

A comparison of electrochemical oxidation performance of PbO₂ and SnO₂ electrodes

X. Y. Duan, J. R. Li, L. M. Chang and C. W. Yang

ABSTRACT

PbO₂ and SnO₂ are two promising anode materials for electrochemical oxidation. In order to highlight the difference between two kinds of electrodes in an electrochemical oxidation process, their morphology, structural, oxygen evolution overpotential (OEP), electrochemical activity and service life-time were compared in detail in this paper. Surface characterization by scanning electron microscope shows that the film of the PbO₂ electrode is even, compact, non-porous, and non-cracked, while many cracks are present on the film of the SnO₂ electrode. Electrochemical studies based on linear sweep voltammetry (LSV) and cyclic voltammetry (CV) prove that the OEP for the SnO₂ electrode was much higher than that of the PbO₂ electrode, and the electron-transfer kinetics and the reversibility of electrode reaction of the SnO₂ electrode were superior to those of the PbO₂ electrode. In electrochemical decomposition of *p*-nitrophenol, the degradation ratios at PbO₂ and SnO₂ anodes achieved 86.9% and 96.5%, respectively, after 120 min electrolysis, which verified the results of LSV and CV. The accelerated lifetime tests show that the service life time of the SnO₂ electrode is far shorter than that of the PbO₂ electrode, even though it was shown to be superior to the PbO₂ in electrocatalytic activity.

Key words | comparison, electrochemical oxidation, electrode, PbO₂, SnO₂

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INTRODUCTION

Fresh water scarcity has been a severe problem in recent years. Moreover, an increase in water pollutant levels is directly threatening the safety of drinking water for humans and animals. Thus, extensive wastewater treatment technologies have been developed, among which electrochemical oxidation is a promising approach for the degradation of refractory organic pollutants in water due to its many distinctive advantages including strong oxidation performance, environmental compatibility, versatility, cost effectiveness and amenability to automation (Zhuo *et al.* 2011; Liu *et al.* 2012).

The degradation efficiency of organic pollutants in an electrochemical oxidation process depends on the activity of the anode materials (Zhao *et al.* 2014). Besides high activity, high chemical stability is one of the basic features for the optimal electrode. Typical anode materials include

graphite (Chen *et al.* 2010), Pt (Torres *et al.* 2003), activated carbon fiber (Yi *et al.* 2008), boron-doped diamond (Nasr & Abdelatif 2009), PbO₂ (Wang *et al.* 2010), SnO₂ (Río *et al.* 2010), IrO₂ (Tolba *et al.* 2010), RuO₂ (Tran *et al.* 2009) and MnO₂ (Lin *et al.* 2012). Among all these anode materials, PbO₂ and SnO₂ are two promising candidates in view of their effective degradation for organic pollutants, simple preparation process and low cost. In previous studies, the degradation applications of a variety of organic wastewaters were reported for these two electrodes, such as dye wastewater (Río *et al.* 2010), landfill leachate (Panizza & Martinez-Huitle 2013), carwash wastewater (Panizza & Cerisola 2010), tannery wastewater (Costa *et al.* 2008), and various toxic organics (Samet *et al.* 2010; Zhu *et al.* 2010; Hamza *et al.* 2011). Thus, in this paper, PbO₂ and SnO₂ electrodes were prepared and their electro-catalytic

characterizations were analyzed and compared by scanning electron microscopy (SEM), X-ray diffraction (XRD), linear sweep voltammetry (LSV), cyclic voltammetry (CV), and electrochemical degradation of *p*-nitrophenol (*p*-NP). Also, the service life of PbO₂ and SnO₂ electrodes was determined by accelerated life tests.

METHODS

Electrode preparation

The PbO₂ electrode was prepared by electro-deposition. The specific details of the preparation method can be found in Duan *et al.* (2013).

The SnO₂ electrode was prepared by thermal deposition. Firstly, Ti substrates underwent a preparation of sandblasting, 10 min of ultrasonic cleaning in acetone, 10 min of ultrasonic cleaning in deionized water, 2 h of etching in boiling aqueous 15% oxalic acid, and rinsing with deionized water. Then, the pretreated Ti substrates were brushed with a solution containing 20 g SnCl₄·5H₂O and 2 g SbCl₃ in 100 mL of isopropanol-HCl mixture, dried at 120 °C for 10 min, and baked at 500 °C for 10 min. This procedure was repeated 10 times. Finally, the Ti substrate was annealed at 500 °C for 1 h.

Electrode characterization

SEM was carried out on a Hitachi S-570 model instrument. XRD patterns of samples were obtained with an XRD (Rigaku D-max/3C) using Cu K α radiation (45 kV, 30 mA). LSV and CV were executed in the PGSTAT302 electrochemical workstation. LSV and CV measurements were both carried out with a conventional three-electrode system. The fabricated PbO₂ and SnO₂ electrodes were used as the working electrode, a platinum sheet as the auxiliary electrode, and a saturated calomel electrode as the reference electrode.

Batch experiment

The electrochemical degradation experiments of *p*-NP were carried out by batch processes and the apparatus mainly consisted of a direct-current power supply, a heat-gathering

style magnetic stirrer and a glass reactor. The anode (PbO₂ or SnO₂ electrode) and cathode (stainless steel sheet) were positioned vertically and parallel to each other at a distance of 1 cm. The initial concentration of *p*-NP during all the experimental runs was 50 mg L⁻¹ of a volume of 200 mL; 0.05 M Na₂SO₄ was used as the supporting electrolyte. The reaction temperature was kept at 30 °C during all the experimental runs. Electrochemical degradation was performed at a current density of 30 mA cm⁻². During the experiments, samples were drawn from the reactor at certain intervals and then analyzed. The disappearance of *p*-NP during electrolysis was analyzed using a spectrophotometric technique ($\lambda = 273$ nm).

Electrode stability

Stability tests for the electrodes were carried out in a three electrode cell in 2 M H₂SO₄ solution at 60 °C with a constant anodic current density of 1 A cm⁻². The fabricated PbO₂ or SnO₂ electrodes were used as the anode, a stainless steel sheet as the cathode, and a saturated Ag/AgCl as the reference electrode. The anode potential was periodically monitored with time. The service lifetime of an electrode is defined as the operation time at which the anodic potential increased rapidly by 5 V (vs. Ag/AgCl).

RESULTS AND DISCUSSION

Surface morphology and phase structure

The SEM images of PbO₂ and SnO₂ electrodes are shown in Figure 1. The PbO₂ electrode (Figure 1(a)) consists of a large number of typical pyramid-structure crystal particles. The film of the PbO₂ electrode is even, compact, non-porous, and non-cracked. However, the SnO₂ electrode presents a 'mud crack' morphology (Figure 1(b)), which was a specific feature of thermal deposition. In addition, there are many cracks on the film of the SnO₂ electrode, which was a result of mechanism tension caused by the plasticity of the coating and the difference of the thermal expansion coefficient between the base metal and the coating (Cominellis & Vercesi 1991; Wang *et al.* 2010).

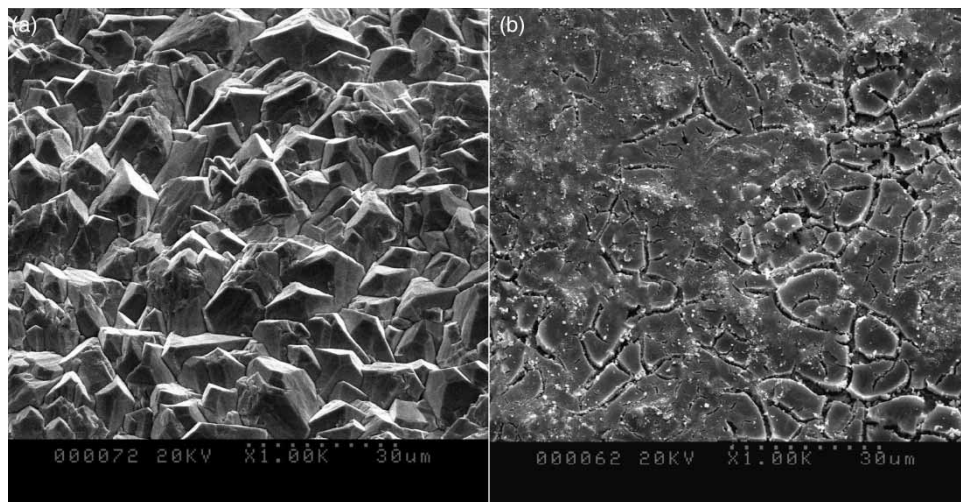


Figure 1 | SEM images of a PbO₂ electrode (a) and an SnO₂ electrode (b).

Figure 2 presents the XRD patterns of PbO₂ and SnO₂ electrodes. The XRD pattern of the PbO₂ electrode presents diffraction peaks of pure β -PbO₂. However, from the XRD pattern of the SnO₂ electrode, two kinds of crystalline structures including SnO₂ and Ti are observed. The presence of diffraction peaks of Ti demonstrates that the formed SnO₂ film was still so thin that the X-ray went to the Ti substrate. In addition, it can be found that no diffraction peak of Sb₂O₃ was observed in the pattern of the SnO₂ electrode because there was too little Sb dopant in the film to be detected by XRD analysis.

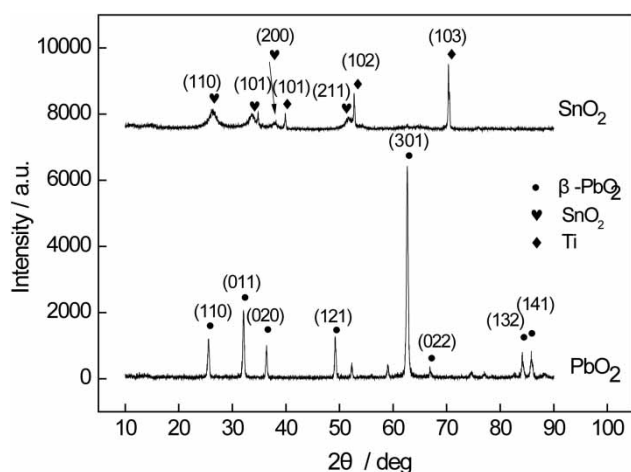


Figure 2 | XRD patterns of PbO₂ and SnO₂ electrodes.

Electrochemical measurements

The oxygen evolution overpotential (OEP) of the PbO₂ and SnO₂ electrodes was measured by means of LSV in 0.5 M Na₂SO₄ solution at a scan rate of 50 mV s⁻¹, and the potential corresponding to the inflection point of the polarization curve was defined as the OEP of the electrode. Figure 3 represents typical polarization curves for two kinds of electrodes. According to the polarization curves, the OEP for the PbO₂ electrode is approximately 1.55 V (vs. SCE), while the OEP value on the SnO₂ electrode is 1.85 V (vs. SCE), much higher than that of the PbO₂ electrode. The

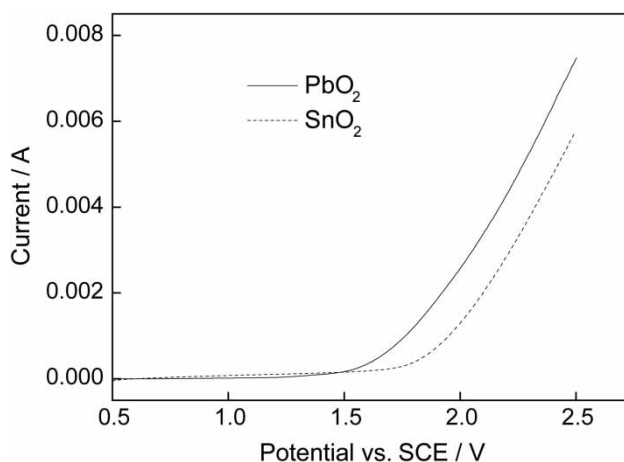


Figure 3 | LSV curves of different electrodes measured in 0.5 M Na₂SO₄ solution at 25 °C, scan rate: 10 mV s⁻¹.

higher OEP of the SnO₂ electrode indicates that the SnO₂ electrode should have better electrocatalytic activity and degradation performance for organic pollutants in the electro-catalytic oxidation process (Amadelli *et al.* 2002; Yao *et al.* 2014). However, this result is not in agreement with the previous reports for the OEP on Pb/PbO₂ and Ti/SnO₂ anodes, in which Pb/PbO₂ material presented higher OEP than Ti/SnO₂ material (Vazquez-Gomez *et al.* 2012). This conflict may be attributed to the difference in the preparation processes of the electrodes.

The CV measurements in 1.0 M KCl solution containing 5.0 mM K₃Fe(CN)₆ and 5.0 mM K₄Fe(CN)₆ were conducted to estimate the electrochemical activity of PbO₂ and SnO₂ electrodes. Figure 4(a) and 4(b) shows the CV curves recorded

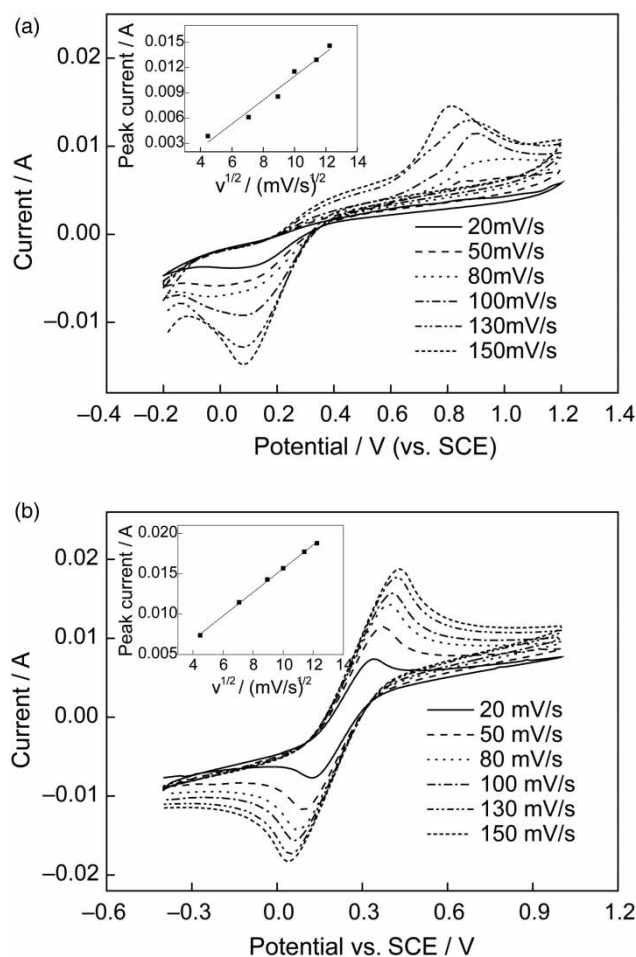


Figure 4 | Cyclic voltammograms of PbO₂ (a) and SnO₂ (b) electrodes in 1.0 mol L⁻¹ KCl containing 5.0 mmol L⁻¹ K₃Fe(CN)₆ and 5.0 mmol L⁻¹ K₄Fe(CN)₆. Insets show the plots of peak current versus the square root of scan rate.

for the PbO₂ and SnO₂ electrodes, respectively, at scan rates of 20 mV s⁻¹, 50 mV s⁻¹, 80 mV s⁻¹, 100 mV s⁻¹, 130 mV s⁻¹, and 150 mV s⁻¹. There are a pair of distinct anodic and cathodic peaks observed for two kinds of electrodes corresponding to the redox reactions through a direct electron-transfer process between Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ at all scans. Comparing two sets of CV curves, it also can be found that sharper, larger and narrower redox peaks appeared on the CV curves of the SnO₂ electrode. Besides, the peak potential separation (ΔE_p) for the SnO₂ electrode was significantly smaller than that of the PbO₂ electrode. For example, at a scan rate of 100 mV s⁻¹, the ΔE_p values were 356 mV and 823 mV for the SnO₂ and PbO₂ electrodes, respectively. All these results suggest that the electron-transfer kinetics and the reversibility of the electrode reaction of the SnO₂ electrode were superior to those of the PbO₂ electrode.

CV measurements were also performed in 0.5 M Na₂SO₄ solution containing 200 mg L⁻¹ *p*-NP to investigate the direct electrochemical oxidation performance of the PbO₂ and SnO₂ electrodes. The cyclic voltammograms are shown in Figure 5(a) and 5(b). For comparison, the cyclic voltammograms in blank Na₂SO₄ solution are also shown in Figure 5(c) and 5(d).

From the curves of the PbO₂ electrode (Figure 5(a) and 5(c)), it can be observed that there were three oxidation peaks in the anodic branches and one reduction peak in the cathodic branch with and without the presence of *p*-NP. Interestingly, the current response of the third oxidation peak (at about 1.2 V vs. SCE) with *p*-NP is much higher than that without *p*-NP in the first cycle, but in the subsequent cycles, if *p*-NP existed in the solution, this peak decreased to total disappearance, if not, it increased slowly and moved negatively. These differences indicate that the third oxidation peak in Figure 5(a) should be attributed to the oxidation reaction of *p*-NP on the surface of the PbO₂ electrode, which may overlap the oxidation peak of formation of PbO₂ in Figure 5(c). The gradual disappearance of peaks in Figure 5(a) with the increase in scan times means that a passivation film was formed on the surface of the PbO₂ electrode during the oxidation of *p*-NP in Na₂SO₄ solution, which prevented all reactions further occurring on the surface of the electrode.

In the voltammogram of the SnO₂ electrode in Na₂SO₄ solution containing *p*-NP (Figure 5(b)), an irreversible oxidation peak presented at 1.25 V vs. SCE in the first cycle.

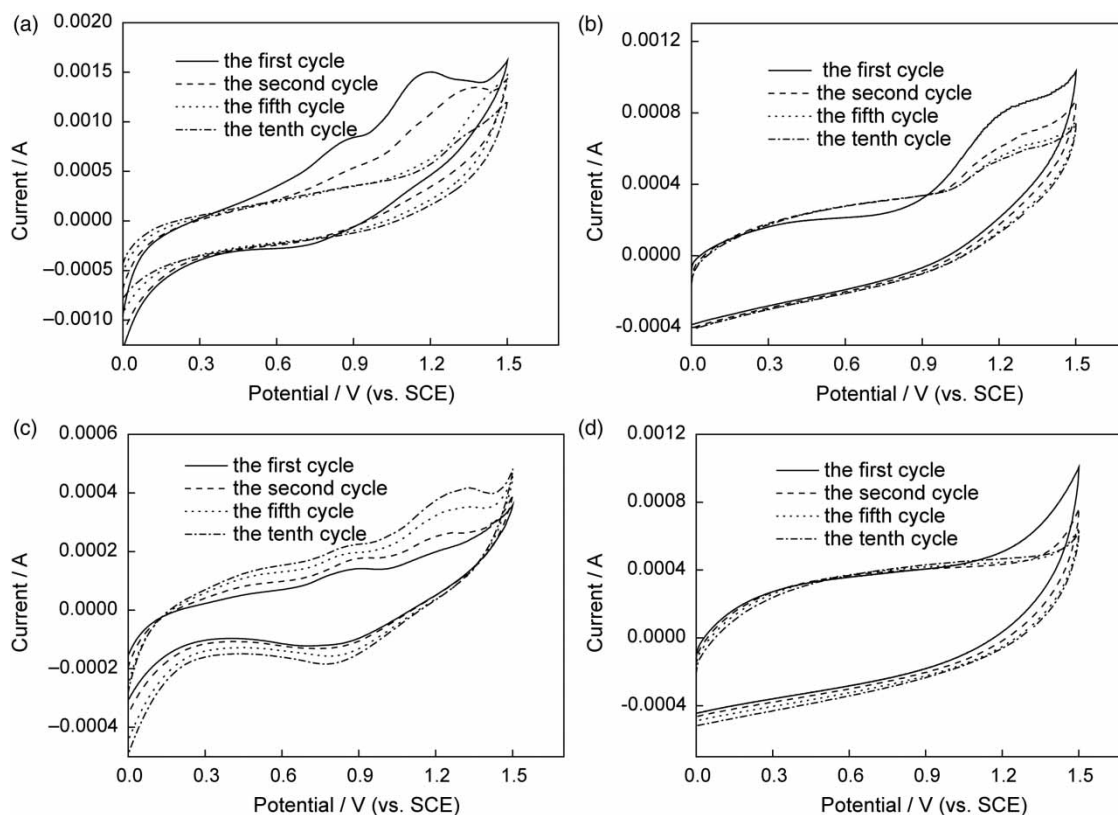


Figure 5 | Cyclic voltammograms of the PbO₂ ((a) and (c)) and SnO₂ ((b) and (d)) electrodes in 1 mol L⁻¹ Na₂SO₄ solution with and without 500 mg L⁻¹ p-NP. Scan rate: 50 mV s⁻¹.

Compared with that in blank Na₂SO₄ solution (Figure 5(d)), it can be determined that this oxidation peak was ascribed to the oxidation of p-NP on the surface of the SnO₂ electrode. It can also be observed that, in subsequent cycles, the oxidation peak decreased gradually during the successive cyclic voltammetric sweeps, but it still exists until the tenth cycle, which shows that passivation also occurred on the SnO₂ electrode, but the rate of passivation was slower than that of the PbO₂ electrode.

Degradation of p-NP on different electrodes

Electrochemical degradation experiments of p-NP at PbO₂ and SnO₂ anodes were performed by applying 30 mA cm⁻² of current density. Figure 6(a) demonstrates the p-NP removal percentage variation by utilizing PbO₂ and SnO₂ as anodes during the electrochemical oxidation process. It can be observed that p-NP could be degraded on these two anodes and the p-NP removal percentages for both electrodes

increased with the increase in reaction time. However, it is also worth noting that the degradation rates of p-NP varied according to the type of anode. At the SnO₂ electrode, the removal percentage was 96.5% after 2 h. However, at the PbO₂ anode, the corresponding removal percentage was 86.9%, a lower value than that obtained at the SnO₂ electrode. The plots of ln(C₀/C) versus time are shown in Figure 6(b). The linear relationships manifest the electrochemical oxidation of p-NP via a pseudo-first-order mechanism, with rate constants of 0.0174 min⁻¹ at the PbO₂ electrode and 0.0285 min⁻¹ at the SnO₂ electrode. Thus, we can conclude that the SnO₂ electrode had a stronger oxidation performance for p-NP, which was in agreement with the above deduction in polarization curves.

Electrode stability

Figure 7 compares the stability of the PbO₂ and SnO₂ electrodes by accelerated life tests. As seen in Figure 7,

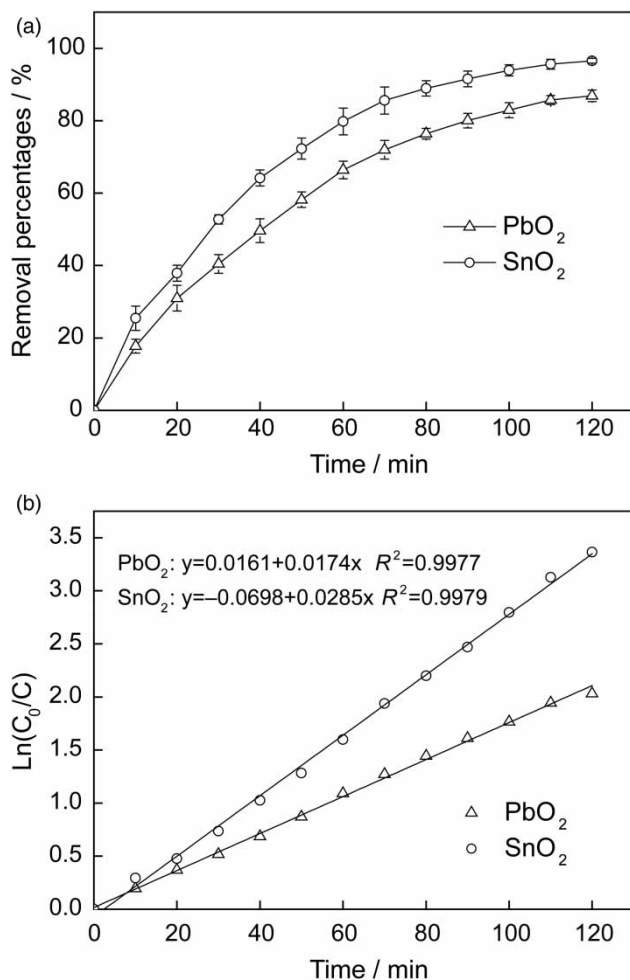


Figure 6 | Variation of *p*-NP removal percentage with time during electrochemical oxidation (a) and pseudo-first-order kinetics fitting curves (b) on PbO₂ and SnO₂ electrodes. Conditions: current density = 50 mA cm⁻²; T = 30 °C; [*p*-NP] = 50 mg L⁻¹; [Na₂SO₄] = 0.05 mol L⁻¹.

the PbO₂ electrode had a service life of 56 h, which was 37 times longer than that of the SnO₂ electrode. This is attributed to the different morphologies of PbO₂ and SnO₂ electrodes. The PbO₂ electrode was prepared by electrodeposition, as shown in Figure 1, its film was compact, non-porous, and non-cracked, which not only reduced the penetration of electrolyte through cracks or pores (Yao *et al.* 2014), but also suppressed the formation of TiO₂ on the Ti substrate and internal O₂ evolution under the film. On the contrary, the electrolyte easily penetrated the cracks on the SnO₂ electrode, leading to the breaking off of the coating.

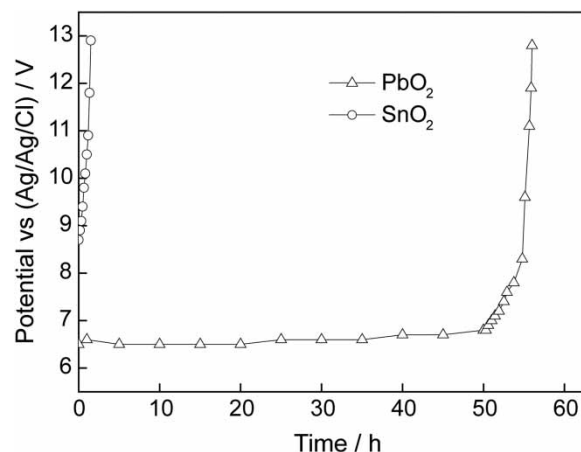


Figure 7 | Electrode stability tests: electrode potential (vs. Ag/AgCl) vs. time for the electrolysis (1 A cm⁻², 60 °C) in 2 mol L⁻¹ H₂SO₄ using PbO₂ and SnO₂ electrodes as anodes.

CONCLUSIONS

In this work, the electro-catalytic activities and service lifetime of PbO₂ and SnO₂ electrodes were compared in detail for the electrochemical oxidation process. The main conclusions are as follows: the film of the PbO₂ electrode is even, compact, non-porous, and non-cracked, while there were many cracks present on the film of the SnO₂ electrode. LSV proves that the OEP for the SnO₂ electrode is much higher than that of the PbO₂ electrode. The electron-transfer kinetics and the reversibility of the electrode reaction of the SnO₂ electrode were superior to those of the PbO₂ electrode in CV measurements. The results of bulk electrolysis show that *p*-NP can be readily degraded at PbO₂ and SnO₂ anodes, and the decay kinetics of *p*-NP on both anodes follow a pseudo-first-order reaction. Although high over voltage anode material SnO₂ was shown to be superior to the PbO₂, a comparison of service lifetime of the two electrode materials showed that the PbO₂ electrode had a service life of 56 h, which is 37 times longer than that of the SnO₂ electrode.

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