Short communication

Study on a high current density redox flow battery with tin(II)/tin as negative couple

Fuyu Chen a, Qing Sun a, Wei Gao a, Jianguo Liu b, Chuanwei Yan b, Qingyu Liu a, *

a College of Engineering, Shenyang Agricultural University, Shenyang 110866, China
b Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

HIGHLIGHTS

- Sn deposition can almost dissolve completely after the charge-discharge process.
- The diffusion coefficient for Sn^2+ is estimated to be 2.86 x 10^{-4} cm^2 s^{-1}.
- The Sn–V battery could work steadily at a high current density of 180 mA cm^{-2}.

ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form 22 December 2014
Accepted 8 January 2015
Available online 9 January 2015

Keywords:
Redox flow battery
Vanadium
Tin
Energy storage
High current density

ABSTRACT

The cyclic voltammetry characteristics of Sn^{2+}/Sn couple in the H_2SO_4 medium on a graphite felt electrode is evaluated. The charge–discharge performance of Sn–V battery with VO_2^+/VO_2^{2+} couple as positive part and Sn^{2+}/Sn couple as negative part is investigated through a small laboratory cell. The result shows that though the deposition/dissolution of Sn is not a normal reversible process, Sn deposits can almost dissolve completely during the charge–discharge tests. It is remarkable that the battery could work normally at a current density of 180 mA cm^{-2} with an average voltage efficiency of 72%.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Redox flow batteries (RFBs) are electrochemical energy storage devices that utilize the oxidation and reduction of soluble redox couples for charging and discharging. Since the RFB concept was first proposed by Thaller [1] in 1974, several types of redox flow batteries have been developed [2]. For example, all-vanadium system [3], Fe/Cr system [4] and polysulphide–bromine system [5] belong to liquid phase batteries while zinc–bromine system [6], zinc–nickel battery [7] and lead-acid system [8] belong to deposition phase batteries, in which the couple of deposition/dissolution of metal ions, such as Zn^{2+}/Zn and Pb^{2+}/Pb, were used as negative part.

RFBs have several advantages over some of the established technologies such as lead-batteries [9–11]: long cycle life and relatively easy maintenance; high battery efficiency; environment friendliness; deep discharge. So the RFB is considered as the most promising electrochemical system for large energy storage [12], and received widespread attention over the past years.

Current density is one of the most important parameters of the redox flow battery and its increase helps improve the specific capacity and to decrease the cost. At the same time, the security of the battery can be effectively enhanced with high tolerable overload current. However, battery performances of some reported single flow batteries decreased markedly with the work current density increasing. For example, the voltage efficiency of Zn/B_2S_3 battery was over 80% at the current density of 30 mA cm^{-2} but drop to only about 45% at 100 mA cm^{-2} [12]. As for the single flow battery, such as zinc–nickel battery [7], lead–acid flow battery [8] and Cu–H_2SO_4–PbO_2 battery [13], the reported current densities were all lower than 50 mA cm^{-2}. It was clear that low work current density is one of the obstacles need to be overcome for the application of energy storage.
In this paper, \( \text{Sn}^{2+}/\text{Sn} \) couple in the acid medium is proposed as negative couple for redox flow battery. When using \( \text{VO}_2^+/\text{VO}_2^{2+} \) couple as positive part, the battery could work steadily at the current density of 180 mA cm\(^{-2}\), with an average columbic, energy and voltage efficiencies were 96%, 70% and 72%, respectively.

2. Experimental

2.1. Electrolytes

Electrolytic solutions were prepared by dissolving \( \text{SnCl}_2 \) in 2 M \( \text{H}_2\text{SO}_4 \). The concentrations of \( \text{Sn}^{2+} \) for CV and charge–discharge experiments were 0.05 M and 1 M, respectively. All chemicals were analytical reagent grade.

2.2. Cyclic voltammetry and surface morphology

Cyclic voltammetry was performed with a Model 273 Potentiostat/Galvanostat (EG&G, U.S.A.), using a three-electrode with a graphite felt electrode of 0.2 cm\(^2\) as the working electrode. A saturated calomel electrode (SCE) electrode as the reference electrode, and a large-area (approximately 2 cm\(^2\)) platinum plate as the counter electrode. The working electrode was ultrasonically cleaned and rinsed thoroughly with distilled water. All solutions were purged with nitrogen prior to the experiments.

The surface morphology of the graphite felt was examined by using scanning electron microscope (SEM) (FEI Company Inspect F, Japan).

2.3. Charge–discharge experiments

The charge–discharge tests were performed in a small test battery with the \( \text{VO}_2^+/\text{VO}_2^{2+} \) couple as positive part. The graphite felts were used as electrodes, conductive plastics as current collectors and the Nafton 212 membrane was used to divide the positive and the negative compartments. The positive compartment was filled with 2 M \( \text{VOSO}_4/2 \text{M H}_2\text{SO}_4 \) solution and the negative compartment was 1 M \( \text{SnCl}_2/2 \text{M H}_2\text{SO}_4 \) solution. Charge–discharge tests were performed with a LAND CT2001A battery test system (Land Wuhan Corp., China) at room temperature. In the charge–discharge cycles, current density increased from 20 to 180 mA cm\(^{-2}\), the battery was charged up to 1.5 V and discharged down to 1.1 V. Cathode was airproof in the charge–discharge tests.
Two compartments were sealed after purging nitrogen for 30 min.

3. Results and discussion

3.1. Voltammetric behavior of Sn$^{2+}$ in H$_2$SO$_4$ solution

Fig. 1 showed cyclic voltammograms on the graphite felt electrode in 0.05 M Sn$^{2+}$/2 M H$_2$SO$_4$ solution. The currents associated with both oxidation and reduction were much larger in the tenth and fortieth cycles than that in the first cycle, probably due to that the wetting property of the graphite felt was improved after soaking in electrolyte. In the multiple scan cycles, both oxidation and reduction peak current densities were stable and the shape of anodic and cathodic peak were symmetrical. This was superior to the classical response for the deposition and stripping of a metal onto a foreign substrate where nucleation and growth of the new phase was required [8].

Fig. 2 showed the typical CVs obtained at different scan rates in a solution of 0.05 M Sn$^{2+}$/2 M H$_2$SO$_4$. The peak separation, $\Delta E_p$, increased from 370 to 826 mV, suggesting that the reaction of Sn$^{2+}$+2e $\rightarrow$ Sn is irreversible at the graphite felt electrode [14,15]. For an irreversible reaction, the peak current, $i_p$, was given by Refs. [16,17]:

$$i_p = 2.99 \times 10^5 n^{3/2} C_0^{1/2} D_0^{1/2} v^{1/2} \left( \text{A cm}^2 \right)$$

where $C_0$ is the bulk concentration of oxidant (moles cm$^{-3}$), $v$ is the potential sweep rate (V s$^{-1}$), $D_0$ is the diffusion coefficient of the oxidant, $\alpha$ is the transfer coefficient and $n$ is the number of electrons involved in the rate determining step.

A plot of $i_p$ vs. $v^{1/2}$ should therefore give a straight line with a slope proportional to $D_0$. The diffusion coefficient for Sn$^{2+}$ in a supporting electrolyte of 2 M H$_2$SO$_4$ was estimated to be $2.86 \times 10^{-4}$ cm$^2$ s$^{-1}$ based on the cathodic peak current for the Sn$^{2+}$/Sn redox couple.

3.2. Charge–discharge performance

The charge–discharge efficiencies for the established Sn–V battery under different current densities were illustrated in Fig. 3. Unlike the columbic efficiency maintained higher than 90%, the energy efficiency and the voltage efficiency decreased continuously.

Fig. 5. Coulombic efficiency, voltage efficiency and energy efficiency of the Sn–V battery at 180 mA cm$^{-2}$ current density (■) Coulombic efficiency, (▲) voltage efficiency, (●) energy efficiency. Temperature 298 K.

Fig. 1. Cyclic voltammograms on the graphite felt electrode in 0.05 M Sn$^{2+}$/2 M H$_2$SO$_4$ solution.

Fig. 2. Cyclic voltammograms at different scan rates in a solution of 0.05 M Sn$^{2+}$/2 M H$_2$SO$_4$.

Fig. 3. Charge–discharge efficiency of the Sn–V battery under different current densities.

Fig. 4. SEM images of graphite felt after 150 cycles: (a) end of charging; (b) end of discharging; (c) enlarged of (a); (d) enlarged of (b).
to about 70% and 74.5%, respectively, when the current density was increased to 180 mA cm$^{-2}$ because of the increasing polarization on the electrode.

Ten cycles charge–discharge curves of Sn–V battery at a current density of 180 mA cm$^{-2}$ was shown in Fig. 4. In all charges, the cell voltage remained almost constant and the value of the cell voltage is the same in all the cycles. This behavior could be ascribed to the fact that the deposition of Sn on the activated graphite felt decreased the negative resistance within the cell. During the discharge cycles at the same current, the curve showed a characteristic voltage drops, indicating a complete discharge [12]. Adsorption of Sn on the graphite felt provided readily available reactive and the discharge process only became mass transport controlled at high reactant conversion levels. The average columbic, energy and voltage efficiencies were 96%, 70% and 72% respectively after 150 cycles of charge and discharge (Fig. 5). The voltage efficiency was higher than that of 45% for Zinc/bromine redox flow cells at a current density of 100 mA cm$^{-2}$ [12].

3.3. SEM characterization for graphite felt in the Sn–V battery

At the end of the charge process, a great deal of Sn was deposited on both surface and the inside of the graphite felt, as shown in Fig. 6a. The deposit of Sn was compact on the surface and relatively uniform inside the graphite felt. At the end of the discharge process, the Sn deposits were dissolved almost completely in the whole felt without any distinct residual Sn even after 150 cycles, as shown in Fig. 6b. The results manifested that the reversibility and rate of Sn deposition/dissolution process were capable enough to provide a high current density during the charge–discharge tests.

4. Conclusions

The Sn$^{2+}$/Sn couple in the H$_2$SO$_4$ medium was evaluated as negative couple for application in deposition phase redox flow battery. Voltammetric results indicated that the deposition/dissolution of Sn was not a normal reversible process on the graphite felt electrode, the diffusion coefficient for Sn$^{2+}$ in a supporting electrolyte of 2 M H$_2$SO$_4$ was estimated to be $2.86 \times 10^{-10}$ cm$^2$ s$^{-1}$. The Sn deposition could almost dissolve completely during the charge–discharge process. With VO$_2^+$/VO$^2^+$ couple as positive part, the Sn–V battery could work steadily at the current density of 180 mA cm$^{-2}$, the average columbic, energy and voltage efficiencies were 96%, 70% and 72% respectively after 150 cycles of charge and discharge.

Although a high current density was obtained for the Sn$^{2+}$/Sn couple used in deposition phase redox flow battery, further studies should be conducted for the application of this couple. For example, an appropriate positive couple and battery combination should be achieved to show a higher cell potential and no crossover pollution in the battery, in which the single flow zinc–nickel battery would be a feasible way. In addition, the concentration characters of Sn$^{2+}$ in the H$_2$SO$_4$ medium and the deposition/dissolution behavior with active additives are needed to be studied systematically to get the optimum battery performance.

Acknowledgments

Financial support from Shenyang Agricultural University Post-doctoral Fund is gratefully acknowledged.

References