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Influence of Trishydroxymethyl Aminomethane as a Positive Electrolyte Additive on Performance of Vanadium Redox Flow Battery

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To improve the stability of 2M V(V) in 3M H_2SO_4 electrolyte in charge-discharge cycles, Trishydroxymethyl aminomethane (Tris) was used as an additive of the electrolyte and first investigated in VRB applicaton. Thermal stability of the V(V) electrolyte at 40 °C was improved by 2-4% Tris additive. The cyclic voltammetry results of 2 M V(IV) in 3M H_2SO_4 electrolyte with various additive amounts showed the electrochemical activity of the electrolyte with 3% Tris additive was improved compared to blank electrolyte, and electrochemical impedance spectroscopy results indicated the electrolyte solution resistance (0.43 ohm) was less than blank sample (0.91 ohm). The VRB employing the vanadium solution with the Tris additive as positive electrolyte exhibited higher voltage efficiency and energy efficiency at the same current densities compared with the blank electrolyte system.

Keywords: Vanadium redox flow battery; additive; stability; electrochemical reversibility

1. INTRODUCTION

The vanadium redox flow battery (VRB) is a type of rechargeable flow battery that employs vanadium ions in different oxidation states to store chemical potential energy [1-3]. VRFB has higher energy efficiency, longer operation life and lower cost compared to other redox batteries, which makes it suitable for the large-scale (MW) grid-connected storage, small- (kW) to large-scale (MW) distributed storage, and small portable batteries [4, 5].

The capacity and power output of VRB are determined by the volume and concentration of the electrolytes. When the volume of the reservoirs for the VRB system is designed completely, the concentration of the vanadium electrolyte could be of importance for raising its energy density [6]. However, the high energy density of VRB (>25 Wh/kg [7]) is a challenge for the poor solubility and stability of the vanadium species, especially the V(V) electrolyte at the elevated temperature (> 40 °C [7]) and concentration (>1.8 M), resulting in decreasing the energy density of VRB [8]. In general, in the sulfuric acid medium V(V) species exists as hydrated penta co-ordinated vanadate ion, i.e. $[VO_2(H_2O)_3]^+$. This hydrated structure would be converted to V_2O_5 precipitation by de-protonation process and condensation reaction at higher temperatures [9]. The thermal stability of V(V) solutions can be enhanced by increasing the concentration of H_2SO_4, which prevents the process of de-protonation or dimerization of VO^{2+} ions to $V_2O_4^{2+}$ and $V_2O_3^{4+}$ species [10]. However, higher concentrations of H_2SO_4 accelerate the precipitation of V(II), V(III) and V(IV) ions [7]. To solve this problem, S. Peng et al. [6] obtained 2 M V(V) electrolyte for VRB application by replacing 1.5 M H_2SO_4 with 1.5 M CH_3SO_3H (a stronger acid than H_2SO_4), and found that the VRB with CH_3SO_3H sample exhibited the higher energy density (39.87 Wh/L) in comparison of H_2SO_4 sample. But the price of CH_3SO_3H is higher than that H_2SO_4 which increases the VRB cost. Adding precipitation inhibitors is an economic and effective method for stabilizing vanadium electrolytes. The stabilizing agent with secondary or tertiary (-OH), ($-NH_2$) and (-SH) groups may resist to oxidation at low concentrations [11]. It was found that the vanadium electrolyte with many organic additives [11, 12], such as d-sorbitol [13], coulter dispersant [14], exhibits superior electrochemical performances compared to the blank electrolyte.

Trishydroxymethyl aminomethane (Tris) is an aqueous dispersant with three hydroxyl groups and one amino and widely used in cosmetics. There are few reports on the effect of Tris on vanadium electrolyte. We found in our recent study that the add addition of trace amount (1-4% wt.) of Tris 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 Tris as an additive into VRB positive electrolyte on the stability and the electrochemical properties of the electrolyte.

2 EXPERIMENTAL

2.1 Thermal stability testing

The 2 M V(V) electrolyte was prepared by oxidizing 2 M $VOSO_4$ in the positive side of a two-compartment electrolysis cell which employed H_2SO_4 with the same concentration as the catholyte. At the end of the electrolysis, the final solutions were analyzed by redox titration to determine the total vanadium concentration. Samples (2 M V(V) + 3.0 M H_2SO_4) with different amount (1-4% wt.) of Tirs were placed in a 40 °C water bath. Periodic aliquots from the all samples were taken and analyzed for vanadium concentration by a titration method.

2.2 Cyclic voltammetry (CV)

CV measurements were carried out by using electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) at a scan rate of 20.0 $mV \cdot s^{-1}$ between 0 V and 1.6 V at room temperature.

A three-electrode cell was used with Pt piece (1.0 cm^2) as a counter electrode, where a saturated calomel electrode (SCE) along with a salt bridge was used as a reference electrode and the graphite electrode with a surface area of 1.0 cm^2 was used as a working electrode. The graphite electrode was polished with 600 (P1200) grit SiC paper, then washed with de-ionized water. To avoid cross-contamination of different ions on the electrodes surface, the graphite electrode was polished and rinsed carefully after each test.

2.3 Electrochemical impedance spectroscopy (EIS)

EIS was performed with a PARAST electrochemistry workstation (USA, AMETEK, Inc.). The sinusoidal excitation voltage applied to the cells was 5 mV with a frequency range from 0.001 Hz to 100 kHz.

2.4 Cell test

A VRB single cell was fabricated by sandwiching the membrane between two pieces of carbon felt (thickness is 5 cm, Shenhe carbon fiber Materials Co., Ltd.) with effective reaction area of 30 cm^2, which was served as the electrodes, and conductive plastic were used as the current collectors. 70 mL 2 M V^{4+} in 3.0 M H_2SO_4 serving as negative electrolyte and 140 mL 2M V^{4+} in 3.0 M H_2SO_4 with 3% Tri additive as positive electrolyte were cyclically pumped into the corresponding half-cell respectively.

The single cell was charged and discharged by a CT2001C-10V/10A battery test system (Wuhan Land Co., Ltd.) with a constant current density of 20-60 mA/cm^2. To avoid the corrosion of the carbon felt electrodes and conductive plastic, the upper limit of charge voltage was 1.7 V and the lower limit of discharge voltage was 0.7 V.

3 RESULTS AND DISCUSSION

3.1 Thermal stability

The energy density of VRB is determined by the solubilities of vanadium ions in the two half-cell electrolytes. The vanadium ion concentrations therefore must be lower than the saturation solubilities of each of the species generated during charge and discharge over the relevant operating temperature range. Earlier studies showed that the rate of thermal precipitation of V(V) to V_2O_5 increases with increasing temperature but decreases with increasing acid concentration [7, 15]. In our experiment, to investigate how the Tris additive affect the thermal precipitation of V(V) to V_2O_5, [VO_2^+] is 2M, [H^+] is 3M, and temperature is 40 °C, respectively. The effect of the Tris additive amount on the solubility of V(V) ion is displayed in Fig. 1. With heating time increasing, V(V) ion concentrations for all samples are decreasing gradually. At the same time, with increasing Tris additive amout from 1 to 4%, the V(V) concentration is increased suggesting Tris additive can effectively inhibit thermal precipitation of V(V) to V_2O_5. Fig.2 displays the difference between the visual images of 2M V(V) electrolyte for blank and 3% Tris samples after heating at 40°C for 48h. It is obvious that there is much red V_2O_5 precipitate in the solution while the solution with 3% Tris sample remains uniform. This suggests Tris additive can effectively improve the thermal stability of V(V) elelctrolyte, probably due to its excellent dispersion of V(V) ions by its three hydroxyl groups and one amino, which is similar to d-sorbitol [13], coulter dispersant [14].

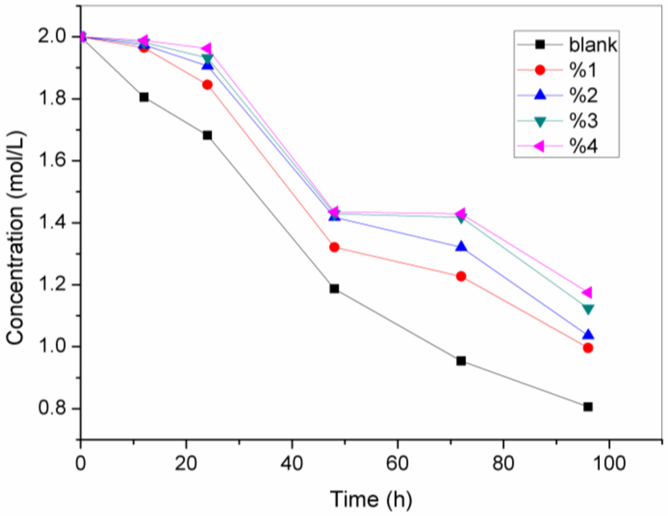

Figure 1. Effect of additive amount on the solubility of V(V) electrolyte.

Figure 2. Visual images of 2M V(V) electrolyte solution for blank and 3% Tris samples after 48h.

3.2 CV

Fig. 3 shows the cyclic voltammograms of 2.0 M $VOSO_4$ in 3M H_2SO_4 solution with various Tris additive amounts at a scan rate of 20mV/s. Firstly, the reduction and oxidation peak current absolute values of blank electrolyte are lower than those of electrolytes with Tris additive, suggesting that Tris additive can be helpful to improve V(IV)/ V(V) redox reaction kinetics [6, 13]. Secondly, the difference between oxidation and reduction peak potential ($\triangle E_p$) for blank sample is more than that for the other electrolytes with Tris additive, suggesting that Tris additive can improve the electrochemically reversibility of V(IV)/V(V) redox reaction [6, 13, 14]. In the same way as the d-sorbitol and glucose, Tris containing three hydroxyl groups and one amino in the opposite orientation, not only can complex with VO^{2+}, but also can be adsorbed easily on the surface of graphite electrode applying more available (–OH) groups for electron transfer[13]. In order to investigate effect of the amount of Tris additive on the reversibility of V(IV)/V(V) redox reaction, cyclic voltammograms data for 2.0M V(IV) solution with various Tris amounts on graphite electrode are calculated and listed in Table 1. When the amount of Tris is lower 3%, the $\triangle E_p$ value is greater than 0.9, and with the amount above 4% $\triangle E_p$ value increases agaian. The result can be describe to the fact that too much amount additive of Tris as an aqueous dispersing agent with multi hydroxyl groups can lower the conductivity of the V(V) electrolyte solution [14]. So the optimal amount of Tris additive was set at 3% for further testing.

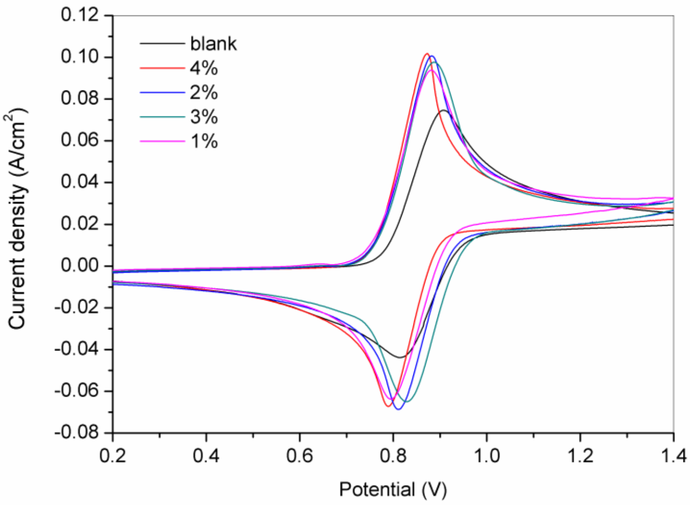

Figure 3. Cyclic voltammograms of the electrolyte (2.0M $VOSO_4$ + 3.0M H_2SO_4) with various Tris amounts at the scan rate of 20mV/s.

Table 1. Cyclic voltammograms data for 2.0M V(IV) solution with various Tris amounts on graphite electrode

Sample	Anodic peak		Cathodic peak		ΔE_p(V)	j_{pa}/j_{pc}
	j_{pa}(mAcm^{-2})	E_{pa}(V)	j_{pa}(mAcm^{-2})	E_{pa}(V)		
Blank	73.54	0.908	56.84	0.816	0.092	1.34
1%	92.08	0.914	74.78	0.822	0.092	1.23
2%	97.73	0.917	83.35	0.827	0.090	1.17
3%	97.47	0.888	78.55	0.828	0.060	1.24
4%	83.31	0.894	69.38	0.814	0.080	1.20

3.3 EIS

In order to clarify the effect of the Tri additive on the impedance of vanadium electrolyte, the electrochemical impedance spectroscopy technique was employed on platinum in the 2M V(IV) / 3M H_2SO_4 solution. The typical ac impedance plots of the electrolytes with and without 3% Tri additive at ambient temperature are shown in Fig. 4. In the complex plane plots, as for blank electrolyte sample, the absence of a well-defined semicircle at high frequencies reflecting the charge transfer process is noted due to the rapid charge transfer reaction kinetics on platinum electrodes in the $VOSO_4$ / H_2SO_4 solution; however, a linear section indicating the diffusion process is observed at low frequencies. This impedance due to mass transport impedance becomes progressively more dominant. But for blank electrolyte the complex plane plot includes a well - defined semicircle and a linear section, which shows that the whole impedance is determined by charge transfer and mass transport together [6, 13, 16]. The difference of the ac impedance plots between them indicates Tri additive can be favorable in improving V(IV) ions charge transfer capability [13]. From the interception at Zre axis where -Zim = 0, the solution resistance can be obtained. For 3% Tri sample, the Zre is 0.43 ohm, which is less than the Zre of blank sample (0.91 ohm).

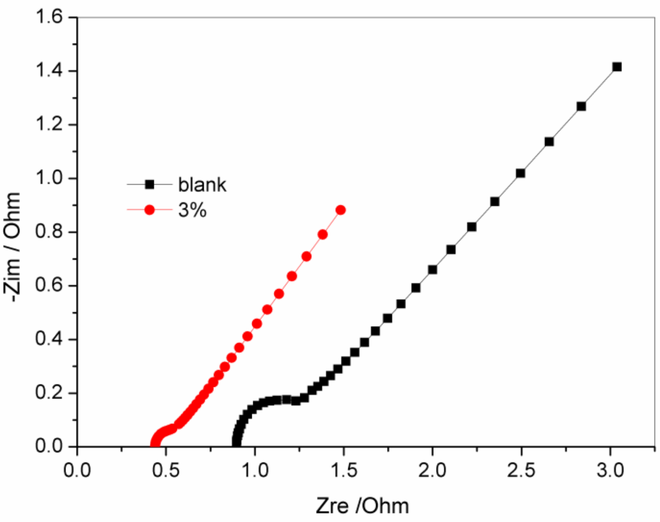

Figure 4. Ac impedance spectroscopy of V(IV) electrolyte with and without 3% Tri additive at ambient temperature.

3.4 Cell test

The charge-discharge curves of VRFB with blank V(IV) electrolyte and with V(IV) electrolyte containing 3% Tri additive as the positive electrolyte are shown in Fig. 5. It can be seen that with the current density varying from 20 to 60 mA / cm^2, the charge and discharge capacities of VRFB with 3% Tri additive electrolyte are higher than those with blank electrolyte, and that charge voltage and discharge voltage platforms for the former are lower and higher than those for the latter, respectively, which is due to the reduction of solution impedance and increased electrochemically reversibility by adding Tri to the vanadium electrolyte. With current density increasing from 20 to 60 mA / cm^2, the charge and discharge capacities of both samples are decreased due to polarization effects [17, 18]. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) for VRFB with blank and 3% Tri additive electrolyte samples at various current densities in the 40 cycles are illustrated in Table 2. For both samples, with current density increasing, the average CE gradually increases due to the reduction of vanadium ions crossover during the shorter charge-discharge time at higher current densities, and VE slowly decrease owing to the increase of ohmic resistance and the overpotentials led by the increase of current densities [17, 18]. Compared to blank electrolyte, the electrolyte with 3% Tris exhibited higher VE and EE at the same current densities, due to its lower solution impedance and higher electrochemically reversibility.

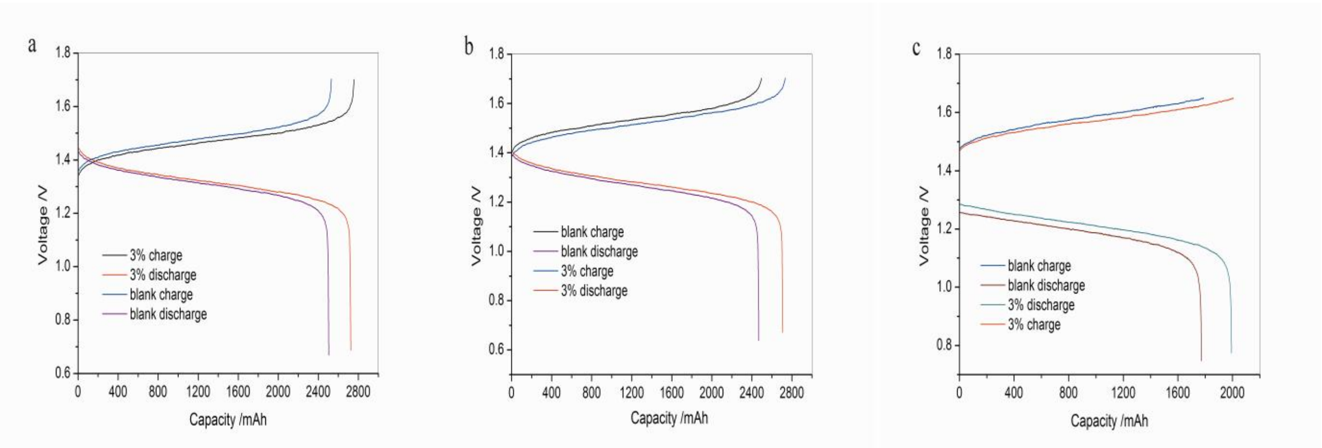

Figure 5. charge and discharge curves for blank sample and 3% Tri sample :(a) at 20 mA/cm^2, (b) at 40 mA/cm^2, (c) at 60mA/cm^2.

Table 2. Performance of VRFB with blank and 3% Tri electrolyte samples in 40 cycles.

Sample	current density /mAcm^2	CE /%	VE /%	EE /%
blank	20	95.34	85.02	81.06
	40	96.03	81.43	78.20
	60	96.51	78.65	75.91
3% Tri	20	95.04	85.91	81.65
	40	95.90	82.75	79.36
	60	96.63	79.49	76.81

4. CONCLUSIONS

In order to improve the stability of 2M V(V) in 3M H_2SO_4 electrolyte, Trishydroxymethyl aminomethane (Tris) was used as an additive of the electrolyte. The stability tests verified that thermal stability of the V(V) electrolyte was improved by 2-4% Tris additive. CV and EIS techniques were used to investigate the electrochemical properties of 2 M V(IV) in 3M H_2SO_4 electrolye with various additive amount of Tris.

The CV results showed the electrochemical activity of the electrolyte with 3% Tris additive was significantly improved compared with blank electrolyte, and EIS indicated the electrolyte solution resistance (0.43 ohm) was less than that of blank sample (0.91 ohm). The VRB using the vanadium solution with the Tris additive as positive electrolyte exhibited higher VE and EE at the same current densities compared with the blank electrolyte system.

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References

1. E. Sum, M. Rychcik, M. Skyllas-kazacos, *J. Power Sources*, 16 (1985) 85
2. E. Sum, M. Skyllas-Kazacos, *J. Power Sources*, 15 (1985) 179
3. K.L. Huang, X.G. Li, S.Q. Liu, N. Tan, L.Q. *Chen, Renew. Energ.*, 33 (2008) 186
4. M. Skyllas-Kazacos, M.H. Chakrabarti, S.A. Hajimolana, F.S. Mjalli, M. Saleem, *J. Electrochem. Soc.*, 158 (2011) R55
5. M. Skyllas-Kazacos, G. Kazacos, G. Poon, H. Verseema, *Int. J. Energ. Res.*, 34 (2010) 182
6. S. Peng, N. Wang, X. Wu, S. Liu, D. Fang, Y. Liu, K. Huang, *Int. J. Electrochem. Sci.*, 7 (2012) 643
7. M. Skyllas-Kazacos, C. Menictas, M. Kazacos, *J. Electrochem. Soc.*, 143 (1996) L86
8. F. Rahman, M. Skyllas-Kazacos, *J. Power Sources*, 72 (1998) 105
9. M. Vijayakumar, L. Li, G. Graff, J. Liu, H. Zhang, Z. Yang, J.Z. Hu, *J. Power Sources*, 196 (2011) 3669
10. C. Madic, G.M. Begun, R.L. Hahn, J.P. Launay, W.E. Thiessen, *Inorg. Chem.*, 23 (1984) 469
11. M. Skyllas-Kazacos, M. Kazacos, *US Patent*, 6, 562, 514 (2003)
12. M. Kazacos, M. Skyllas-Kazacos, *US Patent*, 7, 078, 123 (2006)
13. S. Li, K. Huang, S. Liu, D. Fang, X. Wu, D. Lu, T. Wu, *Electrochim. Acta*, 56 (2011) 5483
14. F. Chang, C. Hu, X. Liu, L. Liu, J. Zhang, *Electrochim. Acta*, 60 (2012) 334
15. M. Kazacos, M. Cheng, M. Skyllas-Kazacos, *J. Appl. Electrochem.*, 20 (1990) 463-467
16. W.H. Wang, X.D. Wang, *Electrochim. Acta*, 52 (2007) 6755-6762
17. M. Skyllas-Kazacos, F. Grossmith, *J. Electrochem. Soc.*, 134 (1987) 2950-2953.
18. N. Wang, S. Peng, D. Lu, S. Liu, Y. Liu, K. Huang, *J. Solid State Electrochem.*, (2011), DOI:10.1007/s10008-011-1560-z.