

Novel phosphorus-doped lead oxide electrode for oxygen evolution reaction

Supporting Information

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Part I. Experimental details

The electrodeposition of P-PbO₂ electrode was achieved through an anodic oxidation technique. The preliminary composition of the deposition solution was 35 g L⁻¹ Na₄P₂O₇ + 16 g L⁻¹ Pb(NO₃)₂. The electrodeposition were carried out in a two-electrode system under constant current, where a 1 cm² pure lead substrate and a 4 cm² platinum plate was used as the anode and cathode, respectively. The deposition temperature and agitation rate were controlled by the DF-101S constant temperature magnetic agitator. Parameters for optimizing the quality and structure of P-PbO₂ deposit were listed in Table S1 in the Supporting Information.

The morphology of P-PbO₂ deposit was observed using JSM-6360 SEM. GENESIS60S EDS was further used for the chemical composition analysis. The mass fraction (wt.%) of phosphorus in the deposit was approximately calculated with equation (1):

$$\text{wt.}\%(P) = \left(1 + \frac{M_{Pb} + 2M_O}{M_P} \times \frac{N_{Pb}}{N_P}\right)^{-1} \times 100\%, \quad (1)$$

where M_{Pb} , M_P and M_O represent the relative atomic mass of lead, phosphorus and oxygen, respectively, and N_{Pb}/N_P is the atomic ratio of lead and phosphorus detected by EDS. TTR-III X-ray Diffractometer (XRD) with Cu Ka ($k = 1.54056 \text{ \AA}$) as radiation source was used to identify the phase composition and crystal structure. Analysis of XRD spectra were carried out in the MDI Jade 6.0 software.

Characterizations of electrocatalytic activity of the Pb/P-PbO₂ electrode for OER were performed on the PARSTAT 2273 Advanced Electrochemical System. The standard three-electrode cell was used. The Pb/P-PbO₂ electrodes were used as anodes. A platinum plate of 4 cm² and the KCl saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials showed in the figures are against SCE. 160 g L⁻¹ H₂SO₄ solution was used as the electrolyte. The characterization process include two steps: (1) preconditioning by galvanostatic polarization at 50 mA cm⁻² for 90 min, (2) electrochemical impedance spectra (EIS) were immediately collected at various anodic potentials. The frequency range was from 100 kHz to 10 mHz, the AC Amplitude was 5 mV. The solution temperature was controlled at 35 °C throughout the characterization. In addition, a plate of pure lead anode (1 cm², Yuguang Gold & Lead, Henan, China) was galvanostatically polarized in 160 g L⁻¹ H₂SO₄ solution for 72 h to form a Pb/PbO₂ anode. The same electrochemical measurements were carried out on this anode as comparison.

Part II. Deposition principle of P-PbO₂

In order to study the formation mechanism of P-PbO₂ at the initial stage of the electrodeposition, both platinum and pure lead were used as the substrates. The cyclic voltammetry was carried out in Na₄P₂O₇ solution as well as the Na₄P₂O₇ + Pb(NO₃)₂ solution. The scanning rate was 10 mV s⁻¹. The potential cycle started from -1.0 to 2.5 V and then reversed to -1.0 V.

As showed in Fig. S1A, the voltammogram on Pt substrate in Na₄P₂O₇ solution only shows an oxygen evolution branch (d) within 1.0~2.5 V, indicating Na₄P₂O₇ solution is chemically stable in the potential region of -1.0 to 2.5 V. When the Pt substrate was cyclically polarized in Na₄P₂O₇ + Pb(NO₃)₂ solution, the voltammogram presents three anodic peaks (a), (b), (c) and an oxygen evolution branch (d) in the positive scanning and two cathodic peaks (e) and (f) in the negative scanning. The appearance of (a) and (b) were considered due to the formation of lead phosphoric salt related intermediate passivation layer. The appearance of peak (c) and (e) represents the formation and reduction of PbO₂, respectively.

In Fig. S1B, peak (a) and (b) on Pb substrate in Na₄P₂O₇ solution are obviously enlarged, and thus one can predict that lead substrate reacted with the pyrophosphate to form the passivation layer. Also, the PbO₂ formation peak (c) and O₂ evolution branch (d) can be considered to combine to one branch. The onset potential (1.6 V) of the combined branch is higher than that of Pt substrate (1.0 V) since the over-potential for oxygen evolution on Pt is much lower than that on Pb. The appearance of anodic peak (a') in the negative scanning further indicates the partially oxidation of lead substrate. With the presence of Pb(NO₃)₂ in the deposition solution, the voltammogram was compressed. One can predict that the lead substrate is prone to form a more compact passivation layer due to the appearance of anodic reaction (b'). This was also confirm by the compression of peak (a') since the contact of deposition solution with the lead substrate become more difficult due to the passivation layer. The layer formed at this case shows lower oxygen evolution activity, rendering the onset potential increase to the positive direction.

To confirm the intermediate product corresponding to anodic peak (a) and (b), constant potential polarization was carried out on the lead substrate (1 cm²) at -0.5 V and -0.1 V in a solution containing 35 g L⁻¹ Na₄P₂O₇ + 16 g L⁻¹ Pb(NO₃)₂. SEM and XRD were used to characterize the corresponding product, as shown in Fig. S2. The intermediate products present similar morphology while overall the later are much more flat and compact. XRD analysis indicates the product at -0.5 V corresponds to Pb₂P₂O₇ and that obtained at -0.1 V corresponds to Pb₂P₂O₇ +

PbP₂O₇. It is worthy to mention that the peak (a) and (b) appeared on Pt substrate is due to the deposited lead in the lower potential region corresponding to peak (f). Thus, we propose that at the initial stage of P-PbO₂ deposition, the electrochemical reactions can be expressed as follows:

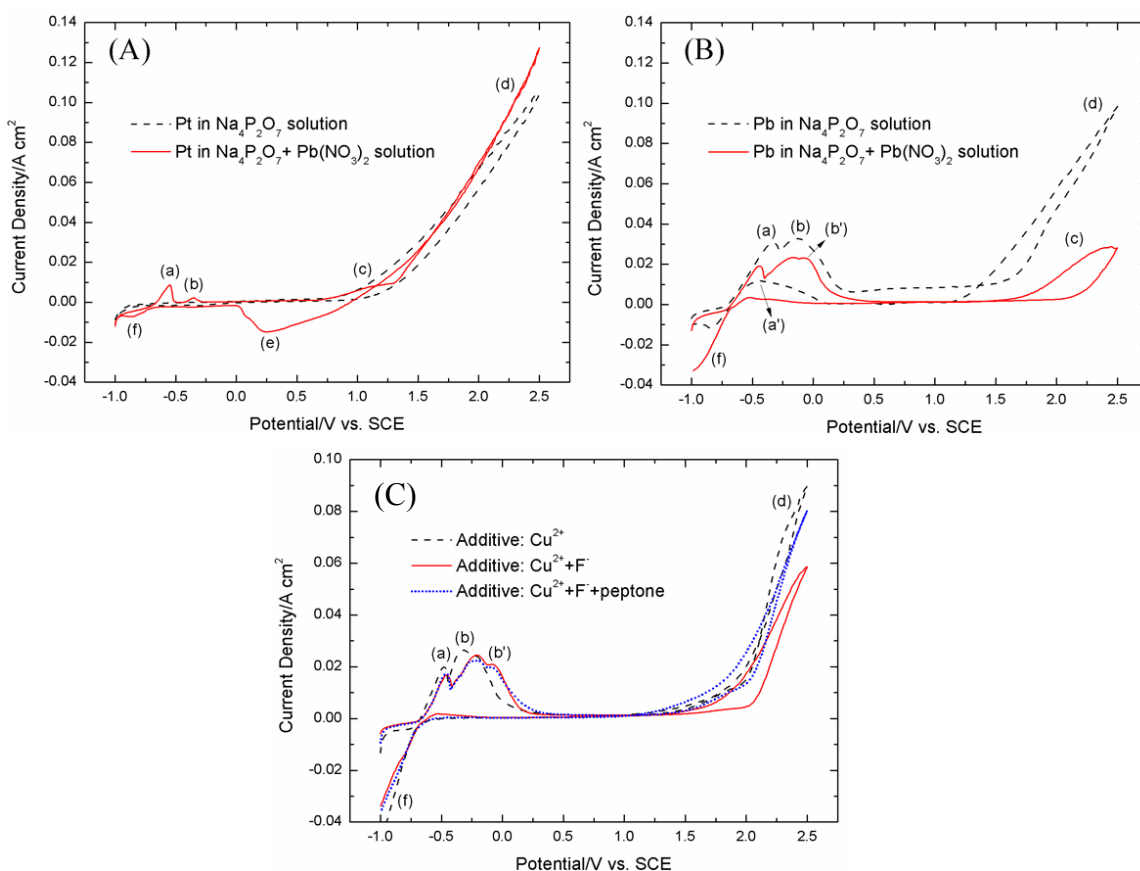
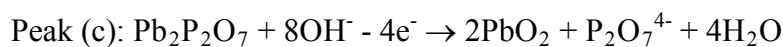
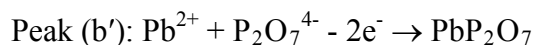
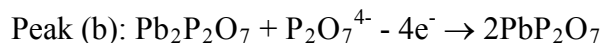
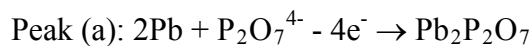


Fig. S1. (A, B) CV of (A) Pt and (B) Pb substrates in solution containing 35 g L⁻¹ Na₄P₂O₇ and 35 g L⁻¹ Na₄P₂O₇ + 16 g L⁻¹ Pb(NO₃)₂, respectively. (C) Influence of additives on CV of lead substrate in the 35 g L⁻¹ Na₄P₂O₇ + 16 g L⁻¹ Pb(NO₃)₂ solution.

Despite electrodeposition of PbO₂ in the Na₄P₂O₇ + Pb(NO₃)₂ solution is theoretically possible according to above proposed principle, it is difficult to obtain a high quality deposit with controlled composition in practice: (1) the deposition potential is high (1.5 V~ 2.5 V), as a result the formation of PbO₂ is largely retarded by the evolution of O₂; (2) the basic Na₄P₂O₇ +

$\text{Pb}(\text{NO}_3)_2$ solution will become turbid during long time deposition, rendering the deposit to be very rough or present a granular shape. Accordingly, several additives were added into the solution to optimize the deposition conditions. Fig. S3 shows the influence of Cu^{2+} (2 g L^{-1} $\text{Cu}(\text{NO}_3)_2$), F^- (1 g L^{-1} NaF) and peptone (0.2 g L^{-1}) on the cyclic voltammograms on lead substrate. With the addition of Cu^{2+} in the deposition solution, the onset potential of branch (d) shifted to the negative direction and the peak height was obviously increased. Cu^{2+} partially deposited on the substrate through the replacement reaction, which will inhibit the formation of passivation layer and render the oxygen evolution and PbO_2 deposition become easier. F^- , as an inhibitor for oxygen evolution [S 1] rendered oxygen evolution potential shift to positive direction, which is prone to the formation of PbO_2 . Peptone can favorably dissolved in the deposition solution and increase its wettability. As a result, the dissolution of evolved O_2 become easier and the branch (d) is heightened. It is worthy to point out that with the addition of these additives, the stability of deposition was largely improved. Experimentally we observed that even during constant current deposition of 120 min, the solution kept clear throughout and no precipitate formed.

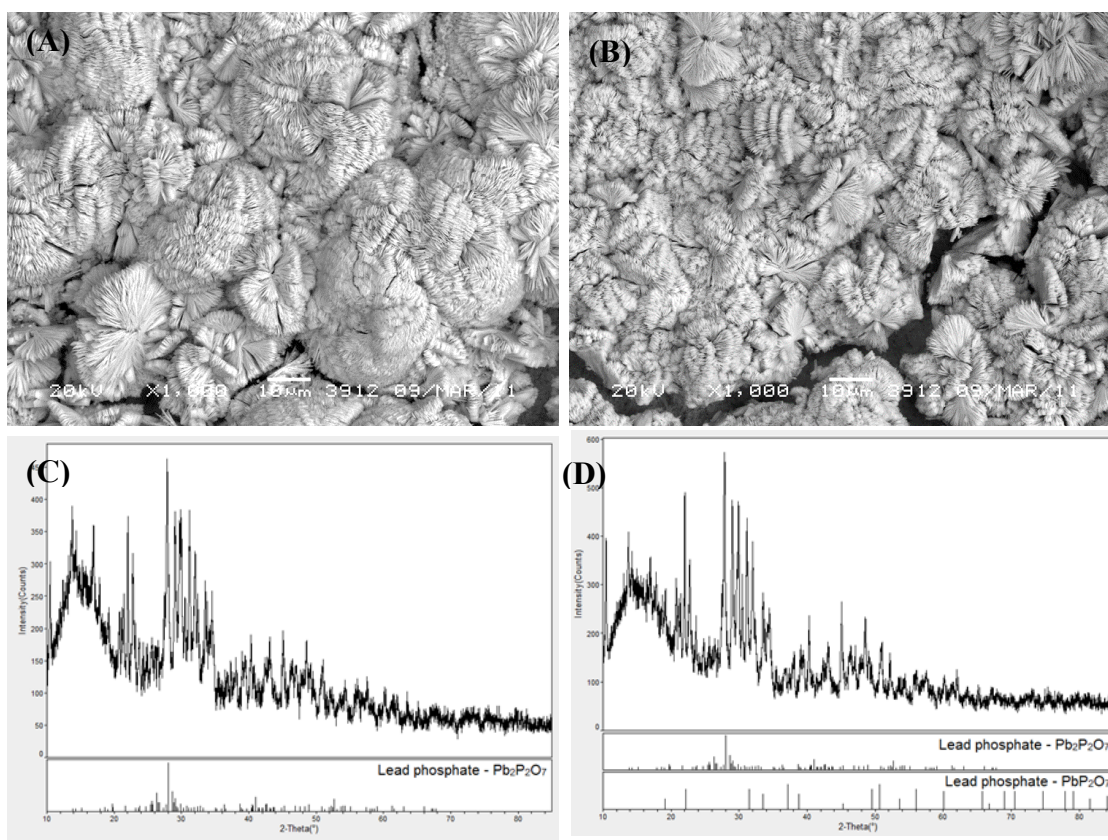


Fig. S2. (A, B) SEM images showing the morphology of intermediate products obtained at -0.5

V (A) and -0.1 V (B). (C, D) XRD patterns corresponding to A and B, respectively.

Part III. Parameter study for the electrodeposition of P-PbO₂

As shown in Table 1, the influence of temperature, additives, current density, agitation and deposition duration on the surface morphology and coating structure was studied in detail. The basic deposition solution was 35 g L⁻¹ Na₄P₂O₇ + 16 g L⁻¹ Pb(NO₃)₂ throughout the study.

Table S1. Experimental parameters used for the electrodeposition of P-PbO₂.

	Temperature (°C)	Additives (g L ⁻¹)			Current (mA cm ²)	Agitation (rpm)	Time (min)
		Cu(NO ₃) ₂	NaF	Peptone			
1	30	2	0	0	10	400	60
2	40	2	0	0	10	400	60
3	50	2	0	0	10	400	60
4	60	2	0	0	10	400	60
5	70	2	0	0	10	400	60
6	70	2	0	0.2	10	400	60
7	70	2	0.5	0	10	400	60
8	70	2	0.5	0.2	10	400	60
9	70	2	1	0.2	10	400	60
10	70	2	1	0.4	10	400	60
10	70	2	1	0.4	10	400	60
11	70	2	1	0.4	15	400	60
12	70	2	1	0.4	20	400	60
13	70	2	1	0.4	10	300	60
10	70	2	1	0.4	10	400	60
14	70	2	1	0.4	10	500	60
15	70	2	1	0.4	10	500	60
16	70	2	1	0.4	10	500	90

2.1. Influence of temperature

Fig. S3 shows the SEM images of P-PbO₂ obtained at different temperature by applying constant current density of 10 mA cm⁻² and agitation rate of 400 rpm. The deposition time was 60 min. At low temperature, the deposit surface was relatively rough, presenting a porous structure with

cauliflower structure. With the increase of temperature, the morphologies become flat and dense, uniform crystal grains with clear crystal edge were observed. This phenomenon can be explained as follows. On the one hand, the ionic migration became easier and the electrochemical activity of electrode was improved with the increase of temperature. As a result, the driving force of PbO_2 nucleation and growth was increased. On the other hand, the formation of PbO_2 is an exothermic process [S2]. With temperature increased, the equilibrium of the reaction shifts negatively, rendering the nucleation process much more difficult. Thus, high temperature presents a function of grain refinement, which makes the surface of PbO_2 more flat and dense.

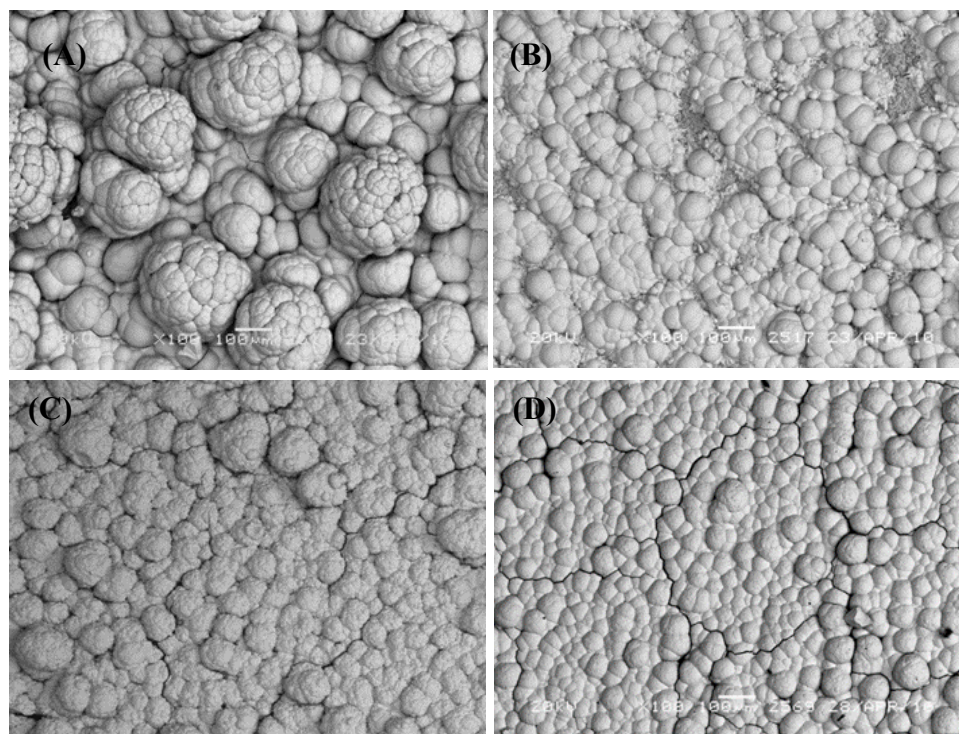


Fig. S3. Influence of temperature on the morphology ($\times 100$) of P- PbO_2 deposited on lead substrate: (A) 30 °C, (B) 40 °C, (C) 50 °C, (D) 60 °C.

2.2. Influence of additives

The influence of F^- and peptone on the surface morphology of P- PbO_2 was shown in Fig. S4. For this group of experiments, the temperature is 70 °C, the current density is 10 mA cm^{-2} , the agitation rate is 400 rpm and the deposition time is 60 min. Generally, the addition of peptone makes the deposits more uniform and denser while F^- makes them more flat [S3]. The collaborative addition of peptone and F^- will further improve the quality of P- PbO_2 deposit. As shown in Fig. S4E-F, the deposit surface becomes smooth, compact and highly ordered. It is

worthy to mention that peptone is an effective surfactant in this deposition system [S4]. On the one hand, the solution became chemically more stable with the addition of peptone. There are neither any precipitates formed nor any color-change during the electrodeposition for even more than 90 min. On the other hand, peptone can be absorbed on the electrode surface and inhibits the electron transfer process, which will refine the PbO_2 grains and render the surface of deposit smooth and dense.

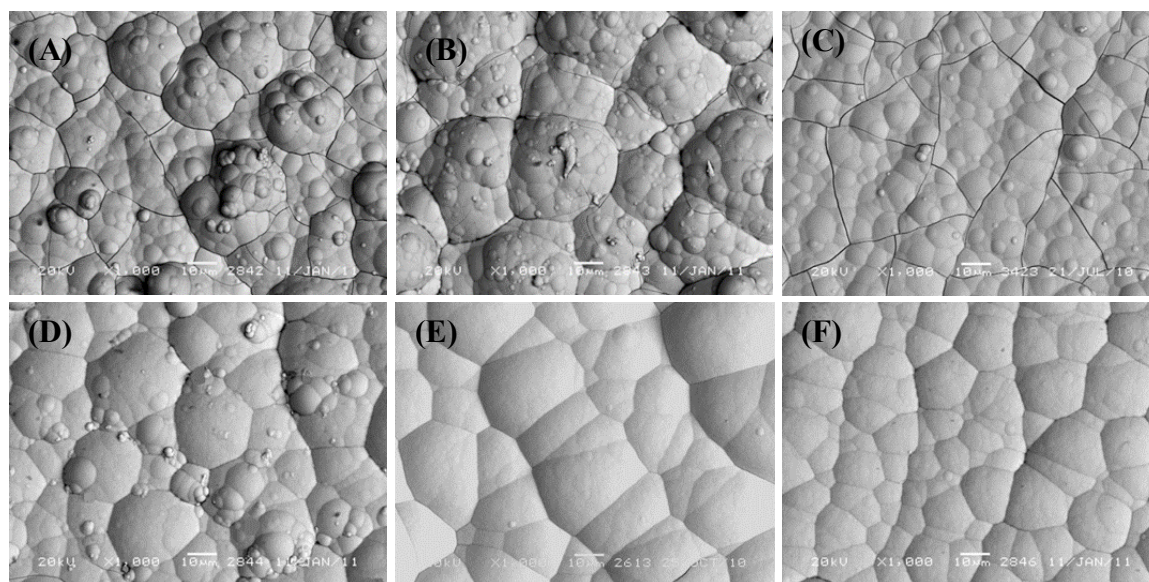


Fig. S4. SEM ($\times 1000$) of P-PbO_2 prepared on Pb substrate with addition of (A) 0 NaF and 0 peptone, (B) 0 NaF and 0.2 g L^{-1} peptone, (C) 0.5 g L^{-1} NaF and 0 peptone, (D) 0.5 g L^{-1} NaF and 0.2 g L^{-1} peptone, (E) 1 g L^{-1} NaF and 0.2 g L^{-1} peptone, (F) 1 g L^{-1} NaF and 0.4 g L^{-1} peptone to the basic deposition solution.

2.3. Influence of current density and agitation

The influence of current density the morphology of P-PbO_2 coatings was shown in Fig. S5A-B and Fig. S4E. With the increase of current density, the deposit surface becomes rough. Threadlike cracks along the grain boundaries can also be observed. The electrodeposition of PbO_2 has been reported to be very sensitive to current density [S5]. On the one hand, the formation of PbO_2 is a process coupled with the evolution of O_2 . At low current density, most of the charges are used in the formation of PbO_2 and thus the crystal grains grow up uniformly. As current density increase, the charges used for oxygen evolution also increased, rendering the deposit a relative rough surface. On the other hand, PbO_2 electrodeposition is a process

controlled by the migration of ions. The previously adsorbed oxygen-containing species are very important for the nucleation and growth of PbO_2 [S6]. At low current density, mass transport process takes a major part compared with the electron transfer and the deposit structure can be uniformly formed. At higher current densities, concentration polarization becomes obvious and Pb-containing ions can't migrate to the electrode surface timely as needed. Hence, the deposit formed will be less ordered and the outward growth of PbO_2 is aggravated. Based on this principle, the deposition process should also have a large dependence on the agitation rate. As shown in Fig. S5C-D and Fig. S4E (400 rpm), the P- PbO_2 deposit presented a rough surface with visible threadlike cracks at agitation of 300 rpm. As the agitation increase to 400 and to 500 rpm, the deposits became smooth and orderly.

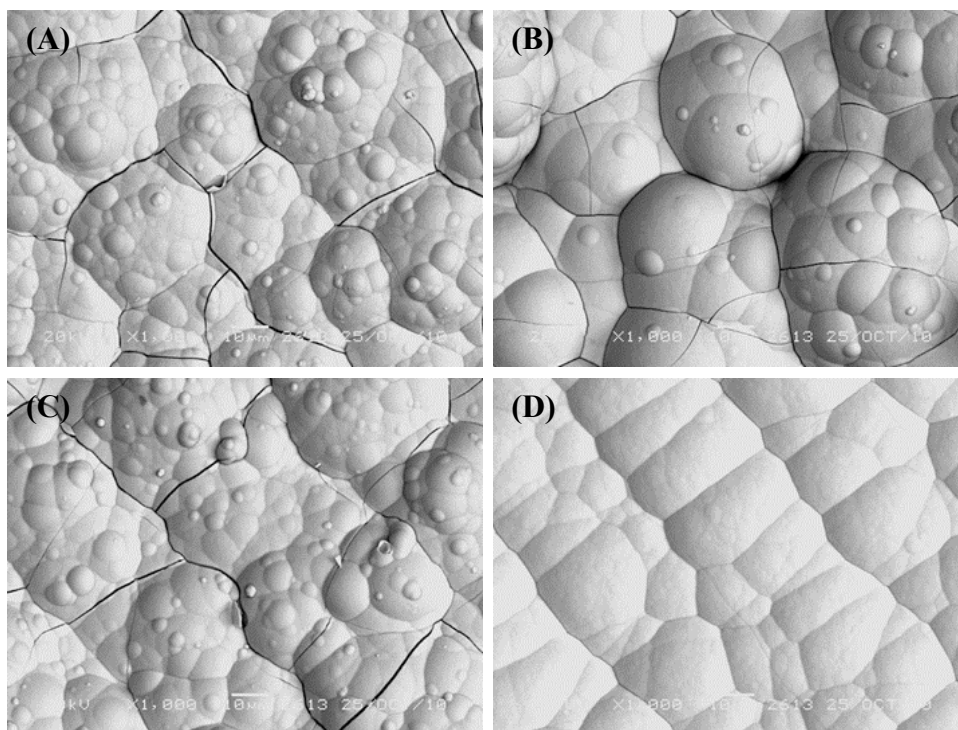


Fig. S5. SEM ($\times 1000$) of P- PbO_2 obtained at current of (A) 15 mA cm^{-2} , (B) 20 mA cm^{-2} , and obtained at agitation rate of (C) 300 rpm, (D) 500 rpm.

2.4. Influence of deposition time

It is well-defined that the electrodeposition processes present an electrochemical leveling function when organic surfactants are used [S7]. In this paper, when the deposition time was increased to 90 min, a highly smooth, uniform and reflective deposit was obtained, as shown in Fig. S6.

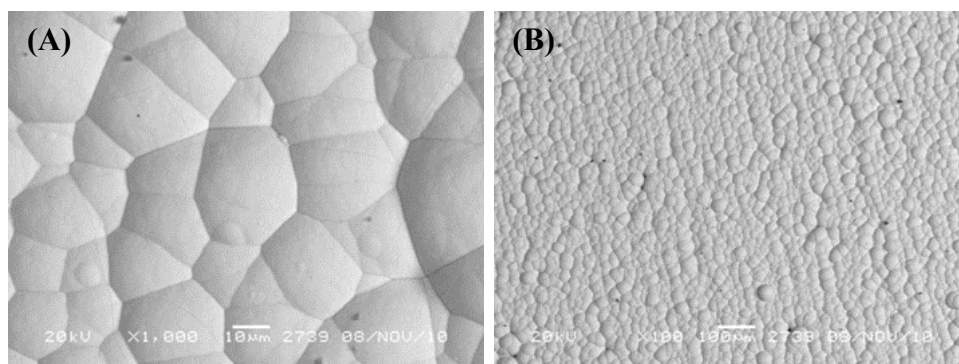


Fig. S6. SEM of P-PbO₂ deposit obtained after electrodeposition for 90 min: (A) ×1000, (B) ×100.

Part IV. Pb/PbO₂ electrode as comparison

The control sample Pb/PbO₂ electrode was obtained by galvanostatically polarizing a 1 cm² pure lead plate at 50 mA cm⁻² for 72 h in 160 g L⁻¹ H₂SO₄ solution. The surface morphology was shown in Fig. S7A-B. Chemical and phase composition were shown in Fig. S7C-D.

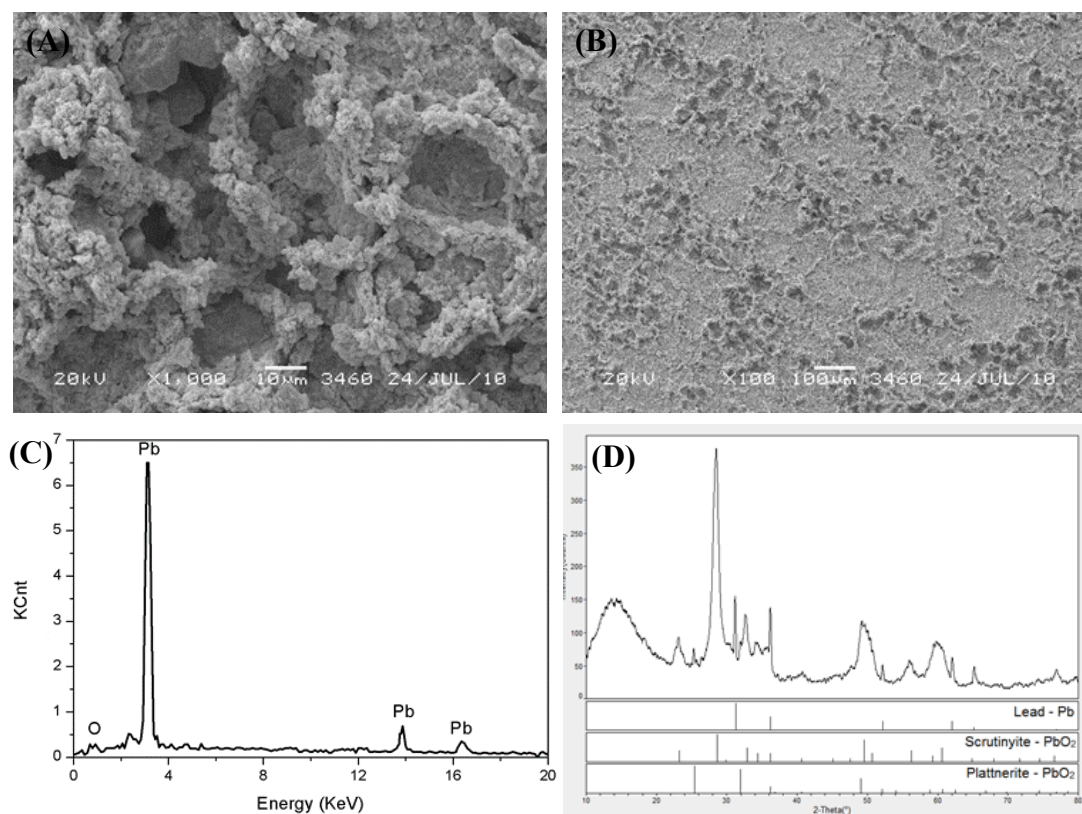


Fig. S7. (A-B) SEM images showing the surface morphology of Pb/PbO₂ electrode: (A) ×1000, (B) ×100. (C) EDS spectrum, (D) XRD pattern for the Pb/PbO₂ electrode.

References

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