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Structural variation of PbO_2 during multi-cycle scanning in mixed gel electrolyte using PAM/PPG/NFS ternary additive

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Abstract. Pb/PbO_2 electrodes are fabricated by the constant current method from sulfuric acid solution. Fabricated electrodes are investigated by the cyclic voltammetric (CV) method in mixed gel electrolyte using PAM/PPG/NFS ternary additive. The results showed that Pb/PbO_2 fabricated at a current density of 5 mA/cm^2 from 1.26 g/cm^3 sulfuric acid solution achieved the best electrochemical activity. Three stages of CV scanning were found. There was only one peak appeared on the oxidation process belonging to the α-PbO_2 modification in the first 15 CVs, but its height decreased gradually with the number of CV, and seems to disappear after 50 CV scans. The second oxidation peak belongs to the β-PbO_2 modification appeared insignificant after 15 CVs and its height increased gradually with cycle number. However, it was almost stable after 140 CVs and the charge factor was 1.4. SEM image analysis results showed that the morphological structure of PbO_2 was very different during CV scanning, the more scanning cycles, the smaller the PbO_2 crystal size.

Keywords: Pb/PbO_2, constant current method, ternary additive, cyclic voltammetry, charge efficiency.

1. Introduction

In the operation of lead-acid batteries, the PbO_2 is interested in a lot of research because it plays a role in determining the capacity and life of the battery [1-5]. Many studies have analyzed and evaluated the structural change of PbO_2 showing that it depends on the parameters used for PbO_2 preparation at the beginning such as preparation methods (CV, constant current or pulse current), changing the electrolysis current, and changing the concentration of electrolyte solution (sulfuric acid) [3,4]. Especially, when PbO_2 works in a gelled electrolyte the geometrical structure as well as the modification form of PbO_2 is affected resulting to inhibiting the release of oxygen compared to that in traditional electrolyte [6,7]. The three-dimensional network in the mixed gel electrolyte using the ternary additive improved the diffusion of HSO_4^- compared with the one using the binary additive [7]. This will positively affect the charge and discharge of the PbO_2 electrode.

This paper presents some results on the structural transformation of PbO_2 during multi-cycle scanning in mixed gel electrolyte using ternary additive and study of morphology as well as charge efficiency of materials.

2. Experimental

2.1. *Material preparation*

PbO_2 electrodes were fabricated by the constant current method (Table 1) in sulfuric acid medium using a three-electrode cell, including PbSb substrate as a working electrode, platin sheet as a counter electrode, and Hg/Hg_2SO_4, sat. K_2SO_4 as a reference electrode on an electrochemical workstation IM6 (Zahner-Elektrik, Germany). Electrode substrates were prepared from PbSb material supplied from TiaSang Battery Company (Haiphong, Vietnam). Alcohol and liquid glass provided from China, PPG and sulfuric acid from Merck, NFS and PAM from Sigma Aldrich.

Table 1. Parameters for PbO_2 fabrication by the constant current method

Sample	Current density (mA/cm^2)	Sulfuric acid concentration (g/cm^3)
1	10	1.05
2	10	1.11
3	10	1.26
4	5	1.26
5	1	1.26

A mixed gel electrolyte using PAM/PPG/NFS (polyacrylamide/propylene glycol/nano fumed silica) ternary additive was prepared by chemical method according to procedure reported in previous research [7] with a ratio of 0.2/0.1/0.6 wt.% comparing to sulfuric acid content.

2.2. *Detection method*

The structural modifications of PbO_2 were detected by CV method using the three-electrode cell as above, but the working electrode was replaced by PbO_2. Charge factor ($= q_+/q_-$) and charge efficiency ($= q_-/q_+$) are calculated based on the calculated data of charge density (q_+) and discharge density (q_-) of anode and cathode partitions due to the integration of anodic and cathodic peak areas [8], respectively. Morphological structure of PbO_2 before and after CV scanning was evaluated through SEM images performed on an equipment FE-SEM Hitachi S-4800 (Japan) by acceleration of potential of 5 kV.

3. Results and discussions

In general, in lead-acid batteries PbO_2 discharges according to the reaction (1), where it will form as α-PbO_2 or/and β-PbO_2 during recharging from $PbSO_4$ depending on the working environment. After PbO_2 is prepared under different conditions, it will be investigated in the mixed gel electrolyte to assess the impact on the PbO_2 form, morphological structure as well as the working ability of PbO_2.

$$PbO_2 + 3H^+ + HSO_4^- + 2e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} PbSO_4 + 2H_2O \qquad (1)$$

3.1. *Influence of some parameters during PbO_2 fabrication*

3.1.1. *Influence of sulfuric acid concentration*

Two forms α and β-PbO_2 were found on the CV spectra similar to previously published work [9], however, their occurrence level depends on the condition using different H_2SO_4 concentrations for PbO_2 fabrication. The peak of α-PbO_2 appears in figure 1(a, b) is relatively clear (in the potential region from 0.9 to 1.2 V) with almost constant height although the position of peak potential is shifted slightly to more negative side, while the β-PbO_2 peak (in the potential region from 1.2 to 1.5 V) appeared indistinct just in the last cycles. Otherwise, the PbO_2 sample synthesized from 1.26 g/cm^3 H_2SO_4 solution (Figure 1c) showed that the α-PbO_2 peak gradually decreased and almost disappeared in the last cycles, while the β-PbO_2 one appeared gradually and clearly. Besides that, the reduction level of PbO_2 to $PbSO_4$ all increased with the number of CV scans, in which the sample (c) reached -180 mA/cm^2 at the 30th cycle, the highest one among the three samples surveyed.

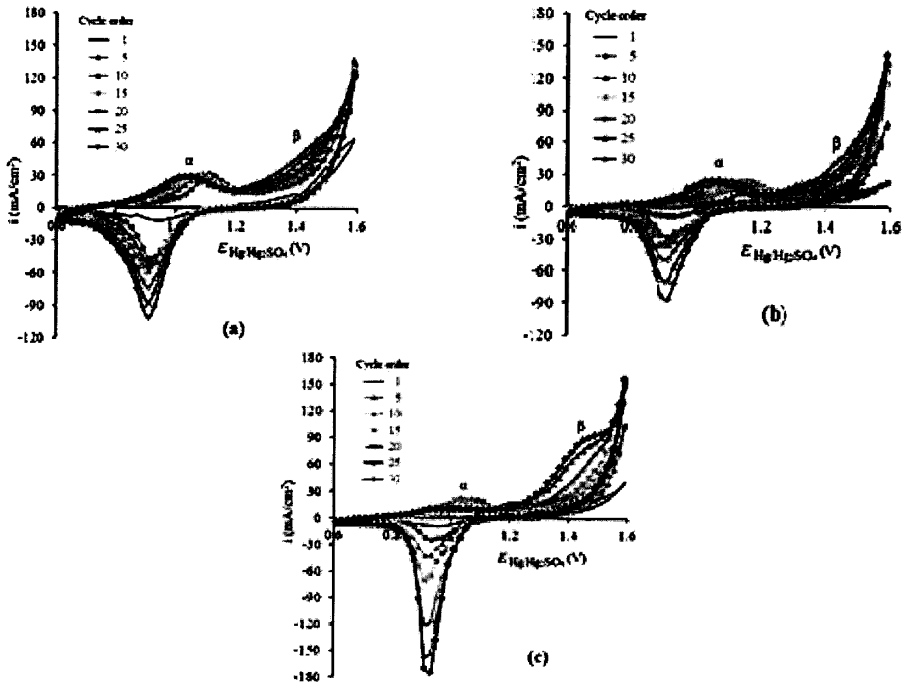

Figure 1. CV curves of PbO_2 measured in mixed gel electrolyte at 100 mV/s. PbO_2 electrodes were fabricated from different sulfuric acid concentrations (a) 1.05 g/cm^3, (b) 1.11 g/cm^3, and (c) 1.26 g/cm^3 at 10 mA/cm^2.

3.1.2. *Influence of current density*

After investigating the influence of acid concentration, we chose 1.26 g/cm^3 H_2SO_4 electrolyte to consider the influence of current density when fabricating PbO_2. Similar to the above, we get CV spectra that also appear two peaks of α and β-PbO_2. They depend strongly on the applied electrolytic current density. At low current density (1 mA/cm^2) only the peak of α-PbO_2 can appear (Figure 2a), while it appears without β-PbO_2 at the beginning under condition of 5 mA/cm^2, however, β-PbO_2 can be observed more prominent with the number of CV scans (Figure 2b). In the case of 10 mA/cm^2 the β-PbO_2 peak is seen quite clearly compared to both above samples, but the α-PbO_2 peak is almost absent in the last cycles (Figure 2c).

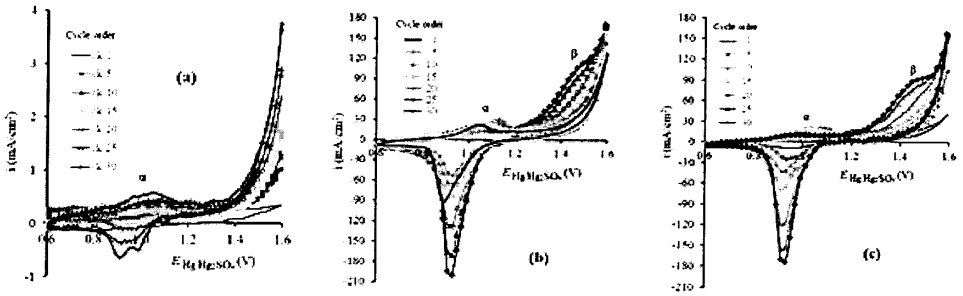

Figure 2. CV curves of PbO_2 measured in mixed gel electrolyte (scan rate of 100 mV/s). PbO_2 electrodes were fabricated at different current density (a) 1 mA/cm^2, (b) 5 mA/cm^2, and (c) 10 mA/cm^2 from 1.26 g/cm^3 sulfuric acid solution.

3.2. *Study on structural modification of PbO_2 during cycling*

From figure 3 it can be seen the peak of α-PbO_2 without β-PbO_2 appeared with decreasing height and its peak position slightly shifted to the left in the first 15 cycles (Figure 3a). After that (16-50 CVs, Figure 3b), α-phase slightly continued to decrease but its peak position was almost unchanged, while β-one appeared gradually increased. From 51-150 CVs (Figure 3c), we do observe only the β-PbO_2 peak without α-PbO_2 existed, indicating that the number of CV scans does indeed influence the appearance of two structural forms of PbO_2.

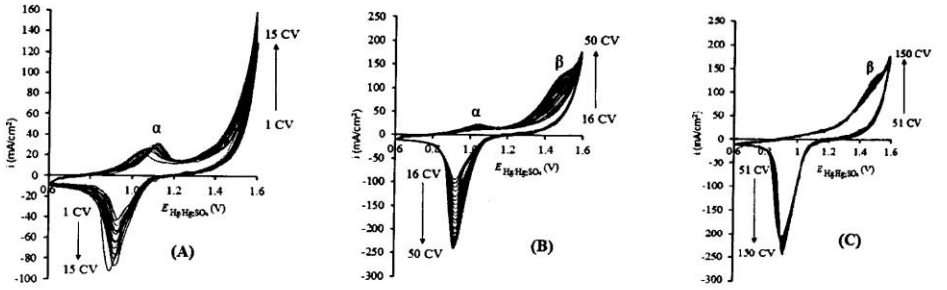

Figure 3. CV curves of PbO_2 measured in mixed gel electrolyte at 100 mV/s (PbO_2 is performed at 5 mA/cm^2 in 1.26 g/cm^3 H_2SO_4 solution).

3.3. *The effect of CV scan number on the discharge and charge process of PbO_2 electrode*

Figure 4 shows that the charge and discharge densities increased almost linearly with number of CV scan during the first 40 cycles and remained relatively stable thereafter. However, the charge density is always higher than the discharge one.

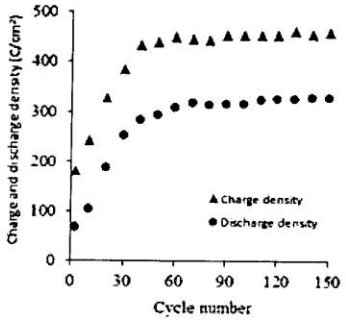

Figure 4. Effect of cycle number on charge & discharge charge density.

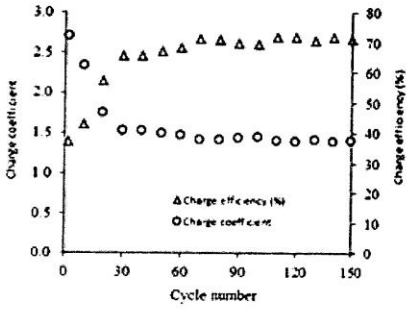

Figure 5. Effect of cycle number on charge coefficient & charge efficiency.

Two reasons for this can be discussed in detail. Firstly, the reduction of PbO_2 to $PbSO_4$ and the recharge (oxidation of $PbSO_4$) so that $PbSO_4$ converts to PbO_2 is reversible, but their volumes are different (25 and 28 cm^3/mol for PbO_2 and $PbSO_4$, respectively) [10], so the amount of PbO_2 formed will hardly be 100% discharged to $PbSO_4$ because some PbO_2 crystals are covered by $PbSO_4$ with larger size. Secondly, it is possible that a very small amount of oxygen may be released along in the oxidation region leading to a little extra energy consumption. The result also shows that the charge and discharge densities are rapidly stable and higher than that of PbO_2 electrodes fabricated on some other substrates [11,12]. The charge factor is reduced from 2.7 to 1.4 at the 70th CV, equivalent to a charge efficiency of 71% (Figure 5), and stay steady from here.

3.4. *Study on morphological structure of PbO_2 by CV*

The SEM image on figure 6 show that the morphology of PbO_2 electrodes is changed very clearly

during the multi-cycle scanning. After 30 cycles, many large crystals (up to 1 μm) appeared next to small ones (< 100 nm) compared to those before CV scanning. Since the particle size of α-PbO_2 is much larger than that of β-PbO_2 [13], it can be seen that both α and β-forms co-exist with the major quantity of α-form, which is consistent with the results of CV scan in figure 3b. As the number of CV scans increases, the crystal size shrinks. At 150 CV, almost only small crystals of relatively uniform size (< 50 um) can be observed, with some places forming large clusters, indicating β-PbO_2 form that is agreed with CV measurement results in figure 3c.

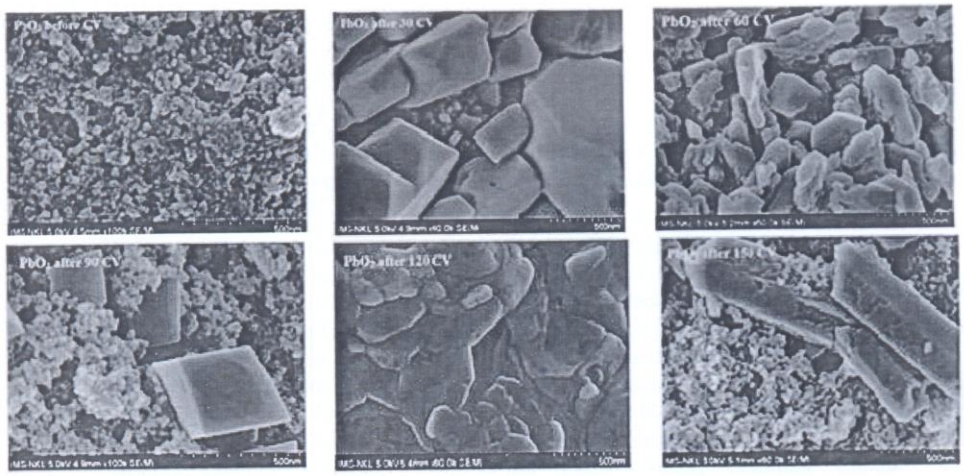

Figure 6. SEM images of PbO_2 after scanning with different CV numbers.

4. Conclusion

PbO_2 electrodes were fabricated by constant current method on PbSb substrate in sulfuric acid solution. The phormological structure and structural form as well as their working ability in mixed gel electrolyte using ternary additive were investigated by SEM images and multi-cycle CV scanning method, respectively. The main results of this study are: (i) The crystal size of PbO_2 is gradually reduced with the number of CV scans; (ii) the appearance of PbO_2 in α or β-form depended on the time of CV scanning. An appearance of α-form was in the first 15 CVs, while both α and β-forms appeared at time of 16-50 CVs, and only β-form was observed after 50 CVs; (iii) the charge efficiency is stable at 71% after 40 CVs.

Acknowledgment

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TABLE OF CONTENT

*Editor's suggestion