Contents lists available at ScienceDirect





Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

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

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ARTICLE INFO

Article history: Received 5 July 2009 Received in revised form 7 September 2009 Accepted 8 September 2009 Available online 15 September 2009

Keywords: Redox flow battery Tiron Electrochemical behavior Acid aqueous solution Tiron/Pb battery

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.

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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 halfcell 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

* Corresponding author. E-mail address: wen_yuehua@126.com (Y.-H. Wen). 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 $3 \text{ M H}_2\text{SO}_4$ 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 threeelectrode 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 H₂SO₄ 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 cm²). 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 cm² 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 cm². Fifty milliliters of 50 mM tiron in 3 M H₂SO₄ medium was used as the feed solution while 3 M H₂SO₄ 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 constantcurrent 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 cationexchange 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 currentcollector. 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 $3 \text{ M H}_2\text{SO}_4$ medium was employed as the positive electrolyte and $3 \text{ M H}_2\text{SO}_4$ 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 constantcurrent 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 pHdependent. 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

рН	0	2	4	6	7	8	10
E_{1A}/V	0.735	0.689	0.650	0.648	0.619	0.629	0.618
$ E_{1A} - E_{1C} /V$	0.159	0.220	0.191	0.184	0.139	0.154	0.142
$ I_{1A}/I_{1C} $	1.42	1.54	1.12	1.12	1.36	1.66	1.87
E_{2A}/V	-	-	0.308	0.295	0.286	0.268	0.254
$ E_{2A} - E_{2C} /V$	-	-	0.103	0.083	0.070	0.055	0.038
$ I_{2A}/I_{2C} $	-	-	1.10	1.28	1.31	1.37	1.19

 Table 1

 Data obtained from cyclic voltammograms of Fig. 1 at various *pH*.

12, multi-oxidation peaks appear on the voltammograms without the corresponding reduction peaks. This indicates that the oxidation products of tiron are difficult to be reduced in strongly alkaline solutions of pH up to 12. It is manifested by the above cycle voltammograms that in acidic solutions of pH lower than 4, the electrode reaction of tiron is simple with a relatively high potential, which is favorable for the application of tiron in RFBs. In solutions of pH higher than 4, the electrode reaction of tiron in RFBs, the pH of electrolytes should be lower than 4. For this reason, we limited our studies to the solutions of pH 0 below.

Some data obtained from Fig. 1 and summarized in Table 1, where E_A stands for the oxidation peak potential, $|E_A - E_C|$ for the peak potential separation and $|I_A/I_C|$ for the peak current ratio, respectively. From Table 1, the voltammetric behavior can be explained except for that at pH 12, (1) with rising the pH, the oxidation potential of tiron decreases progressively; (2) for the electrochemical reaction taking place at the high potential, the potential separation is more than 100 mV and the peak current ratio is ranged from 1.12 to 1.87, which is deviated from the value of unity to varying extents. At pH below 8, the extent of deviation is less than 50%, while it is especially large (>50%) at pH above 8. This suggests that the electrode process at pHabove 8 is far from the ideal reversibility; (3) for the redox reaction taking place at the low potential, the potential separation is basically less than 100 mV, which is particularly small (<60 mV) at *pH* above 8. Nevertheless, the peak current ratio is still higher than 1. It suggests that in solutions of pH below 12, the electrode reaction of tiron displays a quasi-reversible redox process, while at pH 12, the oxidation products of tiron cannot be reduced and the electrode process of tiron has become irreversible.

3.2. Effect of scan rate and cycling

Fig. 2A gives the cycle voltammograms recorded at a graphite electrode at a range of potential scan rates for 0.05 M tiron in 1 M KCl solutions of *p*H 0. A plot of the peak current density (j_p) as a function of the square root of scan rates ($v^{1/2}$) is shown in Fig. 2B. As seen in Fig. 2A, nearly no change in the profile of voltammograms is observed in the range of scan rates studied. But, with increasing the scan rate, the gradual shift of the peak potentials causes the peak potential separation to be increased to a certain degree. It is verified further that the system in strongly acidic aqueous solutions presents a quasi-reversible behavior and an increasing irreversibility for faster scan rates. In parallel, for both the oxidation and reduction processes of tiron, an almost linear response is obtained (see Fig. 2B), indicating relatively fast electrode kinetics and a diffusion-controlled reaction.

In addition, Fig. 2C illustrates the cyclic stability of tiron at the graphite electrode during the initial 100 cycles in the same solution at a scan rate of 50 mV s^{-1} . Compared with the first cycle, almost no variation is observed among the remaining voltammograms. This suggests that the cycling stability and the reversibility of tiron at a graphite electrode are electrochemically favorable.



E vs. SCE / V

Fig. 2. (A) Cyclic voltammograms recorded at potential scan rates (a) 5; (b) 10; (c) 20; (d) 50; (e) 100 mV s⁻¹ at a graphite electrode for 0.05 M tiron in 1 M KCI solutions of *pH* 0. (B) Plots of the peak current density (*j_p*) vs. the square root of scan rate ($v^{1/2}$) for the oxidation and reduction processes in (A). (C) Cyclic voltammograms for 0.05 M tiron in 1 M KCI solutions of *pH* 0 at a graphite electrode with the 1st and 100th scan cycles. Scan rate: 50 mV s⁻¹.

3.3. Rotating disc voltammetry

Fig. 3 reports cyclic voltammograms recorded at a rotating graphite disc electrode with various rotation rates in 0.05 M tiron + 1 M KCl solutions of *pH* 0. In a stationary solution (rotation rate = 0 rpm), the voltammogram shows well-formed reduction and



Fig. 3. Cyclic voltammograms recorded at a rotating graphite disc electrode in 0.05 M tiron + 1 M KCl solutions of *pH* 0, scan rate: 50 mV s^{-1} , rotation speeds: 0, 100, 400 rpm for curves 1–3, respectively.

coupled oxidation peaks at 0.74 and 0.58 V vs. SCE, respectively. The formal potential of tiron is thus seen to be at around 0.66 V vs. SCE, which is somewhat lower than that of the V(V)/V(IV) and Br₂/Br⁻couples. But, the effects of side reactions such as O₂ evolution would be smaller when employing tiron as the positive active species for a RFB since side reactions may be easier to occur at a more positive electrode potential. Moreover, scanning the electrode in the positive direction up to 1.5 V vs. SCE, no anodic side reaction associated with O₂ evolution takes place. No cathodic peak associated with H₂ evolution is observed on the reverse scan to -0.3 V vs. SCE. With increasing the rotation rate, the oxidation peak current increases owing to a decrease in the mass transportation polarization. Scanning the electrode continuously in the positive direction is seen to give rise to an increase in the oxidation current. On the reverse scan, oxidation continues to 0.7 V vs. SCE and then the current becomes cathodic with a lowered reduction peak. When the rotation rate reaches 400 rpm, the oxidation wave shows a welldefined limiting current plateau and no reduction peak appears. This corresponds to the complete diffusion-controlled electrode process.

Fig. 4 shows the dependence of the voltammetry on the rotation rate of the graphite disc electrode in the same solution. It can be seen that a well-formed oxidation wave is observed and the limiting current depends strongly on the rotation rate of the disc. Indeed, a plot of the limiting current density, I_L vs. $w^{1/2}$ is linear passing through the origin, confirming that the oxidation of tiron becomes mass transport controlled and the Levich equation was used to obtain a diffusion coefficient for tiron in this medium; the value calculated was 2.2×10^{-7} cm² s⁻¹ which is one magnitude lower than that of inorganic ions such as vanadium or lead ions.



Fig. 4. Voltammograms at a rotating graphite disc electrode as a function of rotation rate. The solution is 50 mM tiron in $3 \text{ M} \text{ H}_2\text{SO}_4$. Potential scan rate: 5 mV s^{-1} .



Fig. 5. Electrolytic characterization of tiron in 3 M H₂SO₄ at 298 K.

For an electrode reaction that is activation controlled, the exchange current density can be determined by the Butler–Volmer formula [14]; the average value calculated was 3.9×10^{-4} A cm⁻² which is comparable to that of vanadium ions. It can be inferred that the major polarization of tiron may be caused by the mass transportation when the tiron is used as battery active species. Herein, the flow of electrolytes containing active species, tiron, in a RFB would facilitate a significant decrease in the mass transportation polarization.

3.4. Electrolytic characterization of tiron

Electrolytic characterization of the tiron was investigated by constant-current electrolysis of 60 mL of 50 mM tiron in $3 M H_2SO_4$ medium. Fig. 5 shows the electrolytic characterization of tiron in $3 M H_2SO_4$ at 298 K. It is found that the charge potential of tiron on the first cycle is much higher than that on the following cycles, and the time taken for complete oxidization of tiron on the first cycle is more than twice that on the following cycles. This suggests that the first electro-oxidation of tiron may be a four-electron reaction while the succedent electro-oxidation of tiron turns to be a two-electron reaction. A possible explanation [15] is that the electrochemical reaction mechanism of tiron is an ECE process in which the first charge-transfer reaction is followed by a chemical reaction, and then the secondary charge-transfer reaction occurs. The ECE reaction process can be expressed as follows:



Consequently, the structure of tiron is changed. Starting from the secondary electrolysis, only the secondary oxidation/reduction

reaction of tiron takes place. This phenomenon cannot be shown in the cyclic voltammograms. The reason may be that the secondary reaction is much easier to occur than the first one, resulting in only one pair of peaks observed. Of course, this needs to be confirmed with further experiments, e.g. ring-disc electrode experiments.

3.5. Charge–discharge performance of a tiron–Pb redox flow battery

To minimize the cross-contamination of the positive and negative electrolytes through an ion-exchange membrane, a solid lead negative electrode was combined with the tiron redox couple to form a redox flow battery to demonstrate the suitability of tiron as active species in the positive electrolyte of a RFB.

Performance of a RFB employing 0.25 M tiron in 3 M H₂SO₄ as positive active species and the lead electrode as negative active species was evaluated with constant-current charge-discharge tests and open-circuit voltage measurements, respectively. A plot of cell voltage vs. time obtained for the initial five charge-discharge cycles is given in Fig. 6A. The change in coulombic and energy efficiencies of the Pb/tiron battery in the first 10 cycles is given in Fig. 6B. From Fig. 6A, it can be seen that the charge voltage of the battery for the first cycle is much higher than that on the following cycles. In combination with Fig. 6B, the coulombic efficiency is just 38% for the first cycle, indicative of a part of capacity irreversible resulting from the tiron. It suggests that the tiron needs to be activated for the application of a RFB. From the second cycle, the coulombic efficiency is enhanced to be over 90% which has indicated the reversible behavior of the tiron activated electrochemically. And, the battery basically shows no deterioration during the succedent charge-discharge cycles. This corresponds to the electrolytic characterization of tiron. Open-circuit cell voltage after full charging remains constant at 1.10 ± 0.05 V. The average



Fig. 6. (A) Charge–discharge cycling curves for the Pb/tiron redox cell employing 0.25 M tiron in 3 M H_2SO_4 as positive active species and the lead electrode as negative active species. Current density: 10 mA cm⁻². (B) Coulombic and energy efficiencies of the Pb/tiron battery in the first 10 cycles. Current density: 10 mA cm⁻².

coulombic and energy efficiency values except for the first cycle were calculated as 93 and 82%, respectively, which are comparable to that for the all-vanadium and zinc-bromine systems at a relatively low current density. This indicates that the self-discharge due to diffusion of the species of tiron through the membrane is small.

The proposed charge–discharge reactions of the Pb/tiron redox flow cell after the activation can be described as follows:



Negative:

$$Pb + SO_4^{2-} \underset{charge}{\overset{discharge}{\rightleftharpoons}} PbSO_4 + 2e^- \qquad E^0 = -0.35 V$$

While the cell component materials such as electrodes and membranes, and cell design have yet to be optimized, the above results demonstrate that the tiron as active species in the positive electrolyte of a RFB is technically feasible and warrants further investigations to increase the charge–discharge rate and cycling stability of the battery.

4. Conclusions

In this study, the voltammetric behavior of the tiron in aqueous solutions, influence of *pH*, and electrolytic characterization were investigated. The following conclusion can be drawn:

- 1. The *pH* of solutions has a major influence on the electrochemical behavior of tiron. In acidic solutions of *pH* below 4, the electrode reaction of tiron exhibits a simple process at a relatively high potential. In solutions of *pH* above 4, the electrode reactions of tiron tend to be complicated. The acidic aqueous solution of *pH* below 4 is favorable for the tiron as positive active species of a redox flow battery.
- 2. The electrode process of tiron in acidic aqueous solutions of *pH* below 4 is electrochemically quasi-reversible, exhibiting relatively fast electrode kinetics and a diffusion-controlled reaction.
- 3. The electro-reaction mechanism of tiron is an ECE process, leading to a part of capacity irreversible and a change in the structure of tiron for the first electrolysis. As a result, the tiron needs an activation process for the application of a RFB.
- 4. The tiron/Pb battery employing 0.25 M tiron in 3 M H₂SO₄ as positive active species and the lead electrode as negative ones is reported. Coulombic and energy efficiencies of 93 and 82%, respectively, are obtained in a small laboratory cell that has a Nafion 115 membrane and graphite felt electrodes compressed against graphite current-collectors. Self-discharge was small during the short-term cycling. Further work is currently underway to test the long-term effect of electrolyte cross-contamination by tiron transfer across the membrane. A range of modified graphite felt and membrane materials are presently being evaluated over extended cycling periods to improve the long-term performance of the battery.

Acknowledgements

This work was financed by the National Basic Research Program (973 Program) of China (2010CB227204) and the National Natural Science Foundation of China (No. 20573135).

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