

Short communication

A study on the reversibility of Pb(II)/PbO₂ conversion for the application of flow liquid battery

H.Y. Peng, H.Y. Chen, W.S. Li*, S.J. Hu, H. Li, J.M. Nan, Z.H. Xu

Department of Chemistry, South China Normal University, Guangzhou 510631, China

Received 22 September 2006; received in revised form 30 October 2006; accepted 6 November 2006

Available online 18 December 2006

Abstract

The conversion behavior of soluble Pb(II) to deposited PbO₂ on platinum in methanesulfonic acid solution was studied with voltammetry and compared with those on glassy carbon and lead oxides. The effects of methanesulfonic acid concentration and Pb(II) concentration, and temperature were considered. The conversion reaction of Pb(II) to PbO₂ on platinum is irreversible and has a high overpotential, more than 300 mV. Low concentration of methanesulfonic acid, high concentration of Pb(II) and high temperature will favor the conversion reaction of Pb(II) to PbO₂. The conversion reaction depends to a great extent on electrode materials. It is more difficult for the conversion reaction of Pb(II) to PbO₂ to take place on glassy carbon than on platinum. However, the conversion reaction of Pb(II) to PbO₂ becomes easy when it takes place on lead oxides, which was formed by reducing PbO₂ under different potentials.

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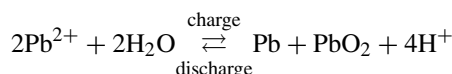
Keywords: Soluble divalent lead; Lead dioxide; Conversion; Flow liquid battery

1. Introduction

Renewable energy becomes more and more important for this society to be sustainable due to the lack of mineral energy sources and the need for environmental protection. One of essential techniques for the use of renewable energy is the energy storage. Flow liquid battery is considered to be an ideal device for the energy storage because it has high energy efficiency (over 80%) and can be used in large scale, which depends on the volume of the electrolyte and the concentration of reactants. More and more scientists are focusing their researches on the flow liquid battery [1–11].

Several redox systems have been developed as the reactants of flow liquid battery, such as all vanadium system, Fe/Cr system and Na₂S_x/Br₂ system. In these systems, a membrane has to be used to avoid the interference of reactants in both anode and cathode. The membrane should be chemically and mechanically stable enough to resist the oxidation and reduction of the reactants and the attack of flow liquid. These requirements make the flow liquid battery complex and expensive.

Recently, Pletcher et al. [12–15] proposed a new concept of flow liquid battery, based on the conventional lead acid battery. In this system, soluble Pb(II), lead methanesulfonate, in flow electrolyte is oxidized to lead dioxide deposited on one electrode and reduced to lead deposited on the other electrode when the battery is charged, and the deposited lead dioxide and the deposited lead turn back to the soluble Pb(II) when the battery is discharged:



Only one reactant, Pb(II), exists in the electrolyte, thus no membrane is needed in this kind of flow liquid battery and the battery can be built in much simpler way than the conventional flow liquid battery. Unfortunately, it is difficult for Pb(II) to be oxidized to lead dioxide, which will result in low energy efficiency. To improve the reaction activity for Pb(II) to be oxidized to PbO₂, it is necessary to understand the reversibility for the conversion of Pb(II) to PbO₂. In this paper, the reversibility for the conversion reaction of Pb(II) to PbO₂ on platinum in methanesulfonic acid solution was studied under different conditions and was compared with that on other electrode materials.

* Corresponding author. Tel.: +86 20 39310256; fax: +86 20 39310256.
E-mail address: liwsh@scnu.edu.cn (W.S. Li).

2. Experimental

Voltammetric experiments were carried out on the electrochemical instrument (Solartron 1480 A). A three electrode cell was used. A platinum microelectrode ($d=600\ \mu\text{m}$) was used as working electrode, a flat platinum was used as counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Potentials in this paper are referenced to SCE. For a comparison, a glassy carbon disc electrode was also used as the working electrode.

The working electrode was pretreated before each experiment as follows: polished with sand papers of number 500, 600 and 1500, successively, and then washed in supersonic deionized water. All the chemicals used were analytical grade reagents. Solutions were prepared with water deionized and distilled twice.

3. Results and discussions

3.1. Conversion between Pb(II) and PbO₂

Scanning the potential between 0.7 and 1.9 V, starting from 0.7 V, on platinum electrode in 0.3 M Pb(CH₃SO₃)₂ + 1 M CH₃SO₃H solution, the voltammogram representing the transformation between soluble Pb(II) and deposited PbO₂ can be obtained, as shown in Fig. 1. As the potential is scanned forward the oxidation current is hardly observed until the potential reaches 1.54 V, which is defined as the potential for the conversion reaction of Pb(II) to PbO₂ to take place and is determined by intersection point of the tangent line of the increasing current-potential relation with potential coordinate. A current peak can be observed at 1.68 V, indicating that the reaction at this potential is controlled by the diffusion of Pb(II). As the potential increases further, the current increases quickly. This is caused by the accompanying oxygen evolution reaction.

When the potential is scanned backward, the oxidation current still exists till the potential reaches 1.46 V, which is 80 mV more negative than the potential for the conversion reaction of

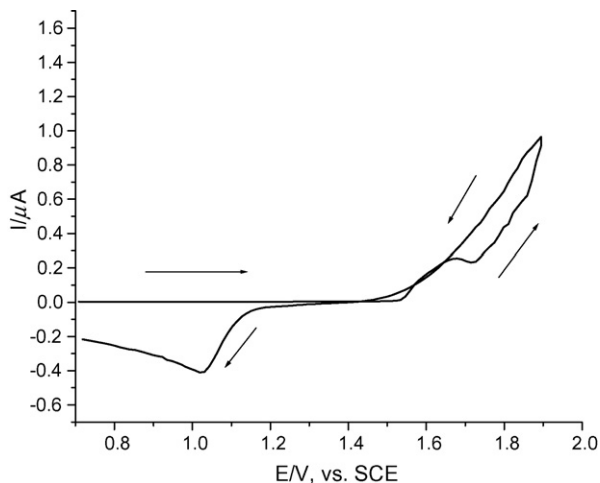


Fig. 1. Voltammogram of platinum electrode in 0.3 M Pb(CH₃SO₃)₂ + 1 M CH₃SO₃H solution at first cycle, scan rate: 50 mV s⁻¹.

Pb(II) to PbO₂ to take place on platinum. This indicates that the conversion reaction of Pb(II) to PbO₂ is more easy on the deposited lead dioxide than directly on platinum. The reduction reaction of the deposited PbO₂ takes place at about 1.2 V. There is a difference of about 300 mV between the potential for the conversion of Pb(II) to PbO₂ and the potential for the conversion of PbO₂ to Pb(II) to take place, indicating that the reversibility for the conversion between Pb(II) and PbO₂ is very poor. The standard equilibrium potential for the conversion between Pb(II) and PbO₂ in acidic solution is 1.46 V (versus SHE), about 1.2 V (versus SCE), therefore the poor reversibility for the conversion between Pb(II) and PbO₂ results mainly from the difficulty in the oxidation of Pb(II) to PbO₂.

Fig. 2 shows the dependence of linear scan voltammograms on the scan rate. There is a linear relationship between peak current and the square root of scan rate, however, the peak potential also depends on the scan rate, as shown in Fig. 2b. This indicates that the conversion for the soluble Pb(II) to the deposited PbO₂ on platinum is an irreversible reaction. The poor reversibility of the conversion Pb(II) to PbO₂ on platinum can be ascribed to the formation of platinum oxide on platinum at high potential. The platinum oxide is inactive to many reactants [16–18].

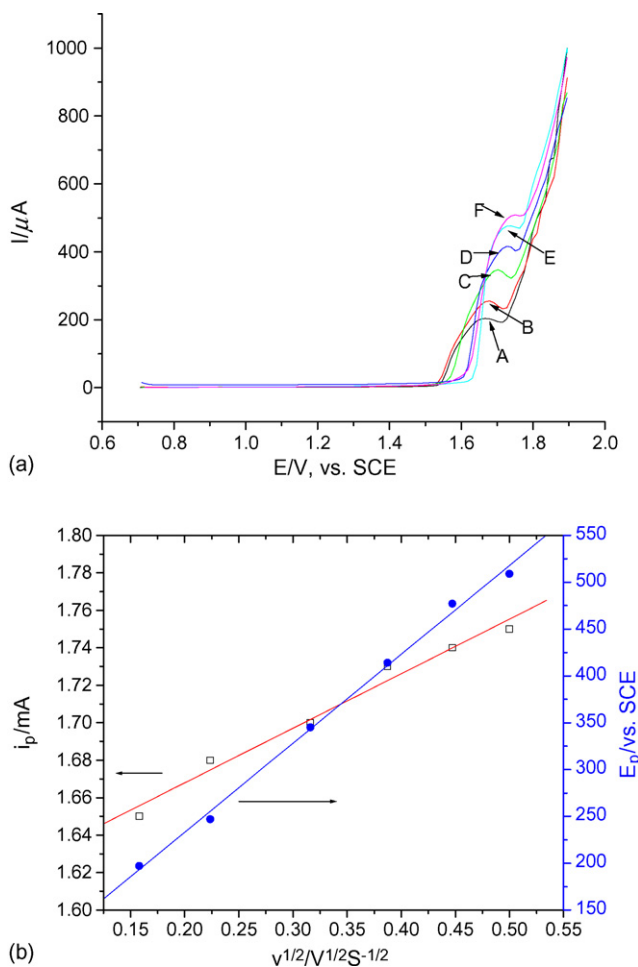


Fig. 2. Linear scan voltammograms for platinum electrode in 0.3 M Pb(CH₃SO₃)₂ + 1 M CH₃SO₃H solution at different scan rate (a), A: 25 mV s⁻¹; B: 50 mV s⁻¹; C: 100 mV s⁻¹; D: 150 mV s⁻¹; E: 200 mV s⁻¹; F: 250 mV s⁻¹; and the relationship of peak current and peak potential with scan rate (b).

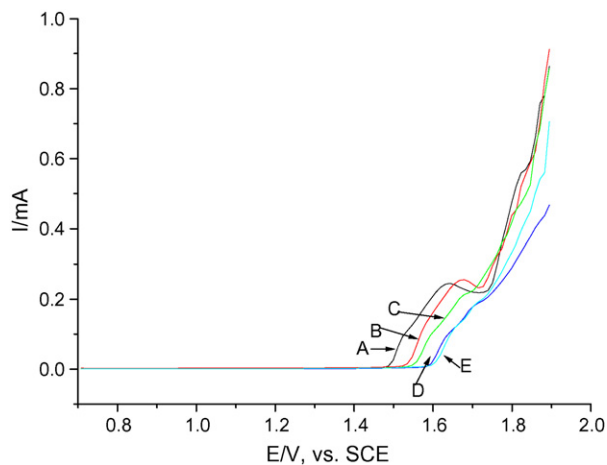


Fig. 3. Linear scan voltammograms of platinum electrode in 0.3 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ solutions with different concentrations of methanesulfonic acid, A: 0.5 M; B: 1.0 M; C: 1.5 M; D: 2.0 M; E: 2.5 M $\text{CH}_3\text{SO}_3\text{H}$, scan rate: 50 mV s^{-1} .

3.2. Effect of concentration of methanesulfonic acid

Fig. 3 shows the linear scan voltammograms of platinum electrode in 0.3 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ solutions with different concentrations of methanesulfonic acid. It can be observed that the potential for the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 to take place becomes more positive and the current for the conversion of $\text{Pb}(\text{II})$ to PbO_2 decreases as the concentration of methanesulfonic acid increases, especially at the concentrations from 0.5 to 2.0 M. It is obvious that higher concentration of methanesulfonic acid inhibits the oxidation reaction of $\text{Pb}(\text{II})$ to PbO_2 , which might be ascribed to the complexity of methanesulfonic ions to the $\text{Pb}(\text{II})$. This suggests that low methanesulfonic acid favors the conversion of $\text{Pb}(\text{II})$ to PbO_2 .

3.3. Effect of concentration of $\text{Pb}(\text{II})$

Fig. 4 shows the linear scan voltammograms of platinum electrode in 1 M $\text{CH}_3\text{SO}_3\text{H}$ solutions with different concentrations

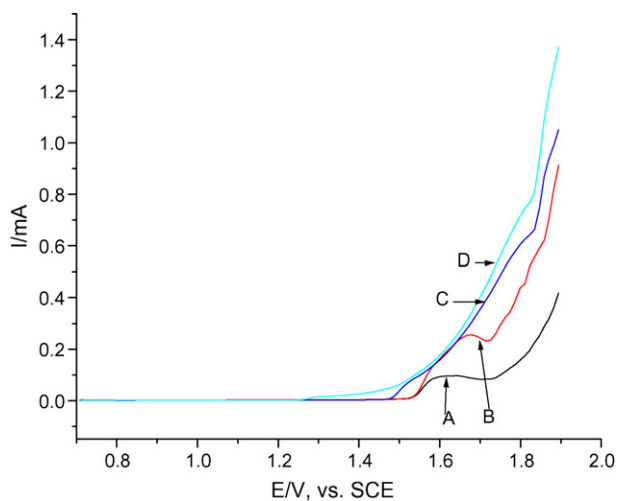


Fig. 4. Linear scan voltammograms of platinum electrode in 1 M $\text{CH}_3\text{SO}_3\text{H}$ solutions with different concentrations of lead methanesulfonate, A: 0.1 M; B: 0.3 M; C: 0.8 M; D: 1.0 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$, scan rate: 50 mV s^{-1} .

of lead methanesulfonate. Current peaks for the conversion of $\text{Pb}(\text{II})$ to PbO_2 can be observed for curves A and B in Fig. 4, the $\text{Pb}(\text{II})$ concentrations of which are 0.3 and 0.5 M, respectively, and that peak current increases with increasing the concentration of $\text{Pb}(\text{II})$. This is characteristic of diffusion control. As the concentration of $\text{Pb}(\text{II})$ increases, the current peak for the conversion of $\text{Pb}(\text{II})$ to PbO_2 disappears, as shown by the curves C and D in Fig. 4, whose concentrations are 0.8 and 1.0 M, respectively. This is characteristic of charge transfer control. It can be found that the potential for the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 to take place becomes more negative as the concentration of $\text{Pb}(\text{II})$ increases. This suggests that high $\text{Pb}(\text{II})$ concentration favors the conversion of $\text{Pb}(\text{II})$ to PbO_2 .

3.4. Effect of temperature

Fig. 5 shows the linear scan voltammograms of platinum electrode in 0.5 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M } \text{CH}_3\text{SO}_3\text{H}$ solution under different temperature. It can be seen from Fig. 5 that the potential for the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 to take place becomes more negative and the current for the conversion of $\text{Pb}(\text{II})$ to PbO_2 increases as the temperature increases. There is about a decrease of 100 mV in taking place potential from 30 to 90°C . This is characteristic of an irreversible reaction and indicates that the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 can be significantly improved by enhancing temperature.

3.5. Effect of electrode materials

Fig. 6 shows the voltammograms of platinum and glassy carbon electrodes under the same conditions. The potential for the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 to take place on glassy carbon is about 1.74 V. It is 200 mV more positive than that on platinum. This indicates that the reversibility for the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 depends to a great extent on the electrode and carbon is poor for the conversion of $\text{Pb}(\text{II})$ to PbO_2 .

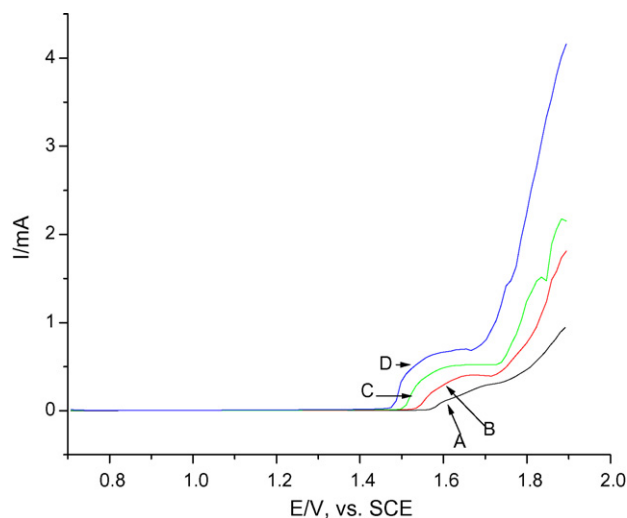


Fig. 5. Linear scan voltammograms of platinum electrode in 0.5 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M } \text{CH}_3\text{SO}_3\text{H}$ solution under different temperature, A: 30°C ; B: 50°C ; C: 70°C ; D: 90°C , scan rate: 50 mV s^{-1} .

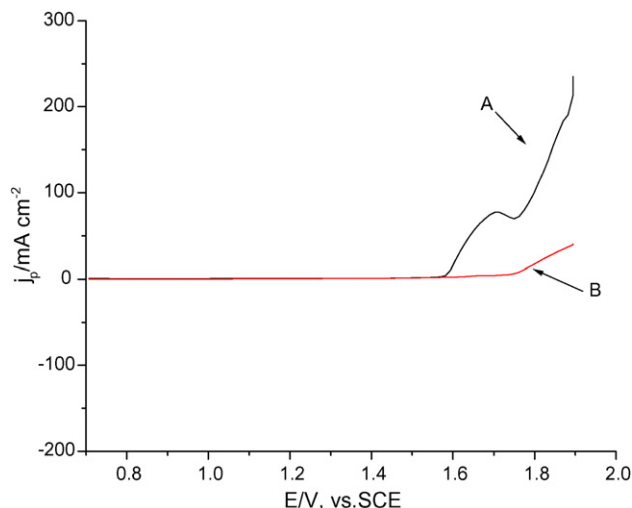


Fig. 6. Linear scan voltammograms of platinum (A) and glassy carbon (B) electrodes in 0.3 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M CH}_3\text{SO}_3\text{H}$ solution, scan rate: 50 mV s^{-1} .

It is noted that during the potential scan the deposited PbO_2 on platinum electrode cannot be reduced completely. As shown in Fig. 1, a large reduction current still exists when the potential is scanned to 0.7 V, indicating that there is residue lead oxide on the surface of platinum electrode after the reduction of deposited lead dioxide. The chemistry and the structure of residue lead oxide worth to understand but they are not the topic of this paper. However, it seems that the residue lead oxide helps to improve the reversibility for the conversion $\text{Pb}(\text{II})$ to PbO_2 . Fig. 7 shows the voltammogram at the sixth cycle for the platinum electrode after successive cycling under the same condition as that in Fig. 1. It can be observed that the oxidation reaction of $\text{Pb}(\text{II})$ to PbO_2 takes place at about 1.2 V, nearly to the standard equilibrium potential for the conversion between $\text{Pb}(\text{II})$ and PbO_2 . This improvement in reversibility should be ascribed to residue lead oxide, which has a similar structure to PbO_2 so as to favor the formation of PbO_2 . This suggests that the over potential for the conversion of $\text{Pb}(\text{II})$ to PbO_2 on platinum or glassy carbon electrodes comes mainly from the difficulty for the formation of

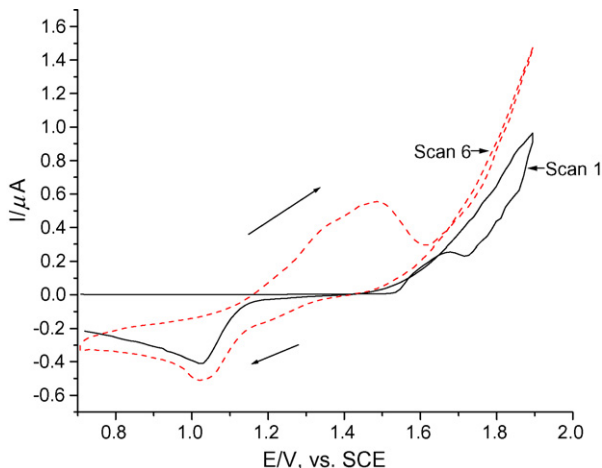


Fig. 7. Comparison of the first and the sixth voltammograms of platinum electrode in 0.3 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M CH}_3\text{SO}_3\text{H}$ solution, scan rate: 50 mV s^{-1} .

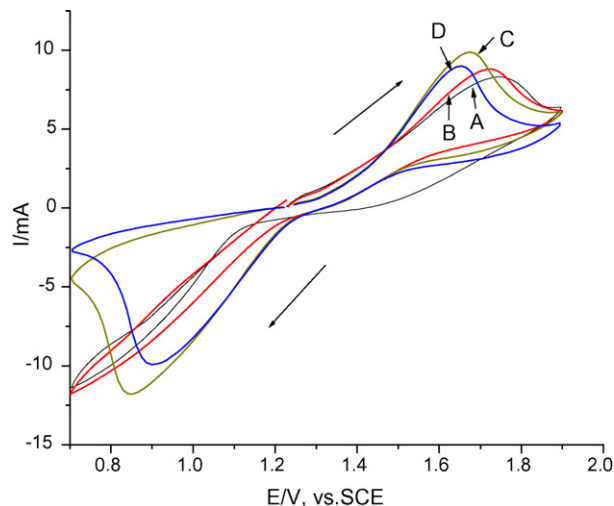


Fig. 8. voltammograms of glassy carbon electrodes with different residue lead oxides in 0.3 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1.0 \text{ M CH}_3\text{SO}_3\text{H}$ solution, starting potential: open circuit potential, scan rate: 50 mV s^{-1} , the glassy carbon electrode was covered with different residue lead oxide by constant potential at 1.8 V for 60 s and then at A: 1.1 V; B: 1.0 V; C: 0.9 V; and D: 0.8 V for 30 s.

PbO_2 and any condition favoring the formation of PbO_2 might improve the reversibility for the conversion $\text{Pb}(\text{II})$ to PbO_2 .

Fig. 8 shows the voltammograms of glassy carbon electrodes with different residue lead oxides in 0.3 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1.0 \text{ M CH}_3\text{SO}_3\text{H}$ solution. The electrodes were prepared as follows: step the potential at 1.8 V and keep constant for 60 s for the formation of PbO_2 and then step to different potentials for the reduction of PbO_2 and the formation of different residue lead oxides. The voltammograms were recorded starting from and ending at open circuit potential. It can be seen from Fig. 8 that the voltammograms during forward scan are similar, indicating that the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 is less influenced by the residue lead oxides formed under different potentials. On the other hand, the voltammograms during backward scan are very different. The reduction of PbO_2 becomes difficult as the potential for the formation of the residue lead oxide increases. This suggests that the chemistry and structure of formed PbO_2 might be influenced by electrode materials.

4. Conclusion

The conversion reaction of soluble $\text{Pb}(\text{II})$ to deposited PbO_2 in methanesulfonic acid solution is influenced by the concentration of methanesulfonic acid, the concentration of $\text{Pb}(\text{II})$, temperature, and electrode materials. The conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 on platinum is irreversible and has a high overpotential, more than 300 mV. Low concentration of methanesulfonic acid, high concentration of $\text{Pb}(\text{II})$ and high temperature will favor the conversion reaction of $\text{Pb}(\text{II})$ to PbO_2 . The conversion rate of $\text{Pb}(\text{II})$ to PbO_2 depends to a great extent on the temperature and electrode materials. Lead oxide electrode favors the conversion of $\text{Pb}(\text{II})$ to PbO_2 , but does not favor the reduction of the formed PbO_2 . This is not good for the flow liquid lead battery. It is interesting to find an oxide electrode similar to lead oxide in structure for positive electrode of flow liquid lead

battery, which favors the conversion of PbO_2 to Pb(II) as well as the conversion of Pb(II) to PbO_2 .

Acknowledgements

This work was financially supported by NSFC (20573039), key project of CISTC (2005DFA60580), key project of Guangdong Province (20042B08, 2005B50101003).

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