Electrodeposition and Characteristics of Highly Ordered Macroporous β-PbO2 Electrodes

Yusairie Mohd

Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

Corresponding email: yusairie@salam.uitm.edu.my

Abstract

Highly ordered macroporous β-PbO$_2$ deposits were successfully produced on gold using polystyrene microsphere templates through electrodeposition technique from acidic nitrate baths containing Pb(II) ions using a constant current at 298 K. The morphology, catalytic activity and chemical stability of the deposits have been investigated. The morphology of the deposits has been analysed by Scanning Electron Microscopy (SEM). The catalytic activity of the deposited β-PbO$_2$ electrodes as anodes for dimethylsulfoxide (DMSO) oxidation has been investigated using cyclic voltammetry. The chemical stability of the electrode in acidic solution was monitored and observed by the SEM. The deposits were shown to be active for the oxidation of DMSO due to their high surface area. It was also found that decomposition of the electrodes occurred when they were kept standing in acidic solution containing an oxidisable organic compound (ie: DMSO) on open circuit.

Keywords: Macroporous β-PbO$_2$; Catalytic Activity; Stability; Electrodeposition

1.   INTRODUCTION

The development of electrolytic processes for the direct oxidation of organic compounds has been limited by the availability of anode materials for such application. Intensive research has been carried out with the aim of producing more efficient and stable anode materials [1-4]. In practice, the materials with large O_2 overpotential are commonly chosen as the anode. Metal oxides are probably the most interesting material for use in electrocatalysis. There are a number of oxides electrodes (RuO_2, IrO_2, SnO_2 and PbO_2) that may be used as anode materials for the oxidation of organic compounds [2 – 7].

PbO_2 clearly emerges as an attractive material as an anode for the direct oxidation of organic compounds due to its high oxygen evolution potential, low price, relatively stable under the high positive potentials required, stability at high temperatures and ease of preparation [1,2]. Its high overpotential for O_2 evolution permits application of potentials to ca. 2.0 V vs Saturated Calomel Electrode (SCE) in acidic media without vigorous O_2 evolution [8]. The PbO_2 electrodes have some disadvantages which they are corroded at high rate under reducing conditions and in some acids as well as their poor mechanical properties.

There are two forms of PbO_2; α-PbO_2 (orthorhombic structure) and β-PbO_2 (tetragonal structure) [9,10]. Electrochemically α-PbO_2 is readily prepared in weakly acidic or alkaline solution by the oxidation of Pb(II) whilst β-PbO_2 can be easily prepared by the electrooxidation of Pb(II) from acidic solutions usually of the perchlorate ($HClO_4$) or nitrate (HNO_3) [1,11-13]. β-PbO_2 also has higher stability in acid solutions than α-PbO_2 [14]. Different electrocatalytic activities of α and β forms of PbO_2 were reported in many studies [15-17]. It was concluded that porous structured PbO_2 with high degrees of crystallinity is more active and has influenced the electrocatalytic properties of the material. The porous structure of β-PbO_2 provides a greater surface area for anodic applications; therefore, the increased in the active surface area will increase the formation of OH radicals and will favour the degradation of organic compounds [18]. The advantage of using of such electrodes is their high surface area and high mass transfer coefficient and hence high rate of electrochemical conversion.

Casellato et al [19] have prepared porous PbO_2 electrodes with high surface roughness by anodic codeposition of β-PbO_2 particles with an electrochemically grown α-PbO_2 matrix; or called α-PbO_2 + β-PbO_2 composites. The steady-state oxygen evolution current density for the porous

α-PbO$_2$ + β-PbO$_2$ composites was found to be 15-18 times higher than α-PbO$_2$ deposits. Another approach of producing porous structure of PbO$_2$ is by using surfactants or emulsions. Blood et al [20] have prepared porous PbO$_2$ via anodic electrodeposition from a stationary high internal phase emulsion (HIPE) on carbon electrode substrates. The resulting deposits are organized in 10-50 μm high pyramidal aggregates, pitted with smaller pores. They reported that the deposits produced by this technique show at least a threefold increase in electroactive surface area per mass of deposit from those produced by normal or plain electrodeposition. Nevertheless, this type of porous PbO$_2$ is not uniform and not well organized. Also, it has still low electroactive surface area due to its low porosity.

Therefore, in this study, a colloidal templating electrodeposition technique was employed to produce highly ordered macroporous deposits with small spherical pores and high porosity in order to increase the electrochemically accessible specific surface area of the electrodes. Macroporous α- and β-PbO$_2$ films arranged in a highly ordered close-packed structure were prepared by electrochemical deposition through self-assembled polystyrene spheres (500 or 750 nm in diameter) assembled on gold and indium tin oxides (ITO) substrates via colloidal crystal templating technique [21]. The macroporous PbO$_2$ frameworks were found to be highly polycrystalline, self-supporting and free from defects.

Generally, the focus of research is the use of PbO$_2$ as an anode, thus efforts are directed at improving the electrode stability in aqueous solutions and electrocatalytic activity. In this study, the stability and catalytic activity of macroporous β-PbO$_2$ electrode prepared by electrodeposition via polystyrene spheres templates have been investigated using dimethylsulfoxide (DMSO) as a model substance in an acidic solution. The improvement of both properties of lead dioxide (PbO$_2$) as an anode material can be used in the oxidation of organic compounds especially for electrosynthesis and wastewater treatment processes.

2.0   EXPERIMENTAL

2.1   Reagents

All aqueous solutions were prepared with water from a Whatman Analyst purifier. All chemicals used were analytical reagent grade from Aldrich, BDH, Avocado or Fisher Chemicals.

2.2   Instrumentation

Voltammetric measurements were performed using a HiTek Instruments type DT2101 potentiostat. A Philips XL 30 SEM scanning electron microscope was used for morphology analysis. The SEM was also equipped with control software for energy dispersive analysis by X-rays (EDAX).

2.3   Preparation of Macroporous β-PbO$_2$ films

The macroporous films were prepared on gold substrate from plating solution containing 100 mM Pb(NO$_3$)$_2$ + 1 M HNO$_3$ using a constant current density 5 mA cm-2 for 75 s at 298K. The PbO$_2$ was grown through a colloidal templating electrodeposition technique which self assembled of polystyrene spheres were used as the template. This technique was employed to produce macroporous films with small spherical pores and high porosity in order to increase the electrochemically accessible specific surface area of the electrodes.

2.3.1   Assembly of Colloidal Templates

Monodispersed polystyrene latex spheres, with diameter of 500 nm ± 20 nm, were obtained from Alfa Aesar as 2.5% solutions in water. Polystyrene sphere templates were assembled by sticking a 0.8 cm internal diameter Teflon ring using double gloss nail's polish onto a polished gold electrode (purity = 99.9%, diameter = 0.008 cm^2). The gold substrate was previously polished on Buehler microcloth with alumina slurries (0.3 and 0.05 μm) and then rinsed with purified water until a mirror finish was obtained.

Approximately, 0.5 cm^3 of an aqueous suspension of the monodisperse polystyrene spheres diluted with water to 1 wt % was spread over the area of the substrate surrounded by the teflon ring. The sample was kept undisturbed in a saturated humidity environment for 2 to 3 days in order to allow the spheres to sediment on to the substrate. A clear water layer subsequently appeared on top of the deposited spheres and this water layer was then allowed to slowly evaporate. Once all of the water had evaporated, the Teflon ring was removed to leave a circular area covered by the template.

2.3.2   Electrodeposition of Macroporous β-PbO$_2$

Prior to electrodeposition process, a series of experiments using cyclic voltammetry was carried out to study the deposition and dissolution of PbO$_2$ at a gold electrode. All potentials recorded were measured versus saturated calomel electrode (SCE). The voltammograms were recorded from +0.40 to

+1.90 V and back to +0.40 V by scanning the potential at a scan rate 100mVs^{-1}.

An electrochemical cell consisting of three electrodes; working electrode (gold), reference electrode (SCE) and counter electrode (Pt), was used for the deposition of β-PbO$_2$ deposits. The plain and macroporous β-PbO$_2$ deposits were prepared at constant current from a solution containing lead (II) nitrate in nitric acid. The electrodeposition of macroporous β-PbO$_2$ deposits was assisted by the self-assembled polystyrene template prepared as in section 2.3.1. After the electrodeposition process, the polystyrene template was completely removed by soaking in toluene for 3 hours to leave behind a macroporous β-PbO$_2$ film with honey-comb structure.

2.4   Catalytic Activity and Stability Analyses

The catalytic activity and stability analyses were carried out to examine the characteristics and performance of the prepared PbO$_2$ electrodes. The catalytic activity of the PbO$_2$ electrodes was performed using the HiTek potentiostat and dimethyl sulfoxide (DMSO) dissolved in 1 M sulphuric acid was used as a test solution. Anodic oxidation of DMSO to DMSO$_2$ (dimethyl sulfone) was used for intercomparison of electrode activities because of DMSO is unreactive at substrate materials (eg: Au, Pt or Carbon). The oxidation of the organic compound can be written as in the following equation.

$$(CH_3)_2SO \quad + \quad H_2O \quad \rightarrow \quad (CH_3)_2SO_2 \quad + \quad 2H^+ \quad + \quad 2e^-$$

The stability analysis on the produced porous PbO$_2$ electrodes on gold substrate on open circuit was carried out by immersing the electrodes in sulfuric acid solution containing DMSO. The changes of the deposits after a period of time were observed by the naked eye and the change in morphology was examined by SEM. The stability of the produced PbO$_2$ electrodes during electrolysis or on load was also investigated by passing the current at constant potential (ie: above the formal potential for Pb^{2+}/PbO$_2$).

3.0   RESULTS AND DISCUSSION

Figure 1 shows a voltammogram of PbO$_2$/Pb^{2+} couple at a gold electrode in solution containing 100 mM Pb(II) + 1 M HNO$_3$ at a scan rate of 100 mV s^{-1}. There is a range of potential where current is higher on reverse scan than on forward scan at E > + 1.60 V. This is evidence for phase formation involving

nucleation and growth of PbO_2. The growth of the deposit is observed by a rapid increase in anodic current for E > +1.80V and continues until ca. +1.60 V on the reverse scan. The rapid increase in current at E > +1.80 V is due to the PbO_2 formation; simultaneously with the O_2 evolution as a competing reaction [22]. This observation is according to the electrochemical reactions in equations 3.1 and 3.2.

$$Pb^{2+} + 2H_2O - 2e \rightarrow PbO_2 + 4H^+ \qquad (3.1)$$

$$2H_2O - 4e \rightarrow O_2 + 4H^+ \qquad (3.2)$$
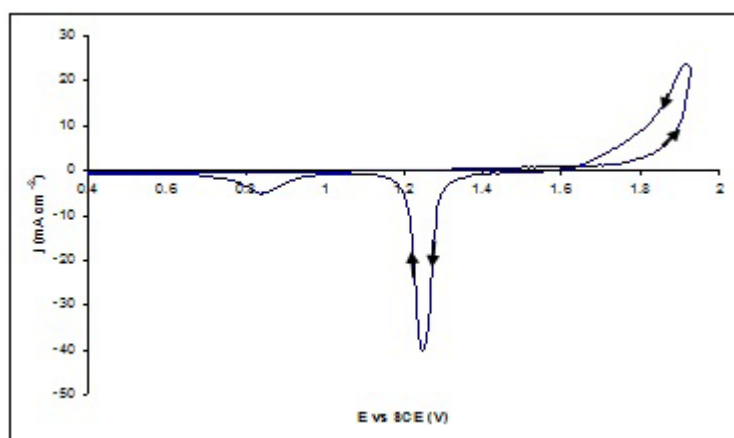
Figure 1: Cyclic voltammogram of gold electrode in 1 M nitric acid containing 100 mM Pb(II) at scan rate 100 mV s^{-1}.

Further on the reverse scan, a sharp symmetrical reduction peak appears at + 1.22 V which corresponds to the dissolution of PbO_2 back to Pb(II). The charge balance ($Q_{Cathodic}/Q_{Anodic}$) for the deposition and dissolution of PbO2 is more than 90% which indicates that the current efficiency for $PbO_2 \leftrightarrow$ Pb(II) is high and the contribution of O_2 evolution to the current is small during PbO_2 deposition in this solution.

It can also be seen in the figure that a small increase in anodic current occurs at E > +1.30 V and an additional peak at +0.85 V on the cathodic scan. These are believed to be the formation and reduction of AuO. A cyclic voltammetry was carried out for the Au disc in 1 M nitric acid solution without the presence of Pb(II) ions in order to confirm these conclusions. Both peaks (anodic and cathodic) appeared about the same potentials as when Pb(II) was

present as in Figure 1. This confirms the formation and dissolution of AuO on the gold surface as reported by several workers [23,24]. In the figure, a rapid increase in current is seen at E > +1.80 V on the anodic scan is due to O_2 evolution on the gold oxide surface. This voltammogram is consistent with those reported by several workers for the deposition and dissolution of PbO_2 at gold electrodes in acidic media [25-27] and results previously presented in nitric acid [28,29].

The electrodeposition potential of PbO_2 deposits was determined from the cyclic voltammetry as shown in Figure 1. A low current density (ie: 5 mA cm^{-2}) was chosen for the deposition which equivalent to E = +1.70 V. At this low current density, the electrodeposition of PbO_2 is controlled by electron transfer process which is a good condition in order to have a well-formed and uniform deposit. Figure 2 shows a SEM micrograph of a macroporous β-PbO_2 film electrodeposited on gold from plating solution containing 100 mM $Pb(NO_3)_2$ + 1 M HNO_3 using a constant current density 5 mA cm^{-2} for 75 s at 298 K. The deposition charge used was calculated to be 0.38 C cm^{-2}. The PbO_2 was grown through a template consisting of a self assembled multilayer of 500 ($\pm$ 20) nm diameter polystyrene spheres.
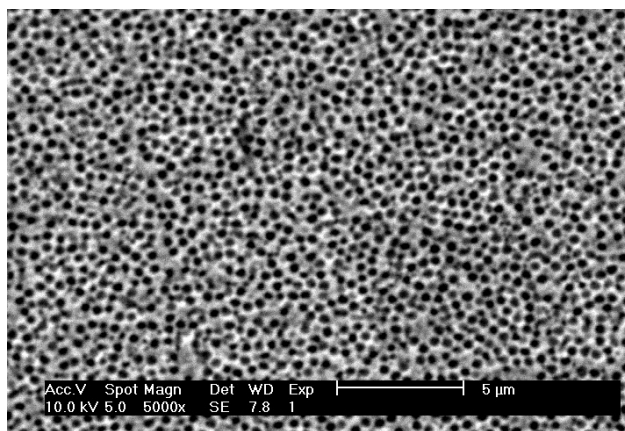
Figure 2: SEM image of a macroporous β-PbO_2 film grown at from 100 mM Pb(II) in 1 M HNO_3 using 5 mA cm^{-2} at 298 K through a template of 500 nm diameter polystyrene spheres.

The SEM image shows that the spherical voids, kept in the PbO_2 film after the removal of the polystyrene spheres by dissolution in toluene, are arranged in a well ordered and close packed structure; resulting in a honeycomb-like structure. From the figure, the measured average pore center

to pore center distance (or between black spots) from the image is ~ 500 nm, which is the same as the diameter of the original spheres used to prepare the templates. This indicates that the PbO_2 film does not suffer any shrinkage after the removal of the polystyrene template by the toluene.

The thickness of the film can be controlled by varying the charge passed for the deposition [30]. The macroporous film produced was good with respect to adhesion to the surface of the gold substrate. The colour of the porous film was dark brown. But when illuminated with white light, the film shows readily visible diffractive colours ranging from blue to red, depending upon the viewing angle. This is an indicator of the formation of a highly ordered pore structure within the film with a pore diameter in the range of the wavelength of visible light [31].

For comparison, a non-templated or plain PbO_2 film was deposited on an identical 1 mm diameter gold substrate using the same deposition solution and deposition charge as used for the templated or porous film. The thickness of the plain PbO_2 was calculated to be 0.5 µm corresponding to a faradaic efficiency for the deposition process of 90 %. Figure 3 shows the SEM image of the plain PbO_2. The image shows that the film is quite smooth with hemispherical crystals and non-porous.
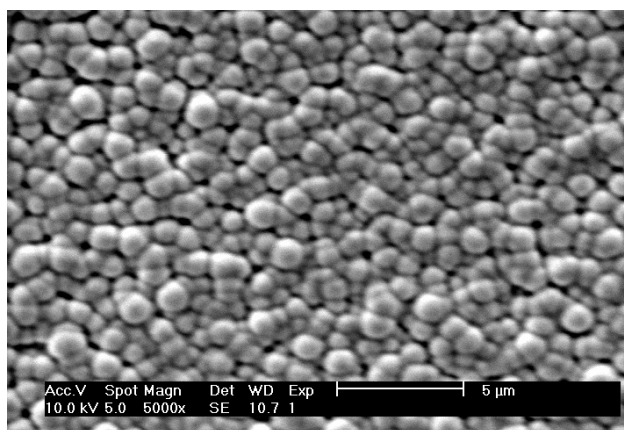
Figure 3: SEM image of a plain β-PbO_2 film deposited on gold from 100 mM Pb(II) in 1 M HNO_3 using 5 mA cm^{-2} for 75 s at 298 K. Deposition charge, Q : 0.38 C cm^{-2}. Magnification: 5000 x

It should be noted that a porous morphology can also be formed if high current density is used for a long time for the deposition of PbO_2. Nevertheless, the deposits produced were less ordered and outward growth as shown in Figure 4a (top view) and 4b (side view). For example the PbO_2 deposits prepared at 25 mA cm^{-2} for 600s at 333 K from solution containing 100 mM Pb(II) + 1 M HNO_3. Under these deposition conditions, the deposition rate is fast and at the same time some oxygen evolution occurs during the deposition leading to isolated nuclei of the PbO_2. These isolated nuclei are overlaid on a more uniform layer and the growth is favourable in vertical direction to form cauliflower-like crystals. Shen and Wei [32] reported that high current density employed is the main factor in the formation of high surface area or porous structured of PbO_2. This type of structure greatly increases its active area, which is a favourable property in view of a possible application as anode materials. Nevertheless, this porous deposit had poor adhesion on gold substrates which it was easily removed by scrapping with tissue.

(a)   (b)
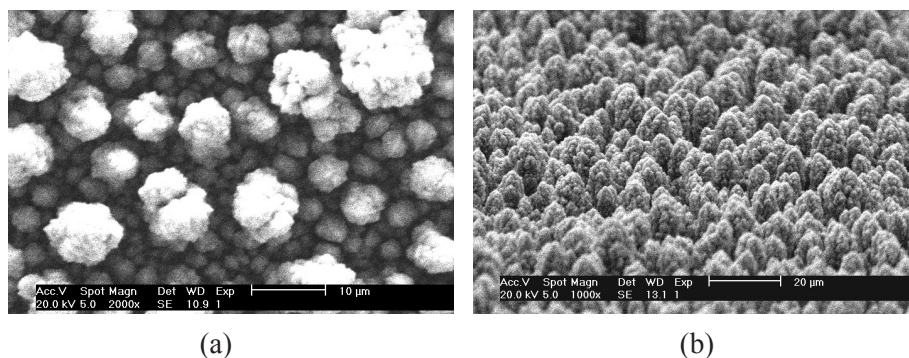
Figure 4: SEM images of β-PbO_2 from (a) top view (b) side view; prepared from 100 mM Pb(II) + 1 M HNO_3 using constant current density of 25 mA cm^{-2} for 600 s at 333 K.

The electrocatalytic activity of the macroporous (SEM image as in Figure 2) and plain or non-templated β-PbO_2 (SEM image as in Figure 3) for the oxidation of DMSO in sulfuric acid was investigated. Figure 5 shows voltammetric response of the two electrodes recorded at 50 mV s^{-1} in 1 M H_2SO_4 containing 50 mM DMSO.
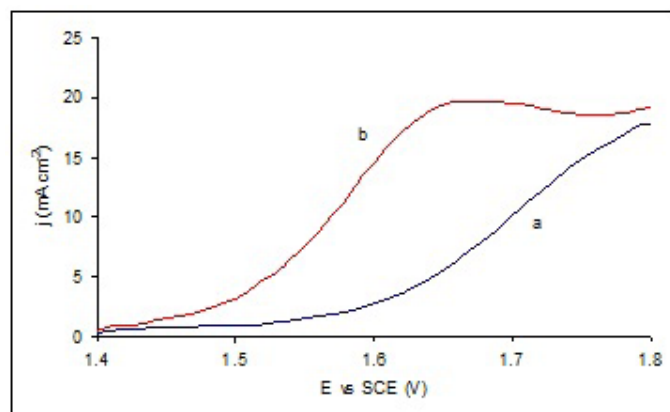
Figure 5: Voltammetric responses for DMSO oxidation on (a) plain and (b) macroporous β-PbO$_2$. Electrolytic solution: 50 mM DMSO + 1 M H$_2$SO$_4$. Deposition charge: 0.38 C cm^{-2}; deposition solution: 100 mM Pb(II) + 1 M HNO$_3$. Scan rate: 50 mV s^{-1}.

Although the two electrodes have the same amount of PbO$_2$ deposited on them, from the figure it can be seen that the catalytic activity for the oxidation of DMSO at the macroporous β-PbO$_2$ is greater than the plain β-PbO$_2$. E$_{1/2}$ potential for the DMSO oxidation occurs at 1.56 V at the macroporous β-PbO$_2$ and at 1.70 V at the plain β-PbO$_2$.

The macroporous β-PbO$_2$ film has higher surface area and more active sites for the oxidation of DMSO taking place than the plain β-PbO$_2$. The combination of the increased specific surface area of the PbO$_2$ electrodes together with the accessibility of active sites has greatly enhanced the electrocatalytic activity for DMSO oxidation. Unfortunately, this macroporous PbO$_2$ is not stable at open circuit in acidic solutions but not during electrolysis or when on load. At open circuit, the PbO$_2$ corrodes to Pb(II) and transforms to PbSO$_4$. The presence of DMSO accelerates the dissolution process and the transformation process of PbO$_2$ to PbSO$_4$ is fast. Figure 6 shows a SEM image of a corroded macroporous PbO$_2$ film with the presence of block particles with the shapes typical of lead sulfate (PbSO$_4$) after immersion in 50 mM DMSO + 1 M H$_2$SO$_4$ for 10 minutes. The presence of PbSO$_4$ was confirmed by EDAX analysis that showed high sulfur content. This is consistent with the stability study of the plain PbO$_2$ on open circuit as reported earlier by Mohd and Pletcher [33]. The plain β-PbO$_2$ films were less stable in open-circuit conditions and dissolved slowly in acids and reduced by DMSO in acidic solutions.
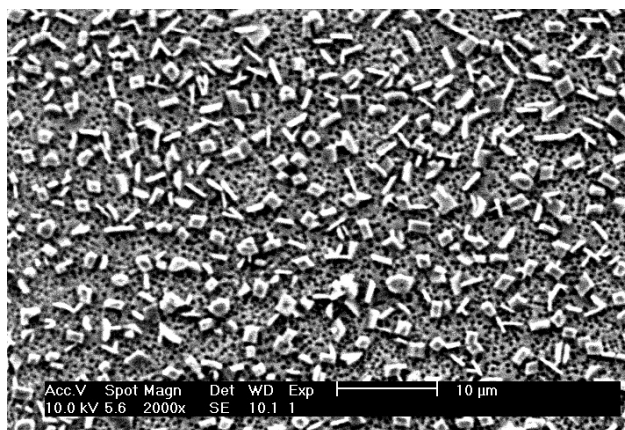
Figure 6: SEM image of a corroded macroporous β-PbO$_2$ film after immersion in 50 mM DMSO + 1 M H$_2$SO$_4$ for 10 minutes.

Hence, the active PbO$_2$ can be useful as anode materials for the oxidation of organic compounds if they are used at potentials positive to the formal potential of the PbO$_2$/Pb(II) couple and immediately washed after use and never left standing for a long time on open circuit.

4.   CONCLUSIONS

Highly ordered, high porosity and high surface area β-PbO$_2$ deposit was successfully produced on gold by deposition into self assembled layers of polystyrene microspheres. It was found that this porous β-PbO$_2$ layer led to a high rate for the oxidation of DMSO. This high activity was attributed to more active sites available on the porous structure for the adsorption of reactant and the oxidation to take place. Nevertheless, the β-PbO$_2$ macroporous deposit was found to be unstable at open-circuit in the acidic solution containing dimethylsulfoxide (ie: 50 mM DMSO + 1 M H$_2$SO$_4$) but not during electrolysis.

REFERENCES

[1]   A. T. Kuhn, Editor, 'The Electrochemistry of Lead', Academic Press, London, (1979) 217

[2]   C.A. Martinez-Huitle and M. Panizza, Application of PbO2 Anodes for wastewater Treatment, In: D.V. zinger (Eds.) Advances in Chemistry Research: Applied Electrochemistry. Nova Science Publishers, Inc. New York, (2010) 269-300.

[3]   M. Zhou and J. He, J. Hazardous Materials, 153 (2008) 357 – 363.

[4]   Y. Samet, S. Chaabane Elaoud, S. Ammar and R. Abdelhedi, J. Hazardous Materials, 138 (2006) 614 – 619.

[5]   S. Kim, T-H Kim, C. Park and E-B Shin, Desalination, 155 (1) (2003) 49 – 57.

[6]   E. Chatzisymeon, A. Dimou, D. Mantzavinos and A. Katsaounis, J. Hazardous Materials, 167 (1-3) (2009) 268-274.

[7]   L. Lipp and D. Pletcher, Electrochim. Acta, 42 (7) (1997) 1091.

[8]   S.E. Treimer, J. Feng, M.D. Scholten, D.C. Johnson and A.J. Davenport, J. Electrochem. Soc., 148 (12) (2001) E459

[9]   J. Gonzalez-Garcia, G. Sanchez-Cano, A. Aldaz, V. Monteil and J.L.G. Fierro, Appl. Surf. Sci., 78 (1994) 457

[10]   M. E. Heron, D. Pletcher and F.C. Walsh, J. Electroanal. Chem., 332 (1992)183

[11]   I. –H. Yeo, Y.S. Lee and D.C. Johnson, Electrochim. Acta, 37 (1992) 1811

[12]   A.B. Velichenko, D.V.Girenko and F.I. Danilov, Electrochim. Acta, 40 (1995) 2803

[13]   K. Pamplin and D.C. Johnson, J.Electrochem. Soc, 143 (1996) 2119

[14] P. Ruetschi, J. Sklarchuk and R.T.Angstadt, Electrochim. Acta, 8 (1963) 333

[15] R. Amadelli, A. Maldotti, A. Molinari, F.I.Danilov and A.B.Velichenko, J. Electroanal. Chem. 534 (2002) 1

[16] D. Pavlov and B. Monahov, J. Electrochem. Soc. 143 (1996) 3616

[17] N. Munichandraiah and S. Sathyanarayana, J. Appl. Electrochem. 18 (1988) 314

[18] H. Bode, Lead-Acid Batteries, Wiley, New York, 1977

[19] U. Casellato, S. Cattarin and M. Musaini, Electrochim. Acta , 48 (2003) 3991

[20] P.J. Blood, I.J. Brown and S. Sotiropoulus, J. Appl. Electrochem., 34 (2004) 1

[21] P. N. Bartlett, T. Dunford and M.A. Ghanem, J. Mat. Chem., 12 (2002) 3130

[22] P. Ribordy, C. Pulgarin, J. Kiwi and P. Peringer, Water Sci. Tech., 35 (1997) 293

[23] E. Plattner and C. Comninellis, in "Process Technologies for Water Treatment", Editor S. Stucki, Plenum Press, 1988

[24] C. Walling, Acc. Chem. Res., 8 (1975) 125

[25] F. Banata and N. Al-Bastakib, Desalination, 170 (1) (2004) 69

[26] G Nakhla, A. Lugowski, J. Patel and V. Rivest, Bioresource Tech., 97 (1) (2005) 1

[27] T. Mohammadi and A. Esmaeelifar, J. Membrane Sci., 254 (2005) 129

[28] R. Kotz, S. Stucki and B. Carcer , J. Appl. Electrochem., 21 (1991) 14

[29]   S. Stucki , R. Kotz, B. Carcer and W. Suter, J. Appl. Electrochem.,
        21 (1991) 99

[30]   P.N. Bartlett, P.R. Birkin and M.A. Ghanem, Chem. Comm.,
        (2000) 1671

[31]   P.N. Bartlett, M.A. Ghanem, I.S. El Hag, P. de Groot and A. Zhukov,
        J. Mater. Chem., 13 (2003) 2596

[32]   P.K.Shen and X.L.Wei, Electrochim. Acta., 48 (2003) 1743

[33]   Y. Mohd and D. Pletcher, J. Electrochem. Soc. 152 (2005) (6)
        D97-D102