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Effects of organic additives containing —NH_2 and —SO_3H on electrochemical properties of vanadium redox flow battery

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ABSTRACT

Effects of methanesulfonic acid (MSA) and aminomethylsulfonic acid (AMSA) as additives for positive electrolyte on thermal stability and electrochemical performance are investigated. Both additives can improve the thermal stability of V(V) electrolyte, and AMSA has better effect, especially. The electrochemical results show that V(IV)/V(V) exhibits superior electrochemical activity and reversibility with additives, and the diffusion coefficient of V(IV) species, exchange current density and reaction rate constant become larger with additives in positive electrolyte. Among the two additives, AMSA has better effect for improvement of electrochemical activity and kinetics. The cell using positive electrolyte with additive of AMSA was assembled and the charge–discharge performance was evaluated. The assembled cell using AMSA as positive electrolyte additive shows good cycling performance, with higher energy efficiency (81.5%) and larger discharge capacity retention (40 cycles: 82.7%). The improved electrochemical performance may be ascribed to more active sites provided by —NH_2 group and the enhanced hydrophilicity of the electrode provided by —NH_2 and —SO_3H groups.

1. Introduction

With the development of new energy, the redox flow battery systems have attracted much attention, such as Br_2/Br^- vs. S/S^{2-} [1,2], Br^-/Br_2 vs. Zn^{2+}/Zn [3], Fe^{3+}/Fe^{2+} vs. Cr^{2+}/Cr^{3+} [4,5], V^{5+}/V^{4+} vs. V^{2+}/V^{3+} [6,7], etc. [8–11]. Among these technologies, vanadium redox flow battery (VRFB), originally proposed by Skyllas-Kazacos et al., has been considered as one of the most promising energy storage systems for intermittently renewable energy because of its long cycle life, high energy efficiency and environmental friendship [12–16]. The commercial application of VRFB significantly promotes the development of VRFB technology and it shows great prospect for use in stationary energy storage, photovoltaic and wind turbine generators [11,17,18].

Low solubility of V(V) and low electrochemical activity of active species on the electrode are two major disadvantages of VRFB. In sulfuric acid solution, hydrated penta co-ordinated vanadate ion of V(V) would convert to V_2O_5 precipitation at high temperature, which limits the energy density of VRFB [19,20]. Increasing concentration of sulfuric acid can enhance the thermal stability of V(V), however, it also aggravates the thermal stability of V(II), V(III) and V(IV) [18,21]. Adding stabilizing agent is one of the most effective methods to improve the thermal stability of V(V) [22,23]. Some inorganic and organic additives have been chosen and achieved good effects. Inorganic additives, such as sodium hexametaphosphate and alkali metal sulfate, were reported as good stabilizing agent for supersaturated vanadyl sulfate solutions [24]. Moreover, organic additives, such as surfactants, dispersants, or other organic chemicals containing —OH and —SH groups, can also enhance the thermal stability of V(V) [22,25,26]. Graphite felt weaved with carbon fiber is the most widely used electrode for VRFB because of its wide operation potential range, good stability, and high specific surface area at reasonable cost, however, graphite felt electrode shows poor hydrophilicity, electrochemical activity and kinetics. Up to now, a variety of modifications of graphite felt have been reported to improve its electrochemical activity, such as heat treatment [13], acid treatment [27], electrochemical oxidation [28] and introducing functional groups onto the graphite felt [29]. Recently, Wu [29] reported hydrothermal treatment by ammonia for graphite felt, by which the polar nitrogenous groups can be introduced on the surface of graphite felt, leading to faster charge transfer between electrode and vanadium ions. However, strict conditions are needed in this case. Can we introduce the

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nitrogenous groups to the electrode through electrolyte? Sulfonic acid exhibits good electrochemical performance in other redox flow batteries [30–32]. Both of —NH_2 and —SO_3H are hydrophilic groups. Thus, it is interesting to know if —NH_2 and —SO_3H groups would be able to improve the thermal stability and electrochemical performance of positive electrolyte.

In this paper, methanesulfonic acid (MSA: CH_3SO_3H) and aminomethylsulfonic acid (AMSA: ($NH_2CH_2SO_3H$) were used as additives to improve the thermal stability and electrochemical performance of positive electrolyte for VRFB. It is found that both additives (MSA, AMSA) can improve the thermal stability and electrochemical performance, of which AMSA shows the best effect.

2. Experimental

2.1. Thermal stability experiment of V(V)

The V(V) electrolyte was prepared by oxidizing $VOSO_4$ in the positive side of a two-compartment electrolysis cell which employed H_2SO_4 with the same concentration as the catholyte in the negative side. The termination of electrolysis was determined by the UV–Vis measurement. Electrolyte of 2.0 M V(V) in 3.0 M H_2SO_4 with additives MSA or AMSA was stored in a temperature-controlled bath at 50 °C for different immersion time (3 h, 6 h, 9 h, 12 h), respectively. The molar ratio of different additives to V(V) in all measurements is 1%. At the end of immersion, the V(V) electrolyte was centrifuged and analyzed by redox titration to determine the change of the vanadium concentration. The concentration of V(V) ions was titrated by $NaNO_2$ with N-phenylanthranilic acid as indicator. The titration was ended when the color was changed to bright green.

2.2. UV–Vis spectrometry of V(IV) electrolyte

UV–Vis spectrometry of vanadium electrolyte was measured on UNIC 3802 UV/Vis spectrophotometer (Shanghai, China) in the range of 400–900 nm using 1.0 cm quartz cell. The measured solutions are 0.04 M V(IV) and 3.0 M H_2SO_4 without and with additives. The molar ratio of additives to V(IV) is 1%. 3.0 M H_2SO_4 solution with 4×10^{-4} M additives was used as the reference solution for the electrolyte with additives, and 3.0 M H_2SO_4 solution was used as the reference solution for the pristine electrolyte.

2.3. Viscosity measurement

Ubbelohde viscometer was used to measure the viscosity of vanadium electrolytes with different additives. Viscosity can be figured out by timing solution with a specified volume flowing through a capillary tube. The viscosity of electrolytes was calculated according to the following equation.

$$\mu = \frac{\pi \rho g d^4 t}{128V}$$

where μ is the viscosity; ρ solution density; d diameter of capillary; t average time of the solution flowing through a capillary tube; V solution volume.

2.4. Electrochemical measurements

Cyclic voltammetry was carried out in the three-electrode system between +0.3 V and +1.4 V vs. SCE at a scan rate range of 5–200 mV s^{-1}. Tafel polarization curve test was carried out in the three-electrode system at a scan rate of 0.5 mV s^{-1}. A 1 cm^2 graphite plate and 4 cm^2 platinum sheet were used as working electrode and counter electrode, respectively. Saturated calomel electrode along with a salt bridge full of saturated potassium chloride solution was used as reference electrode. Prior to each measurement, the working electrode was polished with 600 and 1200 grit SiC paper and then washed with distilled water as described in literature [33]. The reference electrode was washed with distilled water, and the solution in salt bridge was replaced before use. The tests were performed using the CHI660 C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China).

2.5. Charge–discharge test

The VRFB charge–discharge tests were performed in single dynamic cells, which consisted of two pieces of polyacrylonitrile(PAN)-based graphite felt with the size of 5 cm × 6 cm (Shenhe Carbon Fiber Materials Co., Ltd.), two current collectors and a perfluorinated ion-exchange membrane (Best Industrial & Trade Co., Ltd., China). The graphite felt was encircled and fixed with polyurethane with thickness of 5 cm, and the plyurethane and current collector was sealed with silicon rubber. Original electrolyte used in the tests include 160 mL 1.2 M V(IV) in 3.0 M H_2SO_4 as positive electrolyte and 160 mL 1.2 M V(III) in 3.0 M H_2SO_4 as negative electrolyte. The state of charge (SOC) is 0% at the start of cycling. During the operation, the electrolyte was cyclically pumped into the corresponding half-cell with centrifugal pump (MP-10RN, Shanghai Xinxishan Co., Ltd., China) at a flow rate of 50 mL min^{-1}. The charge–discharge tests were carried out by using CT2001C-10V/2A (Wuhan Land Co., China). The battery was galvanostatically charged and discharged between 0.7 V and 1.7 V at a current density of 40 mA cm^{-2}.

2.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the change of elements on the surface of graphite felt after charge–discharge test with additive of AMSA on a K-Alpha 1063 (Thermo Fisher Scientific, UK) with Al Kα X-ray source generated at 12 kV and 6 mA in an ultra-high vacuum of about 10^{-9} mBar. Before testing the XPS, the graphite felt after charge discharge test with additive of AMSA was treated simply as follow: washed with deionized water, then dried for 5 h at 60 °C.

3. Results and discussion

3.1. Thermal stability of V(V)

To investigate the thermal stability of V(V) at elevated temperature, sealed V(V) electrolyte with MSA and AMSA was placed in a water bath at 50 °C, respectively. The effect of additives on the solubility of V(V) ion at 50 °C is displayed in Fig. 1. The original concentration of V(V) ion is 2.02 M. It can be found that the concentration of V(V) decreases with the increase of immersion time for all electrolyte, and the concentration of the electrolyte with additives of MSA and AMSA is higher than that of the pristine electrolyte for the same immersion time. The reduction of the V(V) concentration in the electrolyte with AMSA is less significant than the pristine one and electrolyte with MSA. Moreover, the concentration of V(V) with AMSA remains 1.14 M, 0.22 M higher than that of the pristine electrolyte at 50 °C after 12 h. It indicates that the V(V) electrolyte with additive of AMSA exhibits the best thermal stability. The improved thermal stability of V(V) electrolyte may be due to that AMSA can enhance the dispersibility of V(V) ions which is easy to hydrate and precipitate for synergy of coulombic repulsion and steric hindrance [19,23]. AMSA containing —NH_2 and —SO_3H groups can be adsorbed on the surface of nuclei of V(V) ions, which enhances the dispersibility of V(V) ions to hinder crystal growth [23].