 20	Stable	Color change
2.0	5.0	0.1–2 wt% Saccharin	89 h	
1.8	5.0	7 wt% CH_3SO_3H	236 h	
2.0	5.0	2.1 wt% CH_3SO_3H	140 h	
2.0	5.0	3 wt% CH_3SO_3H	149 h	
1.8	5.0	7 wt% CH_3SO_3H + 0.4 wt% PA	860 h	
2.0	5.0	1.0 wt% Boric acid	72 h	
2.0	5.0	0.3–1.0 wt% Sulfamic acid	72 h	

PA polyacrylic acid, *PEG* polyethylene glycol, *DMSO* dimethyl sulfoxide

Polyacrylic acid can be a potential candidate as a stabilizing agent for a negative electrolyte, and polyacrylic acid and its mixture with CH_3SO_3H are the most promising stabilizing agents for a positive electrolyte. So far, with a total SO_4^{2-} concentration of 5 M, the V(II), V(III), and V(IV) can be stabilized at 2.0 M, and V(V) can be stabilized at 1.8 M in sulfuric acid solutions by adding PA as a stabilizing agent in the temperature range of −5 to 40 °C. Further effort is needed to obtain a stable electrolyte solution with a vanadium concentration higher than 1.8 M at temperatures higher than 40 °C.

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