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Communication

Electrochemical Oscillation Phenomenon of Vanadium Ions

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Abstract: The electrochemical oscillation was first observed in the charging process of anolyte in VRFBs. 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 on energy saving.

Keywords: electrochemical oscillation; vanadium; chronopotentiometry

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1. Introduction

Vanadium is a strategic resource widely used in manufacturing iron, steel non-ferrous metals, and catalyst duo to its excellent properties [1-7]. The vanadium redox flow batteries (VRFBs) which proposed by Skyllas-Kazacos in 1985 [8, 9], was an efficient energy-storage system and had attracted much attention for its long cycle life, flexible design, deep-discharge capability, low pollution emitting and fast response time [10, 11]. The reaction that occurs at the electrode of the VRFBs during charge and discharge process was reacted as Equation (1)-(4):

$VO^{2+}+H_2O-e \rightarrow VO_2^{+}+2H^{+}$ (charge of anode) (1)

$VO_2^{+}+2H^{+}+e \rightarrow VO^{2+}+H_2O$ (discharge of anode) (2)

$V^{3+}+e \rightarrow V^{2+}$ (discharge of cathode) (3)

$V^{2+}-e \rightarrow V^{3+}$ (charge of cathode) (4)

The electricity energy was transferred to chemical energy during the charge process and stored in the electrolytes.

The charge process performed in flowing systems that were 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 [12, 13]. Electrochemical oscillation is an interesting self-organizing phenomenon in which the current or potential periodically fluctuates at a constant external electric field [14, 15]. It existed in systems far from equilibrium and it was an interesting phenomenon of theoretical significance, few studies had reported its influence on the electrolytic efficiency of a practical electrolysis process. In this work, we reported the periodic electrochemical oscillation of the anolyte in a simulated charging process of the VRFBs. The judgment of the electrochemical oscillation phenomenon and the reaction mechanism were also investigated.

2. Materials and Methods

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All chemicals were analytical grade. Water was purified with a water purification system (HMC-WS 10, Korea). The anolyte was composed of $VOSO_4$ (1 M) and H_2SO_4 (2 M), and the catholyte was H_2SO_4 (2 M) with the same volume. The anolyte and catholyte was separated with a Nafion membrane. The anode and cathode used in the experiments was platinum slice (1.5x2 cm) in which no other unexpected side reaction occurred. 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. The signal of the potential was amplified, and the times series were recorded and transferred to a personal computer. The macro-instability frequency, oscillation period, of the potential-time series were obtained using Matlab.

3. Results and Discussion

Electrochemical oscillation was observed during the charging process, while the 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 at room temperature, the potential-time series was showed in Figure 1. As indicated in Figure 1, the potential was increased quickly and then electrochemical oscillation emerged. After then, the period of the electrochemical oscillation slowly decreased with the increasing of current as showed in Figure 2.

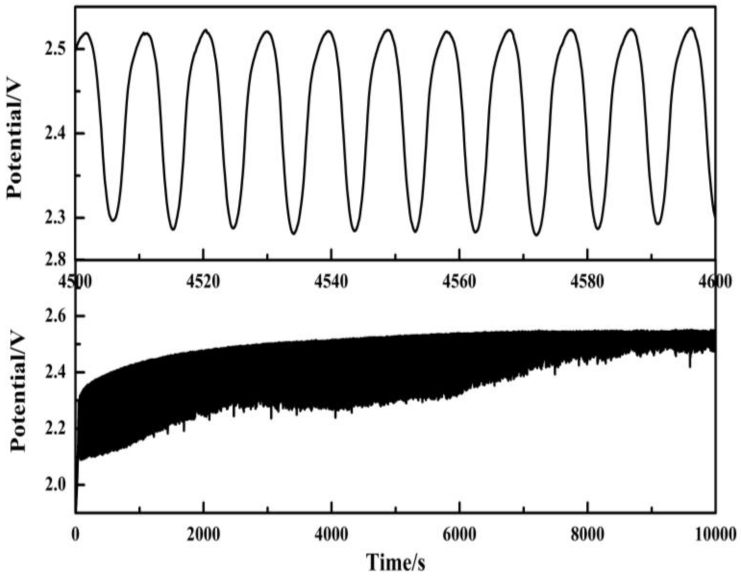

Figure 1 The Potential-time curve (anolyte: 1 M $VOSO_4$ + 2 M H_2SO_4; catholyte: 2 M H_2SO_4)

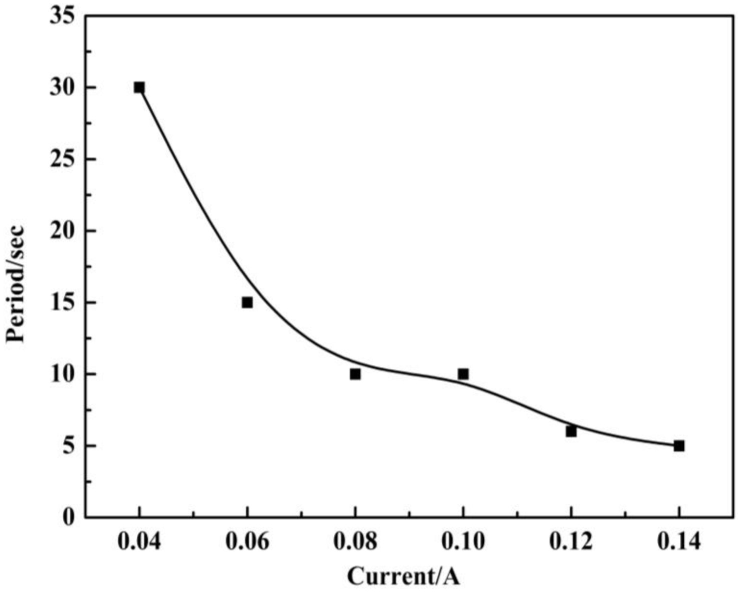

Figure 2 the dependence of oscillation period on the time in different charging current (anolyte: 1 M $VOSO_4$ + 2 M H_2SO_4; catholyte: 2 M H_2SO_4)

The effect of the charge current (I_a) on the threshold value scope and oscillation features of electrochemical oscillation were shown in Figure 3. Before the test, all electrodes were subjected to ultrasonic cleaning in de-ionized water for 30 min to remove residues. When charge current < 0.02 A, no electrochemical oscillation was observed. In the range of 0.03 A—0.19 A (the boxed in Figure 4), the electrochemical oscillation was observed. The chronopotentiometry with current ramp results could be used to judge the appearance of electrochemical oscillation. The induction period decreased with the increasing of charge current, which suggested that the electrochemical oscillation was easy to occur in high charge current within the effective range.

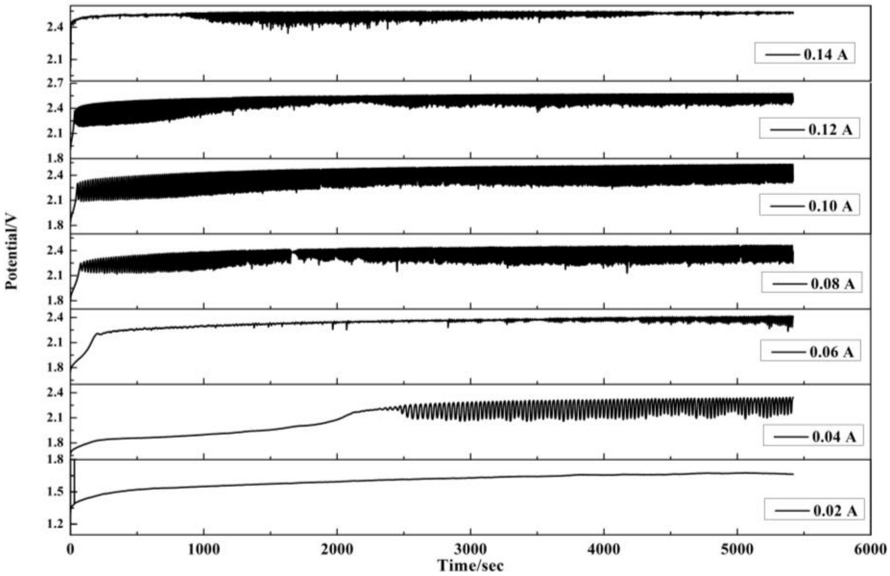

Figure 3 the dependence of oscillation period on the time in different charging current (anolyte: 1 M $VOSO_4$ + 2 M H_2SO_4; catholyte: 2 M H_2SO_4)

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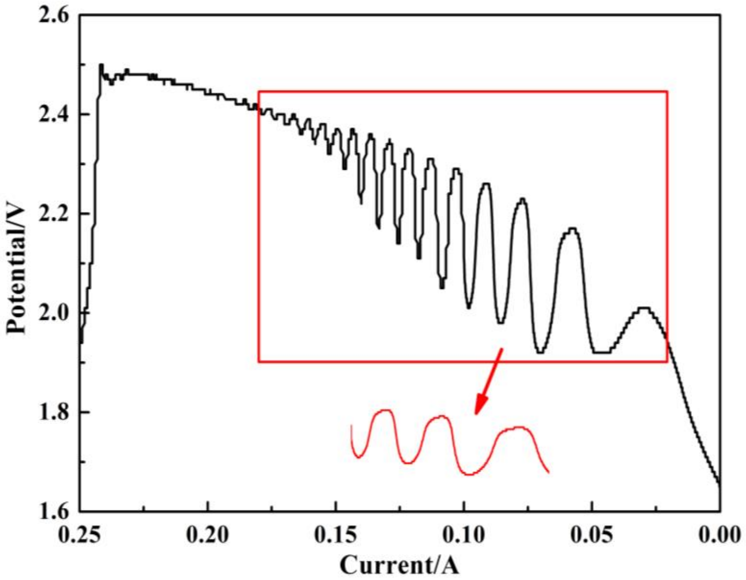

Figure 4 Chronopotentiometry with current ramp results

The power consumption was investigated to reveal the influence of electrochemical oscillation on the charging efficiency. An extra power consume was a result of the electrochemical oscillation. The relative power-consume (PRC) was calculated as PRC= the average power consumption on anode / (Va·Ia), where Va was the potential, Ia was the charging potential. The results were shown in Figure 5. The influence of electrochemical oscillation on the charging efficiency will be enlarging in long-term charging, and much extra power will be consumed. This part of power consumption should exist in practical charging process, even though it is often ignored. It is beneficial for improving the charge efficiency and energy-saving if the electrochemical oscillation could be regulated.

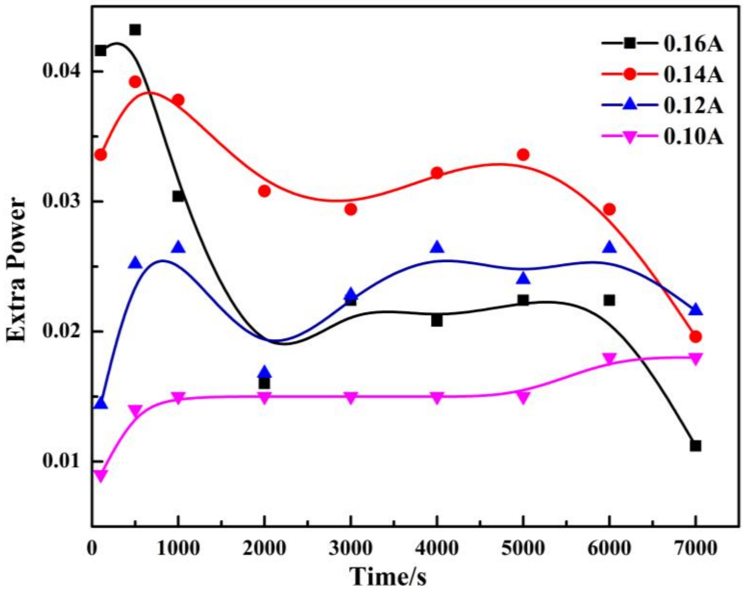

Figure 5 the dependence of extra power-consume on the time in different charging current

(anolyte: 1 M $VOSO_4$ + 2 M H_2SO_4; catholyte: 2 M H_2SO_4)

The mechanism of the electrochemical oscillation was investigated. During the charging process, the main chemical reactions in the system were showed in Figure 6. The VO^{2+} in the anolyte was oxidized to VO_2^+ on the surface of the anode. As V(V) had low solubility in high acidic solution [16-18], VO_2^+ would hydrolysis and formed V_2O_5 according to Equation (5) [18]. And also as the high acidic, V_2O_5 then dissolved according to Equation (6). The competition between the generation and dissolution of V_2O_5 resulting the electrochemical oscillation [19].

$$2\ VO_2^+ + H_2O \rightarrow V_2O_5 + 2H^+ \tag{5}$$

$$V_2O_5 + H^+ \rightarrow 2\ VO_2+ + H_2O \tag{6}$$

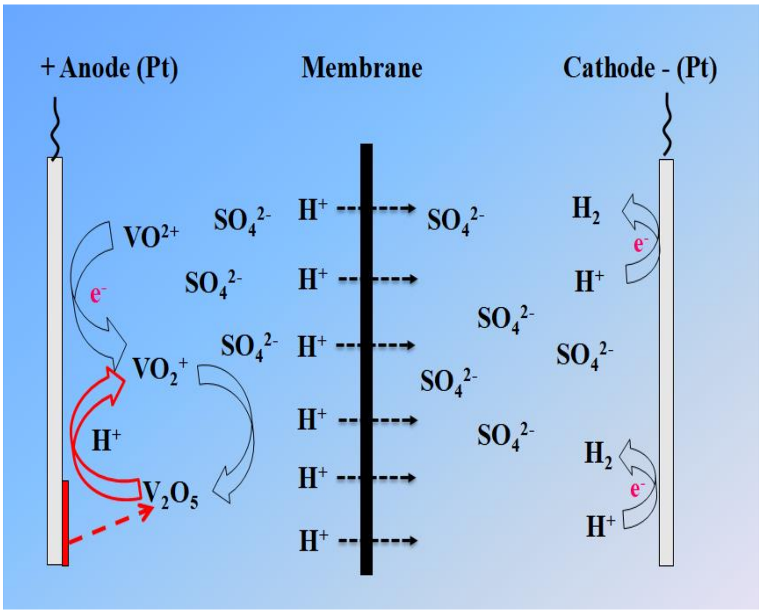

Figure 6 The reaction model in the charging process

4. Conclusions

In summary, the electrochemical oscillation was first observed in the charging process of anolyte in VRFBs. 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 on energy saving.

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Conflicts of Interest: The authors declare no conflict of interest.

References

[1] R.R. Moskalyk, A.M. Alfantazi, Minerals Engineering, 16 (2003) 793-805.

[2] H. Peng, Z. Liu, C. Tao, Energ Fuel, 30 (2016) 7802-7807.

[3] H. Peng, Z. Liu, C. Tao, Journal of Environmental Chemical Engineering, 3 (2015) 1252-1257.

[4] J.A. Valverde, A. Echavarria, J.G. Eon, A.C. Faro, L.A. Palacio, React Kinet Mech Cat, 111 (2014) 679-696.

[5] S.Y. Lu, Q.L. Wang, W.R. Stevens, C.W. Lee, B.K. Gullett, Y.X. Zhao, Appl Catal B-Environ, 147 (2014) 322-329.

[6] J.N. Nicholas, G.d. Silva, S. Kentish, G.W. Stevens, Ind Eng Chem Res, 53 (2014) 3029-3039.

[7] W. Wang, B. Jiang, L.W. Hu, Z.S. Lin, J.G. Hou, S.Q. Jiao, Journal of Power Sources, 250 (2014) 181-187.

[8] C. Ding, H. Zhang, X. Li, T. Liu, F. Xing, J Phys Chem Lett, 4 (2013) 1281-1294.

[9] X. Binyu, Z. Jiyun, K.J. Tseng, S.-K. Maria, L.T. Mariana, Z. Yu, Journal of Power Sources, 242 (2013) 314-324.

[10] E. Sum, M. Rychcik, M. Skyllas-Kazacos, Journal of Power Sources, 16 (1985) 85-95.

[11] V. Viswanathan, A. Crawford, D. Stephenson, S. Kim, W. Wang, B. Li, G. Coffey, E. Thomsen, G. Graff, P. Balducci, M. Kintner-Meyer, V. Sprenkle, Journal of Power Sources, 247 (2014) 1040-1051.

[12] J.A. O'Brien, J.T. Hinkley, S.W. Donne, Electrochimica Acta, 56 (2011) 4224.

[13] W. Huang, Z.L. Li, Y.D. Peng, Z.J. Niu, Chem Commun, 12 (2004) 1380.

[14] X. Fan, J. Hou, D. Sun, S. Xi, Z. Liu, J. Du, J. Luo, C. Tao, Electrochimica Acta, 102 (2013) 466-471.

[15] X. Fan, D. Yang, L. Ding, J. Du, C. Tao, Chemphyschem : a European journal of chemical physics and physical chemistry, 16 (2015) 176-180.

[16] X. Zhou, C. Wei, M. Li, S. Qiu, X. Li, Hydrometallurgy, 106 (2011) 104-112.

[17] S. Banwen, L. Yuji, Inorganic Chemistry Series, Science press., Beijing, 1998.

[18] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, John Wiely, New York, 1976.

[19] V. Alonzo, A. Darchen, E. Le Fur, J.Y. Pivan, Electrochem Commun, 4 (2002) 877-880.