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A study of tiron in aqueous solutions for redox flow battery application

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ABSTRACT

In this study, the electrochemical behavior of tiron in aqueous solutions and the influence of *pH* were investigated. A change of *pH* mainly produces the following results. In acidic solutions of *pH* below 4, the electrode reaction of tiron exhibits a simple process at a relatively high potential with a favorable quasi-reversibility. The tiron redox reaction exhibits fast electrode kinetics and a diffusion-controlled process. In solutions of *pH* above 4, the electrode reaction of tiron tends to be complicated. Thus, acidic aqueous solutions of *pH* below 4 are favorable for the tiron as active species of a redox flow battery (RFB). Constant-current electrolysis shows that a part of capacity is irreversible and the structure of tiron is changed for the first electrolysis, which may result from an ECE process for the tiron electro-oxidation. Thus, the tiron needs an activation process for the application of a RFB. Average coulombic and energy efficiencies of the tiron/Pb battery are 93 and 82%, respectively, showing that self-discharge is small during the short-term cycling. The preliminary exploration shows that the tiron is electrochemically promising for redox flow battery application.

1. Introduction

As a new type of low cost, high-efficiency, large-scale energy storage system [1], the redox flow battery (RFB) allows energy to be stored in two recirculated electrolytes that contain different soluble redox couples. It can not only be used for the electricity storage of renewable energy to ensure the continuity and stabilization of electricity generation and supply, but also can be used for load leveling/peak shaving of electricity supply networks. Over the past years, it has received widespread great attention. Since the redox flow battery concept was proposed by Thaller [2] in 1974, a number of RFB systems, such as chromium/iron [2], zinc/bromine [3], polysulfide/bromine [4], all-vanadium [5], vanadium/bromine [6] and lead-acid [7], have been fabricated and developed. The related battery techniques obtained substantial progresses. Among these systems, the vanadium redox flow battery is the most practical candidate due to the use of the same element in both the half-cells, which avoids problems of cross-contamination of the two half-cell electrolytes during long-term use [5]. However, all the present RFBs are based on inorganic active materials. That is, their development is inevitably restricted by limited mineral resources. For example, with the rapid soaring of the vanadium mineral resources price, the commercialization of all-vanadium redox flow batteries is faced with pressure. In addition, the specific energy of RFBs is relatively low, which is related to the concentration of the redox ions in solutions, to the cell potential and to the number of electrons transferred during discharge. Comparatively, most of organic materials can be synthesized from abundant resources mainly being composed of such elements as C, H and O. Moreover, chemical tunability of organic compounds has made them even more attractive [8]. That is, organic materials can be modified (designed) to give additional chemical and/or electrochemical properties of interest. This characteristic favors the number of electrons transferred during discharge to be adjusted. Therefore, it inspired us to investigate the electrochemical prospect of organic active materials for application in RFBs, expanding the space for the development of RFBs.

Tiron (4,5-dibenzoquione-1,3-benzenedisulfonate) is one kind of weakly acid aromatic organic compound, belonging to the derivative of catechol [9]. Usually, catechol and its derivatives are electrochemically reversible to a certain degree with relatively high electrode potentials in aqueous solutions [10]. Two sulfonic groups on the benzene ring of tiron improve the solubility of tiron. Hence, tiron has the potential to be used as the positive active material of a RFB. To date, however, there has been no literature describing the use of tiron in chemical power sources as an active material. In most cases, tiron is used in chemical [11] and electrochemical analysis [12] as a chelator and an indicator.

In this study, the electrochemical behavior of the tiron is explored deeply in order to assess its suitability as active species in the positive electrolyte of a RFB. On top of it, a preliminary understanding of its electrode reaction mechanism in acidic aqueous solutions is developed. At the same time, the charge–discharge performance of a small tiron/Pb test cell is reported.

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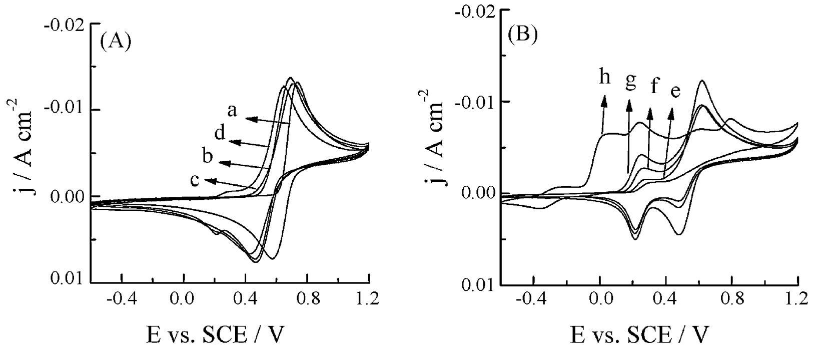

Fig. 1. Cyclic voltammograms for 0.05 M tiron in 1 M KCl solutions of *pH* (a) 0; (b) 2; (c) 4; (d) 6; (e) 7; (f) 8; (g) 10; (h) 12 at a graphite electrode, scan rate: 50 mV s^{-1}.

2. Experimental

2.1. Chemicals and electrode pretreatment

The tiron (hydrated 4,5-dibenzoquione-1,3-benzenedisulfonate) of 98% purity was from Alfa Corp., TianJin, China and all the other reagents were analytical grade.

Prior to test, the working electrodes were pretreated as follows: after grinding with emery paper 1000 grade, the electrodes were washed by ultrasonic cleaning in de-ionized water for 10 min. After cleaning, the electrodes were cycled in 3 M H_2SO_4 solution between −1.0 and 1.0 V (vs. SCE) for 20 min at a scan rate of 10 mV s^{-1}.

2.2. Cyclic voltammetry and electrolysis

Cyclic voltammetry (CV) tests were performed in a three-electrode cell which comprised a graphite rod embedded in epoxy resin as working electrode (0.24 cm^2), with a big area graphite plate and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. The electrolytic solution used was 0.05 M tiron in 1 M KCl aqueous medium with *pH* adjusted with H_2SO_4 or NaOH for the studied *pH* range of 0–12.

To compare with the CV results obtained in stationary solutions and to get the kinetic data, voltammograms were also recorded at a series of rotation rates using a graphite disc electrode (0.1256 cm^2). This electrode was pretreated as above before test. Cyclic voltammograms were measured by CHI1100 electrochemical station (CH Corporation, USA). The rotation rate of the rotating disc electrodes (RDEs) was controlled with an EG & G Model 636 RDE unit. All experiments were conducted at room temperature of 25 °C.

The constant-current electrolysis of the tiron was conducted at 10 mA cm^{-2} with a flow-type cell, in which a cation-exchange membrane (Nafion 115, Du Pont) was used as a separator. A graphite felt electrode (10 mm in thickness) contacted against one graphite plate was used as the working electrode. A lead negative electrode with an area of around 20 cm^2 and a SCE electrode were used as the counter electrode and reference electrode, respectively. The apparent surface area for the working electrode was approximately 5 cm^2. Fifty milliliters of 50 mM tiron in 3 M H_2SO_4 medium was used as the feed solution while 3 M H_2SO_4 was contained in the counter-electrode compartment. One Xishan magnetic drive pump (China) was used to pump the feed solution through the working electrode where the electrolysis reactions occurred. The constant-current electrolysis of the tiron was recorded by an electrochemical test station (Solartron 1280B, England) at the temperature of 298 K.

2.3. Battery fabrication and charge/discharge measurements

A model test cell was applied for the constant-current charge/discharge tests. This test cell consisted of three main parts, the positive and negative electrode compartments and a cation-exchange membrane (Nafion 115, Du Pont) situated between the two compartments. A flange joint held the membrane with rectangle-shaped rubber gaskets. The positive electrode compartment housed a 10 mm thick graphite felt electrode (area: 5 cm^2) contacted against one graphite plate that acted as the current-collector. The negative electrode compartment housed a lead electrode used in valve-regulated lead-acid (VRLA) batteries, the area of which was calculated according to the theoretical capacity needed. Twenty milliliters of 0.25 M tiron in 3 M H_2SO_4 medium was employed as the positive electrolyte and 3 M H_2SO_4 solution of 20 mL was employed as the negative electrolyte. Two Xishan magnetic drive pumps (China) were used to pump each half-cell electrolyte through the corresponding half-cell cavity where the charge–discharge reactions occurred.

The performance of test cells was evaluated with constant-current charge–discharge experiments. A Land CT2000A battery test system (Jinnuo Wuhan Corporation, China) was employed for the charge–discharge cycling experiments. During the charge–discharge cycles, the cell was charged at a current density of 10 mA cm^{-2} up to 1.2 V and discharged down to 0.6 V cut-off at the same current density. After full charging, open-circuit voltage of the battery was measured.

3. Results and discussion

3.1. Effect of pH

The structures of some catechol derivatives are affected greatly by the *pH* of aqueous solutions, thereby exhibiting different electrochemical behaviors with varying the *pH* [13]. As a derivative of catechol, the electrochemical behavior of tiron may be *pH*-dependent. Therefore, this paper firstly deals with the influence of *pH* on the voltammetric behavior of tiron to make sure the suitable *pH* range of solutions for the use of tiron in RFBs as an active material.

Fig. 1 shows the influence of *pH* on the cyclic voltammograms of 0.05 M tiron at a graphite electrode in 1 M KCl aqueous solution of different *pH*. As seen in Fig. 1A, the profile of the *I* vs. *E* curves is almost the same in solutions with *pH* lower than 4. And, only one oxidation peak (E_{pa} = 0.74 V) and a corresponding reduction peak (E_{pc} = 0.58 V) are obtained. However, with the increase of *pH*, the oxidation peak potential shifts toward a less positive value. Also, the peak current is somewhat reduced. When the *pH* of solutions reaches 4, an additional much smaller oxidation peak and a corresponding reduction peak appear at around 0.25 and 0.20 V vs. SCE, respectively. From Fig. 1B, it is found that when the *pH* changes progressively from 4 to 12, the responding currents of the new coupled peaks increase gradually. In contrast, the peak current at the high potential decreases continuously. When the *pH* is up to