



Electrodeposition of PbO₂ on Ti Substrate in Alkaline Solution: Influence of Fluoride Ions Addition

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Titanium-lead dioxide electrode (Ti/PbO₂) has been synthesized by the method of anodic electrodeposition from alkaline solutions with a concentration variation of NaF (0.0048-0.0238 M). The results indicated that the presence of F⁻ ions affects the rate of formation of PbO₂ which may impact on its properties. SEM analysis showed that the PbO₂ film has nanorod-shaped surface morphology with a diameter of 50 nm and a length of 500 nm. X-Ray diffraction study showed that the material was composed of a mixture of α -phase (021; 200; 311) and β -phase (002; 211; 220; 112) whose intensity decreases with an increase on the addition of NaF. Cyclic voltametry results showed a correlation of the electrocatalytic activities with the intensity of phase. The electrocatalytic performance of PbO₂ is more likely to be affected by the β -phase (221 and 220) than by the α -phase (021). In other words, the electrocatalytic activity of PbO₂ is influenced more by the surface area of the conductivity properties.

Key Words: Lead dioxide, Fluoride ions, Electrodeposition, Electrocatalytic, Nanorod.

INTRODUCTION

Lead dioxide (PbO₂) is widely used for producing ozone^{1,2}, for converting organic contaminants electrochemically³⁻⁷, as electrochemical sensors and as electrosynthesis⁸. The advantage of PbO₂ is that it is a low-cost material and it has a stable character physically and chemically as well as a good electrocatalytic activity⁹.

Synthesis of PbO₂ has been done by the method of electrodeposition in acid electrolytes^{1,9-11}. The potential of electrodeposition required is very high *i.e.*, $E = 1.7 \text{ V}^{1,12,13}$ so that a substrate oxide could be formed¹⁴. In addition, the acid method requires more Pb species reactants, *i.e.*, $> 0.1 \text{ mol/L}^{2,6,12,15}$. PbO₂ electrodeposition can also be performed in alkaline condition at low potential and the amounts of Pb species required are fewer than in acid condition^{16,17}. The interesting facts show that acid electrodeposition is more predominant to produce PbO₂ with orientation to the β -phase, while base electrodeposition is more to the α -phase¹².

Electrodeposition is a synthesis method of PbO₂ which is easily controlled by several optimum parameters¹⁸⁻²⁰. Electrodeposition potential and temperature are parameters that can affect the kinetics and diffusion factors¹⁰. Lowering the potential and the increasing temperatures will increase the crystal size and its crystallographic orientation for both α -phase and β -phase.

In this paper we studied the effects of adding F⁻ ions on the formation of PbO₂ by electrodeposition in alkaline condition and the relationship between the properties of the material synthesized with electrocatalytic activity. The addition of F⁻ ions will serve as a regulator of substance in the electrodeposition process based on the fact that the nature of the F⁻ ions is highly electronegative so that it is easy to move to the anode surface without undergoing oxidation reaction because the oxidation potential required is high, which is $E = 2.85 \text{ V}^{21}$. More interesting facts show that the morphology and composition of α -phase and β -phase of PbO₂ can be controlled by the presence of F⁻ ions.

EXPERIMENTAL

All reagents were analytical grade (Merck) and used as received. The substrate Ti (ASTM B.265 Gr.1) was used to deposit PbO₂. Deionized water was used to prepare all solution.

Synthesis of Ti/PbO₂ electrode: Titanium metal plate (4 cm × 0.5 cm) was smoothed using sandpaper and water solvent followed by silicon paste, soaked in a 30 % solution of NaOH and vibrated for 0.5 h in that solution, then with HCl of 3.75 % for 10 min and finally vibrated (Branson 2510E-MT) in acetone for 0.5 h. The plate was heated at a temperature of 60 °C for 0.5 h so that the Ti plate becomes dry. Then 7 g

NaOH was diluted with aquades and cooled in water. It was mixed with the solution of $\text{Pb}(\text{NO}_3)_2$ and NaF which were prepared from 1.2 g of $\text{Pb}(\text{NO}_3)_2$ and NaF solution containing 0.01 g of NaF. The volume of the solution was then set to 50 mL with aquades then stirred with a magnetic stirrer until homogeneous. Electrodeposition was carried out with the DC power supply (GW INSTEK sps-3610) in voltage from $E = 0.5$ -3.4 V for 2 h and Ti plate as auxiliary electrode. Electrode-synthesis was repeated for NaF with the weight of 0.02, 0.03, 0.04 and 0.05 g with the same procedure above.

Physical characterisation: The PbO_2 layers were characterized for their surface morphologies by SEM and the structure of the crystal by XRD. SEM images were carried out on a JEOL (JSM-6360LA) system operating at 20 keV. XRD was performed using a Shimadzu Lab. X 6000 with automatic data acquisition using CuK_α radiation ($\lambda = 0.15406$ nm) and working at 40 kV/30 mA.

Electrocatalytic testing of Ti/ PbO_2 electrode: The electrodes prepared above were removed from their electrodeposition solution and carefully rinsed. Then, they were introduced in a three-electrode cell containing 0.3 M NaCl. A Pt rod was used as auxiliary electrode and an Ag/AgCl system as reference electrode. The electrocatalytic measurements were carried out using a 757 VA Computrace apparatus connected to an IMT 102 interface, controlled by a personal computer through the VoltaMaster 2 software. The electrode geometric area is 2 cm^2 .

RESULTS AND DISCUSSION

Synthesis of Ti/ PbO_2 electrodes: The process of lead dioxide deposit from a solution of 0.0725 M $\text{Pb}(\text{NO}_3)_2$, 3.5 M NaOH and (0.0048-0.0238 M) NaF occurred easily. It is known of the response current density as function of time like shown Fig. 1. The nucleation and growth of the lead dioxide deposit increased rapidly in the early stage then declined slowly during the electrodeposition process. Experimental observations indicated the occurrence of current density increasing highly at 60-300 s with the potential of $E = 0.9$ up to 2.2 V. It represent that this stage is influenced by the migration force that will accelerate the mass transfer²². A strong increase of current density on this voltage indicates that the formation of PbO_2 in alkaline conditions requires critically low potential. This is consistent with the Pourbaix diagram research as demonstrated Carr and Hampson¹³; Rajeshwar and Ibanez²³. After that stage, the formation of PbO_2 declines slowly. Increasing of potential does not increase of the PbO_2 formation. This trend indicates that PbO_2 formation is more predominantly influenced by concentration gradient as explained by Fick's first law²².

The addition of F^- ions in the electrodeposition process affects the speed of PbO_2 formation. The metal oxide formation was likely to increase on the addition of NaF from 0.0048 up to 0.0095 M. This shows that Na^+ ions and F^- ions will serve as an electrolyte or as a carrier of charge. A different phenomenon was shown that when the addition of NaF is larger (0.0143 up to 0.0238 M), the formation of PbO_2 tended to decrease. This is possible because of the competition by the force of migration between $\text{Pb}(\text{OH})_3$ and F^- which are opposite in charge with the substrate of the anode (Ti). The nature

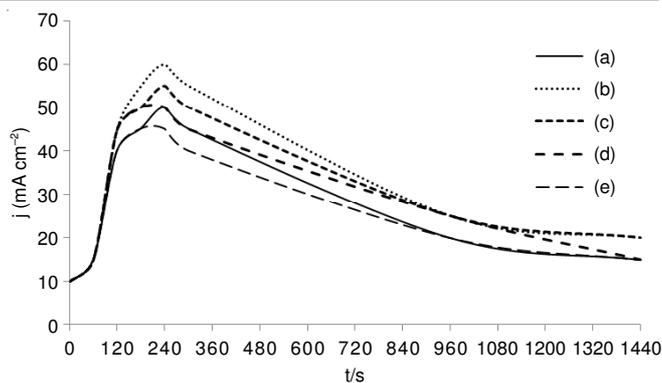
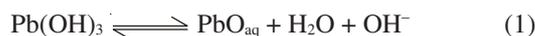


Fig. 1. Chronoamperometric curves for PbO_2 electrodeposition in 0.0725 M $\text{Pb}(\text{NO}_3)_2$, 0.35 M NaOH and different concentration of NaF (a) 0.0048 M, (b) 0.0095 M, (c) 0.0143 M, (d) 0.019 M, (e) 0.0238 M at Ti substrates by applying a potential of 0.5-3.4 V

of the high electronegativity and molecule size of the F^- causes the speed of migration of this ion to be much higher than the $\text{Pb}(\text{OH})_3$ migration speed.

PbO_2 -forming reaction is strongly influenced by the amount of H_2O that is absorbed on the surface of Ti substrate, as the following equation¹³:



The presence of F^- ions can replace the H_2O molecules which are absorbed on Ti so that the formation of PbO_2 will decrease with the increasing concentrations of NaF.

Characterization of the PbO_2 morphology: The surface morphology of the PbO_2 film from the synthesis results was analyzed using SEM (Fig. 2). PbO_2 film was composed of spherical materials with a diameter of *ca.* 20-30 μm which aggregate with each other forming the larger size (*ca.* 80-100 μm). At the magnification of 20000 \times , the PbO_2 film consists of nano-sized, rod-shaped materials that look like roots or fibers (diameter 50 nm and length 500 nm).

The change in the concentration of NaF affects the morphology of the PbO_2 form. The increasing concentrations of NaF make the PbO_2 film have a more homogeneous surface contour with a smaller diameter (Fig. 2e). Declining PbO_2 formation rates also lead to a more oriented surface texture. It is important to note that the decrease in deposition velocity will lead to a more orderly arrangement of material, more uniform and more oriented^{11,16}.

The fiber or rod structure of PbO_2 may have been resulted from the cation Pb complexes in the electrodeposition solution. It has been reported by Campbell *et al.*²⁴ and Delahay *et al.*²⁵, that PbO can be dissolved in alkaline solution in the form of HPbO_2 or polynuclear complex shapes so that the formation of PbO_2 becomes slow. At higher current density solid oxide may be precipitated at a certain distance from the electrode surface due to the increase in concentration of the cation complex. Agglomeration of each deposition on the coating of surface electrode will cause the contour of surface to be randomly oriented. At high currents it can also cause oxidation of HPbO_2 - PbO_2 in the solution and the oxidation of H_2O - O_2 that occur simultaneously¹⁶.

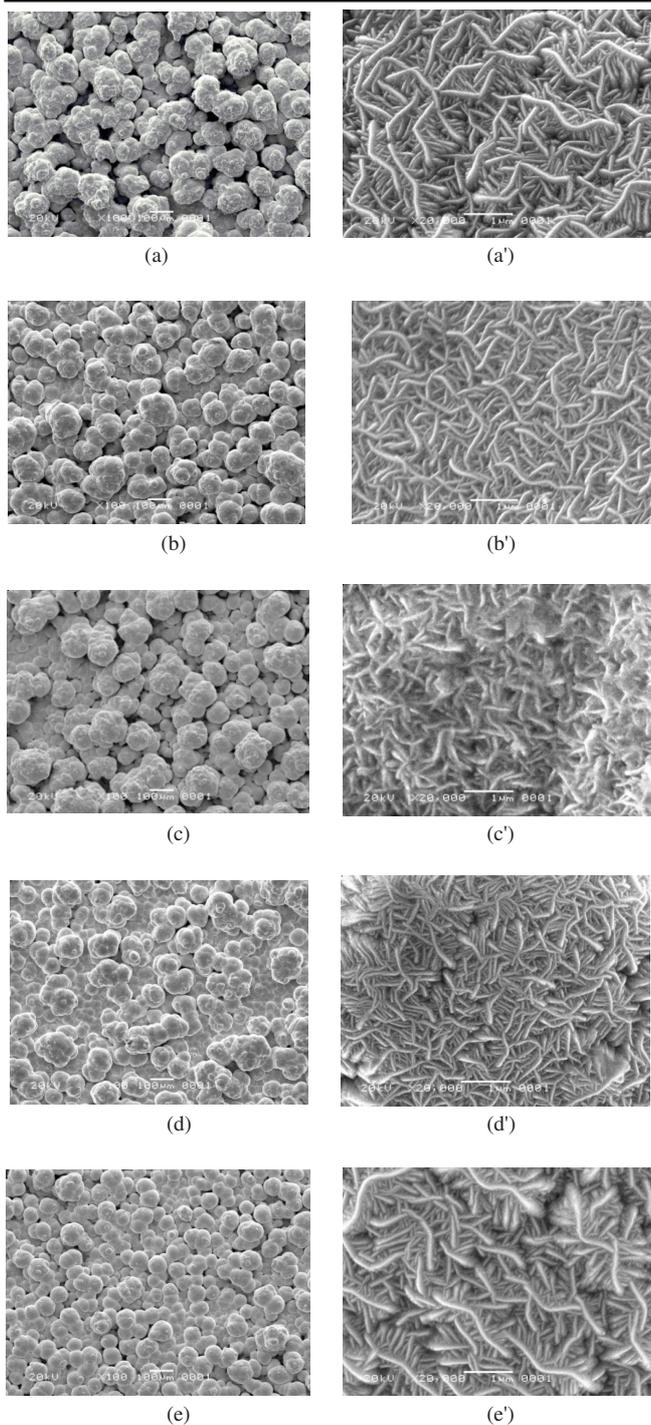


Fig. 2. Scanning electron microscopy images of the synthesized PbO₂ films from a solution containing 0.0725 M Pb(NO₃), 0.35 M NaOH and (a) 0.0048 M, (b) 0.0095 M, (c) 0.0143 M, (d) 0.019 M, (e) 0.0238 M NaF. Overview at the magnification of 100 \times (a, b, c, d, e) and 20000 \times (a', b', c', d', e')

Identification of the PbO₂ structure: The effect of electrodeposition conditions (variations in the concentration of NaF) on the crystallography has been studied by X-ray diffraction. To avoid the influence of the substrate area (Ti), the electrodeposition was performed on Ti width which was constantly maintained.

The XRD patterns show the existence of well-crystallized sample. The diffraction lines were indexed according to JCPDS-ICDD data²⁶ and the results are presented in Fig. 3.

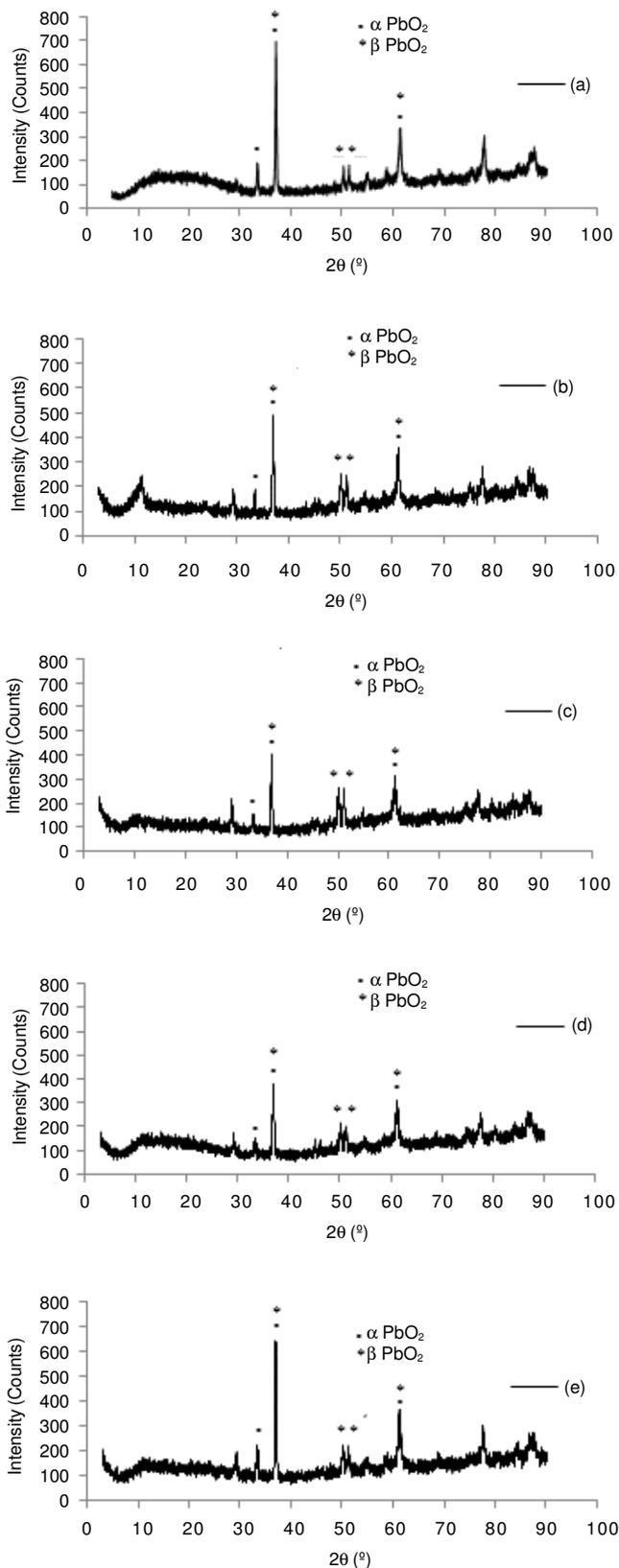


Fig. 3. Diffraction patterns of the PbO₂ films synthesized from a solution containing 0.0725 M Pb(NO₃), 0.35 M NaOH and (a) 0.0048 M, (b) 0.0095 M, (c) 0.0143 M, (d) 0.019 M, (e) 0.0238 M NaF. Symbols represent the ICDD file

All the results of PbO₂ phase synthesis are a mixture of α -phase (orthorhombic) and β -phase (tetragonal). These results are in

contrast to the results of Chen *et al.*¹⁶ which only consists of α -phase. This is possible because of the difference in concentration of NaOH used. Chen *et al.*¹⁶ synthesized PbO_2 in 4 M NaOH solution, while in this study we used 3.5 M NaOH. A smaller concentration of NaOH would accelerate the formation of PbO_2 because the reaction equilibrium 1 (reaction equation above) will tend to the right or PbOaq formation will be faster¹⁷.

Interestingly, we note a change in the relative intensity of β -phase (211 at 49.97° and 220 at 51.04°) which depends on the concentration of NaF. The intensity of the β -phase decreases with the increase in the concentrations of NaF which are used (Fig. 3b-e). This phenomenon is caused by the kinetics factor, where the increase in the concentrations of NaF results in the decrease in the kinetics of formation of PbO_2 . Velinchenko *et al.*¹⁰ reported that the lowering of the kinetics factor will reduce the intensity of the α -phase (021; 200) and β -phase (211; 220). The decrease in phase intensity will cause the grain size to become smaller (Fig. 2e). However, differences in the intensity do not provide sufficient evidence of the existence of an amorphous phase.

Electrocatalytic ability of Ti/ PbO_2 electrode: A PbO_2 electrode is generally used as an active material on the positive electrode of an electrochemical cell⁹. Further investigations have shown that the PbO_2 is a catalytic anodic material¹⁷. More detailed information about the relationship between the catalytic properties of PbO_2 and their characteristics is certainly a very interesting thing to uncover. Electrocatalytic performance measurement on the Ti/ PbO_2 with the difference in its phase intensity can add more information on such relationships.

Cyclic voltammetry studies were performed using the Ti/ PbO_2 electrode prepared on the addition of NaF from 0.0048 up to 0.0238 M. Fig. 4 shows the voltammograms obtained in 0.3 M NaCl aqueous solution at a sweep rate of 100 mV/s, voltage step 0.01 V, start potential at $E = 0.5$ V and end potential at $E = 2.5$ V. All voltammograms data shows an irreversible reaction, which means that the Cl^- oxidation can be followed a chemical reaction to produce another species such as HClO or ClO^- . According to the literature²⁷⁻³⁰, the predominant active chloride species in the conditions are Cl_2 and HClO by a mechanism as follows:

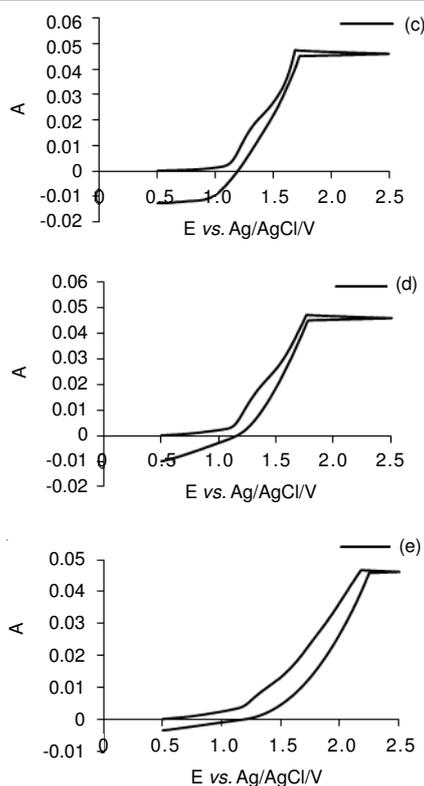
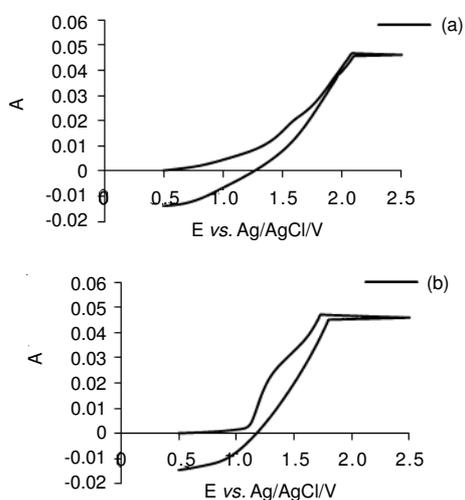


Fig. 4. Cyclic voltammograms, obtained in 0.3 M NaCl for a Ti/ PbO_2 electrode prepared from a solution containing 0.0725 M $\text{Pb}(\text{NO}_3)_2$, 0.35 M NaOH and (a) 0.0048 M, (b) 0.0095 M, (c) 0.0143 M, (d) 0.019 M, (e) 0.0238 M NaF. Sweep rate 100 mV/s. Electrode geometric area = 2 cm^2



These reactions tend to occur because the pH of solution is 7, in which the HClO species is more dominant as demonstrated⁷. The above reaction will be advantageous particularly in the electrochemical application of pollutant degradation because the oxidation potential of HClO is greater than Cl_2 .

Voltammogram data in Fig. 4 also shows a high anodic current wave *i.e.*, $j = 0.0125 \text{ A/cm}^2$ with a center anodic wave at $E = 1.3$ V. This potential accords with the oxidation potential of Cl^- , based on the equation $j = nFv$ ²² so the amount of current density is proportional to the reaction that took place. The sharp increase in current after 1.7 V is due to the oxidation of H_2O into oxygen⁵.

Cyclic voltammetry measurements show the relationship between electrocatalytic properties and the α -phase and β -phase intensity when analyzed according to Figs. 3 and 4 above. The electrocatalytic ability decreases, *i.e.*, $j = 0.0125$ - 0.008 A/cm^2 (Fig. 4b-d) when the intensity of α -phase (021) and β -phase (221 and 220) also decreases (Fig. 3b-d). Different facts occur in Figs. 4a and 4e, where the electrocatalytic activity is low, *i.e.*, $j = 0.0045 \text{ A/cm}^2$ or $j = 0.004 \text{ A/cm}^2$ where as the intensity of α -phase (021 and 200) and β -phase (002) is high. The β -phase (221 and 220) remains low (Figs. 3a and 3e). This phenomenon can be the basis of the conclusion that the electrocatalytic performance of PbO_2 is more likely to be affected by the β -phase (221 and 220) than by the α -phase (021). In other words, the electrocatalytic activity of PbO_2 is

influenced more by the surface area of the conductivity properties.

The trend of higher electrocatalytic activity by β -phase was also reported by Ruetschi and his co-woker³¹ although on different systems. Tafel slope measurement results indicate that on the stage determining the reaction rate on the α -phase involves two-electron transfer, in contrast to the β -phase which involves only a single-electron transfer.

Conclusion

The presence of F⁻ ions has significantly influenced the process of PbO₂ formation. The rate of formation of lead dioxides is likely to increase on the addition of NaF with low concentrations (0.0048-0.0095 M). An addition of more than those can cause the opposite tendency because of the occurrence of migration-force competition between Pb(OH)₃ and F⁻ as well as the substitution factor of H₂O by F⁻ on the surface of Ti. The changes in the NaF concentration affect the morphology of PbO₂. If the concentration of NaF increases, then the contour of the surface will be more homogeneous with a relatively smaller diameter of the material. SEM analysis indicates a nanorod shape that resembles the root or fiber as a constituent of this metal oxide. The PbO₂ is formed from a mixture of α -phase and β -phase, whose intensity changes with the addition of NaF. The intensity of the β -phase (221 and 220) tends to decrease with the increase in the concentrations of NaF. Electrocatalytic activity of PbO₂ is more influenced by the β -phase than the α -phase.

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