

## Stability of Positive Electrolyte Containing Trishydroxymethyl Aminomethane Additive for Vanadium Redox Flow Battery

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Trishydroxymethyl aminomethane (Tris) was used as an additive of the positive electrolyte for all vanadium redox battery (VRB) and cycling and electrochemical stabilities of the positive electrolyte were investigated. The 50 cyclic voltammetry (CV) cycles suggested that the positive electrolyte with the Tri additive after charge-discharge cycles has good cycle stability compared to that before the charge-discharge cycles. The VRB employing the vanadium electrolyte with the Tris additive as positive electrolyte exhibited better charge-discharge behavior and less discharge capacity fade rate with cycles compared with the blank electrolyte system. The UV/visible spectroscopy showed that the vanadium concentration in the positive electrolyte containing Tri additive during 40 charge-discharge cycles remains unchanged. The X-ray photoelectron spectroscopy (XPS) verified that the positive electrolyte with the Tri additive has no etching and oxidation effect on the carbon felt electrode.

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

### 1. INTRODUCTION

All vanadium redox flow battery (VRB) is a promising energy conversion device that employs V(V)/V(II)/V(III) and V(IV)/V(V) couples in the negative and positive half-cells respectively to store chemical potential energy [1-3]. VRB has higher energy efficiency, longer operation life and lower cost compared to the other redox batteries, which makes it suitable for large-scale, renewable and grid energy storage [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 in its tanks is vital to its energy density [6]. However, the

high energy density of VRB ( $>25$  Wh/kg [7]) is a challenge due to the poor solubility and stability of the vanadium species, especially the V(V) electrolyte at the elevated temperature ( $> 40$  °C [7]) and high concentration ( $>1.8$  M), resulting in the decrease of its energy density [8]. Generally, V(V) species in the acid medium exists as hydrated penta co-ordinated vanadate ion (such as  $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ ). This hydrated structure is easily converted to  $\text{V}_2\text{O}_5$  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  $\text{H}_2\text{SO}_4$ , which prevents the process of de-protonation or dimerization of  $\text{VO}^{2+}$  ions to  $\text{V}_2\text{O}_4^{2+}$  and  $\text{V}_2\text{O}_3^{4+}$  species [10]. However, higher concentrations of  $\text{H}_2\text{SO}_4$  accelerate the precipitation of V(II), V(III) and V(IV) ions [7]. To solve this problem, S. Peng et al. [6] obtained a 2 M V(IV) electrolyte in 1.5 M  $\text{H}_2\text{SO}_4$  and 1.5 M  $\text{CH}_3\text{SO}_3\text{H}$  (a stronger acid than  $\text{H}_2\text{SO}_4$ ) mixed acid for VRB application, and found that the VRB with the MAS sample exhibited the higher energy density (39.87 Wh/L) compared to the Pristine sample. But the price of  $\text{CH}_3\text{SO}_3\text{H}$  is higher than that of  $\text{H}_2\text{SO}_4$  which increases the cost of VRB. Adding precipitation inhibitors is an economic and effective method for stabilizing vanadium electrolytes. The stabilizing agent with secondary or tertiary (-OH), (- $\text{NH}_2$ ) 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], coultter 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 industry. S. Peng et al. [15] found 2M vanadium electrolyte with 2-4% Tris additive at 40 °C had better thermal stability than the blank electrolyte, that the VRB employing the vanadium solution with the 3% Tris additive as positive electrolyte exhibited higher voltage efficiency and energy efficiency compared with the blank electrolyte system, due to its better electrochemical activity and lower solution resistance (0.43 ohm vs. 0.91 ohm).

In order to ensure the safety in long-term operation of VRB with the positive vanadium electrolyte with the 3% Tris additive, the effect of the Tris additive on performance of VRB is required to be investigated. In this work, we report in detail the effect of electrolyte containing the Tris additive on the cycling and electrochemical stabilities of VRB using Cyclic voltammetry method, charge and discharge technique, UV/visible spectroscopy and X-ray photoelectron spectroscopy (XPS).

## 2. EXPERIMENTAL

### 2.1 Cyclic voltammetry (CV)

CV measurements were carried out by using electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) at a scan rate of  $20.0 \text{ mV}\cdot\text{s}^{-1}$  between 0 V and 1.6 V at room temperature. A three-electrode cell was used with Pt piece ( $1.0 \text{ cm}^2$ ) 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  $1.0 \text{ cm}^2$  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.

## 2.2 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<sup>2</sup>, which was served as the electrodes, and conductive plastic were used as the current collectors. 70 mL 2 M V<sup>4+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub> serving as negative electrolyte and 140 mL 2M V<sup>4+</sup> in 3.0 M H<sub>2</sub>SO<sub>4</sub> 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<sup>2</sup>. 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.

## 2.3 UV/visible spectroscopy

UV/visible spectroscopy was measured on a UV-vis spectrometer (UV-3802) in the range of 200–900 nm using 2.0 cm quartz cell. 3 M H<sub>2</sub>SO<sub>4</sub> was used as the blank solution. The measured solutions are as follows: draw 1mL solution of 1st and 40th cycle positive electrolyte with 3% Tri additive of VRB charged to 1.7V, respectively, then dilute the 1mL solution samples to 50mL with 3 M H<sub>2</sub>SO<sub>4</sub> (slightly yellow).

## 2.4 XPS

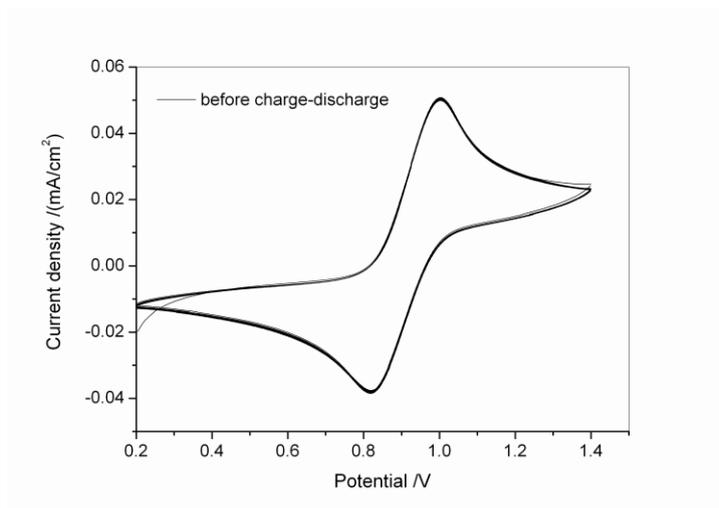
XPS measurements of the carbon felt electrode samples were performed on a K-Alpha 1063 (Thermo Fisher Scientific, UK) in an ultra-high vacuum set-up equipped with Al K $\alpha$  X-ray source generated at 12 kV and 6 mA employing Thermo Avantage survey and analysis system. The base pressure in the measurement chamber was about 10<sup>-9</sup> mBar.

# 3. RESULTS AND DISCUSSION

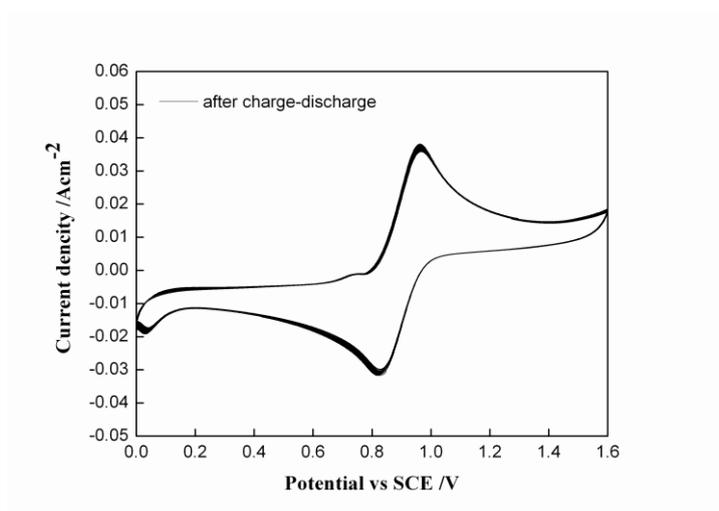
## 3.1 Effect of the additive on the electrolyte cycle stability

Before performing charge-discharge cycles, 3% Tri additive was added to the electrolyte (2.0 M VOSO<sub>4</sub> + 3.0 M H<sub>2</sub>SO<sub>4</sub>) and 50 cycles of continuous voltammetric scans of it was carried out to investigate the electrolyte cycle stability during multiple cycles. Fig.1 shows that the peak shape and difference of the oxidation and reduction peak potential remained unchanged as the scans proceeded. After performing 40 charge-discharge cycles at 40mA/cm<sup>2</sup>, 50 cycles of CV scans of the positive

electrolyte from the VRB tank was carried out and the result was shown in Fig. 2. After undergoing charge-discharge cycles, the peak shape and difference of the oxidation and reduction peak potential seems a little poorer than that before charge-discharge cycles. These results indicate that the positive electrolyte with the Tri additive has good cycle stability [14], which is due to its excellent dispersion of V(V) ions by its three hydroxyl groups and one amino [13, 14].



**Figure 1.** CV of the electrolyte (2.0M VOSO<sub>4</sub> + 3.0M H<sub>2</sub>SO<sub>4</sub>) with 3% Tri before charge-discharge.



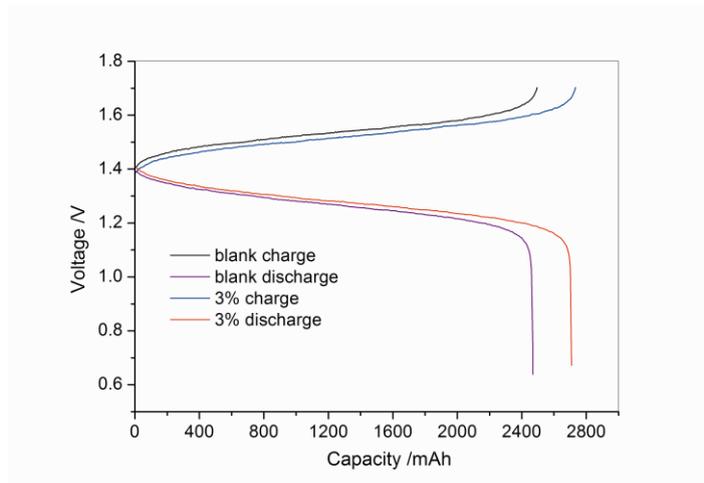
**Figure 2.** CV of the electrolyte (2.0M VOSO<sub>4</sub> + 3.0M H<sub>2</sub>SO<sub>4</sub>) with 3% Tri after charge-discharge.

### 3.4 Cell test

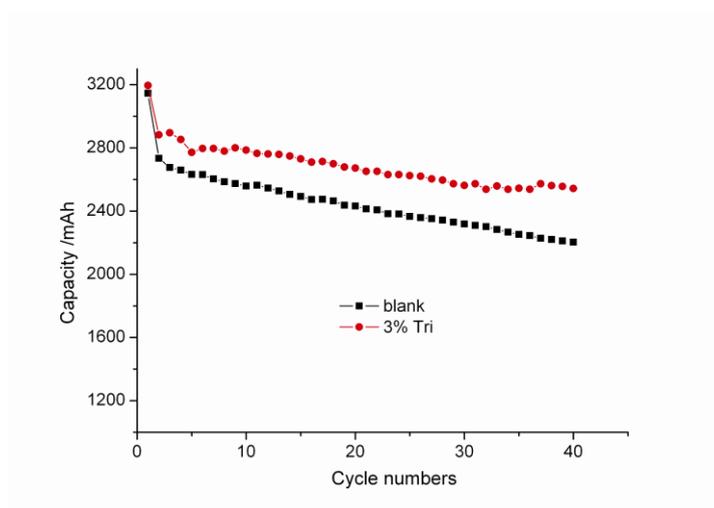
The charge-discharge curves of VRFB with blank V(IV) electrolyte and with V(IV) electrolyte containing 3% Tri additive as the positive electrolyte at 40 mA/cm<sup>2</sup> are shown in Fig. 3. It can be seen that the charge and discharge capacities of VRFB with 3% Tri additive electrolyte are higher than those with blank electrolyte [16, 17], 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 [15].

The decline discharge capacity fade of VRB at  $40 \text{ mA/cm}^2$  for blank and Tri electrolyte samples are presented in Fig. 4. With the cycles increasing, the discharge capacity gradually decreases for the both electrolyte samples due to the vanadium ions transport across the membrane [18, 19]. Compared to blank electrolyte, VRB employing the electrolyte with 3% Tris exhibited less discharge capacity fade, probably described to higher stability of the electrolyte with Tris than that of blank electrolyte.



**Figure 3.** charge and discharge curves for blank sample and 3% Tri sample at  $40 \text{ mA/cm}^2$ .

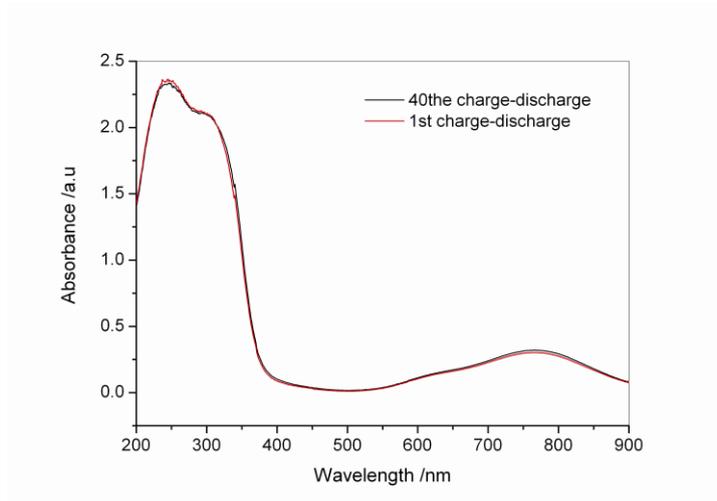


**Figure 4.** Decline discharge capacity of VRB at  $40 \text{ mA/cm}^2$ .

### 3.5 UV-vis spectrometry

Fig. 5 shows the UV-vis spectra of the solutions with Tri additive 1st and 40th charge-discharge cycles list in section 2.3. According to Fig. 5, the max UV absorbance of the two solutions is

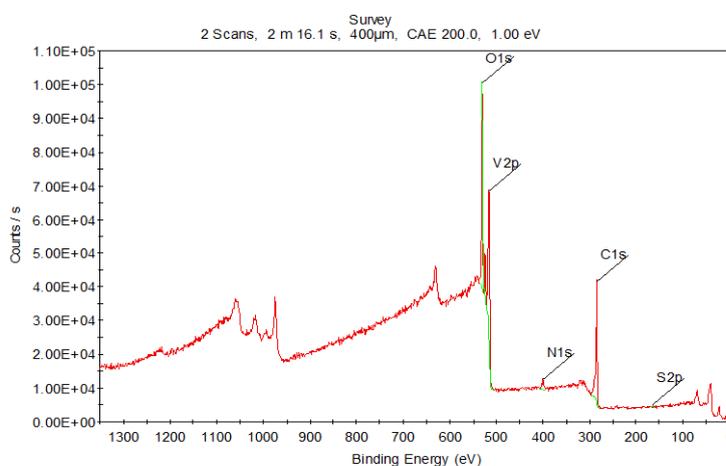
at 200 nm and there is almost no difference between them, which indicating the concentration of the vanadium ion in the positive electrolyte containing Tri additive during 40 charge-discharge cycles remains unchanged and no side reaction is incurred on the carbon felt electrode.



**Figure 5.** UV-vis spectra of electrolyte solutions with Tri additive.

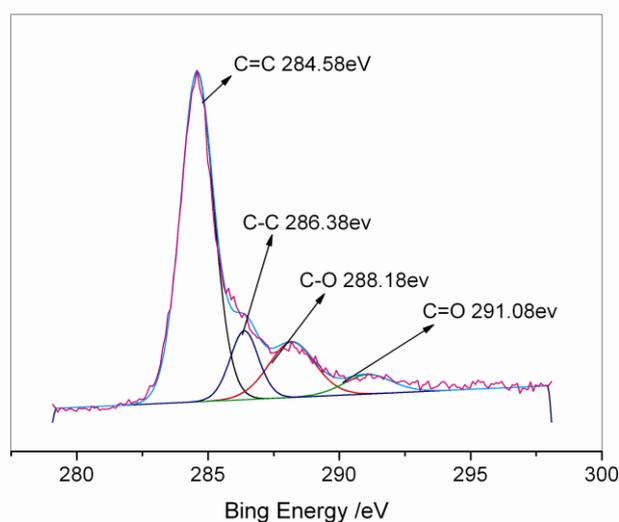
### 3.6 Effect of additive on the carbon felt electrode surface chemistry

To investigate the effect of electrolyte with Tri additive on surface chemistry of the carbon felt electrode after charge-discharge cycles, the XPS was employed. The XPS survey spectra of carbon felt after cycles is shown in Fig. 6. There are five peaks corresponding to O1s, V2p, N1s, C1s, S2p. The intensities of peaks for N1s and S2p are weak indicating the carbon felt surface contains trace N and S elements.

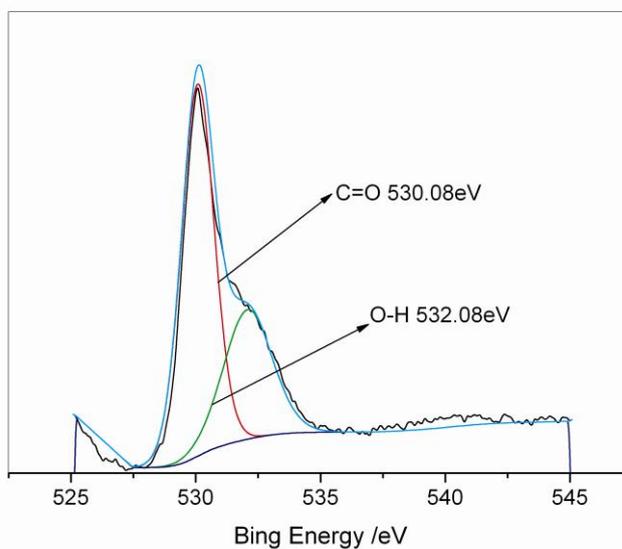


**Figure 6.** XPS survey spectra of carbon felt after 40 cycles

Peak fitting of C1s and O1s was carried out and the results are shown in Fig. 7 and Fig. 8 respectively, and the results are listed in Table 1. The O/C molar ration for the felt for blank electrolyte is slightly higher than that for the Tri electrolyte mainly resulting from higher C=O and C=C groups the lower C-O-C and O-H groups for the Tri sample, indicating the electrolyte with Tri additive has no negative effect on the felt electrode such as the oxidation degradation. However, it can be seen that V content of the felt for blank sample are significantly higher than that for the Tri sample, due to the fact the more  $V_2O_5$  precipitation was formed on the felt for the blank electrolyte during cycles.



**Figure 7.** XPS C1s peaks of carbon felt after 40 cycles



**Figure 8.** XPS O1s peaks of carbon felt after 40 cycles

**Table1** The contents of surface elements and main groups

Name	Peak BE /eV	At. %		Name	Peak BE/eV	At. %	
		blank	additive			blank	additive
S2p	168.1	0.67	0.63	C=C	284.58	70.36	74.54
C1s	284.55	49.75	59.41	C-C	286.38	13.87	12.97
O1s	530.11	32.48	35.0	C-O-C	288.18	12.73	9.41
V2p	530.7	13.8	1.73	C=O	291.08, 530.58	3.04, 65.9	3.08, 73.25
N1s	399.4	3.31	3.23	O-H	532.08	34.1	26.76

#### 4. CONCLUSIONS

The cycling stability of 2M V(V) in 3M H<sub>2</sub>SO<sub>4</sub> electrolyte containing 3% Trishydroxymethyl aminomethane (Tris) was investigated. The 50 cyclic voltammetry (CV) cycles suggested that the positive electrolyte with the Tri additive after charge-discharge cycles has almost the same cycle stability as that before the charge-discharge cycles. The VRB employing the vanadium electrolyte with the Tris additive as positive electrolyte exhibited better charge-discharge behavior and less discharge capacity fade rate with cycles compared with VRB employing the blank electrolyte. The UV/visible spectroscopy showed that the vanadium concentration in the positive electrolyte containing Tri additive during 40 charge-discharge cycles remains unchanged and there no side reaction on the carbon felt electrode. The scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) results showed that the positive electrolyte with the Tri additive has no etching and oxidation effect on the carbon felt electrode.

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