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ARTICLE

Preparation and Characterization of [Emim]BF$_4$ Modified Lead Dioxide Electrodes

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Abstract: Modified PbO$_2$ electrodes were prepared by electrodeposition in the presence of ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF$_4$). The electro-catalytic performance of the prepared electrodes for the electrochemical degradation of phenol in aqueous solution was investigated. The COD removal of phenol simulated wastewater followed pseudo-first-order rate kinetics. The rate constant with [Emim]BF$_4$-modified PbO$_2$ electrodes was 0.007 39 min^{-1}, higher than 0.003 83 min^{-1} obtained with non-modified PbO$_2$ electrodes. The microstructure of the electrodes was characterized by scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The electrochemical properties were investigated by Mott-Schottky, steady-state polarization and linear sweep voltammetry techniques. Results indicate that PbO$_2$ coatings with compact and regular morphology, a higher degree of crystallinity and higher content of oxygen in crystal lattice are anodically grown on Ti substrate from electrolyte containing [Emim]BF$_4$. Steady-state polarization tests show that oxygen evolution overpotential on modified electrodes is significantly higher than that on non-modified ones. Mott-Schottky tests reveal a markedly lower content of oxygen vacancy in modified PbO$_2$ samples as compared with the non-modified ones. It is suggested that the enhanced electro-catalytic activity of the [Emim]BF$_4$-modified PbO$_2$ electrodes towards phenol degradation arises largely from its lower content of oxygen vacancy, which decreases the probability of oxygen transferring from more effective •OH into less desirable O$_{lat}$ at the electrode surface.

Key words: lead dioxide; Mott-Schottky; oxygen vacancy; lattice oxygen; hydroxyl radical

Efficient treatment of waste water is essential to prevent the discharge of pollutants to the environment and to secure public health. In this context, electrochemical oxidation (EO) is a versatile and powerful technique for degradation of a wide range of toxic and recalcitrant organic contaminants [1-4]. One of the foremost parts of EO is the electrode materials. Lead dioxide (PbO$_2$) electrodes have been studied for many years and continue to attract considerable interest due to their good electrical conductivity, high oxygen evolution overpotential and chemical inertness [5-10]. Usually, PbO$_2$ electrodes are prepared by electrochemically coating onto Ti substrates from aqueous electrolyte containing Pb(Ⅱ). However, there are several drawbacks that hinder the practical application of electrodeposited PbO$_2$, including relatively low electro-catalytic activity, high inner stress, and film detachment[1,3,5]. Therefore, much of the recent literature focuses on the developing of PbO$_2$ coatings with high current efficiency and enhanced stability[1,5-10]. The performance of electrodes is proved to be largely determined by their structure, while the structural characteristics of electrodeposited PbO$_2$ are very sensitive to the preparation method[9-11]. Consequently, a lot of research efforts have been devoted into the improvement of preparation technique. For instance, a number of additives, such as Bi, F, Fe, sodium dodecyl sulphonate (SDS), Triton X-100 and polyvinylpyrrolidone (PVP), have been studied extensively to change kinetics of PbO$_2$ electrodeposition and optimize the electrochemical performances of resulting oxide layers [1,5,7-13].

At present, ionic liquids have been widely applied either as electrolyte or as additive in the electrodeposition of metals and

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alloys. Higher current efficiency for preparation and improved products properties were achieved in the presence of certain ionic liquids [14-16]. These findings inspire the interests in applying ionic liquids in the electrosynthesis of metal oxides at anode. In the present work, 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([Emim]BF_4) was used to influence the electrocrystallization behavior of PbO_2 as a novel additive to the deposition electrolyte. It is found that the performance of PbO_2 electrodes on phenol degradation is increased significantly by the modification with [Emim]BF_4. In order to probe into the reason for the increase of the activity by [Emim]BF_4 modification, the surface microstructure of the prepared coatings was characterized by SEM, XRD and XPS, while the electrochemical properties were analyzed by Mott-Schottky plots, linear sweep voltammetry and steady-state polarization technique.

1 Experiment

Titanium plates (99.5% purity, 2 mm thickness) were used as the substrate for PbO_2 coatings. A stainless steel plate with the same area as the titanium plate was used as a cathode in electrodeposition. All chemical reagents were analytical grade and used as received without further purification. Solutions were prepared using deionized Milli-Q water. Ionic liquid [Emim]BF_4 with 99% purity was available commercially from Chengjie Chemicals Company (Shanghai, China).

The Ti plates were pretreated before using by the procedure described in Ref. [7]. Lead dioxides were galvanostatically deposited on Ti substrates at a current density of 10 mA cm^{-2} for 60 min at 50 ℃ using a single compartment cell. The growth solutions were composed of 0.4 mol/L $Pb(NO_3)_2$, 0.3 mol/L HNO_3 and 50 mg L^{-1} [Emim]BF_4 and the resulting PbO_2 samples are labeled as IL-PbO_2. Samples which were prepared under the same experimental conditions except that the solutions were [Emim]BF_4 free are labeled as PbO_2.

The EO experiments were carried out in a batch apparatus consisting of a DC power supply, a magnetic stirrer and a single-compartment glass reactor. The prepared PbO_2 sample was applied as the anode and stainless steel plate of the same size was applied as the cathode. The electrode couple was positioned vertically and paralleled to each other with a gap of 3 cm. 150 mL of electrolysis solution containing 100 mg L^{-1} phenol as model pollutant and 0.25 mol/L Na_2SO_4 as supporting electrolyte was oxidized at a constant current density of 10 mA cm^{-2} and ambient temperature. During the experiments, samples were drawn from the reactor at certain intervals and analyzed. The chemical oxygen demands (CODs) of the phenol aqueous solution were measured by the titrimetric method using dichromate as the oxidant in acidic solution at 458 K for 2 h.

The accelerated life tests were performed to assess electrode stability. The prepared PbO_2 sample was used as the working electrode, graphite sheet as the counter electrode, and a standard calomel electrode as the reference electrode. The tests were conducted at 1 A cm^{-2} in the electrolyte of 1 mol L^{-1} H_2SO_4, keeping the cell temperature at 60 ℃. During the testing, the potential of the working electrode was periodically measured. In the present work, the service life of an electrode was defined as the operation time when the anodic potential increased rapidly by 5 V or more.

X-ray diffraction (XRD) was used to study the phase composition and changes in crystallinity of prepared samples. XRD were performed on a Shimadzu XRD-7000 diffractometer with Cu Kα (λ=0.154 18 nm) radiation at 40 kV and 40 mA. The morphology of the samples was investigated by scanning electron microscope (SEM, JSM-6390A). Atomic valence states of the PbO_2 samples were determined by X-ray photoelectron spectroscopy (XPS) with a K-Alpha spectrometer, and an Al Kα monochromatized radiation was employed as X-ray source.

The electrochemical tests were performed by employing model PARSTAT4000 potentiostat/galvanostat instrument (Ametek, USA) using VersaStudio software. Measurements were conducted in a conventional three-compartment cell. PbO_2 sample was used as the working electrode. The counter electrode was a platinum flag. A saturated calomel electrode (SCE) was used as the reference. It was in contact with the working electrode through a Luggin tip. The Mott-Schottky, linear sweep voltammetry, and steady-state polarization measurements were all performed in a working solution containing 1 mol/L H_2SO_4 at 30 ℃. In the Mott-Schottky test, capacitance of the interface was measured at constant frequency of 1 kHz in the potential range of –0.4~1.0 V. The perturbing AC amplitude was 10 mV and the scan rate was 20 mV s^{-1}. Tafel plots of E versus logi were obtained from steady-state polarization measurements. The current was read at each potential (1.7~2.0 V) after it reached a constant value, which required at least 10 min.

2 Results and Discussion

2.1 Electro-catalytic performance of PbO_2 anodes

Electrocatalytic activities of prepared PbO_2 electrodes were evaluated by means of electrochemical oxidation of phenol simulated waste water at ambient temperature. The rates of COD removal as a function of time were fitted with first-order reaction rate equation and the results are shown in Fig.1 and Table 1. The rate constant of electrochemical oxidation of phenol on IL-PbO_2 is 0.00739 min^{-1}, almost two times that on PbO_2, indicating a much higher electrocatalytic activity of [Emim]BF_4-modified PbO_2 electrodes. Structure characterizations were performed later to investigate the underlying reasons for the improved activity.

PbO_2 and IL-PbO_2 samples were subjected to accelerated life tests to compare their electrochemical stability (Fig.2). It can be seen that the potential rose rapidly after 30 min for PbO_2. Whereas, a sharp potential increase is not observed until

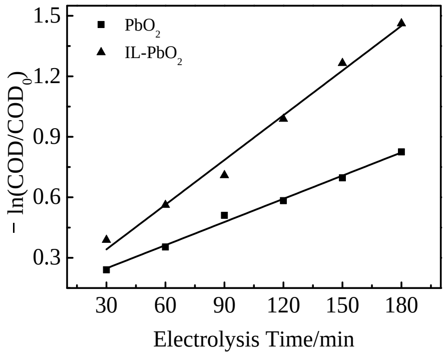

Fig.1 COD removal as a function of time during electrolysis of 100 mg·L^{-1} phenol at a current density of 10 mA·cm^{-2} by different PbO_2 anodes

Table 1 **Kinetic parameters of COD removal in phenol degradation process by different PbO_2 electrodes**

Electrode sample	k/min^{-1}	R^2
PbO_2	0.00383	0.9924
IL-PbO_2	0.00739	0.9860

120 min for IL-PbO_2. Clearly, the [Emim]BF_4-modified PbO_2 coating possesses better adhesion to substrate and much longer service time than non-modified one. The deactivation mechanism of Ti-based PbO_2 anodes in sulfuric acid is thought to be a developing process which involves diffusion of active oxygen atoms produced toward PbO_2 layer first and then Ti substrate [17]. Therefore, the prolonged life of IL-PbO_2 may result from the intrinsic characteristics of its coating which makes it less accessible to the active oxygen diffusion.

2.2 Physicochemical properties of PbO_2 coatings

The SEM micrographs of PbO_2 films deposited in the absence and presence of [Emim]BF_4 are shown in Fig.3. Defects in the form of cracks and pores are observed for sample grown in the absence of [Emim]BF_4 (Fig.3a). However, smooth surface, densely packed structure and a more regular morphology is obtained in the presence of [Emim]BF_4 (Fig.3b). Besides, the crystalline structure of modified PbO_2 is essentially enhanced with more pronounced edges and apexes.

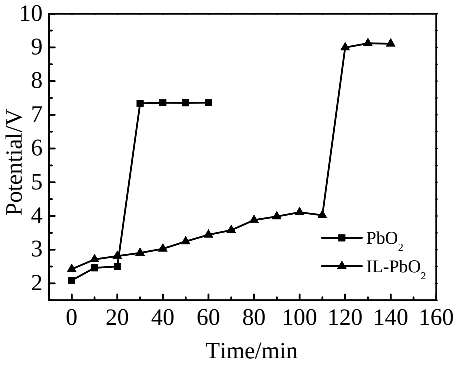

Fig.2 Accelerated life tests of different PbO_2 samples in 1 mol·L^{-1} H_2SO_4 solution under 1 A·cm^{-2} at 60 ℃

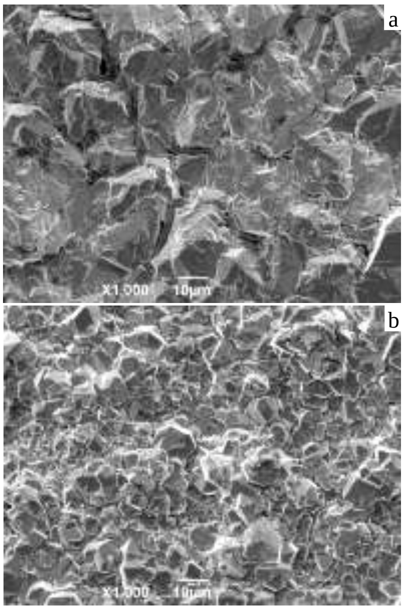

Fig.3 SEM images of PbO_2-coatings surfaces: (a) PbO_2 and (b) IL-PbO_2

Fig.4 shows the XRD patterns of PbO_2 samples prepared in the absence and presence of [EMIM]BF_4. It can be seen that β-PbO_2 is mainly obtained. Meanwhile, the addition of ionic liquid to the deposition electrolyte results in significant changes in the reflection patterns of resulting deposits. The sample IL-PbO_2 was characterized by a preferential orientation in the (110) direction, indicating a highly textured structure of [EMIM]BF_4-modified samples. It has been known that some crystals employed in electrocatalytic or photo-catalytic processes have their unique shape and facet-dependent activities due to the differences in surface energies between different planes [18-20]. Therefore, the higher electro-catalytic activity of the modified sample IL-PbO_2 on phenol degradation could be related to its stronger (110) plane to some extent. Besides, IL-PbO_2 is featured with a higher degree of crystallinity with a significant increase in peak intensity.

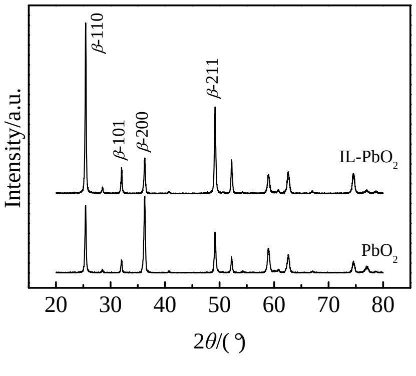

Fig.4 XRD patterns of PbO_2-coatings surfaces

The surface layers of prepared samples were also investigated by X-ray photoelectron spectroscopy to get insight into the atomic valence states and elemental composition (Fig.5). The XPS signal in the O 1s binding energy region consists of a sharp peak at 528.8 eV and a more or less pronounced shoulder at higher binding energy of 531.2 eV. The first signal is assigned to strongly bound (lattice) oxygen; the shoulder is assigned to weakly bound oxygen species: adsorbed OH^- and H_2O [21]. A marked decrease of peak intensity for the weakly bound oxygen signal and an increase of peak intensity for the lattice oxygen signal were observed for IL-PbO_2 as compared with PbO_2, which indicate that there is more lattice oxygen formed in the sample grown in the presence of [EMIM]BF_4 than that of the control.

By a comparative study of crystalline microstructure of IL-PbO_2 with that of PbO_2, it can be deduced that the electrocrystallization behavior of lead dioxide is greatly influenced by the ionic liquid. As a result, a better defined crystal of lead dioxide is obtained by [EMIM]BF_4 modification. It is well known that [Emim]BF_4 is capable of adsorption on metallic surface due to the lone electron pairs in nitrogen atoms of imidazolium cation[22]. So the influence of imidazole-based ionic liquid on electrocrystallization of lead dioxide may result from its selective adsorption on the electrode surface, just in the similar way to surfactants [12, 13].

2.3 Electrochemical properties of PbO_2 electrodes

The capacities of the prepared PbO_2 coatings were analyzed by Mott-Schottky test. The Mott-Schottky relation describes the potential dependence of the space charge capacity C for a semiconductor electrode under depletion condition.

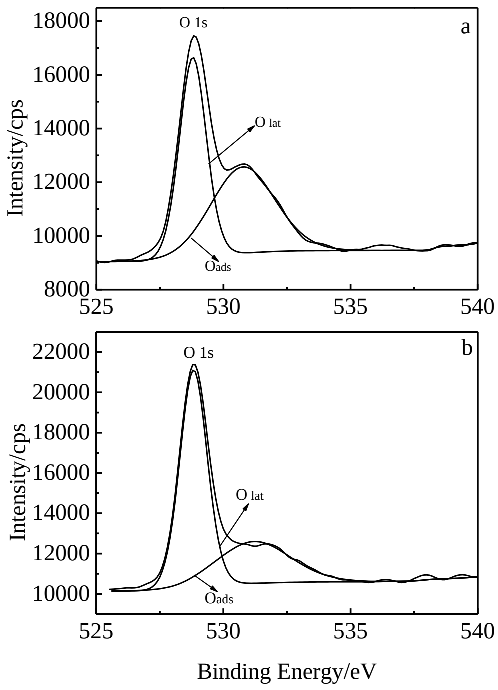

Fig.5 XPS spectra of O1s for PbO_2 (a) and IL-PbO_2 (b)

$$\frac{1}{C^2}=\frac{2}{\varepsilon\varepsilon_0 \mathrm{e} N_\mathrm{D}}\left(E-E_\mathrm{FB}-\frac{kT}{\mathrm{e}}\right) \qquad (1)$$

Where ε is the dielectric constant of PbO_2, taken as 3.91 [23], ε_0 is the vacuum permittivity, e is the electron charge, N_D denotes the donor density, E and E_{FB} are the applied and flat-band potentials, respectively, T is the absolute temperature, k is the Boltzmann constant. A plot of C^{-2} vs. E should give a straight line, the slope of which is inversely proportional to the number of carriers N_D. Straight lines are indeed observed in Fig.6 with a positive slope (n-type conductivity) for PbO_2 and modified IL-PbO_2 from which the calculated values of N_D are 4.506×10^{21} and 6.100×10^{20} cm^{-3}, respectively. The intercept with the potential axis yields the flat band potential E_{FB} [24]. The values of E_{FB} as obtained from this plot are –0.445 V for PbO_2 and –0.143 V for modified IL-PbO_2.

Electrodeposited PbO_2 is widely considered to be a narrow band gap (1.4 V) semiconductor with high electron conductivity due to non-stoichiometry [25, 26]. W. Mindt [25] held that the nonstoichiometric composition of PbO_2 is mainly due to oxygen vacancies. Payne et al. [23] also suggested that the metallic nature of PbO_2 arises from occupation of conduction band states above the Fermi level of stoichiometric PbO_2, probably arising from oxygen vacancy defects. In a word, oxygen vacancies are expected to be the predominant donors for PbO_2 semiconductor. Therefore, the decrease of N_D for sample IL-PbO_2 indicated a decline of oxygen vacancies for [EMIM]BF_4-modified PbO_2 films.

Tafel plots of E versus log$j$, obtained from quasi-steady polarization measurements are given in Fig.7. According to obtained results, oxygen evolution overpotential on modified IL-PbO_2 is significantly higher than that on non-modified PbO_2 electrodes. Additionally, the Tafel slope increased from 173 mV dec^{-1} for non-modified PbO_2 to 179 mV dec^{-1} for modified IL-PbO_2. The higher oxygen evolution overpotential is helpful to restrain the side reaction of oxygen evolution so as to improve the current efficiency of PbO_2 electrodes [3].

In the reported literatures[26-28], reduction of PbO_2 electrodeposited under different conditions has been investigated frequently in order to gain insight into property related to film

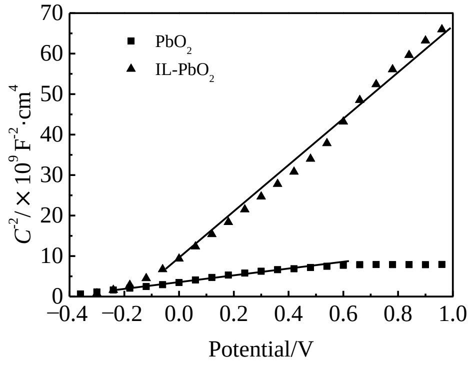

Fig.6 Mott-Schottky plots for different PbO_2 electrodes in 1 mol L^{-1} H_2SO_4 at 30 ℃

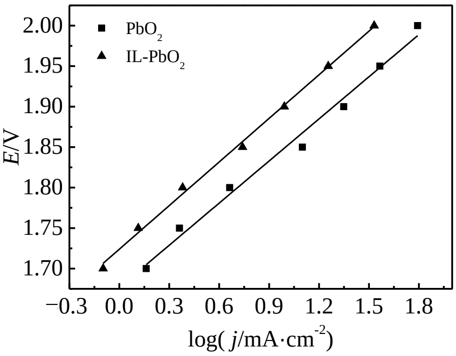

Fig.7 Tafel plots for different PbO_2 electrodes in 1 mol L^{-1} H_2SO_4 at 30 ℃

morphology. For example, films with structural characteristics such as accessibility to species in the electrolyte and fast surface and subsurface exchange of protons are expected to be more easily reduced [27]. Therefore, linear sweep voltammetry curves for the reduction of different PbO_2 samples in 1 mol L^{-1} H_2SO_4 solutions were performed (Fig.8). It appeared that for non-modified sample reduction peak was more broad and larger and reduction occurred at more positive potentials. This can be explained through its lower mechanical strength and/or higher morphological defects, which allow an easy diffusion of sulfuric acid into the sample.

2.4 Proposed function of [EMIM]BF_4 modification

It is widely believed that electro-oxidation of pollutants occurs on anodes by generating physically adsorbed “active oxygen” (adsorbed hydroxyl radicals, •OH) or chemisorbed “active oxygen” (oxygen in the oxide lattice, O_{lat}) [3,29,30]. In any case, the initial step is the discharge of water molecules to form adsorbed hydroxyl radicals (Reaction 1). The physically adsorbed •OH causes the complete combustion of organic compounds R to CO_2 and H_2O (Reaction 2, where actual values of *m* and *n* depend on the elemental composition of *R* to be oxidized). Possible oxygen transition may occur from adsorbed hydroxyl radicals to the crystal lattice of the oxide anode, forming so-called higher metal oxides MO_{x+1} (Reaction 3). And the chemisorbed “active oxygen” (MO_{x+1}) participates in the formation of selective oxidation products (Reaction 4), which means more intermediates production. Obviously, physically adsorbed •OH is more effective and desirable for organic pollutant degradation than O_{lat} in MO_{x+1}[3,29-32].

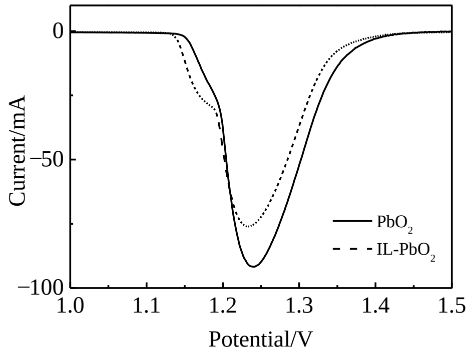

Fig.8 Linear sweep voltammetry curves for the reduction of different PbO_2 electrodes in 1 mol L^{-1} H_2SO_4 at a scan rate of 20 mV s^{-1}

$$MO_x + H_2O \rightarrow MO_x[\bullet OH] + H^+ + e^- \quad (1)$$

$$MO_x[\bullet OH] + R \rightarrow MO_x + mCO_2 + nH_2O + H^+ + e^- \quad (2)$$

$$MO_x[\bullet OH] \rightarrow MO_{x+1} + H^+ + e^- \quad (3)$$

$$MO_{x+1} + R \rightarrow RO + MO_x \quad (4)$$

It has been proved that oxygen vacancies in the oxide anode could make allowance for the oxygen transfer from adsorbed •OH to oxygen in the oxide lattice, O_{lat} [31]. Thus, the concentration of oxygen vacancies would influence the ratio of MO_x[•OH] versus MO_{x+1} on the anode surface, and therefore the catalytic performance of anode material [32]. For [EMIM]BF_4-modified PbO_2 films a marked decline of oxygen vacancies was revealed by the Mott-Schottky tests (Fig.6), which provided lower possibility of oxygen transfer from •OH into O_{lat}. On the other hand, the XPS results (Fig.5) indicated that there was more lattice oxygen formed in the [EMIM]BF_4-modified PbO_2 electrode than that of the control. The higher content of O_{lat} suggests lower content of oxygen vacancy in metal oxide. Therefore, both electrochemical and XPS tests supported that the enhanced performance of the [EMIM]BF_4-modified PbO_2 electrode arose from its lower content of oxygen vacancy, which is more favorable for the physical adsorption of •OH.

3 Conclusions

1) The microstructure of electrodeposited PbO_2 electrodes is strongly affected by the modification of ionic liquid [EMIM]BF_4. The modified coatings exhibit a better defined crystal of PbO_2 with compact and regular morphology, a higher degree of crystallinity and a higher content of oxygen in crystal lattice.

2) The electro-catalytic activity towards phenol degradation and stability of the [EMIM]BF_4-modified PbO_2 electrodes are greatly improved as compared with the non-modified electrodes.

3) Oxygen evolution overpotential on [EMIM]BF_4-modified PbO_2 electrodes is significantly higher than that on non-modified electrodes.

4) The higher electro-catalytic activity of [EMIM]BF_4-modified PbO_2 electrodes could be related to its lower content of oxygen vacancy in crystalline structure, which mean lower probability of oxygen transfers from more effective •OH into less desirable O_{lat} at the electrode surface.

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离子液体[Emim]BF_4改性二氧化铅电极的制备与表征

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摘　要：采用电沉积法制备了离子液体[Emim]BF_4改性 PbO_2 电极。通过电化学氧化降解苯酚实验对电极催化性能进行了考察，发现苯酚模拟废水的 COD 去除率符合一级反应动力学，[Emim]BF_4改性 PbO_2 电极的速率常数为 0.007 39 min^{-1}，明显高于未改性 PbO_2 电极的速率常数 0.003 83 min^{-1}。采用 SEM、XRD、XPS 对电极表面结构进行表征。结果显示，[Emim]BF_4改性钛基 PbO_2 涂层表面致密规整、结晶度高、晶格氧含量高。通过莫特-肖特基曲线、稳态极化和线性扫描伏安法考察了电极的电化学性质。结果表明，改性电极表面氧空位含量相比未改性电极大大降低，改性电极的析氧过电位相比未改性电极有明显提高。通过与未改性电极结构和电化学性质的对比研究，得出改性电极催化活性的提高主要是由于其氧空位含量较低，从而降低了氧化物电极表面羟基自由基(•OH)向晶格氧(O_{lat})转移的发生率。

关键词：二氧化铅；莫特-肖特基曲线；氧空位；晶格氧；羟基自由基

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