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Original scientific paper

Electrochemical oscillation of vanadium ions in anolyte

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Abstract

Periodic electrochemical oscillation of the anolyte was reported for the first time in a simulated charging process of the vanadium redox flow batteries. The electrochemical oscillation could be explained in terms of the competition between the growth and the chemical dissolution of V_2O_5 film. Also, the oscillation phenomenon was possible to regular extra power consumption. The results of this paper might enable new methods to improve the charge efficiency and energy saving for vanadium redox flow batteries.

Keywords

vanadyl sulphate; oscillation phenomenon; redox flow battery

Introduction

Vanadium is an important metal used for manufacturing iron, steel non-ferrous metals, and petrochemicals because of its excellent physicochemical properties [1-4]. It is applied in energy storage [5]. The all-vanadium redox flow batteries (VRFBs) proposed by Skyllas-Kazacos *et al.* as an efficient energy-storage systems [6] have attracted attention for their long life time, flexible design, high efficiency and fast response time [7]. The main components of VRFB are electrolytes, membranes [8-10] and electrodes [11-13]. The reaction that occurs at the positive electrode of the VRFB during charge and discharge process is defined as follows:

$$VO^{2+} + H_2O - e \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} VO_2^{\ +} + 2H^+ \tag{1}$$

The electrical energy is transferred to the chemical energy during the charge process and stored in the electrolytes.

The charge process performed in flowing systems is driven far from equilibrium. Calculations based on Prigogine's dissipative structure equilibrium indicated that the kinetics of electrochemical system far from equilibrium is much more complicated than that near the equilibrium [14,15].

Electrochemical oscillation is an interesting self-organizing phenomenon in which the current or potential periodically fluctuates in constant external electric field [16,17]. Oscillations existed in systems far from equilibrium and are interesting phenomena of theoretical significance. There are, however, only few studies that reported influence of oscillation on the electrolytic efficiency of a practical electrolysis process.

In this work, we have reported the periodic electrochemical oscillation of the anolyte in a simulated charging process of the VRFB. A connection between the electrochemical oscillation phenomenon and the reaction mechanism was also investigated.

Experimental

The experimental process was nearly the same as presented before [10]. The anolyte was composed of $VOSO_4$ (varied from 0.5 M to 1.5 M) and H_2SO_4 (2 M), and the catholyte was H_2SO_4 (2 M) with the same volume. The anolyte and catholyte were separated with a Nafion membrane. The anode and cathode used in the experiments were platinum slices (1.5×2 cm) in which no other unexpected side reaction occurred except water oxidation. They were subjected to ultrasonic cleaning in de-ionized water for 30 min to remove residues before testing. Electrochemical tests were carried out on CHI660D electrochemical workstation (Shanghai Chenhua, China). All chemicals were of analytical grade and de-ionized water was used for all experimental solution.

Results and discussion

To explore electrochemical oscillation in a simulated charging process of the VRFBs, electrochemical tests were carried out on CHI660D electrochemical workstation with the anolyte of 1 M $VOSO_4$ + 2 M H_2SO_4, and the catholyte of 2 M H_2SO_4. As shown in Figure 1a, the period of electrochemical oscillation emerged during the charging process. The potential increased quickly at the beginning, and then the periodic electrochemical oscillation emerged. After then, the oscillation period slowly decreased, while the amplitude increased within the initial 500 s and then decreased what is shown in Figure 1b.

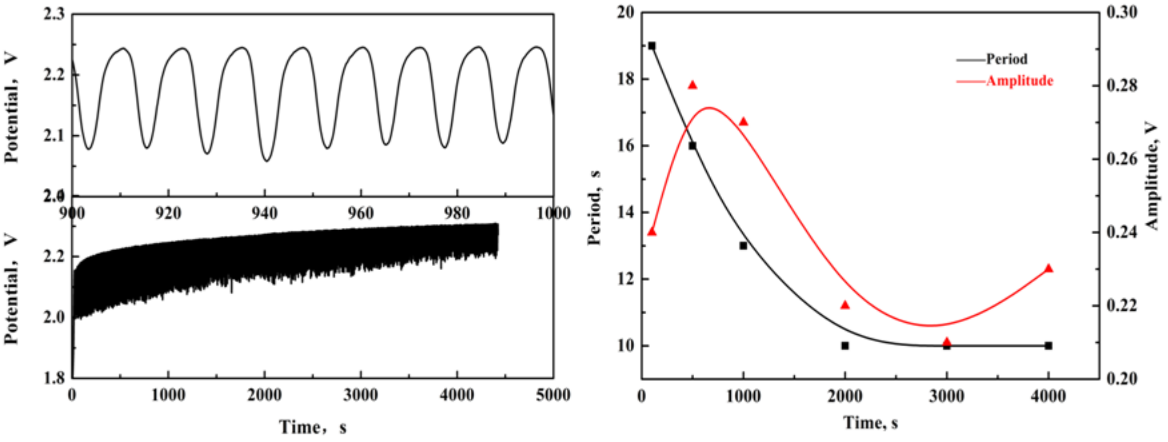

Figure 1. *Oscillation phenomenon at j = 0.07 A cm^{-2} a) the potential-time curve; b) time dependence of oscillation period and amplitude*

The effect of the charge current density on the threshold potential value scope and oscillation features of electrochemical oscillation are shown in Figure 2. Before the test, all electrodes were subjected to ultrasonic cleaning in de-ionized water for 30 min to remove residues. When charge current density < 0.0067 A cm^{-2}, no electrochemical oscillation was observed. In the range of 0.01 - 0.063 A cm^{-2} (boxed in Figure 3a), the electrochemical oscillation was observed. The results of chronopotentiometry with current ramp experiments are used to judge the appearance of electrochemical oscillation. It is shown in Figure 3b that induction period decreased with the increasing of charge current, which suggested that the electrochemical oscillation was easy to occur at high charge current within the effective range. In addition, the oscillation period was also decreased with charge current and the trend was consistent with the induction period.

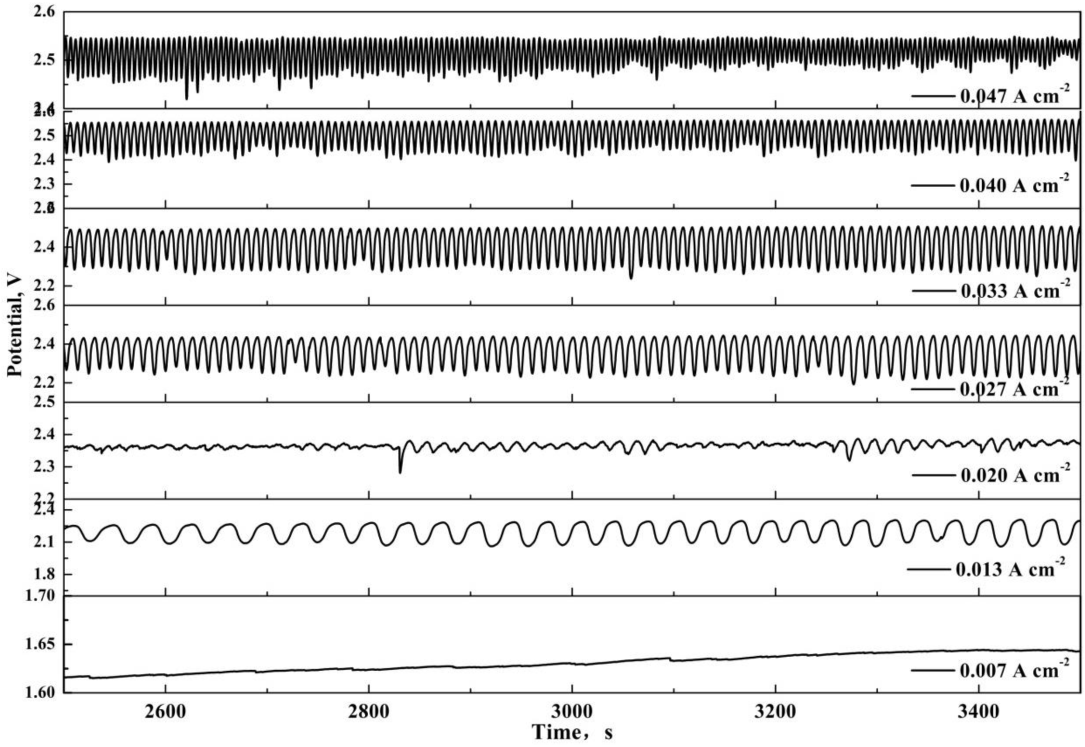

Figure 2. *The potential-time curve at different charge current densities*

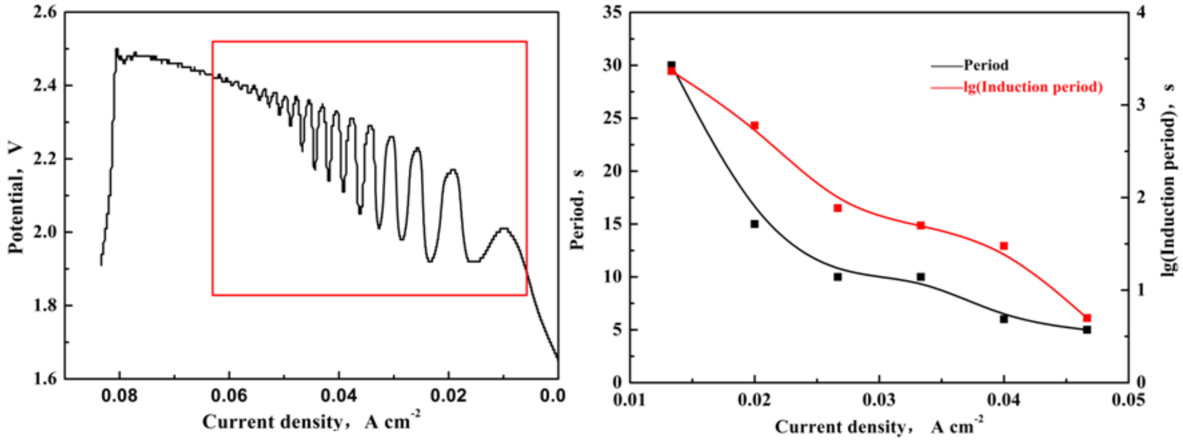

Figure 3. *a) Chronopotentiometry with current ramp results; b) oscillation and induction periods in dependence on charge current density*

If no electrochemical oscillation occurred, the average power consumption (P_a) was usually calculated using the product of potential and current described by equation (2):

$$P_a = V\,I \tag{2}$$

If electrochemical oscillation occurred, the calculation of P_a was more complicated. At constant current condition, the calculation of average power consumption could be calculated through the integration method shown by equation (3) [17]:

$$P_{\text{aver}}=V_{\text{baseline}}I+I(\int V-V_{\text{baseline}})\mathrm{d}t/\Delta t \qquad (3)$$

The term $I(\int V-V_{\text{baseline}})\mathrm{d}t/\Delta t$ is denoted as the alternating potential part of power consumption (P_e). The results shown in Figure 1 indicated that the potential have increased at a constant current, what resulted in an extra power and energy consumption.

The effect of concentration of $VOSO_4$ on oscillation was also investigated, and the results are shown in Figure 4. The electrochemical oscillation did not occur at low concentration (Figure 4a), while at increased concentrations, electrochemical oscillations occurred (Figure 4b-d). These results indicated that the electrochemical oscillation was not a result of the O_2 coverage and release but a special reaction in the anolyte.

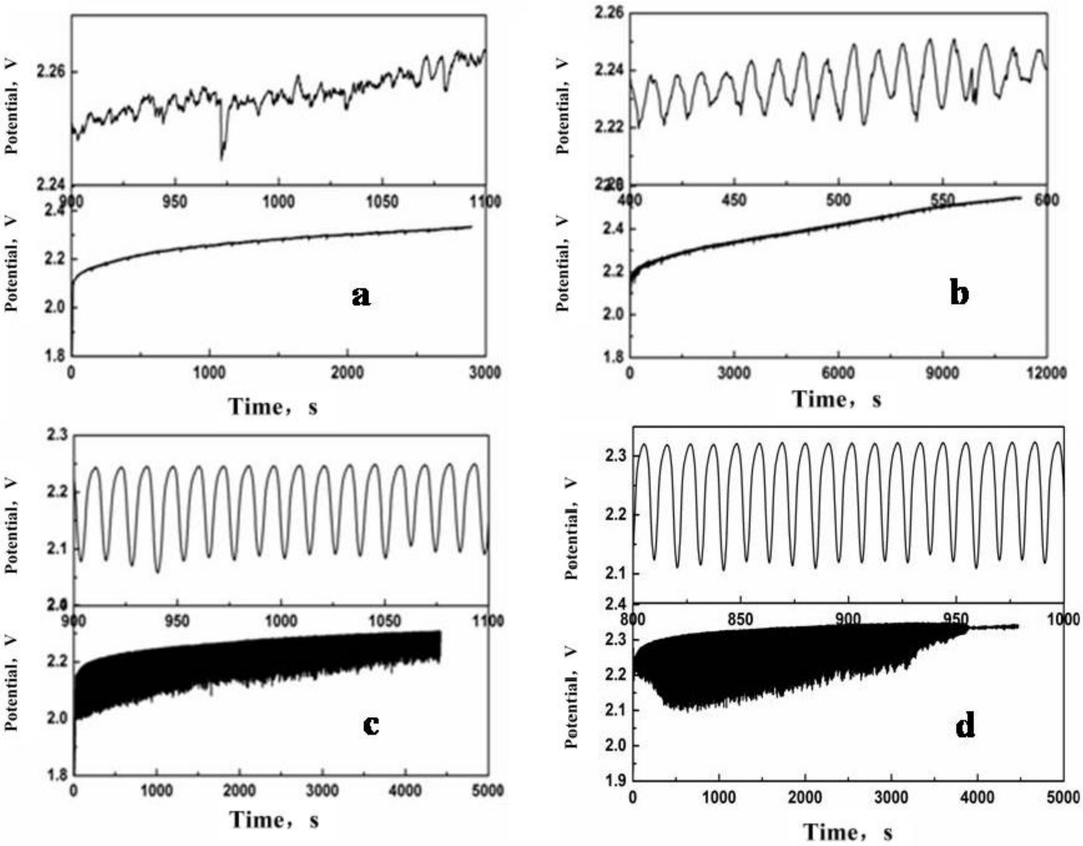

Figure 4. *The potential-time curve in different anolyte at j= 0.07 Acm^{-2}: a) 0.5 M $VOSO_4$+2 M H_2SO_4; b) 0.75 M $VOSO_4$+2 M H_2SO_4; c) 1.0 M $VOSO_4$+2 M H_2SO_4; d) 1.5 M $VOSO_4$+2 M H_2SO_4*

In order to investigate the reaction mechanism of the electrochemical oscillation, the solvent was also changed. As is shown in Figure 5a, no electrochemical oscillation phenomenon occurred in the water solution and red film, probably V_2O_5, is produced around the anode (Figure 5c). As the solvent was changed to H_2SO_4, the electrochemical oscillation was observed (Figure 5b) and the red film disappeared (Figure 5d).

During the charging process described by equation (1), the VO^{2+} was oxidized to VO_2^+ and in water solution hydrolyzed to form V_2O_5 film according to the equation (4). This V_2O_5film becomes absorbed on the anode in the water solution. In the H_2SO_4 solution, however, the V_2O_5 is dissolved due to the presence of large amount of H^+ what can be described by equation (5).

$$2VO_2^+ + H_2O \rightarrow V_2O_5 + 2H^+ \qquad (4)$$

$$V_2O_5 + 2H^+ \rightarrow 2VO_2^+ + H_2O \qquad (5)$$

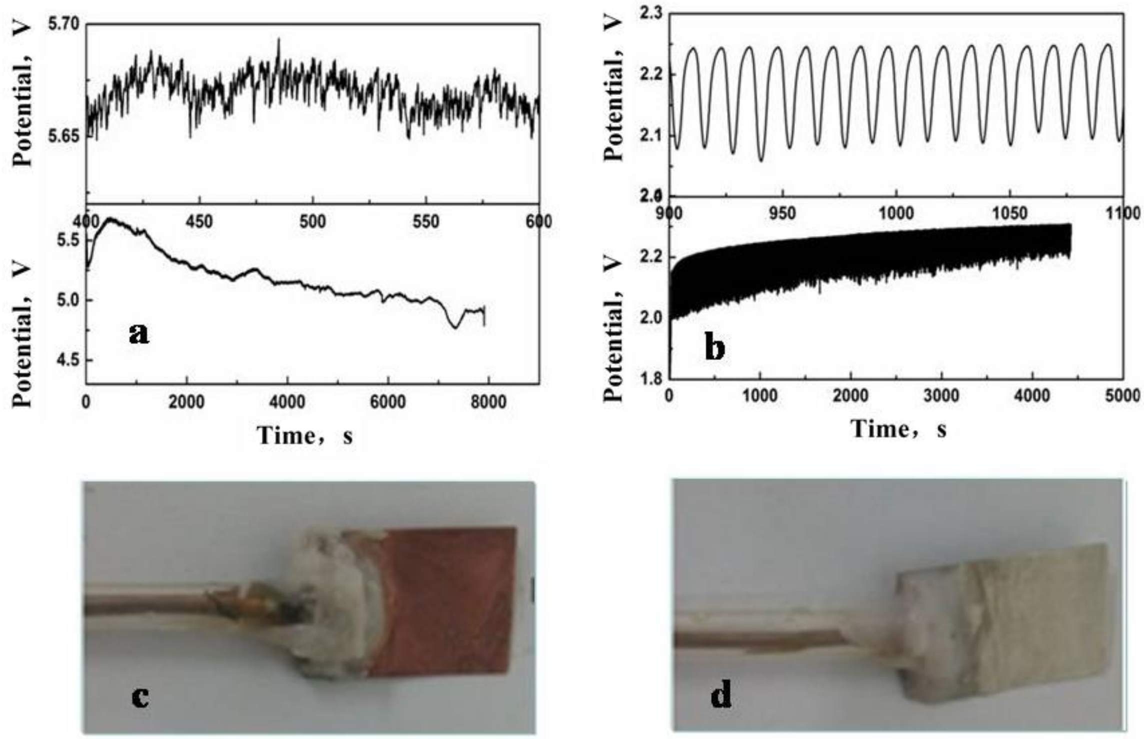

Figure 5. *The potential-time curve in different anolytes at* j= *0.07 Acm*$^{-2}$*: a) 1 M VOSO*$_4$*+ water; b) 1 M VOSO*$_4$*+ H*$_2$*SO*$_4$ *c) anode in the water solution; d) anode in H*$_2$*SO*$_4$ *solution*

From all results and discussion mentioned above, the electrochemical oscillation could be explained in terms of the competition between the growth and the chemical dissolution of V_2O_5 film [18,19].

Conclusions

In summary, the periodic electrochemical oscillation was first observed in the charging process of anolyte in simulated VRFB. The chronopotentiometry with current ramp results could be used to judge the appearance of electrochemical oscillation. The electrochemical oscillation could be explained in terms of the competition between the growth and the chemical dissolution of V_2O_5 film in the H_2SO_4 solution. It was possible to regular the extra power consumption resulted by the electrochemical oscillation. This work might provide new focus on the charging process of the VRFBs and guide for new methods in energy saving.

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