Pb-0.6%Sb/ α -PbO₂/ β -PbO₂-MnO₂ Electrode Electrodeposited In Methanesulfonic Acid With Application To The Electrocatalytic Degradation of AYR Wastewater

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Research Article

Keywords: Lead dioxide electrodeposition, Methanesulfonic acid, Wastewater treatment, Physicochemical properties, Electrocatalytic degradation

Posted Date: June 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-546712/v1>

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Abstract

In the present work, a novel Pb-0.6%Sb/ α -PbO₂/ β -PbO₂-MnO₂ composite electrode with high electrocatalytic activity was obtained by electrodeposition in methanesulfonic acid and further investigated in the electrochemical degradation of alizarin yellow R (AYR) wastewater. The selection of temperature ranges was found to cause a quantitative difference in the formation of α / β -PbO₂ phases. In this way, both phases were simultaneously electrodeposited in the same methanesulfonic acid, and electrodes with corresponding proportions of phases were fabricated. Furthermore, performance tests indicated that composite electrodes with the most appropriate corresponding proportions of phases co-deposited with proper amount of MnO₂ could obviously improve the COD removal efficiency and degradation efficiency of AYR to 78.1% and 80.3%. They also showed commendable recyclability and fine economic applicability. Ultimately, the paper proposed a proper electrocatalytic degradation pathway of AYR based on the identification of the major intermediate products. The results proved that MnO₂-co-doped composite electrodes had more promising application potential in the electrocatalytic degradation of AYR wastewater.

Introduction

Followed the development of modern electrochemical technology and environmental protection, more and more researchers are gradually paying close attention to the utilization of electrode coating materials [1–3]. Lead dioxide (PbO₂) is counted as such a kind of electrode coating material of superior performance and has been used in quite a few applications, especially in the wastewater treatment [4–6]. AYR wastewater is a typical representative azo dye wastewater, which has impacted the growth of aquatic creatures and human health for ages [7,8]. For the composition of benzene rings and azo bond of the AYR molecule, AYR wastewater is hard to be degraded. Former scholars' researches proved that electrocatalysis could be considered as an eco-friendly method in AYR wastewater treatment due to its high efficiency and little pollution [9,10]. Based on this, the application of PbO₂ composite electrode in electrocatalysis, where reactive oxygen species are produced to degrade organics in effluent, is naturally recognized as of particular interest. However, previous studies mainly focus on PbO₂ coatings obtained in situ on lead or lead alloys. Even later researches were only limited to single or stochastic phase structures of PbO₂. All these electrodes were facing the problem of easy corrosion or other inefficiencies problems [11–13]. It is urgent to make full use of the phase structures composition of α - and β -PbO₂ that separately show corresponding performance characteristics to finally possess longer service life and better removal efficiency of organic pollutant in AYR wastewater treatment.

Among the current preparation methods of PbO₂, electrodeposition has always been favored for its advantages in obtaining stable coatings of different phase structures with minimum pollution [14,15]. Up to now, α - and β -PbO₂ are mainly obtained in alkaline and acid solutions separately by electrodeposition. Orthorhombic α -PbO₂ is relative compact and can promote longer life cycles of electrodes. Whereas tetragonal β -PbO₂ is porous and provides more active surface area [16]. It's rare to simultaneously

prepare both phase structures of PbO_2 in the same solution, as well as the crystal proportion be quantitatively controlled. Through a large number of researches and experiments, our previous study has worked out the problem and put forward a method of preparing PbO_2 coating materials composed of two phase structures in the same methanesulfonic acid (MSA) solution by electrodeposition, which not only avoids the difficulty of preparing different phase structures in separate solutions, but also makes the PbO_2 coating materials performance more stable since MSA is an environmentally friendly electrolyte for its chemical stability and excellent solubilisation of metal salts [17]. Based on this, the further promotion on chemical stability and oxidation activity of PbO_2 coatings by introducing active particles (MnO_2 , CNTs etc.) appears to be of interest to practice [18–20].

In this connection, herein we first presented a thorough study of the temperature influence on the nucleation and growth process of α - or β - PbO_2 obtained by electrodeposition in MSA solutions so as to judge the guiding factors for obtaining different crystal forms of PbO_2 and prepare anodes with ideal crystal ratio. Afterwards, the co-deposition of MnO_2 was realized and its content influence upon $\text{Pb-0.6\%Sb}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2\text{-MnO}_2$ electrodes in the electrocatalytic degradation of AYR, namely the oxygen evolution potentials, charge transfer resistances, corrosion potential and accelerated service life, were systematically studied. Ultimately, LC-MS was employed to identify the oxidization intermediates. The electrocatalytic degradation pathways of AYR on MnO_2 -co-doped PbO_2 composite electrodes were accordingly elucidated.

Experimental Conditions

$\text{Pb-0.6\%Sb}$ sheets prepared by hot rolling with the dimension of 12 mm x 22 mm x 2 mm were used as the substrates for the composite materials. The pretreatments of the $\text{Pb-0.6\%Sb}$ substrates were performed by procedures as polishing, sand blasting, chemical degreasing and zinc galvanizing twice. Then, $\text{Pb-0.6\%Sb}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2\text{-MnO}_2$ electrodes were obtained by electrodeposition in MSA solutions (Electrodeposition time, $\alpha\text{-PbO}_2$ 2 h, $\beta\text{-PbO}_2$ 2 h) and assessed at PARSTAT 2273 electrochemical workstation with a three-electrode system ($\text{Pb-0.6\%Sb}$ sheet as working electrode. Saturated calomel electrode as Reference electrode. Graphite as counter electrode). Besides, the physical and chemical properties of the electrodeposited composite anodes were tested by means of Scanning Electron Microscope (SEM), Energy Dispersive Spectrometer (EDS), Anodic polarization curves, Electrochemical Impedance Spectroscopy (EIS), Tafel curves (Tafel) and Accelerated service life curves. Therein, EIS test was achieved at open-circuit potential conditions and AC potential with the amplitude of 10 mV and normally a frequency range of 100 kHz to 10 mHz. Accelerated service life curves were tested in 0.50 M H_2SO_4 solution at current density of 250 mA cm^{-2} . Composite electrodes well prepared by electrodeposition were then used for the electrocatalytic degradation of AYR. A stainless steel electrode with the same surface area was used as cathode. Add 0.1 L AYR wastewater (80.0 mg L^{-1}) and Na_2SO_4 electrolyte (9.0 g L^{-1}) into the electrolytic cell. Adjust the pH at 5. Control the plate space between anode

and cathode at 3.0 cm. The COD removal efficiency and degradation efficiency of AYR were determined per 30 min. The UV-Vis spectra wavelength ranged from 600 nm to 200 nm.

Results And Discussion

3.1 Electrodeposition process of Pb-0.6%Sb/ α -PbO₂/ β -PbO₂-MnO₂ electrodes

During the whole nucleation process, the growth of PbO₂ particles was closely related to the diffusive transport of metal ions controlled by the current density across the electrodes that directly determined the overpotential of the solution. All these factors were influenced by the experimental conditions [21]. It should be noted that neither of the two modifications of PbO₂ were fully stoichiometric and initial crystal forms could be converted to each other to some extent [22,23]. Compared to MSA and lead(II) methanesulfonate concentrations, temperature and current density showed more obvious effect on the overpotential of the solution thus on PbO₂ nucleation process [24]. When maintaining overpotential at a lower range, Pb(II) and OH_{ads} could continuously and stably react over the electrode surface. As particles had similar deposition trails, the differences of particle size and morphology mainly depended on the nucleation moment. A uniform and compact α -PbO₂ film was easy to obtain then. However, the increase of overpotential would lead to the increase of charge transfer, which directly caused the lack of Pb(II) and OH_{ads} around growing particles. New particles then tended to form on the growing particles, thus the transition and proliferation of lead dioxide were easier to happen in a 3-dimensional growth way. Comprehensively, particles obtained always first accomplished the full growth of metastable α -PbO₂ and then prefer to be the growth of porous β -PbO₂ (Fig. 1) [25]. The key step to separately obtain either phase form was to effectively control the overpotential.

Through a large number of experimental studies, our researches found that keep the solution concentration and current density stable while control the temperature at 25 °C could continuous and stable supply of Pb(II) and OH_{ads} be ensured to get relative pure α phases. Besides, the temperature of 60 °C was discovered to be an appropriate boundary of obtaining relative better pure β phases [26]. Since the increase of current density could cause the change of magnetic field force in the solution, two different phase forms of PbO₂ prefer to be obtained more stably by controlling the temperature limit. Having in mind that a proper proportion of the crystalline composition was essential, MnO₂ were further optimized by ultrasonic dispersion and then used in the co-deposition with β -PbO₂ to promote the chemical stability and oxidation activity of PbO₂ coatings.

3.2. Electrochemical behavior of Pb-0.6%Sb/ α -PbO₂/ β -PbO₂-MnO₂ electrodes

3.2.1 Surface topography analysis

As follows from the SEM data, PbO_2 obtained in the first 30 s was a set of large polycrystalline blocks with a slightly pronounced predominant orientation (Fig. 2a). While the co-deposition of MnO_2 allowed one to obtain PbO_2 (Fig. 2e), of which the surface tended to be more compact and the crystalline size was evidently reduced.

In Fig. 2, within 30 s after the beginning of the co-deposition process, the nucleation and growth of $\beta\text{-PbO}_2$ were the main reactions that carried out on the surface of the composite anode. Since the conductivity of MnO_2 active particles were not that ideal [27–29], they hadn't been adsorbed on the surface of composite anode then. After 2 min, MnO_2 active particles began to co-deposited on the surface of the composite anode, which agglomerated in a small range under the action of electric field force, providing nucleation sites for the deposition of PbO_2 in the system. As the co-deposition proceeded on a constantly renewable surface, complex particles could be adsorbed on the surface of the growing oxide, which were probably involved in the oxidation of Pb(II) and thus lead to different effects, in particular reduced crystal size. The heterogeneous nucleation rate was thus accelerated and nucleation growth of new PbO_2 squints towards the sides around MnO_2 active particles. When the deposition process reached 5 min, PbO_2 around MnO_2 active particles had grown larger and new formed PbO_2 grains were refined as well. When they grew to a certain extent, original MnO_2 active particles were covered and new MnO_2 were continuously adsorbed around them. The continuous diffusion co-deposition and growth of the two particles were realized alternately, till most MnO_2 were co-deposited into the $\beta\text{-PbO}_2$ deposition layer. The surface of the composite anode was compact and smooth then.

As been suggested from the EDS data in Fig. 3a, the agglomeration of MnO_2 active particles at point 1 was not as obvious as that at point 2. Moreover, the proportion of Pb atoms at point 1 was higher than that at point 2, while the proportion of Mn atoms was opposite, which was consistent with the results of SEM analysis in previous studies, indicating that the effective dispersion and adsorption of MnO_2 active particles could provide more nucleation sites for PbO_2 deposition. In Fig. 3b, point 1 and 2 separately represented MnO_2 active particles exposed outside and coated inside the $\beta\text{-PbO}_2$ grains. The increase of Pb and Mn atoms proportion showed that MnO_2 had been effectively coated in the $\beta\text{-PbO}_2$ grains. Besides, there was a slight raise of Pb proportion at point 1 and 2, which proved that the $\beta\text{-PbO}_2$ deposition layer was also growing and thickening then. In Fig. 3c, the adsorption position of MnO_2 was higher at point 1 and lower at point 2. It could be found from the Pb and Mn atoms proportion that PbO_2 grains seemed to grow preferentially around MnO_2 active particles close to the surface of the matrix. Also the proportion of Pb atoms then was lower than that at 5 min, which suggested the nucleation and growth of $\beta\text{-PbO}_2$ deposition layer had become slow.

3.2.2. Electrochemical performance test

The data in Fig. 4 was combined data from studies, which comprehensively analyzed the effects of MnO_2 co-deposition on the performance of composite anodes by separately presenting the anodic polarization curves, EIS curves, Tafel curves and accelerated service life curves.

As could be seen from Fig. 4a that the oxygen evolution potential of the co-deposited composite electrode (1.79 V vs. SCE) was higher than that of Pb-0.6%Sb/ α -PbO₂/ β -PbO₂ electrode (1.77 V vs. SCE), which demonstrated that the co-deposition of MnO₂ could increase the electrochemical oxidation efficiency of organic pollutants by inhibiting the oxygen evolution reaction. The Nyquist diagrams in Fig. 4b illustrated the same conclusion, of which the radius decreased as MnO₂ co-deposited. Theoretically, the radius semicircle objectively reflected the charge-transfer resistance. A smaller radius semicircle represents the lower oxygen evolution overpotential and electron transfer resistance of composite anode. The co-deposition of MnO₂ had effectively achieved the decrease and promoted the charge transfer. In Fig. 4c, the corrosion potential of the composite anodes were compared, between which the one was higher when MnO₂ was co-deposited. It should be noted that as the ductility of MnO₂ was poor [29], an excessive co-deposition of MnO₂ may result in the self-corrosion area of the composite anode increase correspondingly and should be avoided in the optimization of degradation AYR wastewater conditions. Figure 4d presented the accelerated service life curves, from which the co-deposition of MnO₂ had made the accelerated lifetime of the Pb-0.6%Sb/ α -PbO₂/ β -PbO₂ electrode (15 h) extended by 0.8 times (27 h). A more compact surface of Pb-0.6%Sb/ α -PbO₂/ β -PbO₂-MnO₂ electrode had made it possible that the corrosion of electrolyte be prevented, the conductivity be less influenced, as well as the oxygen evolution process be reduced, thus prolonging the lifetime in the electrocatalytic degradation treatment of AYR wastewater.

3.3 Electrocatalytic degradation process of AYR

3.3.1. Effects of composite anodes with different MnO₂ content on electrocatalytic degradation of AYR

We conducted potassium dichromate method (GB-11914-89), where excessive K₂Cr₂O₇ was titrated with calibrated (NH₄)₂Fe(SO₄)₂ solution, to investigate the effects of composite anodes with different MnO₂ content on the COD removal efficiency and degradation efficiency of AYR calculated by the following formulas:

	C_1 , concentration of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ (M)
$\text{COD}(\text{mg L}^{-1}) = \frac{C_1(V_1 - V_2) \times 8000}{V_0}$	V_0 , volume of AYR wastewater (mL)
	V_1 & V_2 , volumes of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ solution applied to blank sample and AYR wastewater (mL)
$\eta (\text{COD}, \%) = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100$	COD_0 & COD_t , chemical oxygen demands of samples at electrolytic time 0 and t
$\eta (\text{AYR}, \%) = \frac{A_0 - A_t}{A_0} \times 100$	A_0 & A_t , initial and final values of the absorbance intensity of AYR

The observed effect in Fig. 5 indicated that MnO_2 content in composite anodes has a great effect on the degradation efficiency of AYR. With the increase of MnO_2 content from 10 to 40 $\text{g}\cdot\text{L}^{-1}$, the COD removal efficiency significantly increased from 53.6–78.1% after 150 min (Fig. 5a), while the degradation efficiency of AYR increased from 54.4–80.3% (Fig. 5b). By further observing the growth rate could we summarized that both two kinds of efficiencies changed slightly in the presence of a higher MnO_2 content of more than 30 $\text{g}\cdot\text{L}^{-1}$, indicating that excessive MnO_2 was not entirely conducive to the degradation of pollutants. Moreover, the COD removal efficiency and degradation efficiency of AYR could still be reached up to 72.3% and 73.4% after ten successive cycles of electrocatalytic degradation, which indicated that $\text{Pb-0.6\%Sb}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2\text{-MnO}_2$ electrodes had commendable recyclability and fine economic applicability.

3.3.2. Degradation mechanism of AYR on $\text{Pb-0.6\%Sb}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2\text{-MnO}_2$ electrode

During the electrochemical degradation process, series of precursor-product relationships of the intermediates were emerged. Theoretically, persulfate ions $\text{S}_2\text{O}_8^{2-}$ were generated via direct electron transfer of O_4^{2-} and then activated to create sulfate $\text{SO}_4^{\cdot-}$, which could rapidly attack oxidisable compounds including organics and inorganics [30]. Besides, vast amounts of $\cdot\text{OH}$ were generated from the reaction between $\text{SO}_4^{\cdot-}$ and water to accelerate the electrochemical degradation of AYR [31]. Compared with $\text{SO}_4^{\cdot-}$, the degradation effect of $\cdot\text{OH}$ tended to be more significant.

Figure 6 showed the snail shaped UV-Vis spectra of composite anodes at different degradation time. The rapid peak value decrease of the maximum absorption band (360 nm) indicated that azo bond ($-\text{N}=\text{N}-$)

had been gradually broken. Four possible degradation pathways were proposed according to different initial attacking positions, including C-N cracking, N-N cracking, denitration and decarboxylation.

In order to verify this, LC-MS was employed to identify the oxidization intermediates. The observed organic compounds indicated us three steps of organic degradation. Step 1, CAN bond and NAN bond were cleaved into organic intermediates by $\cdot\text{OH}$ [32]. Step 2, single-chain small molecules were formed from the organic intermediates by denitration and decarboxylation. Step 3, these single-chain small molecules were rearranged by further oxidation, reduction, and partial mineralization until completely mineralized into CO_2 , H_2O and inorganic ions [33]. The whole electrochemical degradation process could be simulated in Fig. 7.

Conclusions

In summary, $\text{Pb-0.6\%Sb}/\alpha\text{-PbO}_2/\beta\text{-PbO}_2\text{-MnO}_2$ composite electrode with high electrocatalytic activity was successfully prepared by electrodeposition in methanesulfonic acid and further applied in the electrochemical degradation of alizarin yellow R (AYR) wastewater. Keep the solution concentration and current density stable while control the temperature at $25\text{ }^\circ\text{C}$ could continuous and stable supply of Pb(II) and OH_{ads} be ensured to get relative pure α phases. Besides, the temperature of $60\text{ }^\circ\text{C}$ was discovered to be an appropriate boundary of obtaining relative better pure β phases. Meanwhile, the co-deposition of MnO_2 allowed one to obtain PbO_2 layers, of which the surface tended to be more compact and the crystalline size was evidently reduced. With the increase of MnO_2 content from 10 to $40\text{ g}\cdot\text{L}^{-1}$, the COD removal efficiency significantly increased from 53.6–78.1% after 150 min, while the degradation efficiency of AYR increased from 54.4–80.3%. Moreover, the COD removal efficiency and degradation efficiency of AYR still exhibited superior stability after ten successive cycles of electrocatalytic degradation. Based on the identification of the major intermediate products, the paper proposed a proper electrocatalytic degradation pathway of AYR. The results proved that MnO_2 -co-doped composite electrodes had more promising application potential in the electrocatalytic degradation of AYR wastewater.

Declarations

Ethical Approval

All analyses were based on previous published studies, thus no ethical approval and patient consent are required.

Consent to Participate and Publish

All participants provided informed verbal consent. They all agree to publish.

Authors Contributions

Bohao Yu is responsible for experimental design, Zhenyu Zhan is responsible for data analysis, Yunbo Yang and Xuanbing Wang are responsible for instrument operation, Ruidong Xu is responsible for providing overall thinking.

Funding

This work was supported by the Applied Basic Research Foundation of Yunnan Province and Yunnan Normal University Doctoral Research Project. Also we are grateful for the help of Analytical and Testing Center of Southwest University of Science and Technology.

Competing Interests

The authors do not have any possible conflicts of interest

Availability of data and materials

All data, models, or code generated or used during the study are available in a repository or online in accordance with funder data retention policies.

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Figures

Figure 1

Simulation diagram of PbO_2 phase growth by electrodeposition in methanesulfonic acid

Figure 2

SEM photos of Pb-0.6%Sb/ α -PbO₂/ β -PbO₂-MnO₂ composite anodes prepared at different MnO₂ & β -PbO₂ co-deposition time (a: 30 s, b: 2 min, c: 5 min, d: 30 min, e: 60 min)

Figure 3

EDS data of Pb-0.6%Sb/ α -PbO₂/ β -PbO₂-MnO₂ composite anodes prepared at different MnO₂ & β -PbO₂ co-deposition time (a: 30 s, b: 5 min, c: 30 min)

Figure 4

Effects of MnO_2 co-deposition on the performance of composite anodes

Figure 5

Effects of composite anodes with different MnO₂ content on COD removal efficiency (a) and degradation efficiency (b) of AYR.

Figure 6

UV-Vis spectra change with electrolysis time for electrocatalytic degradation of AYR

Figure 7

Electrochemical degradation pathway simulation of AYR.