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Effects of organic additives with oxygen- and nitrogen-containing functional groups on the negative electrolyte of vanadium redox flow battery

Jianlei Liu, Suqin Liu*, Zhangxing He, Huiguo Han, Yong Chen

Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, School of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, China

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ABSTRACT

DL-malic acid and L-aspartic acid are investigated as additives for the negative electrolyte of vanadium redox flow battery (VFRB) to improve its stability and electrochemical performance. The stability experiments indicate that the addition of L-aspartic acid into the 2 M V(III) electrolyte can stabilize the electrolyte by delaying its precipitation. The results of cyclic voltammetry and electrochemical impedance spectroscopy show that the V(III) electrolyte with both additives demonstrates enhanced electrochemical activity and reversibility. The introduction of DL-malic acid and L-aspartic acid can increase the diffusion coefficient of V(III) species and facilitate the charge transfer of V(III)/V(II) redox reaction. Between the two additives, the effect of L-aspartic acid is more remarkable. Moreover, the VFRB cell employing negative electrolyte with L-aspartic acid exhibits excellent cycling stability and achieves higher average energy efficiency (76.4%) compared to the pristine cell (73.8%). The comparison results with the cell employing L-aspartic acid pre-treated electrode confirm that L-aspartic acid in the electrolyte can modify the electrode by constantly providing oxygen- and nitrogen-containing groups, leading to the enhancement of electrochemical performance.

1. Introduction

Redox flow battery (RFB) is one of the most suitable energy storage systems for large-scale intermittently renewable energy. Unlike conventional energy storages, the reactants of redox flow battery are dissolved in the electrolyte and stored in external tanks while the chemical energy is converted to electrical energy in the cell stack [1,2]. The separation of storage and reaction decouples the energy and power characteristics of RFB, providing great flexibility in matching the energy capacity and power capability with different applications. Other attractive advantages of RFB include long lifetime, quick response, easy system configuration and thermal management [3]. Among various RFB systems, vanadium redox flow battery (VRFB), initially proposed by Skyllas-Kazacos [3–5], has excited the most extensive attention due to its utilization of four different valence state of vanadium species that can significantly diminish the cross-contamination of active components. However, the widespread commercialization of VRFB is still restricted by some limitations, including high cost, capacity decay, stability of the key materials (e.g. the membrane and current collector), electrochemical inertness of its electrode towards the vanadium redox couples and the low energy density of its electrolyte.

The surface properties of electrode play a crucial role in the activity and reversibility of V(IV)/V(V) and V(III)/V(II) redox reaction. A large number of modification processes have been applied to the commonly used carbon electrode, including electrochemical oxidation [6], thermal treatment [7], acid treatment [8,9], hydrothermal treatment [10], nitrogen doping [11], electrodeposition of bismuth nanoparticle[12], deposition of metal oxide nanoparticle[13] and the fabrication of composite electrode [14,15]. These techniques achieved to activate the carbon electrodes by formation of different functional groups. The exploration of more technologically simple and energy-saving approaches to modify the electrode is still under way.

The energy density of electrolyte is determined by the solubility of vanadium species. Lower concentration of sulfuric acid or higher temperature could quicken up the precipitation of V(V) species but favor the stability of negative electrolyte [16,17]. Most of the researches are focused on improving the solubility of V(V) species. The solubility of vanadium ions can be promoted by

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* Corresponding author. Tel.: +86 731 88879850; fax: +86 731 88879850.
E-mail address: sqliu2003@163.com (S. Liu).

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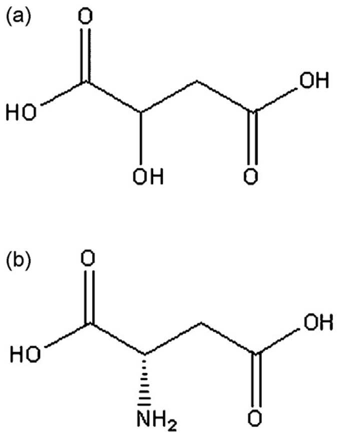

Fig. 1. The structure of (a) DL-malic acid and (b) L-aspartic acid.

optimization of the supporting acid electrolyte. A mixture of sulfuric and hydrochloric acid employed as solvent can considerably improve the thermal stability of V(V) ions [18,19]. The addition of stabilizing agent is another approach to delay the precipitation of vanadium species in sulfuric acid system [20,21]. Organic additives containing oxygen and nitrogen groups such as D-sorbitol, L-glutamic acid and coulter dispersant are reported as effective precipitation inhibitors for V(V) cations at elevated temperature [22–24]. In the meantime, the positive electrolyte with the polyhydroxy compounds [22,25] or amino acids [23] also exhibit enhanced electrochemical performance.

Currently, the electrochemical property of V(IV)/V(V) couple has been enhanced by various approaches employed to modify the electrode or optimize the electrolyte, which makes V(III)/V(II) redox reaction a relatively limiting factor for the electrochemical performance of the cell. Organic additives were commonly used in positive electrolyte for VRFB to improve its stability and electrochemical activity, but few researches have been reported to investigate whether the additives containing oxygen or nitrogen groups would have positive influences on the negative electrolyte. In this research, the effects of DL-malic acid and L-aspartic acid (Fig. 1) on the precipitation behaviour and electrochemical performance of V(III) electrolyte for VRFB are examined.

2. Experimental

2.1. Preparation of electrolyte

V(III) electrolyte containing 2.0 M V(III) and 3.0 M H_2SO_4 was prepared by electrolytic dissolution and reduction of V_2O_5 in sulfuric acid in a two-compartment electrolysis cell which employed sulfuric acid of the same concentration as the anolyte. The termination of electrolysis was determined by UV-vis measurement. The vanadium concentration was analyzed by redox titration. Electrolyte with additives was obtained by adding 3 mol% (mole percentage of the additive to V(III) species) DL-malic acid(99.7%) or L-aspartic acid(99.7%) into the V(III) electrolyte.

2.2. Thermal stability experiment of V(III)

The V(III) electrolyte without and with organic additives was statically stored in a temperature-controlled container at different temperatures (4 °C and 25 °C). The electrolyte was observed at regular intervals to record the time required for visible precipitation.

2.3. Spectrometry Measurements

UV-vis spectrometry of the electrolyte was measured on UNIC 3802 UV-vis spectrophotometer (Shanghai, China) in the range of 200-900 nm using 1.0 cm quartz cell. 3.0 M H_2SO_4 was used as the pristine solution.

Raman spectrometry measurement of the electrolyte was conducted on Labram-010 spectrophotometer (Jobin Yvon-Instruments SA).

X-ray photoelectron spectroscopy (XPS) of electrodes was conducted on 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. The graphite felt obtained from the charge-discharge tests was washed with and soaked in the deionized water to remove the electrolyte and impurities, followed by being dried for 5 h at 60 °C.

2.4. Viscosity measurement

Viscosity measurements of 2 M V(III) electrolyte with and without different additives were conducted with an Ubbelohde viscometer. The diameter of the capillary is 1.0 mm. The temperature was maintained at 20 °C.

2.5. Electrochemical measurements

Cyclic voltammetry measurement was conducted in a three-electrode system on RST5200 electrochemical workstation (Zhengzhou Shiruisi Technology Co., Ltd., China) at a scan rate range of 10-200 mV s^{-1} between -0.9 V and 0 V at room temperature. The system employed a 1 cm^2 graphite plate as working electrode, a 4 cm^2 platinum sheet as counter electrode and a saturated calomel electrode along with a salt bridge filled with saturated potassium chloride solution as reference electrode. The graphite plate was polished with 600 and 1200 grit SiC paper and then washed with deionised water before each test.

Electrochemical impedance spectroscopy was conducted on PARAST electrochemistry workstation (USA, AMETEK, Inc.). The sinusoidal excitation voltage applied to the cells was 5 mV. The frequency range was from 0.005 Hz to 100 kHz.

2.6. Charge-discharge test

The charge-discharge tests were performed in a VRFB single dynamic cell, which was assembled by employing a perfluorinated ion-exchange membrane (Best Industrial & Trade Co., Ltd., China) as separator, two pieces of polyacrylonitrile (PAN)-based graphite felt (Shenhe Carbon Fiber Materials Co., Ltd.) with an area of 30 cm^2 as electrodes and conductive plastics as current collectors. All of the above components were sealed with silicon rubber. 160 mL 1.2 M V(IV) in 3.0 M H_2SO_4 and 160 mL 1.2 M V(III) in 3.0 M H_2SO_4 were used as original positive and negative electrolyte respectively. The electrolyte was cyclically pumped into the corresponding half-cell and flowed through the electrode compartment during operation. The cell tests were conducted on CT2001C-10 V/2A battery test system (Wuhan Land Co., China) between 0.7 V and 1.7 V at a constant current density of 60 mA cm^{-2}.

3. Results and discussion

3.1. Thermal stability of V(III) electrolyte

To investigate the effects of organic additives on the thermal stability of V(III) electrolyte, 2 M V(III) ions in different concentrations of sulfuric acid were sealed and stored in a temperature-controlled