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Influence of Molecular Structure of Imidazolium Based Ionic Liquids on the Electrochemical Oxidation Performances of Resulting PbO_2 Deposits

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The PbO_2 coatings were electrodeposited on titanium sheet from aqueous solution containing lead nitrate and imidazolium based ionic liquids (ILs) additive. Effects of molecular structure of ILs on electro-catalytic activities of resulting PbO_2 electrodes were investigated. Electrochemical treatment of simulated wastewater containing phenol was carried out to investigate the electro-catalytic activities of the PbO_2 electrodes modified by ILs. High performance liquid chromatography (HPLC) was employed to determine the amount of hydroxyl radicals (·OH) generated on the electrodes by using salicylic acid (SA) as a probe. The electrochemical properties of the samples were investigated by polarization curves tests. The surface structure and wetting ability of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and contact angle test respectively. The results showed that the electro-catalytic activities of PbO_2 electrodes modified by $[Emim]BF_4$ were significantly higher than that of PbO_2 electrodes modified by [Emim]Br or $[Emim]PF_6$. With BF_4^- fixed, the improvement order for the activity of modified PbO_2 electrodes was as follows: $[Bmim]BF_4 > [Emim]BF_4 > [Hmim]BF_4$. XRD patterns and SEM micrographs showed a highly textured structure and controlled morphology of the PbO_2 coatings by ILs modification. Both the anions and cation chain lengths of imidazolium based ILs had a significant effect on the surface properties and electro-catalytic activities of resulting PbO_2 electrodes, with the influence of the former being more prominent than that of the latter. The modification may be attributed to the adsorption of ILs molecule on the anode surface during the electrodeposition of PbO_2 coating. Meanwhile, the higher COD removal efficiency on PbO_2 electrodes modified by $[Bmim]BF_4$ can be attributed to its preferential orientation along (110) plane as well as its larger specific surface area and more active sites for the generation of hydroxyl radical. Furthermore, $[Bmim]BF_4$ had the most significant positive impact on the reusability and stability of PbO_2 coatings.

Keywords: PbO_2 electrodes; ionic liquids; electrochemical oxidation; phenol degradation; hydroxyl radicals (·OH), COD removal

1. INTRODUCTION

Lead dioxide (PbO_2) coatings have always been one of the most promising electrode materials for the treatment of organic pollutants in wastewater by electrochemical oxidation technique [1-7]. In order to enhance the electro-catalytic performance of PbO_2 electrodes, 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, 2, 4-10]. Searching the alternative additives with significant modification effects to the physical properties and catalytic activities of the PbO_2 coatings is still making progress. At present, ionic liquids (ILs) have attracted considerable interests in the area of electrochemistry due to their high charge density, thermal and electrochemical stability, a wide electrochemical potential window and low volatility [11-13]. Among a wide range of ILs with different structure, imidazolium based ILs have been widely applied either in the electrodeposition of metals/alloys on cathode or in the electrosynthesis of metal oxides on anode owing to its amenability to synthesis, stability in properties and relatively low cost [14-17]. As previously reported, Ti-based PbO_2 electrodes with small crystal size, large specific surface area and high electro-catalytic activity were constructed by electrodeposition of PbO_2 on Ti in the ILs/water two-phase electrodeposition solution [16, 17]. Unfortunately, this method was high in cost and poor in economical efficiency due to the large volume dosage of ILs as co-solvent plus the rather high commercial price of ILs at present. In view of this problem, a novel way to achieve the modification of PbO_2 electrodes by using ILs [Emim]BF_4 as an additive in aqueous electrodeposition solutions was proposed and proved to be feasible and effective by our research group [18, 19]. Apparently, this method is more adaptable to commercial application owing to its pretty low dosage (mg/L level) and significant modification effects.

It was suggested that ILs were capable to influence the electrodeposition behaviour of metal by its strong adsorption on electrode surface [20]. Accordingly, the modification effects of ILs on PbO_2 electro-oxidation may be attributed to the adsorption of the compound on the anode surface. So it’s necessary to get an insight into the adsorption characteristics of ILs on electrode surface in order to reveal the modification mechanism of PbO_2 electrodes by ILs. Indeed, the adsorption performance of ILs was first studied extensively in the field of corrosion and corrosion protection of metals [21-22]. For instance, Zhou claimed that the adsorption of imidazolium based ILs on carbon steel surface occurred by sharing lone electron pair in N atoms and/or π electrons in benzimidazolium ring with the unoccupied d orbital of iron atoms to form coordinate covalent bond [21]. With respect to the adsorption of ILs on the electrode surface under polarization, Zhang concluded on the basis of frontier orbital theory analysis that -C=N- and imidazolium ring functional groups in imidazolium-based compounds made great contributions to the adsorption, and the adsorption of imidazolium-based compounds on cathode occurred via electrovalent bond between imidazolium cations and negatively charged cathode surface [23]. However, the adsorption behaviour of imidazolium based ILs on anode surface under anodic polarization remains unknown yet. In order to elucidate the adsorption characteristics of imidazolium based ILs during the electrodeposition of PbO_2, as well as better understand the relationship between ILs in electrodeposition, resulting deposit morphology and catalytic activity of the deposit, five imidazolium based ILs with different cation chain lengths and anions were applied as additives in the electro-deposition solutions for the construction of modified PbO_2 electrodes in this work. The effects of anion types（BF_4^-、Br^-、PF_6^-）and alkyl branched chain lengths of imidazolium cation（ethyl、butyl、hexyl）on the electro-catalytic activity and surface properties of resulting modified PbO_2 electrodes were investigated in detail.

With respect to modification mechanism for PbO_2 electrodes, some researchers [24] attributed the improvement of electrode activity to the change in wetting ability of electrode surface. It was suggested that the oxygen evolution potential can be improved and utilization rate of hydroxyl radicals (·OH) can be enhanced by highly hydrophobic electrode surface due to the different adsorption behaviors for ·OH [24]. This perspective presents a novel way of improving the electro-oxidation efficiencies for electrodes. In order to probe the dependence of catalytic activity on composition and structure of active layer, the surface wetting ability and electrochemical polarization curve of PbO_2 electrodes modified with ILs were analyzed in this work.

The oxidation of aqueous organic species by electrochemical technique has been demonstrated to involve hydroxyl radicals as electro-generated intermediates [24-26]. Hence, quantitative determination of the concentrations and the generation rate of ·OH in the electrochemical degradation process were necessary for understanding the role and function of ·OH in the electro-catalytic oxidation of aromatic compounds. The half-life of ·OH is estimated to be around 10^{-9}s [27]. Therefore, the quantification of ·OH is usually carried out by trapping of the ·OH with salicylic acid (SA) to produce hydroxylated derivatives of SA as 2, 3- and 2, 5-dihydroxybenzoic acid (DHBA) [28-30]. High-performance liquid chromatography (HPLC) with a UV detector was used to monitor the hydroxylated derivatives and salicylic acid after they had been separated. From the total concentration of hydroxylated derivatives, the ·OH used for hydroxylation can be obtained, and the formation of ·OH under the specified conditions can be estimated relatively.

2. EXPERIMENTAL METHODS

2.1 Materials

Brominated 1-ethyl-3-methyl-imidazolium ([Emim]Br), 1-ethyl-3-methyl-imidazolium hexafluorophosphate ($[Emim]PF_6$), 1-ethyl-3-methyl-imidazolium tetrafluoroborate ($[Emim]BF_4$), 1-butyl-3-methyl-imidazolium tetrafluoroborate ($[Bmim]BF_4$) and 1-hexyl-3-methyl-imidazolium tetrafluoroborate ($[Hmim]BF_4$) were obtained from Chengjie Chemicals Company (Shanghai, China). They were 99% purity, water content < 0.2%, halogen content < 50ppm and used as received without further purification. Methanol was chromatographical grade, other chemicals were analytical grade. Solutions were prepared using deionized Milli-Q water.

2.2 Preparation and Characterization of PbO_2 electrodes

Lead dioxide coatings were galvanostatically deposited on pretreated Ti substrate (30 mm × 40 mm × 1 mm) 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 M $Pb(NO_3)_2$, 0.1 M HNO_3 and 50 $mg \cdot L^{-1}$ ILs. X-ray diffraction (XRD) was used to study the phase composition and crystallinity of prepared samples on a Shimadzu XRD-7000 diffractometer with Cu K (λ=0.15418 nm) radiation. Surface morphology of samples was studied by using scanning electron microscopy (Jeol JSM-6390A). The surface wetting ability of PbO_2 electrodes were measured by sessile drop method using polar water as liquid phase on Kenuo SL200A contact angle tester.

2.3 Electrochemical tests of PbO_2 electrodes

The electrochemical tests were performed by employing model PARSTAT4000 potentiostat/galvanostat instrument (Princeton Applied Research company, 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 linear polarization measurements were performed in a working solution containing 1 M H_2SO_4 in the potential range from 0 V~2.1 V at a scan rate of 10 $mV \cdot s^{-1}$.

2.4 Electrocatalytic degradation of phenol simulated wastewater

The electrochemical oxidation experiments were carried out in a batch apparatus consisting of a DC power supply, a magnetic stirrer and a single-compartment glass reactor. The self-made PbO_2 electrode 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 parallel 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 0.2 M 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 180°C for 2 h. The results of experiments were averages of three repeated experiments with the relative standard deviations (RSD) being less than 5%.

2.5 Quantitative measurements of ·OH generated

Ultimate 3000 DGLC (dual-gradient high performance liquid chromatography) ThermoFischer Sci. equipment with variable wavelength ultraviolet detector was employed to measure quantitatively ·OH generated by using SA as a trap. Electrolysis of SA in aqueous solution was carried out using a one-compartment cell at 25℃, 10 mA·cm^{-2}. The self-made PbO_2 was used as the working electrode and stainless steel sheet as the counter electrode. Samples were then taken for analysis at various times throughout the reaction process. Chromatographic separation was performed by using Acclaim120 C18 injection column (250×4.6 mm I.D., 5µm) under isocratic conditions. The mobile phase at flow rate of 1.0 mL·min^{-1} was a mixture of methanol and water (40:60; V/V). The pH value of mobile phase was 3.5 and adjusted by phosphoric acid. The column temperature was set at 30℃. The wavelength of UV detector was set at 320nm. All solvents were filtered through a 0.45µm PVDF film before entering the apparatus. According to our previous research, the ratio of 2,5-DHBA to 2,3-DHBA was about 40. Therefore, the amount of 2,3-DHBA was negligible. The detection of 2,5-DHBA was used to estimate the formation amount of ·OH in this work.

3. RESULTS AND DISCUSSION

3.1 Electro-catalytic activity of PbO_2 electrodes modified by different ILs

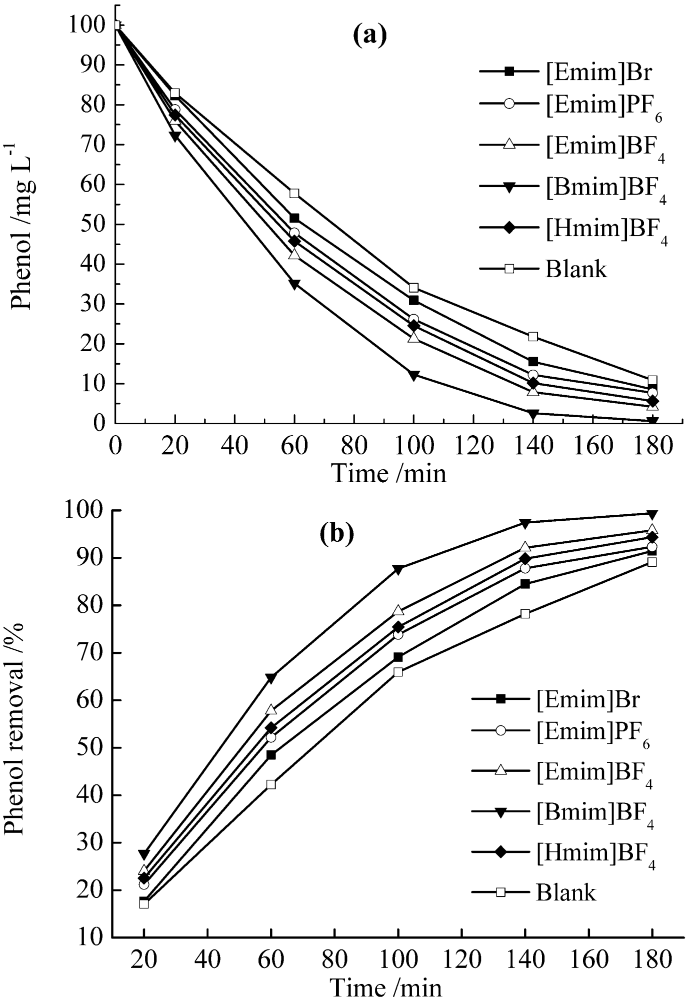

Figure 1. Phenol degradation (a) and removal rate (b) on PbO_2 electrodes modified by different imidazolium based ILs (current density 10 mA cm^{-2}, 100 mg L^{-1} phenol, supporting electrolyte 0.2 M Na_2SO_4).

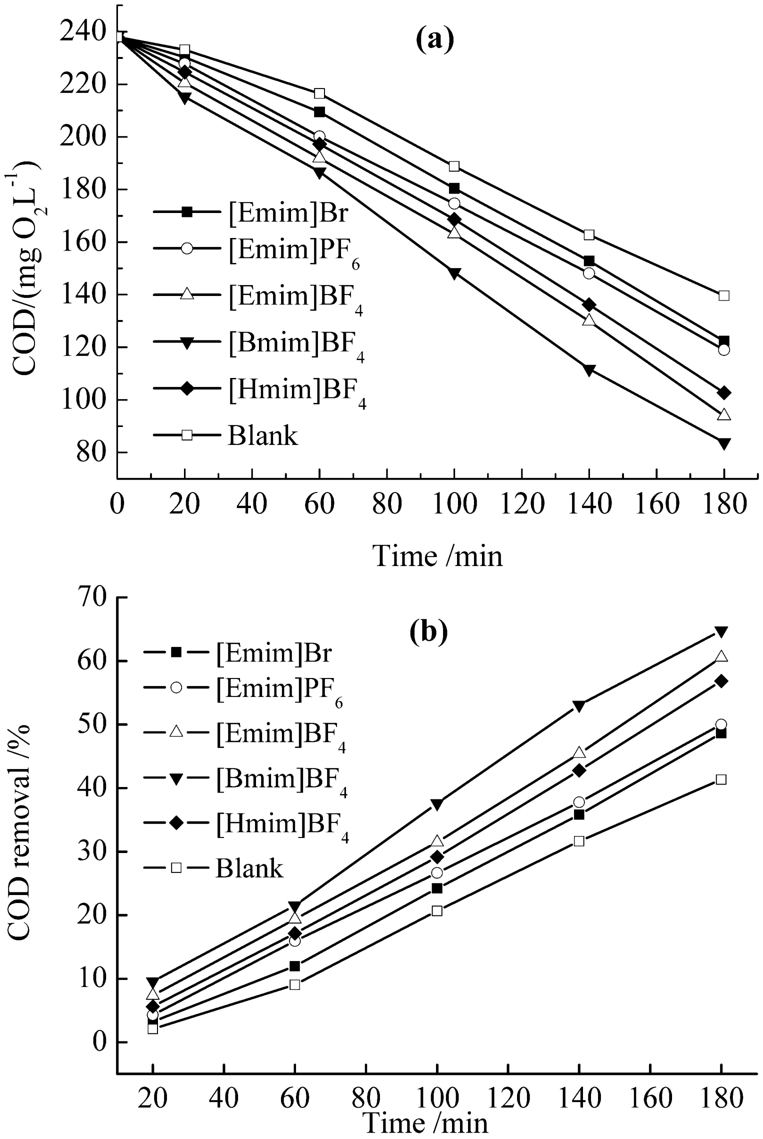

Figure 2. COD degradation (a) and removal rate (b) on PbO_2 electrodes modified by different imidazolium based ILs (current density 10 mA cm^{-2}, 100 mg L^{-1} phenol, supporting electrolyte 0.2 M Na_2SO_4).

Phenol along with chemical oxygen demand (COD) removal rate was used to evaluate the electro-catalytic activity of PbO_2 electrodes modified by different ILs. Fig.1 and Fig.2 shows the phenol and COD removal rate during bulk electrolysis of phenol simulated wastewater respectively. It can be seen that the phenol and COD removal rates, especially the latter, were significantly improved on modified PbO_2 electrodes. Only 41% COD removal was achieved on non-modified PbO_2 electrode within 180 min. Whereas, the removal of COD could reach 64% on PbO_2–ILs ([Bmim]BF_4) electrode. The electro-catalytic activity of PbO_2 electrodes modified by [Emim]BF_4 was significantly higher than that of PbO_2 electrodes modified by [Emim]Br or [Emim]PF_6. With BF_4^- fixed, the improvement order for electro-catalytic activity of PbO_2 electrodes modified by different ILs was as follows: [Bmim]BF_4 > [Emim]BF_4 > [Hmim]BF_4. As previously discussed, ILs additives in the deposition electrolyte solution could influence the electro-crystallization process of PbO_2 through its adsorption on the anode surface.

Therefore, the different modification effect of ILs with different molecular structure can be attributed to their varied adsorption behaviours on anode surface under anodic polarization. It's well known that the performances of PbO_2 coatings are very sensitive to their microscopic composition, structure, morphology and surface area [1, 31]. Therefore, the surface characterization for the diverse modified electrodes was performed later in this work to discuss the reasons for their activity differences.

3.2 The amount of ·OH generated on PbO_2 electrodes modified by different ILs

The concentration of ·OH generated on the PbO_2 electrodes modified with different ILs under a current density of 10 mA·cm^{-2} is depicted in Fig.3.

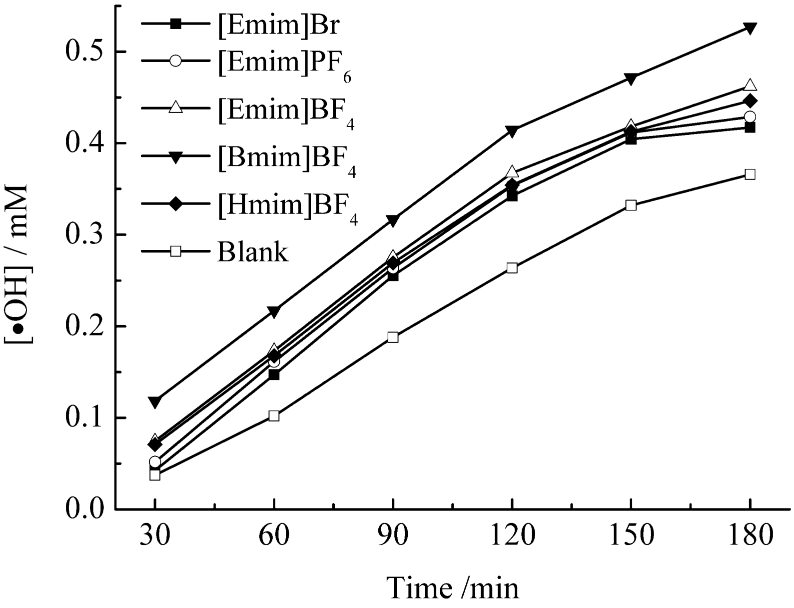

Figure 3. Hydroxyl radical generated on PbO_2 electrodes modified by different imidazolium based ILs

It was found that ·OH generated on modified electrodes was significantly more than that on unmodified ones. Besides, the generation concentration of ·OH on $[Bmim]BF_4$-PbO_2 was apparently higher than that on the electrodes modified by other ILs. The improvement sequence for the generation capacity of ·OH on PbO_2 electrodes modified by different ILs was as follows: $[Bmim]BF_4$ > $[Emim]BF_4$ > $[Hmim]BF_4$ > $[Emim]PF_4$ > [Emim]Br. The improvement order was consistent with the results of the removal effectiveness of phenol and COD. In other words, the increase of the concentration of ·OH on modified PbO_2 electrodes was accompanied with the improvement of the COD removal of phenol simulated wastewater. The results clearly indicated that ·OH generated on PbO_2 anodes played a key role in the electrochemical oxidation of organic pollutants in aqueous solution. That was in good agreement with the statements [4, 32] that the yield of ·OH was closely concerned with the electrocatalytic activity of electrodes and the oxidation efficiency of electrodes depended greatly on their generation capacity of ·OH. It was also good evidence for the claims made by Johnson [33]. They believed that the electrocatalytic mineralization of organic compounds was dominated by oxygen transfer mechanism and the prerequisite of the anodic O-transfer reactions was the discharge of H_2O to generate adsorbed ·OH.

3.3 Electrochemical polarization curves for PbO_2 electrodes modified by different ILs

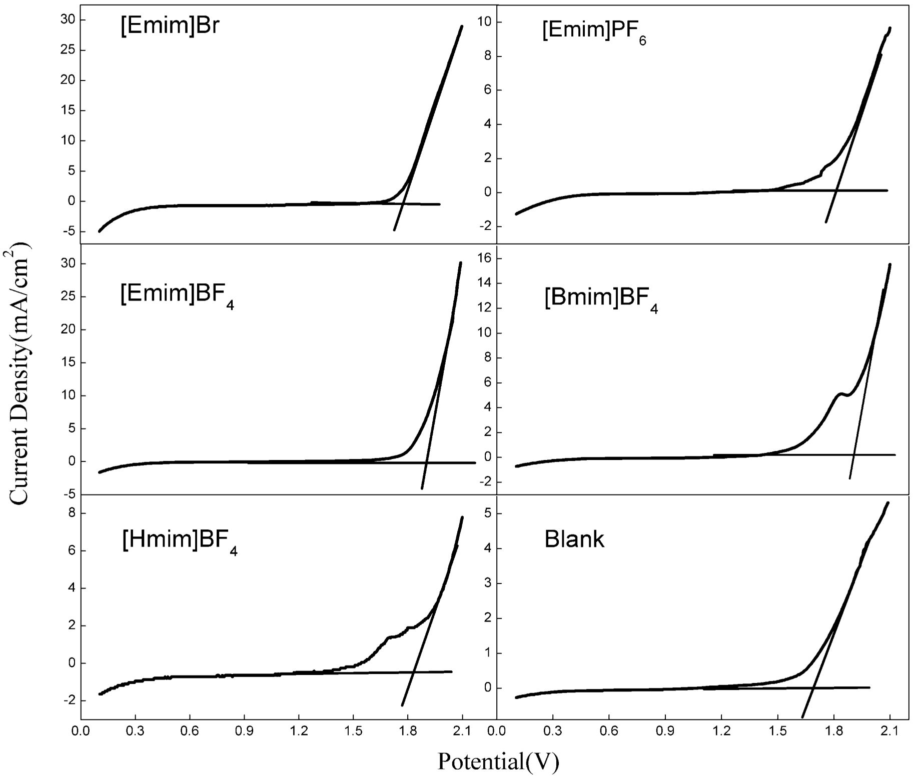

Figure 4. Polarization curves of PbO_2 electrodes modified by different imidazolium based ILs in 1 M H_2SO_4 solution with scan rate of 10 mV s^{-1}.

Oxygen evolution potentials (OEPs) are usually used as an index to evaluate the trend of the oxygen evolution reaction on anodes. Steady-state polarization curves in 1 M H_2SO_4 were investigated to examine the OEPs of unmodified PbO_2 electrodes and ILs modified PbO_2 electrodes. As shown in Fig.4, OEPs on modified electrodes was significantly higher than that on the unmodified ones. Obviously, ILs modification enhanced the OEPs of PbO_2 electrode. The OEPs increased positively in the order of non-modified PbO_2, [Emim]Br-PbO_2, [Emim]PF_6-PbO_2, [Hmim]BF_4-PbO_2, [Emim]BF_4-PbO_2, [Bmim]BF_4-PbO_2. Again, the order was in good agreement with the generation capacity of ·OH and degradation efficiency of organic pollutants. It is widely believed that there exists a competition for the current supplied between the oxygen evolution reaction and electrochemical oxidation of organic pollutants [25, 34]. Therefore, the increased OEPs would restrain the oxygen evolution reaction and be beneficial for the incineration of organic pollutants. Based on the steady-state polarization tests, the PbO_2 modified by [Bmim]BF_4 possessed the best electrochemical performance compared with other modified electrodes.

3.4 Crystalline structure of PbO_2 electrodes modified by different ILs

Fig.5 shows the XRD patterns of the PbO_2 electrodes modified by different imidazolium based ILs. In the absence of ILs, the crystallographic orientation sequence of non-modified electrodes was (200) (110) (211) (101), which were in good agreement with standard data of the JCPDS card (No. 76-0564) for β-PbO_2 with a tetragonal structure. When different ILs were added to the electrolyte during electrodeposition process, significant changes in the reflection patterns of resulting deposits occurred. A highly textured structure of PbO_2 coatings was obtained as a result of ILs modification. For PbO_2 modified by ILs with BF_4^- or PF_6^- the main crystal plane was (110), while for PbO_2 electrodes modified by ILs with Br^- the preferential orientation shifted to (301) (200) (211) (110).

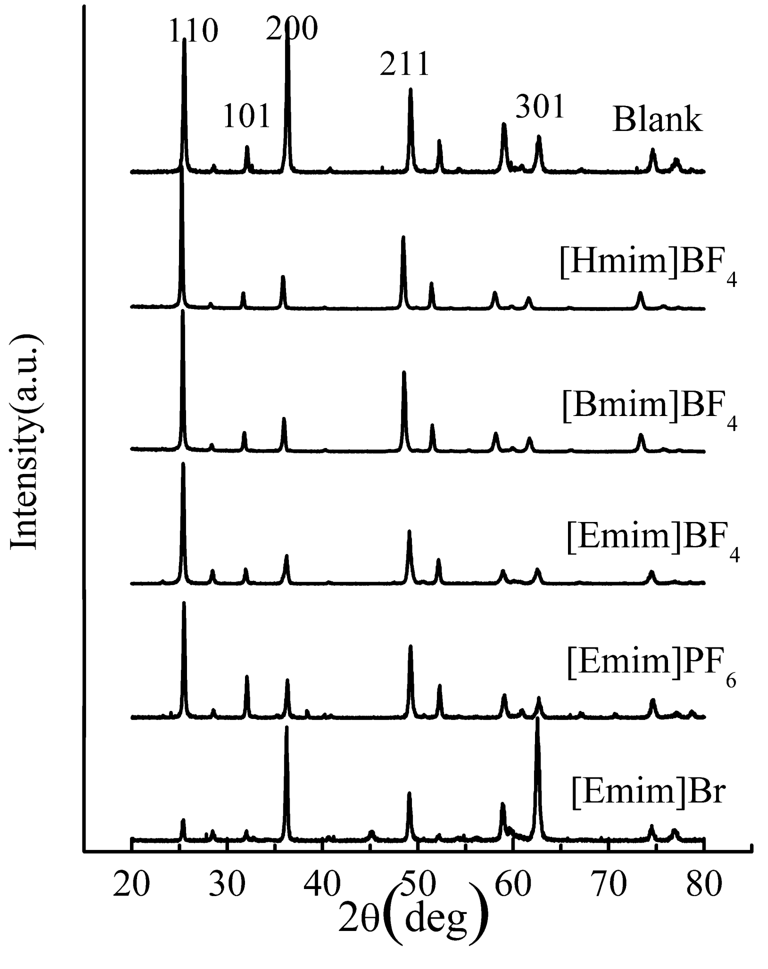

Figure 5. XRD patterns of prepared PbO_2 electrodes modified by different imidazolium based ILs. Temperature of electrolyte: 50 °C, current density: 10 mA cm^{-2} and deposition time: 60min.

The formation of textured crystals depends strongly on the growth direction, growth rate and growth mode of crystal plane [35, 36]. Upon addition of ILs to electrolyte, the growth of certain plane was inhibited due to the selective adsorption of the ILs molecule on the plane. Finally, the preferential orientation of this plane was obtained. By comparing the XRD patterns of PbO_2 electrodes modified by various ILs, it could be deduced that the influence of anions on the adsorption behavior of ILs was more significant than the chain length of imidazole ring substituent. Therefore, the adsorption of ILs on anode surface occurred probably by the electrostatic interaction between negative-charged anions and the anode. In other words it was anions rather than imidazolium ring that played a dominant role in the adsorption of ILs on anode surface. Apparently, owing to the anode polarization the adsorption properties of imidazolium based ILs on anode surface was totally different from that on general metal surface or that on cathode surface under cathode polarization.

The crystal size was calculated by Scherrer equation and presented in Table 1. It can be seen that with the increase of carbon numbers in imidazolium substituent from 2 to 6, the average crystal size of PbO_2 increased significantly from 29.2 nm to 42.8 nm. The crystal size was related to the relative speed of nucleation and growth of crystals. When the nucleation rate rather than growth rate was inhibited, crystals of large size would be obtained [37]. Hence, it could be deduced that imidazolium cation may also enter the anode zone with the guidance of anion, increasing the anode polarization and influencing the nucleation rate of the crystals. The longer the substituent chain was, the stronger the restrain effect on the crystal nucleation rate was, and consequently the larger the resulting crystal was.

Table 1. Average crystal sizes of PbO_2 electrodes modified by different imidazolium ILs

Additives	[Emim]Br	[Emim]PF_6	[Emim]BF_4
grain size, nm	32.1	36.2	29.2
Additives	[Bmim]BF_4	[Hmim]BF_4	Blank
grain size, nm	37.0	42.8	33.2

A variety of research works have demonstrated that deposits with highly preferential orientation posses particular facet-dependent catalytic performances compared with deposits of random orientation [38, 39]. For example, the (111) faces of Cu_2O were catalytically more active than the (100) faces because surface copper atoms contained in the (111) face had dangling bonds which interacted more strongly with methyl orange [38, 39]. Therefore, the higher electrocatalytic acitivity of PbO_2 modified by ILs with BF_4^- may be attributed to their preferential orientation along (110) plane. Meanwhile, the relatively low activity of PbO_2 modified by ILs with Br^- demonstrated that preferential orientation along (301) plane was unfavorable for the activity improvement of β-PbO_2. Indeed, the electrochemical oxidation was a complex process involving many factors such as electron transfer, liquid diffusion and adsorption/desorption of various substances on electrode surface. Therefore, more fundamental experimental explorations and theoretical studies are required before the exact correlation between the microstructure of the electrode surface and the oxidation capacity is obtained.

3.5 Surface Morphology of PbO_2 electrodes modified by different ILs

Fig.6 presents the scanning electron micrographs of PbO_2 samples modified by different ILs. There were remarkable differences between the microstructural features of these samples. Defects in the form of cracks and pores were observed for sample grown in the absence of ILs (Fig.6f). However, samples prepared in the presence of various ILs showed a relatively smooth, regular morphology and densely packed structure. Meanwhile, sample prepared in the presence of [Emim]Br exhibited a obviously different morphology with column-like shape(Fig.6a). Furthermore, when modified with BF_4^- type ILs, the grain size increased with the increase of the carbon number of substitute of imidazolium ring. This observation was in agreement with the calculated crystal size shown in Table 1. The surface morphology can reflect the growth mode of the coating to some extent [40]. Therefore, the diversity of the morphology may be attributed to the variation of PbO_2 crystal growth mode in the presence of various ILs. The SEM observation combined with XRD results indicated that the molecular structure of imidazolium based ILs had a major influence on the structure of resulting deposits, with the anions being more influential than the cations.

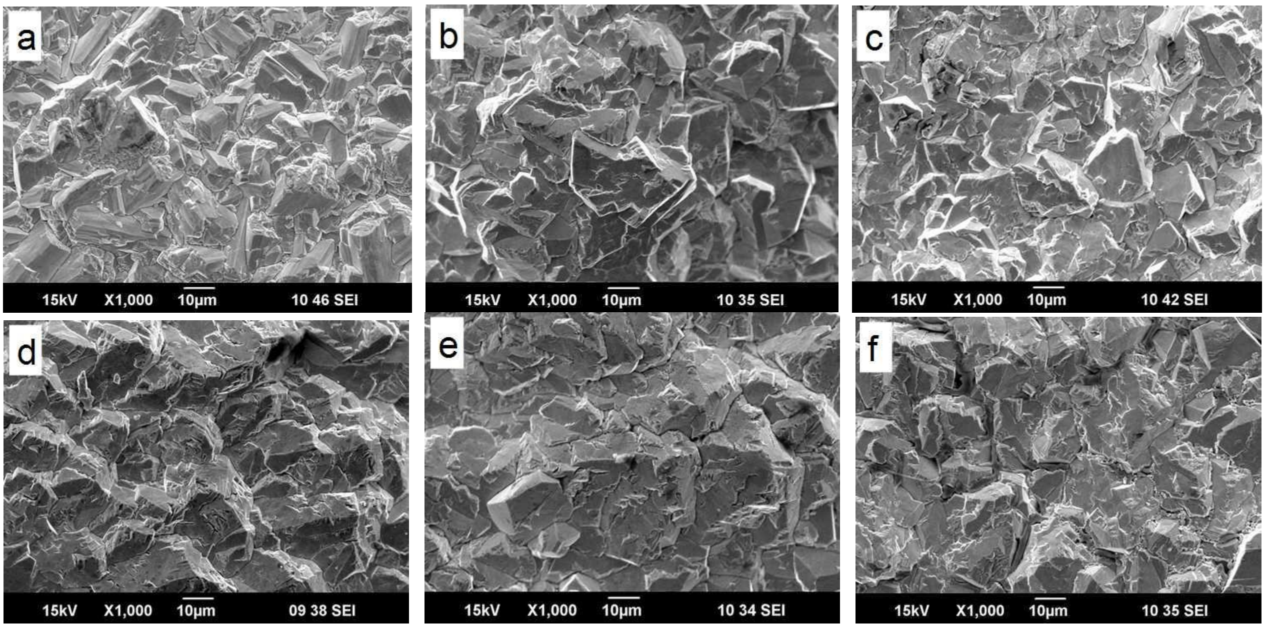

Figure 6. Surface scanning electron micrographs of PbO_2 modified by (a)[Emim]Br (b)[Emim]PF_6 (c)[Emim]BF_4 (d)[Bmim]BF_4 (e)[Hmim]BF_4 (f)Blank. Temperature of electrolyte: 50 °C, current density: 10 mA cm^{-2} and deposition time: 60min.

3.6 Contact angle on surface of PbO_2 electrodes modified by different ILs

The electrochemical oxidation of organic species in aqueous solution by electrodes could be influenced by the wetting ability of electrode through affecting the adsorption behaviors of water, organic pollutants or ·OH on electrode surface. The wetting ability was evaluated via contact angle tests. The decrease of the contact angle of water on the electrode surface means the increase of the wetting ability of electrode by water. Fig.7 shows the contact angles of water on the PbO_2 electrodes modified by different ILs. The surface free energy of the electrode was calculated by using the contact angle and shown in Table 2.

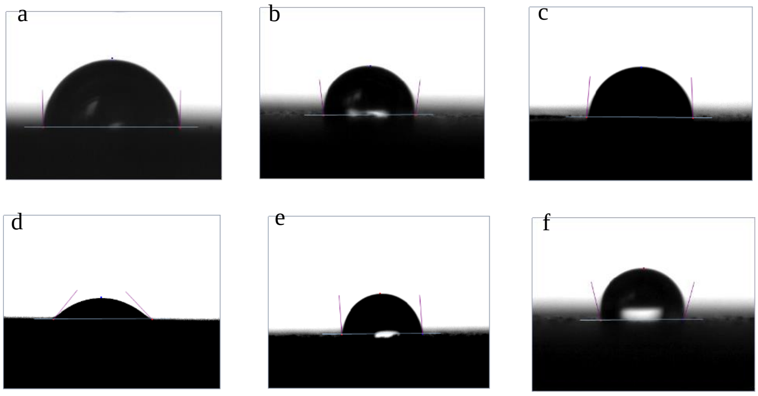

Figure 7. Contact angles of the PbO_2 electrodes modified by (a)[Emim]Br (b)[Emim]PF_6 (c)[Emim]BF_4 (d)[Bmim]BF_4 (e)[Hmim]BF_4 (f)Blank. Temperature of electrolyte: 50 °C, current density: 10 mA cm^{-2} and deposition time: 60min.

As shown in Fig. 7 and Table 2, the non-modified electrode surface was hydrophobic with the contact angle of 106.62°. Whereas, the surface hydrophilicity increased for electrodes modified by various ILs. When the electrode was modified by ILs with BF_4^-, the electrode surface was changed from hydrophobic to hydrophilic with the contact angle changing from 106.62° to $<$90°. The sequence of the hydrophilicity of different electrodes was as follows: [Bmim]BF_4-PbO_2 > [Emim]BF_4-PbO_2 > [Hmim]BF_4-PbO_2 > [Emim]PF_4 -PbO_2 > [Emim]Br-PbO_2. Interestingly, this order was consistent with the results of the removal effectiveness of phenol and COD too. So it can be concluded that the higher degradation efficiency was achieved on electrodes with better hydrophilicity. It’s worth noting that the hydrophilicity of the PbO_2 electrode modified by [Bmim]BF_4 was prominently higher than that of other modified electrodes, which was corresponding to its much greater electro-catalytic capacity.

Table 2. Contact angle and surface energy of the PbO_2 electrodes modified by different imidazolium based ILs

Additives	Contact angle, °	Surface free energy, mJ·cm^{-2}
[Emim]Br	91.72	23.05
[Emim]PF_6	95.44	21.52
[Emim]BF_4	84.85	31.35
[Bmim]BF_4	48.07	54.46
[Hmim]BF_4	88.37	25.68
Blank	106.62	14.71

Zhao [24] proposed that fluorine resin (FR) doping can increase the utilization rate of ·OH and improve the oxidation efficiency of PbO_2 electrodes. The enhancement mechanism was that resin doping resulted in the surface changing from hydrophilicity to hydrophobicity, thus reducing the ·OH adsorption on electrode and improving the oxygen evolution over-potential. The results obtained in this work, however, were obviously not in agreement with this statement. Therefore, it is not reliable to simply attribute the performance improvement to the change of hydrophilicity of electrode surface. Actually, it is well known that the surface roughness of material has a close connection with its contact angles in aqueous solution. According to Wenzel Equation [41], the smaller the contact angle, the rougher the surface of materials. The rougher the surface, the greater the surface area. Therefore, more specific surface area and active sites for the generation of hydroxyl radical were provided for electrodes with lower contact angle. Hence the improved oxidation capacity of [Bmim]BF_4-PbO_2 can be attributed to its higher specific surface area. This was in agreement with the findings by An [42] and statements from Trasatti [43]. They both highlighted the importance of surface area on the electrocatalysis of electrodes. An [42] investigated the influence of electrochemical deposition time of PbO_2 coatings on the electrocatalytic capability of prepared electrodes, and found that although increasing electrodeposition time resulted in a smoother electrode surface, but the electrocatalytic activity of electrodes was decreased due to the lower specific surface area. Trasatti [43] proposed that electrocatalysis depended on electronic factors and geometric factors. The former affected the surface-intermediate bond strength and depend on surface chemical structure. The latter were those related to the extension of the surface area. A concept of "·OH utilization rate" was recently proposed and used by Zhao [24] and other researchers [44, 45]. It was defined as the value of $[\cdot OH]_{free}/[\cdot OH]_{total}$ and reflected by the value of $\triangle COD/[\cdot OH]_{total}$, where $[\cdot OH]_{total}$ was determined with dimethyl sulfoxide (DMSO) trapping and HPLC. The ratios of △COD to the amount of ·OH generated on PbO_2 electrodes modified by different ILs were calculated and shown in Fig. 8.

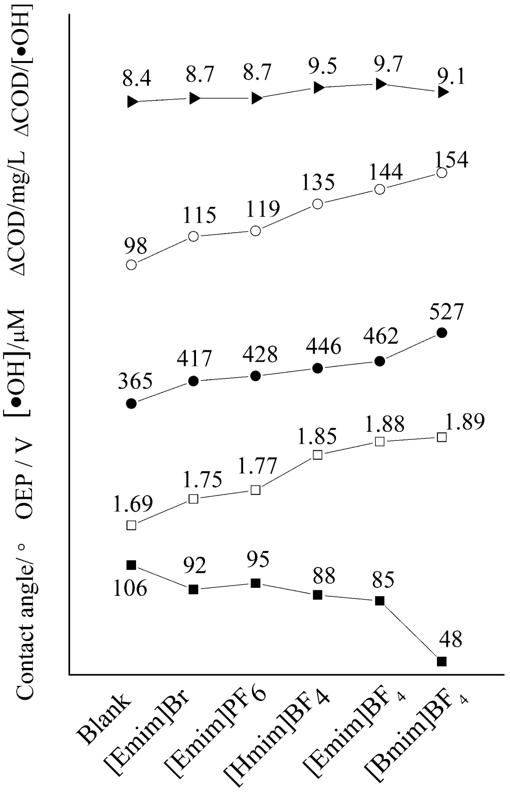

Figure 8. Oxidation capacity and electrochemical properties of PbO_2 electrodes modified by different imidazolium based ILs

It ranged from 8.4 to 9.7. Only slight changes occurred and no direct correlation between the value and electrolytic activity was found for PbO_2 electrodes modified by different ILs.

3.7 Reusability and stability of PbO_2 electrodes modified with ILs

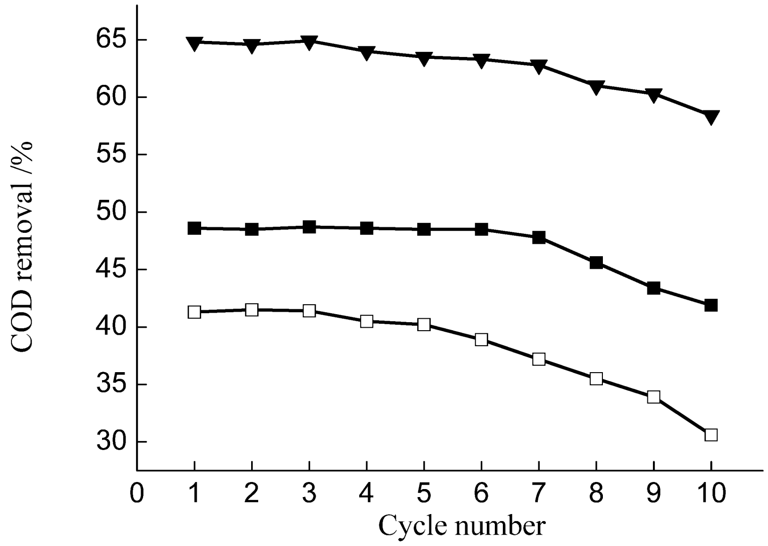

Figure 9. Electrochemical degradation of phenol for ten successive reactions on -■- [Emim]Br modified PbO_2 electrode; -▼- [Bmim]BF_4 modified PbO_2 electrode; -□- non-modified PbO_2 electrode

The reusability and stability of the electrode are important for its real application[44]. Fig.9 shows the COD removal rates by three different PbO_2 electrodes after 3 h degradation reusing 10 cycles. The degradation efficiencies were tested one after another reaction successively. It was found that electrocatalytic activity of PbO_2 electrodes modified with ILs was significantly higher than that of non-modified ones for all the ten cycles tested, which confirmed the improvement of electrocatalytic activity by ILs modification as indicated in previous section. Besides, there was an evident decrease on COD removal efficiency since the sixth cycle for non-modified electrode, whereas it was from eighth cycle that degradation efficiency began to drop apparently for the electrodes modified by ILs. Furthermore, the falling speed of COD removal efficiency for electrodes modified by [Emim]BF_4 was obviously slower than that for electrodes modified by [Emim]Br. The results indicated that the introduction of imidazolium-based ILs, particularly [Bmim]BF_4, to the electrodepostion solution could stabilize the resulting PbO_2 coating and significantly improve the reusability and stability of the electrodes.

4. CONCLUSIONS

1) The electrocatalytic activities of PbO_2 electrodes modified by [Emim]BF_4 were significantly higher than that of PbO_2 electrodes modified by [Emim]Br or [Emim]PF_6. With BF_4^- fixed, the

improvement order for electrocatalytic activity of modified PbO_2 electrodes by different ionic liquids was as follows: $[Bmim]BF_4$>$[Emim]BF_4$>$[Hmim]BF_4$. The improvement order for the generation capacity of ·OH on PbO_2 electrodes modified by different ILs was consistent with the results of the removal effectiveness of phenol and COD, indicating that the oxidation efficiency of electrodes depended greatly on their generation capacity of ·OH.

2) The molecular structure of imidazolium based ILs had a major influence on the surface morphology and microstructure of resulting PbO_2 deposits. A highly textured structure and controlled morphology of the PbO_2 coatings was obtained due to the selective adsorption of the ILs molecule on the anode plane. β-PbO_2 modified by ILs with anion BF_4^- was characterized by the preferential crystallographic orientation along (110) plane.

3) A decrease in surface contact angles of modified electrodes resulted in an improved electrode activity. The higher activity of PbO_2 electrodes modified by $[Bmim]BF_4$ can be attributed to its preferential orientation in the (110) direction along with its larger specific surface area and more active sites for the generation of hydroxyl radical.

4) The reusability and stability of PbO_2 electrodes was improved greatly after modification with ILs. The PbO_2 electrodes modified by $[Bmim]BF_4$ exhibited the best reusability and stability in successive degradation tests.

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