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Electrochemical properties of powder-pressed Pb−Ag−PbO_2 anodes

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Abstract: Pb−Ag−PbO_2 composite anodes with different mass fractions (1%, 2%, 3%, 4% and 5%) of β-PbO_2 were prepared by powder-pressed (PP) method. The galvanostatic polarization curves, Tafel curves and anodic polarization curves were tested in sulfuric acid solution. The morphologies and phase compositions of the anodic layers formed after galvanostatic polarization were investigated by using scanning electron microscope (SEM) and X-ray diffractometer (XRD), respectively. The results showed that β-PbO_2 can improve the electrocatalytic activity of anodic oxide. The anode containing 3% β-PbO_2 had the lowest overpotential of oxygen evolution reaction (OER) and the best corrosion resistance. The morphologies of the anode surfaces were gradually transformed from regular crystals to amorphous ones as the content of β-PbO_2 increased in anodes.
Key words: power-pressed Pb−Ag−PbO_2 anode; oxygen evolution overpotential; electrochemical properties; zinc electrowinning

1 Introduction

Electrowinning has become a very important method for producing zinc by hydrometallurgy in the past few decades [1−3], in which the oxygen evolution reaction (OER) is a significant anodic reaction [4,5]. The cast Pb−(0.3%−1%)Ag anodes are widely used in zinc electrowinning for their available raw materials and stability [6−8]. For the cast Pb−(0.3%−1%)Ag anodes, the addition of Ag can effectively reduce the overpotential of OER, and the produced PbO_2 coating on the anodes exhibits good properties, such as good corrosion resistance to Cl^-, which can even be eliminated [9]. However, because there are several problems for the cast Pb−Ag anodes in the zinc electrowinning, such as worse corrosion resistance which reduces the service lifetime of the Pb−Ag anodes (only 1−3 a) [10−12], a lot of precious metal Ag particles are consumed [13]. Most important of all, the cast anodes still have high overpotential of OER in zinc electrowinning [14−16], which results in 20%−30% energy wasted during zinc electrowinning [17].

To solve these problems, many alternative anodes have been put forward, such as Pb-based multi-variant alloy anodes, porous alloy anodes, dimensionally stable anodes (DSAs), polyaniline anodes, and powder-rolled/powder-pressed (PP) anodes. The Pb-based multi-variant alloys have good mechanical properties, but have little reduction to the overpotential of OER [18]. The porous alloy anodes have larger inner surface, which helps lower the overpotential of OER [19]. However, they are not easy to obtain because of the complex preparation process. The anodes with particle coatings, usually RuO_2, IrO_2, and MnO_2 [20−22], formed on the Pb matrix show good electrocatalytic properties, but they show poor corrosion resistance and instability [23]. In addition, the preparation process of these anodes is complex. Compared with the cast Pb−Ag anodes, the powder-rolled/powder-pressed anodes show better creep resistance, lower overpotential of OER and better corrosion resistance [24], which are considered to be a more promising candidate for zinc electrolysis.

In our previous work [25], it has been found that the electrochemical performance of PP Pb−0.4%Ag anode is better than that of the cast Pb−0.6%Ag anode. In addition, it is reported that the β-PbO_2 has good corrosion resistance and electrocatalytic properties,

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which could improve the electrochemical properties of the anodes [9]. In order to further study the effect of β-PbO_2 on the performance of anode, in this study, the PP Pb−Ag−PbO_2 composite anodes were prepared with the fixed 0.4% Ag content and various β-PbO_2 contents (1%, 2%, 3%, 4% and 5%, mass fraction). For comparison, the performances of cast Pb–0.6%Ag anode and PP Pb–0.4%Ag anode were also investigated. The electrochemical properties of the anodes were systematically tested. The micromorphologies and phase compositions of the oxide layer after galvanostatic polarization were also studied.

2 Experimental

2.1 Preparation of sample

The β-PbO_2 powders with particle size <5 μm (99.00% purity, Shanghai Macklin Biochemical Co., Ltd., China), Ag powders with particle size <8 μm (99.99% purity, Chengdu Lianhe Chemical Pharmaceutical Co., Ltd., China) and Pb powders with particle size <42 μm (99.95% purity, Sinopharm Chemical Reagent Co., Ltd., China) were used as raw materials. The XRD pattern and SEM image of the β-PbO_2 powders are shown in Figs. 1 and 2, respectively.

To obtain the uniformly distributed powder particles, the mixture containing 0.4% Ag, different contents (0, 1%, 2%, 3%, 4% and 5%) of β-PbO_2 powder and Pb powders was milled in a plastic tube at a rotating speed of 65 r/min for 48 h in air. The mixture was put into a steel mold and pressed under a pressure of 65 MPa for 5 min. And then, the compacts were sintered at 310 °C for 10 h and a H_2 flow rate of 0.2 L/min under normal pressure. Finally, the sintered samples were cooled to room temperature at a H_2 flow rate of 0.2 L/min. For comparison, the Pb−0.6%Ag anode was also prepared by melt casting method. The process flow diagram of PP anodes and the sketch of the mould are shown in Fig. 3.

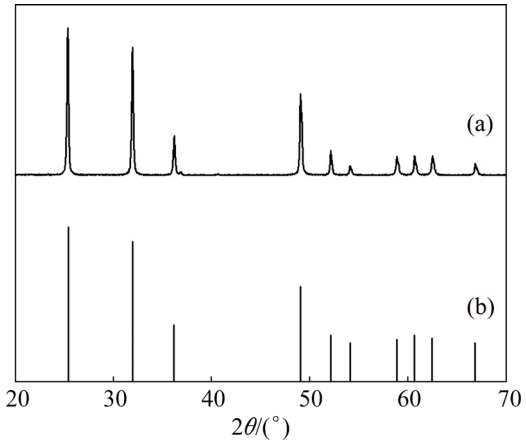

Fig. 1 XRD patterns of powders: (a) Prepared PbO_2; (b) Standard β-PbO_2

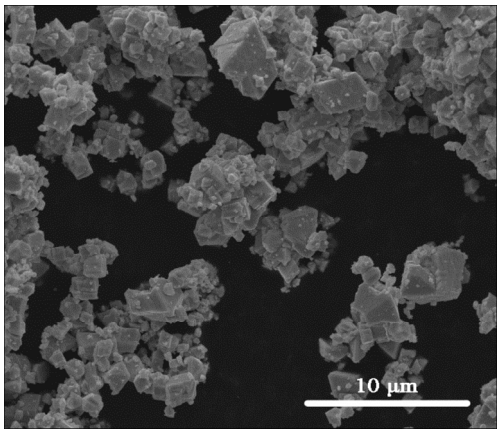

Fig. 2 SEM image of β-PbO_2 powders

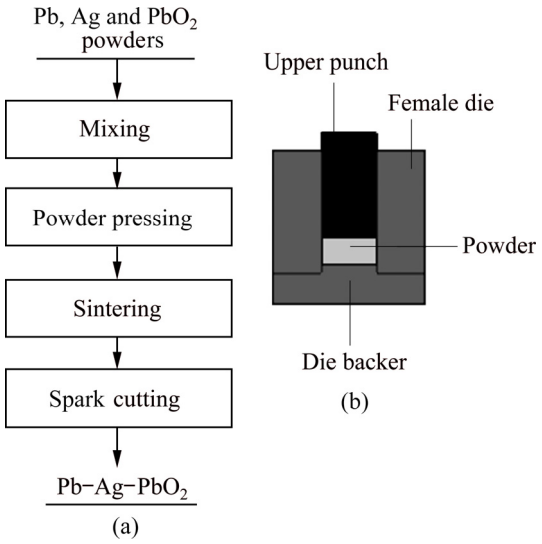

Fig. 3 Process flow diagram of PP anodes (a) and sketch of mould (b)

2.2 Electrochemical measurements

Galvanostatic polarization curves, Tafel curves and anodic polarization curves were obtained with an electrochemical workstation (CHI 760E, Huachen, China) in 500 mL electrolyte solution at 35 °C. The galvanostatic polarization tests were performed in a solution of 160 g/L H_2SO_4 at a current density of 50 mA/cm^2 for 72 h. The Tafel and anodic polarization tests were done in a solution containing 50 g/L Zn^{2+} and 160 g/L H_2SO_4 after galvanostatic polarization at the scanning rates of 3 and 0.5 mV/s from 1.4 to 1.8 V (vs SCE), respectively. A three-electrode cell was used, in which the reference electrode was a saturated calomel electrode (SCE), the counter electrode was a platinum plate, and the working electrode was the sample with an exposed area of 1.0 cm^2. The assembly diagram of the anode is shown in Fig. 4.

All the samples were polished with 1500-grit SiC paper before galvanostatic polarization tests, and they

were washed with distilled water and dried with warm air after each electrochemical test.

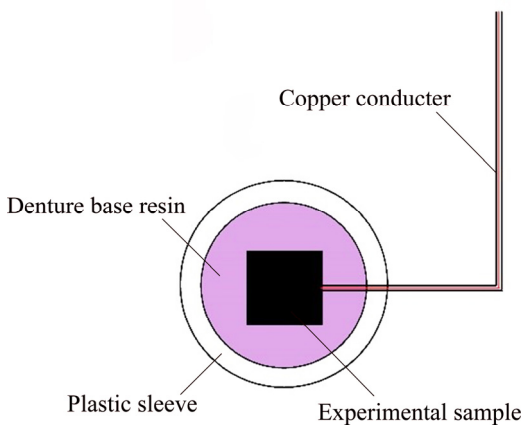

Fig. 4 Sketch diagram of experimental sample

2.3 Characterization

The morphologies of the samples after galvanostatic polarization tests of 72 h were observed by SEM (Nova Nano SEM 230). The phases of the oxide layer formed on the anode surface after galvanostatic polarization tests of 72 h were identified by XRD (Rigaku D/MAX−2250) with Cu K_α radiation.

3 Result and discussion

3.1 Galvanostatic polarization

In order to study the effects of different anodes on the overpotentials of OER, the galvanostatic polarization tests were carried out under a current density of 50 mA/cm^2 in a solution of 160 g/L H_2SO_4 at 35 °C and the results are shown in Fig. 5.

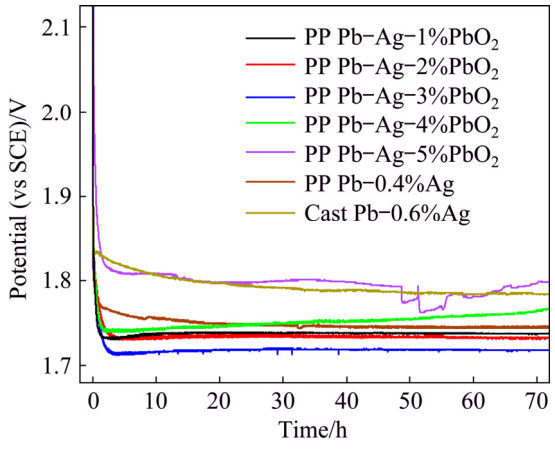

Fig. 5 Galvanostatic polarization curves of different anodes

All the anodes showed different anodic behaviors. At the initial stage of galvanostatic polarization test, the potential of all the anodes dropped dramatically with time, and eventually kept stable except for the PP Pb−Ag−5%PbO_2 anode. With the continuous formation of oxide layer on the anode surface [22,26,27], the potential of the cast Pb−0.6%Ag anode was stabilized around 1.79 V (vs SCE) after 44 h of polarization test. Compared with the cast Pb−0.6%Ag anode, the PP Pb−0.4%Ag anode showed lower stable potential in the galvanostatic polarization test which was around 1.73 V (vs SCE) after 44 h, which is consistent with our previous study.

As for the PP Pb−Ag−PbO_2 composite anodes, with the increase of β-PbO_2 content, the potential of anode was firstly decreased and then increased. More specifically, the potentials of PP anodes containing 1%, 2% and 3% PbO_2 were stabilized around 1.72, 1.72 and 1.71 V (vs SCE) after 55, 30, and 13 h of polarization tests, respectively. The potential of the anode containing 4% PbO_2 was firstly decreased and then increased, which is obviously distinguished with the other anodes; while, the potential of the anode containing 5% PbO_2 presented obvious fluctuation and was significantly higher than that of the other anodes at the end of the test.

According to Fig. 5, the overpotential of OER decreased with the increase of β-PbO_2 content (≤ 3%) in the anode during the galvanostatic polarization test, which can be explained as follows: (1) OER can be facilitated by β-PbO_2; (2) the increase of β-PbO_2 content is conducive to the increase of surface area of the anode. However, when the content of β-PbO_2 is higher than 3%, it will have great impact on the mechanical strength of the anode, which is not conducive to the formation of dense oxide layer and can even cause the shedding of the oxide layer. The cracks and loose structures of the oxide layers may be the reasons for the fluctuation of potential.

In conclusion, according to the results shown in Fig. 5, the β-PbO_2 powders (≤3%) could improve the electrocatalytic activity of the anodes and the PP Pb−Ag−3%PbO_2 anode showed the lowest overpotential of OER and the best stability among the studied samples, which makes it promising alternative for zinc electrolysis.

3.2 Tafel curves

The corrosion resistance of the PP Pb−Ag−PbO_2 composite anodes was evaluated by the Tafel curves obtained in the solution containing 50 g/L Zn^{2+} and 160 g/L H_2SO_4 under a scanning rate of 3 mV/s at 35 °C after galvanostatic polarization. The results are shown in Fig. 6.

Table 1 shows the corrosion potential (φ_{corr}) and corrosion current density (J_{corr}), which were obtained by the linear fitting of Tafel curves (Fig. 6). As well known, J_{corr} is a kinetic parameter and φ_{corr} is a thermodynamic parameter, and J_{corr} is usually used to evaluate the corrosion resistance of the anode [28]:

$$v=\frac{MJ_{corr}}{nF} \quad (1)$$

where v is the corrosion rate, n is the valence of metal, F is the Faraday constant, and M is the mole mass of metal.

As shown in Table 1, compared with the PP Pb−0.4%Ag anode, for all the PP Pb−Ag−PbO_2 composite anodes, the current densities are decreased firstly at β-PbO_2 content ≤3% and then increased at β-PbO_2 content >3%, and the anode containing 3% PbO_2 has the lowest J_{corr} (3.50×10^{-5} A/cm^2) and φ_{corr} (−0.338 V), which exhibits the best corrosion resistance. This means that appropriate addition of β-PbO_2 can improve the corrosion resistance of the anode [29], while excessive addition of β-PbO_2 will cause the decrease of corrosion resistance of the anode. The corrosion resistance of the anode is closely related to the morphology of the surface oxide layer.

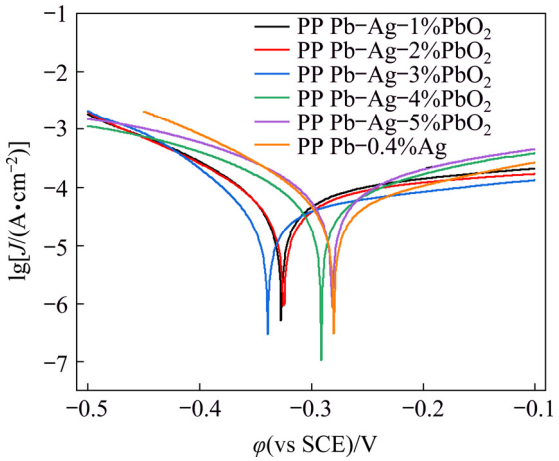

Fig. 6 Tafel curves of different anodes

Table 1 Corrosion potentials and corrosion current densities of different anodes

Anode	φ_{corr}(vs SCE)/V	J_{corr}/(A·cm^{-2})
PP Pb−Ag−1%PbO_2	−0.327	6.14×10^{-5}
PP Pb−Ag−2%PbO_2	−0.325	5.30×10^{-5}
PP Pb−Ag−3%PbO_2	−0.338	3.50×10^{-5}
PP Pb−Ag−4%PbO_2	−0.291	6.36×10^{-5}
PP Pb−Ag−5%PbO_2	−0.281	8.57×10^{-5}
PP Pb−0.4%Ag	−0.298	6.20×10^{-5}

3.3 Anodic polarization

To study the oxygen evolution behaviors of different anodes after galvanostatic polarization, anodic polarization tests were carried out at a scanning speed of 0.5 mV/s in a solution containing 50 g/L Zn^{2+} and 160 g/L H_2SO_4 at 35 °C, and the results are shown in Fig. 7. The order of oxygen evolution potentials from low to high is: Pb−Ag−3%PbO_2 < Pb−Ag−2%PbO_2 < Pb−Ag−1%PbO_2 < Pb−Ag−4%PbO_2 < Pb−Ag−5%PbO_2 < Pb−0.4%Ag. This trend is consistent with the final potential of galvanostatic polarization in Fig. 5 and the Pb−Ag−3%PbO_2 anode has the lowest overpotential of OER.

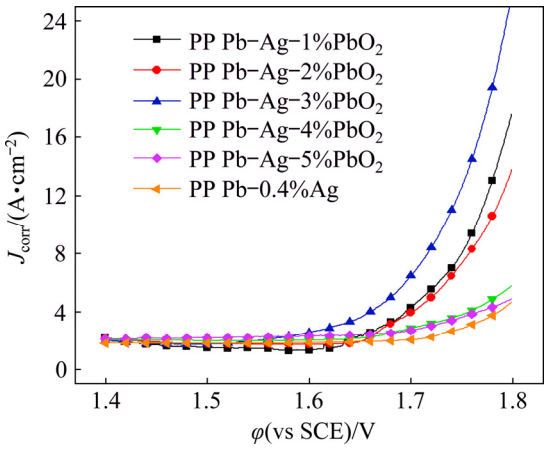

Fig. 7 Anodic polarization curves of different anodes

Table 2 lists the kinetic parameters (a, b and J_0) and the overpotential of OER (η) for all the Pb−Ag−PbO_2 composite anodes obtained at a current density of 50 mA/cm^2. The value of η is calculated with Eq. (2) [30,31].

$$\eta=\varphi+0.2373-1.260-JR_s \quad (2)$$

where R_s is the solution resistance between the working electrode and the reference electrode, J is the current density corresponding to φ, φ is the anodic potential, 1.260 is the equilibrium potential of OER, and 0.2373 is the potential of SCE. And then, a, b can be obtained by linear fitting of R_s-corrected lines (η−lg J) according to Eq. (3), and the exchange current density (J_0) can also be calculated through Eq. (3) at η=0.

$$\eta=a+b\lg J \quad (3)$$

From Table 2, it can be seen that the order of J_0 from low to high is: Pb−0.4%Ag < Pb−Ag−5%PbO_2 < Pb−Ag−4%PbO_2 < Pb−Ag−1%PbO_2 < Pb−Ag−2%PbO_2 < Pb−Ag−3%PbO_2, and the Pb−Ag−3%PbO_2 anode has the highest J_0 value (1.02×10^{-5} A/cm^2). We usually

Table 2 Kinetic parameters of oxygen evolution reaction of anodes

Anode	a	b	J_0/(A·cm^{-2})	η(vs SCE)/V
PP Pb−Ag−1%PbO_2	1.150	0.215	4.46×10^{-6}	0.870
PP Pb−Ag−2%PbO_2	1.120	0.212	5.27×10^{-6}	0.844
PP Pb−Ag−3%PbO_2	1.064	0.213	1.02×10^{-5}	0.786
PP Pb−Ag−4%PbO_2	1.727	0.319	3.89×10^{-6}	1.311
PP Pb−Ag−5%PbO_2	1.774	0.324	3.31×10^{-6}	1.353
PP Pb−0.4%Ag	1.791	0.325	3.08×10^{-6}	1.368

evaluate the reversibility of electrode reactions and electrode polarization with the value of J_0 [28]. A higher J_0 indicates that the electrode cannot be easily polarized and has higher electrochemical activity and better reversibility [32]. Table 2 also shows that the Pb−Ag−3%PbO_2 anode has the the lowest η value (0.786 V), which means that the anode has the best energy saving property among all the PP Pb−Ag−PbO_2 composite anodes. Therefore, the Pb−Ag−3%PbO_2 anode has the highest electrochemical activity.

3.4 Surface morphology

To find out the reason for the difference of electrochemical properties of different anodes, the morphologies of the anodes after galvanostatic polarization tests were characterized by SEM, as shown in Fig. 8.

For the PP Pb−0.4%Ag anode (Fig. 8(a)), the oxide layers formed on the anode surface were mainly composed of small crystals/particles, on some of which, small cavities could be found. In comparison, when the low amount of β-PbO_2 is introduced (PP Pb−Ag−1%PbO_2) (Fig. 8(b)), the oxide layer was mainly composed of smaller regular crystals/particles than PP Pb−0.4%Ag anode (Fig. 8(a)) with different sizes and amorphous particles. When the β-PbO_2 content was further increased to 2% (Fig. 8(c)), the particles/crystals became smaller in size and the proportion of amorphous

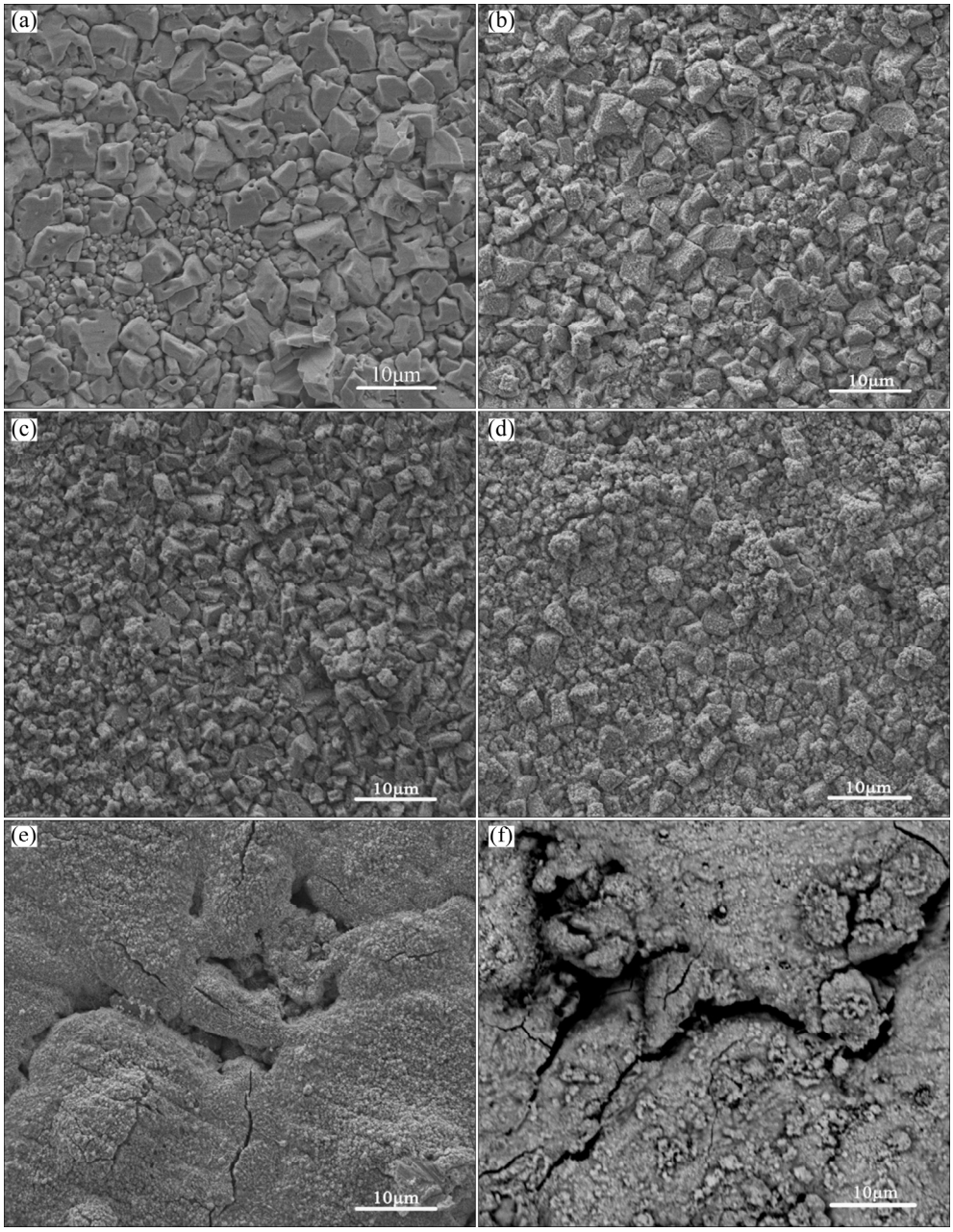

Fig. 8 SEM images of PP Pb−0.4%Ag (a), PP Pb−Ag−1%PbO_2 (b), PP Pb−Ag−2%PbO_2 (c), PP Pb−Ag−3%PbO_2 (d), PP Pb−Ag−4%PbO_2 (e), and PP Pb−Ag−5%PbO_2 (f)

particles increased significantly. When the β-PbO_2 content was 3% (Fig. 8(d)), the oxide layer was mainly composed of amorphous particles and some regular particles. The results above indicate that the introduction of β-PbO_2 into the PP Pb−0.4%Ag anode is beneficial to the formation of amorphous particles, and the higher content of β-PbO_2 induces the formation of more amorphous particles in the oxide layer. However, when the β-PbO_2 content was increased to 4% (Fig. 8(e)), the oxide layer was composed of amorphous particles and the crystals/particles disappeared, most importantly, some cracks were observed in the oxide layer. With further increase of β-PbO_2 content to 5% (Fig. 8(f)), cracks became significantly larger. The obvious cracks mean that the oxide layer is loose and has weak adhesion, which is easy to fall off during galvanostatic polarization tests. The loose structure and the cracks may be the main reasons for the poor corrosion resistance of PP Pb−Ag−4%PbO_2 and PP Pb−Ag−5%PbO_2 anodes, and are also responsible for the potential fluctuation in the process of galvanostatic polarization test.

3.5 Phase analysis

The influence of β-PbO_2 content on the composition and phases of the anodic oxide layer was studied by XRD and the results are shown in Fig. 9.

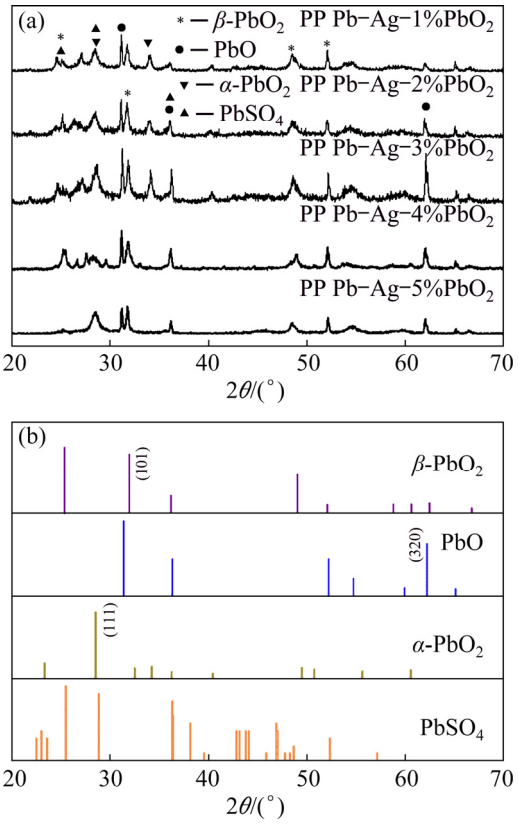

Fig. 9 XRD patterns of oxide layer of PP anodes after 72 h polarization at 50 mA/cm^2 and 35 °C (a) and diffraction standard cards of β-PbO_2, PbO, α-PbO_2 and $PbSO_4$ (b)

The results showed that for all the Pb−Ag−PbO_2 composite anodes, the oxide layers were mainly composed of PbO, α-PbO_2, β-PbO_2, and $PbSO_4$. However, the characteristic absorption peaks of each anode were different. Compared with the anodes containing 4% and 5% β-PbO_2, the anodes containing 1%, 2% and 3% β-PbO_2 had obvious diffraction peaks of α-PbO_2 (111). The intensity of the peak of PbO (320) increased with the β-PbO_2 content (≤3%), then it decreased when the β-PbO_2 content exceeded 3%. It is worth noting that the increase of β-PbO_2 content in fresh composite anodes had great effect on the intensity of the peak of β-PbO_2 (101) of oxide layers and the changing trend of the absorption peak of β-PbO_2 was consistent with the potential of galvanostatic polarization of Pb−Ag−PbO_2 composite anodes. Therefore, the content of β-PbO_2 in anodes has certain influence on the formation of α-PbO_2, β-PbO_2 and PbO. The powder of β-PbO_2 in the anodes may provide some active sites for the formation of transformation of Pb to $PbSO_4$ and $PbSO_4$ to β-PbO_2 [29,33]. However, the excessive addition of β-PbO_2 leads to the formation of unstable oxides, which may be the reason for the decline of intensity of PbO.

4 Conclusions

(1) As the content of β-PbO_2 increased in the powder-pressed anode, the overpotential of oxygen evolution reaction decreased firstly and then increased. The Pb−Ag−3%PbO_2 anode had the lowest potential.

(2) The addition of an appropriate amount of β-PbO_2 can improve the corrosion resistance of the powder-pressed anodes. The Pb−Ag−3%PbO_2 anode showed the best corrosion resistance.

(3) With increasing the content of β-PbO_2, the morphologies of the oxide layer changed from regular crystals/particles to amorphous particles. However, excessive addition of β-PbO_2 in the anodes was not conducive to the formation of a highly adhesive oxide layer.

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粉末压制 Pb−Ag−PbO_2 阳极的电化学性能

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摘 要：采用粉末压制方法制备 Pb–Ag–PbO_2 阳极，其中，β-PbO_2 的质量分数分别为 1%，2%，3%，4%和 5%。在硫酸电解液中测试恒电流极化、塔菲尔和阳极极化曲线。采用扫描电镜(SEM)和 X 射线衍射仪分别观察和测试恒电流极化后阳极表面的形貌和相成分。研究结果表明，β-PbO_2 能提高阳极表面氧化层的电催化活性；含 3% β-PbO_2(质量分数)的阳极具有最低的析氧过电位和最好的抗腐蚀性能；随着 β-PbO_2 含量的增加，阳极表面的形貌从规则晶体转变到无定型状态。

关键词：粉末压制 Pb−Ag−PbO_2 阳极；析氧过电位；电化学性能；锌电泳

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