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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-methyl-imidazolium 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 $mA\cdot cm^{-2}$ for 60 min at 50 °C 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 $mg\cdot L^{-1}$ [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 $mg\cdot L^{-1}$ phenol as model pollutant and 0.25 mol/L Na_2SO_4 as supporting electrolyte was oxidized at a constant current density of 10 $mA\cdot cm^{-2}$ 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 $A\cdot cm^{-2}$ in the electrolyte of 1 $mol\cdot L^{-1}$ H_2SO_4, keeping the cell temperature at 60 °C. 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 °C. 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 $mV\cdot s^{-1}$. 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