# The Effect of Electrocatalytic Activity and Crystal Structure of $PbO_2$ Surfaces on Polyphenylene Oxide (PPO) Production in Acetonitrile

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The crystallographic nature of $PbO_2$ films was changed by optimizing the electrolysis conditions in an electrodeposition solution of $PbO_2$. These $PbO_2$ films were then used to prepare PPO films. It was determined that $\alpha$ and $\beta$ modifications, and relative degrees of crystallinity had profound effects on the electrocatalytic performance of $PbO_2$ films in the production PPO films.

**Key Words:** $\alpha$-$PbO_2$, $\beta$-$PbO_2$, phenol, electrocatalysis, PPO.

## Introduction

$PbO_2$ has been extensively used as an electrocatalyst for the degradation of various organic species in aqueous solution,[1−3] production of ozone,[4−5] anodic oxygen transfer reactions,[6−10] and polymerization.[11,12] $PbO_2$ is the cheapest metal-oxide electrode and provides a good alternative to more costly materials, such as platinized titanium or mixtures of precious metal oxides on titanium. It is chemically inert, stable, and highly conductive. $PbO_2$ comes in 2 crystallographic forms ($\alpha$ and $\beta$). $\alpha$-$PbO_2$ has an orthorhombic structure, whereas $\beta$-$PbO_2$ has a tetragonal structure. $\alpha$ and $\beta$-$PbO_2$ can be distinguished from each other by means of X-ray diffraction patterns, which are used to estimate the proportions of the polymorphs in a mixture of the two.[13] The degree of crystallinity or the quantity of the amorphous form can be estimated by the half-width of the diffraction lines. The half-width decreases as the degree of crystallinity increases.[14] The properties of $\alpha$ and $\beta$ modifications of $PbO_2$ are different. $\beta$-$PbO_2$ has a porous structure, whereas $\alpha$-$PbO_2$ has a compact structure. It is known

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that $\beta$-PbO$_2$ is more stable in acid solutions than $\alpha$-PbO$_2$ and that $\beta$-PbO$_2$ has greater conductivity than $\alpha$-PbO$_2$.[15,16] The surface areas of both modifications are also different. BET surface area measurements indicate that $\beta$ modification results in a larger surface area than $\alpha$ modification.[17]

It was proposed that the crystallographic nature of PbO$_2$ significantly influences its electrocatalytic activity. Ho et al.[18] used impedance and potential relaxation methods to conduct a comparative analysis of adsorbed reaction intermediates—OH and O—on $\alpha$ and $\beta$ allotropic forms of PbO$_2$. They concluded that the structure affected both the behavior of adsorbed species and electrocatalytic activity in O$_2$ evolution. The effects of surface structures were also evident in the work of Pavlov and Monahov,[19,20] who proposed a mechanism of O$_2$ evolution on Pb/PbO$_2$ electrodes in sulfuric acid. Compton et al.[21] conducted an AFM study of PbO$_2$ surfaces and correlated the observed morphology with electrochemical activity on glucose oxidation. Velichenko et al.[22] changed the crystallinity of PbO$_2$ surfaces by changing the temperature of the electrolysis solution, and determined that increasing the temperature resulted in the formation of better crystalline PbO$_2$ surfaces and that better crystalline PbO$_2$ films had better electrochemical activity.

We recently reported that the polymorphic composition and relative degree of crystallinity of PbO$_2$ films can be controlled by optimizing different electrochemical parameters, such as water concentration, acidity, Pb$^{2+}$ concentration, and applied current density, during the electrodeposition of PbO$_2$ surfaces.[23]

PPO is a widely studied polymer. It can be used in several areas, including sensors, corrosion protection, water pumps, automotive and electrical components, and foams in superior foam sandwich structures.[24−26] The properties of PPOs depend largely on electropolymerization conditions, such as solvent, electrolyte, pH, monomer concentration, and metallic substrate.[27] In the present study PPO films were produced from a phenol solution by using PbO$_2$ surfaces. Efforts were directed at correlating the electrocatalytic activity of the PbO$_2$ surfaces with their crystallographic nature.

# Experimental

## Chemicals

Acetonitrile was purified as described elsewhere.[28,29] Tetrabutylammonium perchlorate (TBAP) was prepared by reacting a concentrated perchloric acid solution (Analar) with a 40% aqueous solution of tetrabutylammonium hydroxide (Aldrich). Lead perchlorate (Pb[ClO$_4$]$_2$) was prepared by reacting concentrated perchloric acid with lead monoxide (Analar). Double distilled water was used for all experiments.

## The Electrochemical Cell and Instrumentation

We used was a 3-electrode-type electrochemical cell, with separate compartments for the reference electrodes and the counter electrode (platinum spiral and lead). All electrochemical experiments were carried out under a nitrogen atmosphere. The electrochemical instrumentation consisted of a PAR model 173 potentiostat-galvanostat coupled to a PAR model 175 universal programmer and a PAR model 179 digital coulometer, as well as a PAR model 273 potentiostat-galvanostat.

## Preparation of $PbO_2$ Films

$PbO_2$ films with different $\alpha$ and $\beta$ modifications, and relative degrees of crystallinity were prepared according to a previously described procedure.[23] $PbO_2 \alpha$ and $\beta$ modifications were distinguished from each other by means of X-ray diffraction patterns; these patterns were used to estimate the proportions of polymorphs in mixtures of the two. The relative degree of the films' crystallinity was calculated using the half-width values of the XRD lines; the half-width decreased as the relative degree of crystallinity increased.

The films were 40 $\mu$m thick. The adherence of the $PbO_2$ layers to the Pt substrates was extraordinary; only chemical treatment was able to remove these layers. The surfaces were also smooth and homogeneous.

## Analysis of Phenol and PPO

The GC-MS technique was used to monitor the consumption of phenol in the polymerization solution. The GC-MS instrument consisted of a Hewlett-Packard model 6890 gas chromatograph combined with a Hewlett-Packard model 5972 A MS detector.

The PPO samples for FT-IR analysis were prepared as follows: the PPO-deposited electrode (after electrolysis) was removed from the electrolysis solution and dipped into an acetonitrile solution several times to remove the supporting electrolyte residue. Then, the PPO-coated electrodes were mechanically peeled off and powdered PPO samples were pelleted under high pressure. FT-IR analysis was conducted with a Bruker-type Vector model spectrophotometer.

Elemental composition of the PPOs was determined using Carlo Erba EA1108 elemental analysis instruments. XRD analysis was conducted using a General Electric XRD instrument with Ni-filtered 40 kV Cu K$\alpha$ radiation

# Results and Discussion

Oxidation of the phenol forms of the phenoxy radical ($C_6H_5O^\bullet$) occurred either by reaction with a hydroxyl radical ($OH^\bullet$) or by direct electron transfer.

$C_6H_5OH + OH^\bullet \rightarrow C_6H_5O^\bullet + H_2O$ (1)

$C_6H_5OH \rightarrow C_6H_5O^\bullet + H^+ + 1e^-$ (2)
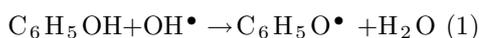
These phenoxy radicals may react with OH radicals and can form benzoquinone, and further reaction of OH radicals with benzoquinone leads to the formation of aliphatic products, such as maleic acid, fumaric acid, and $CO_2$, in the presence of water. However, in the absence of water, these phenoxy radicals react with each other and PPO formation occur as follows:

$C_6H_5O^\cdot + C_6H_5O^\cdot \rightarrow Dimer$ (then polymers) (3)

As can be deduced from the above mechanism, the acetonitrile to water ratio has a critical role in phenol decomposition. It was reported in one of our previous studies that phenol can be completely degraded into aliphatic products on $PbO_2$ surfaces in aqueous solutions.[3] When a suitable quantity of acetonitrile is added to water, benzoquinone can be obtained.[30] A nonaqueous environment was chosen for polymerization and acetonitrile was used. To polymerize phenol, constant current electrolysis (10 mA/cm$^2$) was applied via $\alpha$-$PbO_2$ and $\beta$-$PbO_2$ electrodes from a solution containing 20 mM phenol and 100 mM TBAP in acetonitrile. The

solid products of electrolysis were analyzed by elemental analysis. The Table provides the elemental analysis results of each product, as well as the theoretical values for PPO. As can be seen, the C/H ratios of the products were very close to the ratio for PPO; however, C/O ratios were quite different. It is also clear that total percentage of C, H, and O did not equal 100% for the products of the $\alpha$ and $\beta$ modifications. On the basis of these data, it can be concluded that anion insertion $(ClO_4^-)$ into the polymeric backbone occurred and that this insertion caused deviations from the expected values.

**Table.** Comparison of elemental analysis results of PPO films that were formed on $\alpha$-PbO$_2$ and $\beta$-PbO$_2$ surfaces, with theoretical PPO values.

| Element | $\alpha-$PbO$_2$ % by weight | $\beta-$PbO$_2$ % by weight | PO % by weight |
|:---:|:---:|:---:|:---:|
| C | 51.1 | 46.6 | 77.4 |
| H | 3.7 | 3.4 | 5.4 |
| O | 40.1 | 32.5 | 17.2 |
| C/H | 13.8 | 13.7 | 14.3 |
| C/O | 1.3 | 1.4 | 4.5 |

FT-IR analysis of the PPO deposits was conducted. The spectra of each product were the same, except the peak intensities, and were similar to the spectra previously reported for PPO.[31] The spectrum for the product that formed on the $\beta$-PbO$_2$ surface from a solution containing 20 mM phenol and 100 mM TBAP is shown in Figure 1.
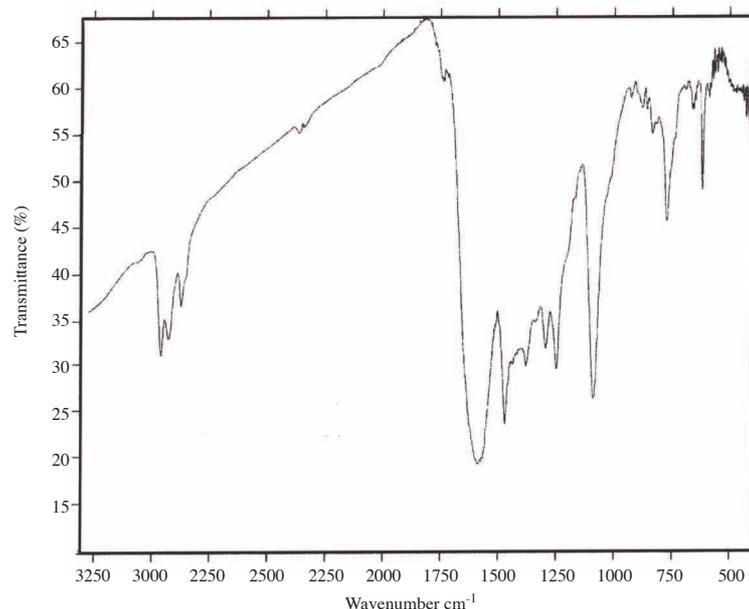


**Figure 1.** FT-IR results of PPO film that was formed on a $\beta$-PbO$_2$ surface.

Bands that appeared in the 700-850-cm$^{-1}$ region were aromatic out-of-plane C-H deformation vibrations. The band at 1530 cm$^{-1}$ corresponded to the aromatic C–C stretching vibration. The broad band at 900-1150

cm$^{-1}$ might be related to the ether C-O symmetric and asymmetric stretching vibration (-C-O-C- ring). Peaks at $625\,\mathrm{cm}^{-1}$ and $1100\,\mathrm{cm}^{-1}$ also prove that insertion of the counter-anion ($ClO_4^-$) into the polymeric backbone occurred. This counter-anion insertion was also verified using the TBAPF$_6$ electrolyte instead of the TBAP, by observing a peak around $830\,\mathrm{cm}^{-1}$, which can be attributed to the PF$_6^-$ anion.

Powder XRD analysis of the PPO deposits was also performed (Figure 2). XRD spectra were very different than the PbO$_2$ spectra reported by Abaci et al.,[23] which indicates that the quantity of PbO$_2$ in the PPO deposits was insignificant. High-intensity peaks could not be obtained because the PPO deposits were generally amorphous in character.
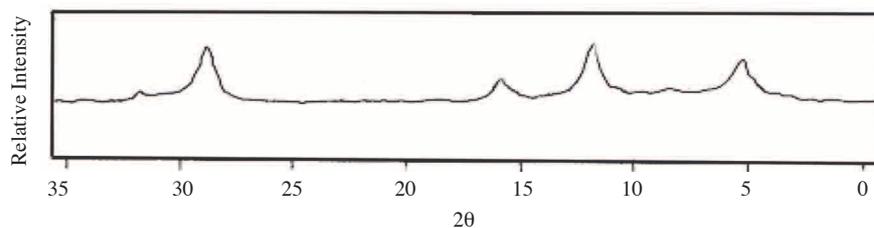


**Figure 2.** XRD results of PPO deposited from a solution containing 20 mM phenol and 100 mM TBAP in acetonitrile at $10\,\mathrm{mA/cm}^2$.

In order to investigate a possible correlation between the electrocatalytic activity of PbO$_2$ surfaces, and $\alpha$ and $\beta$ modifications, electrolysis was carried out for 60 min under the same conditions mentioned above; however, in this case, PbO$_2$ surfaces with varying amounts of $\alpha$ and $\beta$ modifications were used as working electrodes, and the consumption of phenol and the production of PPO were monitored. PbO$_2$ surfaces with varying amounts of $\alpha$ and $\beta$ forms were prepared by changing the water concentration, current density, electrolyte, and acid concentration in the electrodeposition solution of PbO$_2$, as described in our previous report.[23] Electrolysis results indicate that the rate of phenol consumption and current efficiency for PPO production were different for each PbO$_2$ surface.

As can be seen from Figure 3, current efficiency increased as $\beta$ modification increased in the PbO$_2$ composition; however, phenol remained in the solution after electrolysis increased in response to increased $\alpha$ modification of the PbO$_2$ surface. Both data can be used as an indication of lower electrocatalytic performance of the $\alpha$ surface. Improved electrocatalytic performance of the $\beta$ surfaces can be attributed to the larger surface area of $\beta$ modification, as compared to $\alpha$ modification, which has been experimentally proven.[17] An increase in the active surface area will cause a concurrent increase in the formation of phenoxy radicals, which will increase the conversion to PPO. The difference in conductivity, which is approximately 100-fold greater for the $\beta$ modification of PbO$_2$, could be another reason for the enhanced electrocatalytic activity of the $\beta$-PbO$_2$ films

The influence of the relative degrees of crystallinity of the PbO$_2$ surfaces on PPO production was also investigated. $\beta$-PbO$_2$ surfaces with different degrees of crystallinity were prepared according to a procedure previously given.[23] Electrolysis was carried out under the same conditions mentioned above, and the phenol remained in the solution and current efficiency was determined for each surface. The results are given in Figure 4.
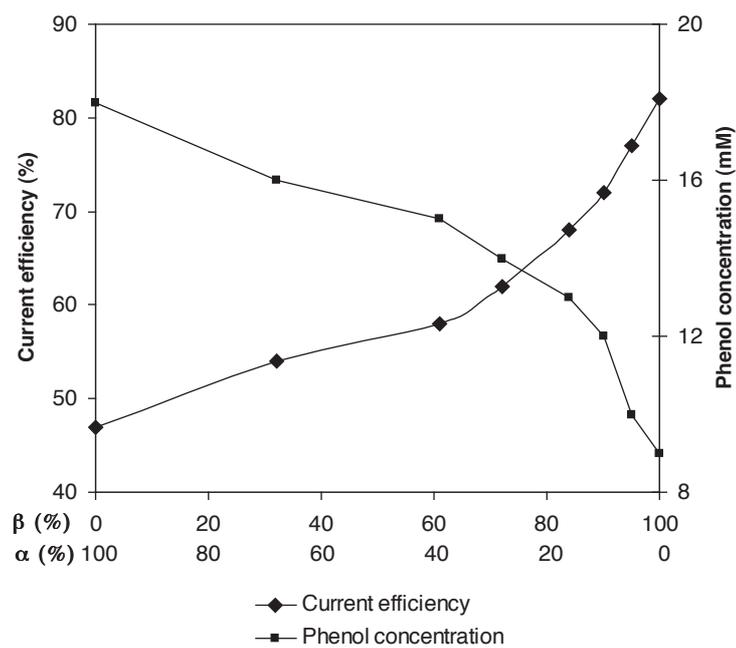
**Figure 3.** The change in current efficiency for PPO production and concentration of phenol that remained in the solution after 60 min of electrolysis, with respect to the polymorphic composition of $PbO_2$.
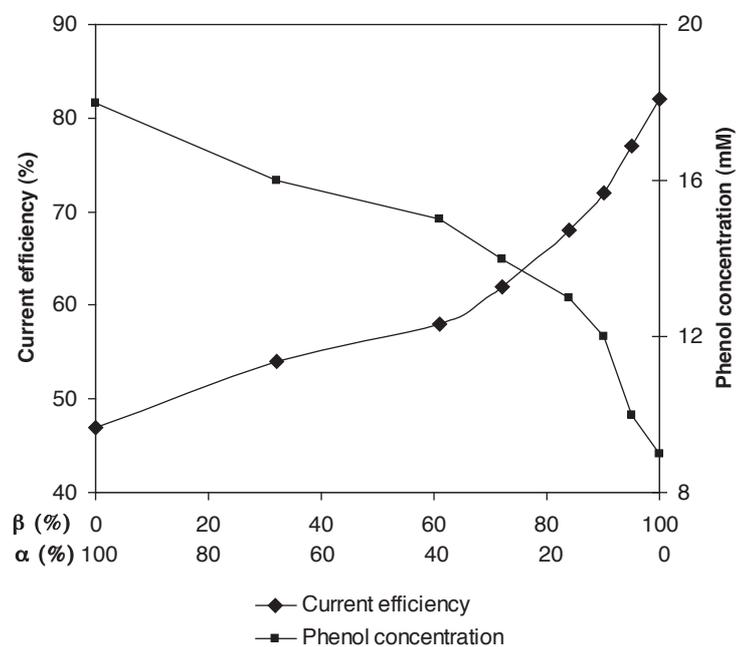


**Figure 4.** The change in current efficiency for PPO production and the concentration of phenol that remained in the solution after 60 min of electrolysis, with respect to the relative degree of crystallinity of $PbO_2$.

As can be seen, the increase in relative degrees of crystallinity of $PbO_2$ surfaces resulted in higher current efficiency. The concentration of phenol in the solution after electrolysis was higher for $PbO_2$ films with lower relative degrees of crystallinity. The cause of this effect could have been the relative inactivity of amorphous forms during polymerization. When the degree of crystallinity of $PbO_2$ increased, $PbO_2$ grain size increased and more defined crystals were obtained; these films had much better electrocatalytic activity.

It should be noted that a transition from a $\beta$ structure to a $\alpha$ structure may occur during electrolysis,[32] which could lead to a decrease in electrocatalytic activity. To test the possible transition, $PbO_2$ films were subjected to XRD analysis after electrolysis, but significant differences were not detected in the crystal structure of the $PbO_2$ films, with respect to their structure before electrolysis.

# Conclusion

It was determined that PPO can be produced on $\alpha$-$PbO_2$ and $\beta$-$PbO_2$ surfaces. The formation of PPO films was verified by electrochemical and spectroscopic techniques. It was also determined that the electrocatalytic performance of $PbO_2$ films changed in response to varying amounts of $\alpha$ and $\beta$ modification, and relative degrees of crystallinity.

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