# Electrochemical Deposition of Lead dioxide ($PbO_2$) on different Metals and its Characterization

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# DECLARATION

This is to certify that this dissertation entitled ***"Electrochemical deposition of $PbO_2$ on different metals and its characterization"*** submitted by ***Mr.Muhammad Ali*** is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, as satisfying the dissertation requirements for the degree of ***Master of Philosophy in Physical Chemistry.***

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Dedicated to

My loving
Parents

بسم الله الرحمن الرحيم

*In the Name of Allah, the Most Beneficent, the Most Merciful*

* * *

*(1) Read! In the Name of your Lord, Who has created (all that exists), (2) Has created man from a clot (a piece of thick coagulated blood). (3) Read! And your Lord is the Most Generous, (4) Who has taught (the writing) by the pen (5) Has taught man that which he knew not. (6) Nay! Verily, man does transgress all bounds (in disbelief and evil deed, etc.). (7) Because he considers himself self-sufficient. (8) Surely! Unto your Lord is the return.*

*(al-alaq, Verses1-8)*

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# Abstract

Search to develop stable, cost effective and efficient electrodes made $PbO_2$ a potential candidate with desired properties. However, to date there are factors to be addressed to achieve the desired electrode material. Present work deals with the electrochemical deposition of pure and modified $PbO_2$ on different metal substrates such as Ti, Pd, Pt, W and Au. The electrochemical deposition was carried out employing glavanostatic mode at a constant current density of 10 $mA/cm^2$ for varied time periods. The surface of $PbO_2$ was modified by changing the deposition conditions such as concentration of deposition solution, current density and time period. The process was optimized to acquire the enhanced stability and efficiency of the electrode material. For the purpose different binding agents (nafion, polyvinyl pyrollidone (PVP), sodium dodecyl sulphate (SDS) and halides ($F^-$, $Cl^-$, $Br^-$ and $I^-$) were investigated and optimized. PVP and $F^-$ were proven to be better candidates for the desired electrochemical activity. An attempt has also been made to add some metal ion dopants (like $Bi^{3+,}$ $Ni^{2+}$ and $Ag^+$) for the improvement of electrode properties. The obtained samples were characterized with the help of cyclic voltammetry (CV), XRD and AFM techniques. Some typical redox systems (ferrocene, dinitro benzene, phenol) were tested and reasonable CV response was observed. Out of the five metal substrates and the analysis carried out Au was found to be the most suitable substrate. The results of the new electrode showed improvement in potential window, increase in oxygen evolution potential and stability in the material. For the developed material 'function' dependency on the surface morphology was also deliberated upon.

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Chapter: 1

# Introduction

The binary compound of oxygen with any other element is called oxide and metals on combining with oxygen form metal oxides. Lead (Pb) a metal element of group IV is capable to form oxides in which it exhibits oxidation states 2+ and 4+. Lead oxide may refer to PbO (litharge, massicot), $Pb_3O_4$ (II, II, IV) *(red lead)* and $PbO_2$ (IV) (Lead dioxide or plumbic oxide). Less common lead oxides are· $Pb_2O_3$ (II, IV) (lead sesquioxide) and $Pb_{12}O_{19}$ (monoclinic, black crystals). Black lead oxide is a mixture of PbO and fine-powdered metal Pb.

Lead dioxide, $PbO_2$ (the poor man's platinum), is an odorless dark-brown crystalline powder and is nearly insoluble in water (Mary 1994). It exists in two crystalline forms; α-$PbO_2$ (orthorhombic) and β-$PbO_2$ (tetragonal). Plattnerite is the beta crystalline form of lead dioxide, scrutinyite being the other, alpha form. Both the phases exist in nature and in synthetic forms (Haidinger 1845, Taggard 1988, Harada et.al. 1981). In both the lattices, each metal ion is in the center of a distorted octahedron; however, β-form is more stable crystalline state (Pauling 1923, Goldschmidt 1960, McQueen 1967, Sasvari 1960, White 1961, Fedorova 1966). Lead dioxide is an amphoteric compound with prevalent acidic properties. It dissolves in strong bases to form the hydroxyplumbate ion, $Pb(OH)_6^{2-}$(Mary 1994). Being a good oxidizing agent, lead dioxide oxidizes manganese, chromium and others, as reported in number of reactions (Anil 2007). When heated in air, lead dioxide decomposes to form various lead oxides in industries like $Pb_{12}O_{19}$, $Pb_{12}O_{17}$, $Pb_3O_4$ and PbO (Greenwood, Earnshaw 1997).

Lead dioxide is a strong oxidizing agent found its applications in match, dye, pyrotechnic and high-voltage lightning arresters industries (Greenwood 1997). Several applications exist in electrochemistry e.g; extensively used in lead acid batteries as cathode, as oxygen anodes for electroplating copper and zinc in sulfate baths, organic synthesis and as anode for the regeneration of potassium dichromate (Francois 2008). One of the reasons of excessive use of $PbO_2$ is its anomalous metallic conductivity. The lead acid battery stores and releases energy by shifting the equilibrium between metallic lead, lead dioxide and lead (II) salts in sulfuric acid.

Although the formula of lead dioxide is normally written as $PbO_2$, the actual oxygen to lead ratio is from1.90 to 1.98 depending on the preparation method. Deficiency of oxygen (or excess of lead) leads to the characteristic metallic conductivity of lead dioxide. Like metals, lead dioxide has a characteristic electrode potential and can be polarized both anodically and cathodically in electrolytes. Dual action of $PbO_2$ electrodes is due to the fact that both lead and oxygen ions take part in the electrochemical reactions (Barak 1980). Generally, oxides are nonconducting or semiconducting, however, a limited number such as $PbO_2$, show electrical conductivity and have close similarities to metals. Like a metal electrode an electrical double layer forms at the interface between the lead dioxide and the electrolyte solution.

Lead dioxide is produced commercially by several methods. These include oxidation of $Pb_3O_4$ in alkaline slurry in a chlorine atmosphere (Greenwood 1997), reaction of lead(II) acetate with calcium chloride, or reacting $Pb_3O_4$ with dilute nitric acid (Mary 1994). Galvanostatic electrodeposition of lead dioxide on pure lead is carried out by applying a current of about 100 $A/m^2$ for about 30 minutes. The drawback of the lead electrode is its softness, especially compared to the hard and brittle $PbO_2$. This mismatch results in weak coating. Therefore, electrodeposition is preferred over harder substrates, such as titanium, niobium, tantalum or graphite. The purification of the substrate from other oxides and impurities is highly recommended to achieve good adhesion for the stable $PbO_2$ coatings (Francois 2008). Due to poisoning nature of the lead having permissible limit of 10 ppb, precautionary measures must be taken when exposed to it.

*Mechanism of $PbO_2$ electrodeposition*

The documented electrodeposition mechanism of $PbO_2$ on metal substrates by most of the scientists is given below.

$$H_2O \rightarrow OH^{\bullet} + H^+ + e^- \qquad (1)$$

$$Pb^{2+} + OH^{\bullet} \rightarrow Pb(OH)^{2+} \qquad (2)$$

$$Pb(OH)^{2+} + H_2O \rightarrow Pb(OH)_2^{2+} + H^+ + e^- \qquad (3)$$

$$Pb(OH)_2^{2+} \rightarrow PbO_2 + 2H^+ \qquad (4)$$

The first stage involves the formation of oxygen-containing particles as $OH_{ads}$, chemisorbed on the electrode. In a second chemical stage, these particles interact with lead species forming a soluble intermediate product, $Pb(OH)^{2+}$. This is further oxidized electrochemically with transfer of the second electron in the third step forming a soluble oxidized Pb (IV) compound. The last stage is the chemical decomposition of the soluble product to form colloidal $PbO_2$ particles in the electrolyte volume that crystallize on the surface. At low overpotential, the rate determining stage is the second electron transfer reaction (Equ.3) and at high overpotential, the process is controlled by diffusion of $Pb^{2+}$ (Equ.2). The activation energy of the reaction has been reported as 70 kJ/mol at low overpotential and it decreased with increasing electrode potential up to 13 kJ/mol (Velichenko 1996, Velichenko 2006, Velichenko 2007).

## Literature review:

Persistent organic pollutants in water, particularly phenol derivatives, cause hindrance during electrochemical analysis and eradication by passivating the working electrode surface. Thus electrodes with high stability, good activity and of low cost are desirable for such type of applications (Feng, Lib 2003, Minghua et.al. 2005). Intensive research has been undertaken to discover more efficient electrode materials and the so far outcome presents boron-doped diamond (BDD) electrode as a best choice both for electroanalysis and electrosynthesis (Pleskov et.al. 2003, Swain et.al. 2004). However, the cost of the material is still high. The other includes metal oxide film electrodes such as, $PbO_2$, $SnO_2$ and $RuO_2$.

Among the metal oxide electrodes, $PbO_2$ has been regarded as excellent electrode material, because of its lower cost compared to noble metals, chemical stability in corrosive media, higher overpotential for oxygen evolution reaction (Jiangtao et.al. 2007), relative stability under the high positive potentials (Rossano, Velichenko 2001), chemical inertness, good electrical conductivity (Huiling et.al. 2008) and relatively high service life (Chen, et.al. 2010). Because of the high overpotential for oxygen evolution, the electrochemical synthesis of strong oxidants, like ozone and hydroxyl free radical can be done with ease and in less time (Pei, Xiao 2003). In addition to this significant work has been performed on the improvement of $PbO_2$ to be used in other areas. These include as electrode material for lead acid batteries (Shahram et.al. 2007), electrosynthesis, ozone generation (Velichenko et.al. 1998), oxidation of phenol (Ai et.al. 2003) and other organic compounds in waste water (Johnson et.al. 2000), $Cr^{3+}$ (Devilliers et.al. 2003) and glucose (Hyde et.al. 2004). Some other applications of $PbO_2$ are that it is used as electrocatalyst for salicyclic acid, 2-naphtol and trans-3,4-dihydroxy cinnamic acid formation (Shahram et.al. 2007), anode material as analytical transducer with high electrocatalytic activity for anodic oxidation transfer processes (Velichenko et.al. 1998).

To improve the physicochemical properties of the $PbO_2$ doping of different metal cations have been tried by several workers (Huiling et.al. 2008). The properties like electrochemical activity towards various anodic reactions in acidic media (Velichenko et.al. 1998), oxygen atom transfer properties including $O_3$ formatoin (Huiling et.al. 2008, Rossano, Velichenko 2001) and stability (Rossano, Velichenko 2001) of pure $PbO_2$ can be improved to a greater extent by the incorporation of some ions. The work reported so far include $Co^{2+}$ (Rossano, Velichenko 2001), $Bi^{3+,}$ $As^{3+}$, $Fe^{3+}$, $F^-$, $Cl^-$ (Velichenko, Devilliers 2007) and $SO_4^{2-}$ (Feng, Johnson1990).

Some active metals like Bi, Ni, La, Ce and Er have been used as catalyst for the oxidation of organics. It has been reported that introducing these metals in the $PbO_2$ increases the oxidation capacity of the anode (Kong et.al. 2007). For the electrogeneration of ozone, Fe and Co doped $PbO_2$ showed a current efficiency of 15–20% for this process (Rossano, Velichenko 2001). Jiangtao added $Gd_2O_3$ and $CeO_2$ in the $PbO_2$ films, which improved the oxygen evolution potentials (Jiangtao et.al. 2007).

Y. Mohd introduced Bi in the $PbO_2$ electrodes as a dopant which modifies the structure and improves the oxidation kinetics of several organic compounds, due to the formation of a low surface density at the bismuth oxide sites (Mohd, Pletcher 2005). S.Y. Ai added rare earth element Ce (III) as a doping agent into $PbO_2$ electrode which changes the crystallite size and increases the catalytic activity in the oxidation of DMSO (Ai et.al. 2005). It has been determined that the doping controls the amount of structural water in an oxide (Rossano, Velichinko 2001). In most cases, the details of the dopant effects on the lead dioxide are unknown and demand to explore further.

There is a consensus that the properties of $PbO_2$ electrodes are largely determined by the composition of the deposited film (Jiangtao et.al. 2007). Apart from metal ions some other species e.g. $F^-$, binding agents and surfactants were also found effective to improve the surface properties of the electrode material. Fluoride ions give very good $PbO_2$ electrodes for oxygen transfer reactions. $F^-$ not only enhances the oxygen evolution potential to some extent, but also greatly increases the life of $PbO_2$ electrode (Guohua et.al. 2010). Doping of $PbO_2$ by cations, by $F^-$ and by cations and $F^-$ simultaneously enhances the stability and electrochemical activity in processes occurring at high potentials (Rossano, Velichinko 2001).

The redox activity of the $PbO_2$ relates to its morphology and structure ($\alpha$-$PbO_2$ or ß-$PbO_2$) (Pei, Xiao 2003). The morphology and phase composition of electrochemically deposited lead dioxide depend on a number of parameters. These include type of substrate, the electrochemical method used, deposition conditions including pH of solution (acidic or basic solution) and presence of forming agents such as $F^-$ and nafion (Shahram et.al. 2007). So far used electrochemical techniques to prepare lead dioxide coating include constant potential, constant current density, pulse current and cyclic voltammetry (Huiling 2008, Shahram 2007, Hassan 2009).

The crystal structure of electrodeposited $PbO_2$ depends mainly on the pH of the electroplating solution. $\alpha$-$PbO_2$ is obtained from bases, while $\beta$-$PbO_2$ from acids. The structure of former allotrope is more compact than later due to better contact between the particles (Chen et.al. 2010). ß-$PbO_2$ has high efficiency in the detoxification and waste electrodegradation (Feng, Lib 2003). However, $\alpha$-$PbO_2$ showed a higher catalytic activity than $\beta$-$PbO_2$ in dilute $H_2SO_4$ solution (Chen et.al. 2010). It has been reported that porous structured $PbO_2$ should give more active properties irrespective of the preparation method used (Pei, Xiao 2003).

## Aims and objectives:

As discussed above lead dioxide is an excellent electrode material, as compared to the conventional electrodes, like platinum, gold and glassy carbon. This is because of its low price, stability at high potential, good electrical conductivity, high over potential for oxygen evolution and high service life. Moreover $PbO_2$ encompasses a number of applications as mentioned in the introductory paras. Literature shows that there is a growing interest in the improvement of $PbO_2$ electrode for several applications. A major goal is to tune the properties of the resulting oxide to a particular electrocatalytic process. In this respect, two aspects are important to be concentrated upon: (i) modification of the oxide surface with suitable dopants (ii) understanding the chemistry behind the observed changes.

The present work deals with the galvanostatic electrodeposition of $PbO_2$ on Ti, Pd, Pt, W and Au as metal substrates. To have effective metal-metal oxide binding nafion, PVP (Polyvinyl pyrrolidone) and surfactant SDS (sodium dodecyl sulphate) were employed. Effect of some metal ion dopants and halides was also investigated. The electrochemical activity and stability of the deposited lead dioxide electrode was checked using some typical redox systems. Following features were attempted with the self fabricated pure and modified lead dioxide electrode.

1) The working potential window both in the aqueous and non-aqueous media.
2) The oxygen evolution potential in aqueous medium.
3) Proposal for a suitable substrate material for the electrochemical deposition of lead dioxide, of the available metals.
4) Surface studies with the atomic force microscopy.

The present work collected preliminary results for the fabrication of formal modified $PbO_2$ electrode for conventional electrochemistry. Moreover the findings are also helpful to design a $PbO_2$ based electrode in future for the removal of organic pollutants from water.

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Chapter: 2

# Theory

The present chapter is devoted to essential theoretical aspects relevant to the research work carried out in this particular project. It is divided in two parts; (i) properties and application of $PbO_2$ (ii) theory behind the characterization techniques used.

## 2.1 Lead Dioxide ($PbO_2$)

Lead dioxide, $PbO_2$, is a metal oxide of lead in oxidation state +4. The basic structural properties have already been listed in Chapter 1. An interesting property of the lead dioxide is its behaviour as an inert electrode in much the same way as Pt rather than showing any specific electrode catalytic activity. It can withstand at high positive potentials more effectively than graphite (which undergoes degradation) and at the same time cheaper than platinum and may be readily electrodeposited.

**Applications**

Being a very good oxidizing agent lead dioxide is used in the production of matches, pyrotechnics, dyes and the curing of sulfide polymers. It is also used in the construction of high-voltage lightning arresters (Greenwood, Earnshaw 1997). Beta-$PbO_2$ is more attractive for lead acid batteries than the alpha form because it has relatively low resistivity, good corrosion resistance even in low-pH medium and a high overvoltage for the evolution of oxygen in sulfuric acid and nitric acid based electrolytes. Lead dioxide can also withstand chlorine evolution in hydrochloric acid. Lead dioxide anodes are inexpensive and are used instead of conventional platinum and graphite electrodes for regenerating potassium dichromate. They are also applied as oxygen anodes for electroplating copper and zinc in sulfate baths. In organic synthesis, lead dioxide anodes were applied for the production of glyoxylic acid from oxalic acid in a sulfuric acid electrolyte (Francois 2008).

The most important use of lead dioxide as the cathode of lead acid batteries is because of its anomalous metallic conductivity. The lead acid battery stores and releases energy by shifting the equilibrium (a comproportionation) between metallic lead, lead dioxide, and lead (II) salts in sulfuric acid. The chemical process can be presented as;

$Pb + PbO_2 + 2\ HSO_4^- + 2\ H^+ \rightarrow 2\ PbSO_4 + 2\ H_2O$, E = +2.05 V

## Chemical reactivity

1. Lead dioxide is an amphoteric compound with prevalent acidic properties. It dissolves in strong bases to form the hydroxyplumbate ion, $Pb(OH)_6^{2-}$ (Mary 1994). It also reacts with basic oxides in the melt yielding orthoplumbates $M_4[PbO_4]$.

$$PbO_2 + 2\ NaOH + 2\ H_2O \rightarrow Na_2[Pb(OH)_6]$$

2. Since its $Pb^{4+}$ cation is unstable, lead dioxide reacts with warm acids, converting to the more stable $Pb^{2+}$ state with liberation of oxygen (Greenwood, Earnshaw 1997).

$$2\ PbO_2 + 2\ H_2SO_4 \rightarrow 2\ PbSO_4 + H_2O + O_2$$
$$2\ PbO_2 + 4\ HNO_3 \rightarrow 2\ Pb(NO_3)_2 + H_2O + O_2$$
$$PbO_2 + 4\ HCl \rightarrow PbCl_2 + 2\ H_2O + Cl_2$$

3. As an oxidizing agent it behaves as shown below (Anil 2007).

$$2\ MnSO_4 + 5\ PbO_2 + 6\ HNO_3 \rightarrow 2\ HMnO_4 + 2\ PbSO_4 + 3\ Pb(NO_3)_2 + 2\ H_2O$$
$$2\ Cr(OH)_3 + 10\ KOH + 3\ PbO_2 \rightarrow 2\ K_2CrO_4 + 3\ K_2PbO_2 + 8\ H_2O$$

4. When heated in air, lead dioxide decomposes to form various lead oxides.

$$PbO_2 \rightarrow Pb_{12}O_{19} \rightarrow Pb_{12}O_{17} \rightarrow Pb_3O_4 \rightarrow PbO$$

The reaction is common in industries. The stoichiometry of the end product is controlled by changing the temperature; for example, the first step in the above reaction, takes place at 290 °C, second at 350 °C, third at 375 °C and fourth at 600 °C. In addition, $Pb_2O_3$ can be obtained by decomposing $PbO_2$ at 580–620 °C under oxygen pressure of 1.4 kbar (Greenwood, Earnshaw 1997).

### Electrochemical

Like metals, lead dioxide has a characteristic electrode potential, and in electrolytes it can be polarized both anodically and cathodically. Lead dioxide electrodes have a dual action, that is both the lead and oxygen ions take part in the electrochemical reactions (Barak 1980).

### Production

1. Lead dioxide is produced commercially by several methods, which include oxidation of $Pb_3O_4$ in alkaline slurry in a chlorine atmosphere, (Greenwood, Earnshaw 1997) reaction of lead(II) acetate with calcium chloride, or reacting $Pb_3O_4$ with dilute nitric acid (Mary 1994).

$$Pb_3O_4 + 4\,HNO_3 \rightarrow PbO_2 + 2\,Pb(NO_3)_2 + 2\,H_2O$$

2. For large scale industrial production of $PbO_2$ anodes, lead dioxide forms on pure lead, in dilute sulfuric acid, when polarized anodically at electrode potential about +1.5 V at room temperature. Lead and copper electrodes are immersed in sulfuric acid flowing at a rate of 5–10 L/min. The electrodeposition is carried out galvanostatically by applying a current of about 100 $A/m^2$ for about 30 minutes.

### Safety

Being a strong oxidant, lead dioxide is a poison when ingested. The associated symptoms include abdominal pain and spasms, nausea, vomiting and headache. Acute poisoning can lead to muscle weakness, metallic taste, loss of appetite, insomnia, dizziness, with shock, coma and death in extreme cases. The poisoning also results in high lead levels in blood and urine. Contact with skin or eyes results in local irritation and pain.

## 2.2 Electrochemical Deposition

The process in which a coating is formed on a substrate by the help of electric current is called electrochemical deposition or electrodeposition or electroplating. The coating is usually of a metal or some times it is a metal oxide. Similarly most of the substrates are also metals however other materials such as glass, alloy, and ceramic may also be used. This is done by creating a negative charge on the object to be coated while putting it into a solution containing a salt of the metal to be deposited. Thus the substrate acts as a cathode and positive metal ions are reduced here. The anode is made of another metal or graphite (Poyner 1986, Jim 2006). **Fig. 2.1** is a schematic presentation of such an electrolytic cell for electrodeposition of a metal "M" from an aqueous solution of metal salt "MA".

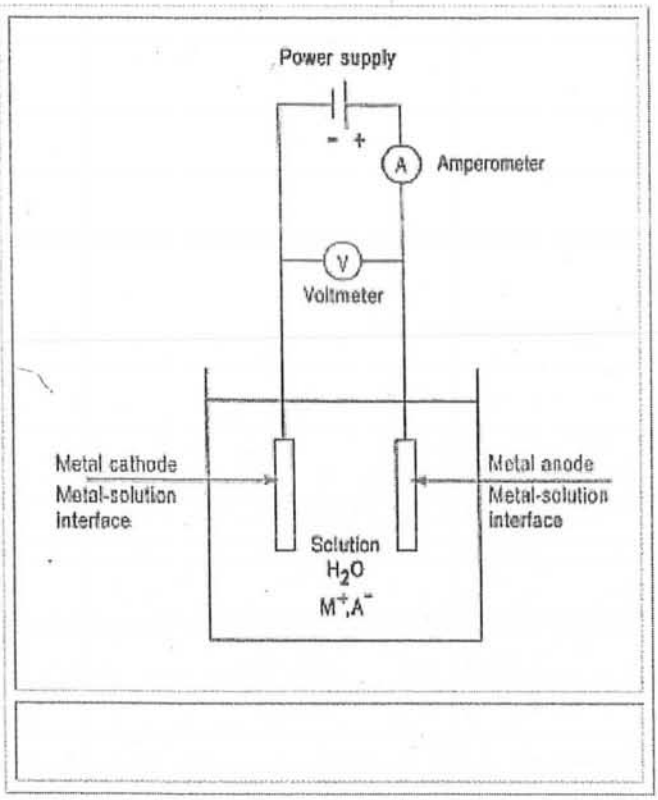

**Fig. 2.1** Schematics of an electrolytic cell for plating metal "M" from a solution of the metal salt "MA" (Schlesinger, Milan 2000).

There are several reasons for the electroplating process. The major rationale is to change the properties of the substrate partially or wholly. This could be done to change (enhance or decrease) the conductivity, to improve the shining and appearance or even sometimes to create dullness. A major application is protection against the corrosion of metals. Artificial jewelry is a major user of this process for centuries. Similarly in automobile and space industry electrodeposition is inevitable.

Over recent decades, electrodeposition has evolved from an art into a regular science. The development in the field can be seen from the wide spread applications nearly in 80% of the industry. Moreover the advent of nanotechnology created a very wide gate for electrodeposition process both in terms of applications and methodologies. Some of the areas are: macro and micro, nano and submicro, electronics, magnetisms, optics, opto-electronics and sensors of most types, electrodes and ultra micro electrodes, SEM, TEM and AFM technologies, to name only a few. That is so for reasons of economy and convenience in applying the process. Modern electroplating equips the practitioner with the ability to pre-design the properties of surfaces and thus saves a lot of time and finance. Furthermore, the ability to deposit very thin multilayers at nano-scale level via different techniques such as CVD made electroplating a strong competitor and developed yet a new avenue of producing new materials.

The recent increase of interest in electrodeposition is because of three main factors/technologies (Paunovic, Schlesinger 1998).

- Metal deposition for the fabrication of integrated circuits. .
- Deposition of magnetic recording devices (heads, discs).
- Deposition of multilayer structures.

### Pretreatment and Surface preparation

A very essential and important part of the electrodeposition process is the pretreatment or surface preparation. To achieve the desired electroplating half of the results depend upon pretreatment of the substrate. It is commonly accepted that one can not make a good use of electroplated surface without excellent pretreatment however having a very good surface preparation with poor electrodeposition can work significantly good. Surface pretreatment can be done with different methods including chemical, mechanical means and also electrochemical. Most of the metal surface treatment and plating operations have three basic steps (Schlesinger, Milan 2000).

- Surface cleaning or preparation. This is done by employing solvents, alkaline cleaners, acid cleaners, abrasive materials or water.
- Surface modification. To change in surface attributes, such as softening or hardening, creating etching.
- Rinsing finishing operations to produce the desired product.

Why the surface treatment is necessary? The answer lies in the intrinsic and extrinsic factors that affect the surface properties. This includes contaminants and films on the substrate, organic matter already deposited there, mineral dust, one example being of the native oxide layer. Cleaning methods are designed to minimize the substrate damage while removing the undesired films. Having the knowledge of the substrate and its surface the most suitable cleaning method can be anticipated.

An other important feature of the electrodeposition is the thickness of the deposited layer. This depends upon the time duration of the plating, area of the electrode surface and the current applied. Longer time the object remains in the bath the thicker the resulting electroplated layer will be. Typically, layer thicknesses varies from 0.1 to 30 microns (micron = one millionth of a meter), however, it can be increased or decreased as desired. The geometric shape and contour of the substrate also affects the thickness of the deposited layer. In general, objects with sharp corners and features will tend to have thicker deposits on the outside corners and thinner ones insides: This is due to the fact that dc current flows more densely to sharp edges than to the less accessible recessed areas. In the case of electroplating the most important factor is the judicial placement of the anode(s) to obtain a uniform thickness.

To characterize the electrochemical process reliable information can be obtained from the current potential curve such as shown in **Fig. 2.2.** Such a curve helps to select the appropriate potential for the reduction of a desired metal when using two or more than two metal solutions simultaneously. The reduction potentials appeared as reduction peaks in the voltammograms are the criteria for selective deposition. The onset of the reduction potentials of the metals present in solution help to see the possibility of separate, successive or mixed deposition as the case may be. In contrast to this a precautionary measure is to remain in the potential region where the metals (in solution or the substrate) do not get destroyed or decomposed. Thus moving beyond some potential values may start "over-potential reactions" as indicated in **Fig. 2.2**. Any current causing such changes is considered "wasted". Faraday's law helps to calculate very precisely the overall amount of chemical change produced by any given quantity of electricity. This defines the current efficiency; the ratio between the actual amounts of metal deposited to that expected theoretically from Faraday's law.

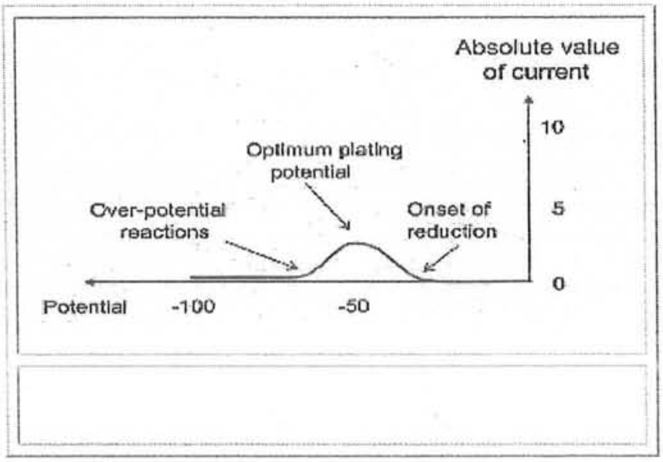

**Fig. 2.2** Typical voltammogram for a single-metal deposition (scales are arbitrary) (Paunovic, Schlesinger 1998).

### Electrochemical Deposition of Lead dioxide

$PbO_2$ coating can be prepared from the solution of low-valence lead ions by anodic deposition on a substrate. The preparation methods include constant potential, constant current density, pulse current and cyclic voltammetry (Hassan, Mahboobeh 2009, Shahram et.al. 2007). The morphology and structure of $PbO_2$ depends on different electrochemical methods. $PbO_2$ anodic layers prepared galvanostatically had a compact continuous structure, while $PbO_2$ potentiostatically prepared electrode showed a higher degree of porosity. The compact structure with higher degree of interconnected particles led to lower internal resistance thus higher capacity and the porous surface layer would result in high transfer resistance and diminished capacity. Discharge capacity was related to film structure and internal resistance of $PbO_2$. Preparation methods can controllably affect the structure of the $PbO_2$ films, which further play important role in discharge capacity (Donglan, Lijun 2007).

## 2.3 Cyclic voltammetry

Cyclic voltammetry is a precise electrochemical method which enables one to obtain redox potential properties, heterogeneous and homogeneous kinetics and thermodynamic feasibility of a process with good certainty. The standard accepted procedure in CV experiment is scanning linearly the potential of a stationary working electrode and then reversing it at some suitable switching potential. Depending on the information sought, single or multiple cycles can be used. During the potential sweep, the potentiostat measures the current resulting from the applied potential. The resulting plot of current vs. potential is termed as cyclic voltammogram. A typical cyclic voltammogram is shown in **Fig. 2.3**. This i-E curve is a complicated, time dependent function of a number of physical and chemical parameters but with full of information about the system and medium under run. A significant amount of information on the subject matter has been documented in literature (Bard 2001, Wang 1994, Faulkner 1983, Evans 1983, Gary 1983).

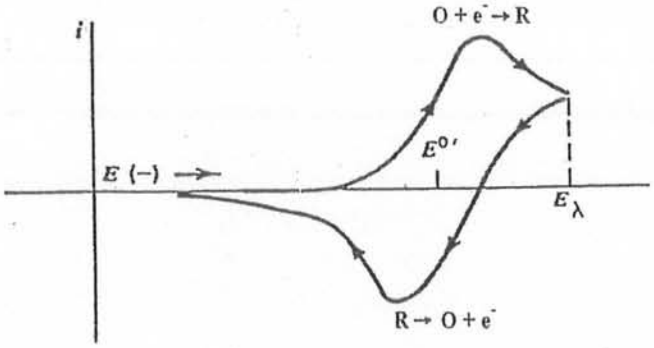

**Fig. 2.3** Typical cyclic voltammogram for single electron transfer reversible process.

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Chapter: 3

# Experimental

The present work was aimed to develop electrochemically the pure and modified forms of $PbO_2$ and characterize them for their morphological and electrochemical properties. This chapter presents the chemicals used, instrumentation employed and the procedure adopted to achieve the goals.

## 3.1 Chemicals

To deposit $PbO_2$ five different metal substrates were selected which include; Ti, Pd, Pt, W and Au. All of them were used in the form of cylindrical rods except Pd which was used in the form of a strip. However, the current results were normalized by converting into current densities. The chemicals used for the electrochemical deposition of $PbO_2$ on different substrates along with their specifications are listed below in table 3.1. The electrochemical response of the fabricated electrodes was checked using three typical redox systems namely Ferrocene ($C_{10}H_{10}Fe$), 1,3-Dinitrobenzene ($C_6H_4(NO_2)_2$) and Phenol ($C_6H_5OH$). First two compounds were tested in Acetonitrile (99 %, Fluka) using Tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. For Phenol aqueous solution of Britton-Robinson buffer (BRB) containing 0.04 M each of Boric acid, Acetic acid and Phosphoric acid titrated against 0.2 M NaOH solution for adjusting the pH was used. When required, doubly distilled water was used.

**Table 3.1** The chemicals used for the electrochemical deposition of $PbO_2$ on different substrates.

| S.No | Chemical Name | Chemical Formula | Source / %Purity |
|---|---|---|---|
| 1 | Lead Nitrate | $Pb(NO_3)_2$ | Riedel-de Haen / 99.6 % |
| 2 | Ethanol | $C_2H_5OH$ | Analytical grade / 99 % |
| 3 | Nafion 117 | $C_7HF_{13}O_5S.C_2F_4$ | Sigma Aldrich / 99.5 % |
| 4 | Polyvinylpyrrolidone (PVP) | $(C_6H_9NO)n$ | Amresco / 88% |
| 5 | Potassium Floride | KF | Riedel-de Haen / 99% |
| 6 | Potassium Chloride | KCl | Merk 99% |
| 7 | Potassium Bromide | KBr | Riedel-de Haen / 99% |
| 8 | Potassium Iodide | KI | Riedel-de Haen / 99% |
| 9 | Perchloric Acid | $HClO_4$ | UNI-CHEM / 72% |
| 10 | Bismith Nitrate | $Bi(NO_3)_3.5H_2O$ | UNI-CHEM / 98% |
| 11 | Nickle Nitrate | $Ni(NO_3)_2.6H_2O$ | UNI-CHEM / 98% |
| 12 | Silver Nitrate | $AgNO_3$ | Fluka / 99.95% |

## 3.2 Instrumentation:

### 3.2.1 Potentiostat/Galvanostat

Galvanostatic deposition and cyclic voltammetric measurements were carried out using Eco Chemie Autolab PGSTAT 302 potentiostat/galvanostat (Utrecht, The Netherlands) with the electrochemical software package GPES 4.9. The instrument is capable of working with high accuracy both in the applied potential (± 2mV) and in the current (±0.2%).

#### *Electrochemical Cell*

The electrochemical cell was a double walled cylindrical cell (Model K-64 PARC) with self mounting plastic cap. The cell cap has five 14/20 standard taper ports for insertion of working electrode, reference electrode, counter electrode, thermometer and inert gas like argon or nitrogen. The cell also contains a side opening through which it is connected to thermostat LAUDA Model K-4R for the maintenance of temperature during the measurement. For electrodeposition two electrode systems was exercised where metal substrate was employed as anode and platinum as cathode. Conventional three electrode system was used throughout for voltammetric studies.

#### *Working Electrode*

Pure $PbO_2$ and modified $PbO_2$ electrodeposited on polished metal substrates (Ti, Pd, Pt, W and Au) of appropriate areas were used as working electrodes.

#### *Reference Electrode*

Saturated calomel electrode (SCE), (Aldrich scientific company Milwaukee, Wisconsin 53233) was used as a reference electrode. In the calomel electrode a paste of mercury and calomel ($Hg_2Cl_2$) is covered with a pool of mercury and filled with saturated KCl acting as an electrolyte, this electrode can be represented by the following electrode notation Hg/ $Hg_2Cl_2$/KCl.

#### *Counter or Auxiliary Electrode*

Platinum wire was used as counter electrode throughout CV measurements. The electrode is 1.0 mm diameter thick and about 3 cm long sealed in a pyrex glass tube with the help of transparent epoxy having exposed portion of about 2 cm at one end. The Pt wire is connected with copper wire for external connection through mercury at the other end.

### 3.2.2. X-Ray Diffraction (XRD)

Powdered X-ray diffraction (XRD) analysis was carried out by a Philips X' Pert PRO 3040/60 diffractometer (Panalytical, Netherland) equipped with Cu K$\alpha$ radiation ($\lambda$=1.54 A°) as a radiation source operated at 40 kV and 30mA to characterize the phase composition of the powdered sample. Usually a 2$\theta$ range of 5 to 70 degrees is sufficient to cover the most useful part of the powder pattern.

### 3.2.3. Atomic Force Microscopy (AFM)

The Atomic Force Micrograph used was Alpha-Contec, GmbH, Germany. Its lateral and vertical resolution was 2 nm and less than 1 nm respectively. It was used in contact mode.

### 3.2.4 Balance

For the determination of mass, an electrical balance of A&D Company of Tokyo Japan was used. The resolution of the instrument was ± 0.0001g.

## 3.3 Procedure:

### 3.3.1. Electrochemical Deposition:

Electrodeposition of both pure and modified lead dioxide was done galvanostatically. The deposition was carried out with a two electrode system at optimized constant current density of 10 mAcm$^{-2}$ for 5 minutes for all of the substrates except for Ti where it took 15 minutes. First the deposition was carried out for pure $PbO_2$ from an aqueous solution of 0.1M $Pb(NO_3)_2$. Next the modification in the $PbO_2$ was conceded by adding different binding and stabilizing agents one by one or in combinations. These include Nafion, Polyvinylpyrrolidone (PVP), Sodium dodecyl sulphate surfactant (SDS), halide salts and some metal salts. The substrates used were extensively polished with sand papers of grades 400, 800, 1200 and 4000 and washed with acetone and distilled water before deposition of the $PbO_2$ under different conditions.

### 3.3.2 Experimental Procedure for Cyclic Voltammetry:

The CV response of three redox systems was obtained utilizing conventional three electrode system in suitable media. This helped to investigate the stability and electrochemical activity of the pure and modified lead dioxide electrode. Solutions of 2mM of Ferrocene and 6mM of 1,3-Dinitrobenzene were prepared in a medium of acetonitrile with 0.1M TBAP supporting electrolyte. Deaeration of the blank and analytes was done using argon gas for 3-5 minutes. Cyclic voltammograms of the medium (blank) were run prior to the analytes to ensure the electro-inactivity of the medium. Phenol solution (0.5 mM) of pH 2 was prepared in Britton-Robinson Buffer. All the measurements were performed under argon atmosphere at about 25°C.

### 3.3.3. X-Ray Diffraction (XRD)

$PbO_2$ electrochemically deposited on Pd substrate was scratched with the help of a spatula and the sample was powdered. The powdered sample was given to the operator for its XRD analysis and the results were obtained.

### 3.3.4 Atomic force Microscopy (AFM)

The AFM micrographs for surface topography were obtained in contact mode. The micrographs were aquaired in two dimensional and three dimensional forms. These were recorded for $PbO_2$ coating carried out under different conditions. Each sample probe was scanned at different resolutions such as 2, 5, 10 and 15 micrometer.

Chapter: 4

# Results and Discussion

The current chapter presents the results and discussion of the work carried out. The chapter is divided into three main parts. Part I presents the electrochemical deposition protocol under varied conditions and fabrication of the desired $PbO_2$ surface. Part II discusses the morphological aspects. Here, the XRD and AFM techniques were employed to assess the crystalline nature of the resulting $PbO_2$ layer(s) and their homogeneity on the substrate respectively. Part III is specified to check the improvements in the applications of the fabricated electrodes. This includes the potential window of the prepared $PbO_2$ electrode in aqueous and non aqueous media (along with the $O_2$ evolution status in aqueous medium), cyclic voltammetric response of some typical redox systems and rationalization of the additives used to prepare modified $PbO_2$ electrodes. At the end discussion is concluded and possible future work pieces are pointed out.

## 4.1 Electrochemical deposition of pure and modified lead dioxide

Out of the practiced methods to deposit lead dioxide on metal substrates (or for that matter on any substrate) constant current (galvanostatic) method was employed in the present studies. The other schemes include constant potential deposition, pulse current technique and cyclic voltammetric deposition. It is understandable that during constant current density (normalizing the constant current by dividing it with area of working electrode) method the potential variations are obvious and are indicative of the nature of the substrate surface. Such plots are discussed below for the modified $PbO_2$ under optimized conditions.

The conditions were optimized for the deposition of the $PbO_2$ on different substrates. Although deposition of the $PbO_2$ on different substrates takes place at higher current density, the optimized current density was found to be 10 $mA/cm^2$. Deposition did not occur below this current density. Minimum amount of the $Pb(NO_3)_2$ deposition solution was tried to be used. The optimum concentration of the lead nitrate deposition solution used was 0.1M. The time given to the deposition process of $PbO_2$ was 5 minutes for all the substrates except that of Ti. For sufficient deposition on titanium substrate, the time required was 15 minutes.

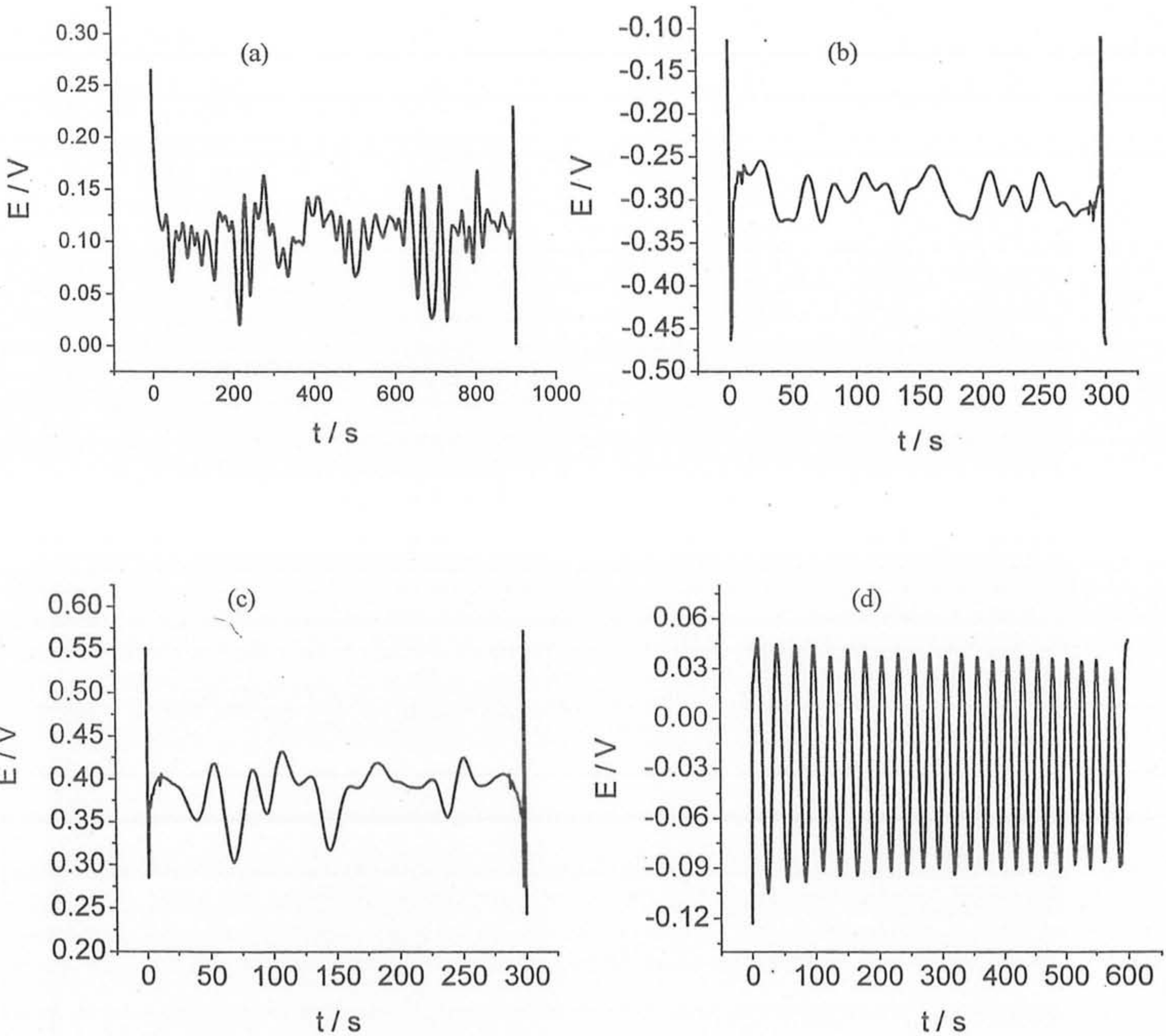
First $PbO_2$ was electrodeposited on five self-made metal substrates including Ti, Pd, Pt, W and Au from the aqueous deposition solution containing only $Pb(NO_3)_2$. Although deposition occurred on these substrates, but the adsorption of the lead dioxide with the substrate surface was weak. The respective prepared electrodes were tried to be tested for their electroactivity but were found unstable for precise analysis. For strong substrate-$PbO_2$ adhesion nafion (a conductive copolymer with chemical formula $C_7HF_{13}O_5S.C_2F_4$) was added to the lead nitrate solution in 50 % ethanol. Nafion strengthened the binding, however, electrochemical activity of the electrode was not improved. Though some workers (Chen et.al. 2010) have reported to achieve good electrochemical performance of the $PbO_2$ electrodes in presence of nafion but did not show the respective voltammetric curves. It is worth to be mentioned for the experimentalists that the chemical nature and composition of the nafion are important factors to be cared before its application.

Next Polyvinyl pyrrolidone (PVP) having chemical formula $(C_6H_9NO)n$ and KF along with $HClO_4$ were added to the aqueous $Pb(NO_3)_2$ solution instead of nafion. PVP is again a conductive polymer and also owes adhesive properties. The addition of KF provided $F^-$ ions which have been reported (Shahram et.al. 2007) for their ability to decrease the particle size of $PbO_2$ and thus create compactness in the structure. This deposition solution gave modified $PbO_2$ electrode with better stability and activity. PVP leads to more adhesion to the substrate surface. It also affects the morphology and particle size of the prepared $PbO_2$ and enhances the over potential for the oxygen evolution during electrodeposition of $PbO_2$. The presence of $F^-$ improves the morphology and decreases the particle size of the prepared $PbO_2$ as assessed from the imaging analysis.

Keeping in view the favoring result of the $F^-$ ions the effect of other halides such as $Cl^-$, $Br^-$ and $I^-$ on the stability and activity of $PbO_2$ film electrode was also investigated. The obtained $PbO_2$ films in presence of these halogen ions did not show good deposition behavior and in some cases the changes in the colour or state of the electrolyte solution were also observed. A separated discussion for $PbO_2$ deposited on Au substrate in presence of different halides is presented in section 4.5. An attempt was also made to improve the properties of the $PbO_2$ by doping some metal ions. The metal ions used were $Bi^{3+}$, $Ni^{2+}$ and $Ag^+$ and in their presence the activity of PVP plus $F^-$ modified electrode was observed. The findings were not encouraging but we feel a systematic and in-depth empirical approach is needed to explore the effect further. This was not possible due to time limitations and placed for future work.

The electrochemical deposition of $PbO_2$ from different aqueous solutions on metal substrates was associated with changes observed in the plot of electrode potential variation with time at a constant current density between the electrodes. These potential variations as a function of time are shown in **Fig. 4.1** for the deposition of $PbO_2$ at a current density of 10 mA/cm$^2$ on Ti for 15 minutes and Pd, Pt, W and Au for 5 minutes. The results are interesting, for Ti substrate as shown in **Fig. 4.1a** the potential varied between 0.02 to 0.17V (positive range), for Pt the range is 0.3 to 0.43V **(Fig. 4.1c)**, for Pd **(Fig. 4.1b)** the variation is in negative potential (-0.32 to -0.25V), for W **(Fig. 4.1d)** it is -0.1 to +0.05 and for Au **(Fig. 4.1e)** the range is -0.04 to +0.04V· i.e. in both the positive and negative side in the last two cases. The negative and positive potential may arise due to the intrinsic properties of the substrate used under the particular conditions applied. The variation in the potential with the passage of time shows the electrodeposition of the $PbO_2$ on the inhomogeneous surface of the metal. In the present studies the Ti, Pt, W and Au were used as disc electrodes of areas about 0.34 cm$^2$, 0.0154 cm$^2$, 0.13 cm$^2$ and 0.031 cm$^2$ respectively, on the other hand Pd strip of 0.5mm thickness with area of about 0.33 cm$^2$ was used. It appears that the surface of the disc electrodes was more inhomogeneous and thus the variation in the potential is large.

Moreover, deposition of $PbO_2$ was also carried out from solutions containing $Pb(NO_3)_2$, sodium dodecyl sulfate (SDS) surfactant, KF and pH was adjusted to 2 with $HNO_3$ solution, also from $Pb(NO_3)_2$, $HClO_4$ and NaF in 30% methanol. The electrodeposited $PbO_2$ from these solutions was checked for its suitability but was not found good enough to be further investigated.


(a)
E / V
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
200
400
600
800
1000
t / s
(b)
E / V
-0.10
-0.15
-0.20
-0.25
-0.30
-0.35
-0.40
-0.45
-0.50
0
50
100
150
200
250
300
t / s
(c)
E / V
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0
50
100
150
200
250
300
t / s
(d)
E / V
0.06
0.03
0.00
-0.03
-0.06
-0.09
-0.12
0
100
200
300
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t / s

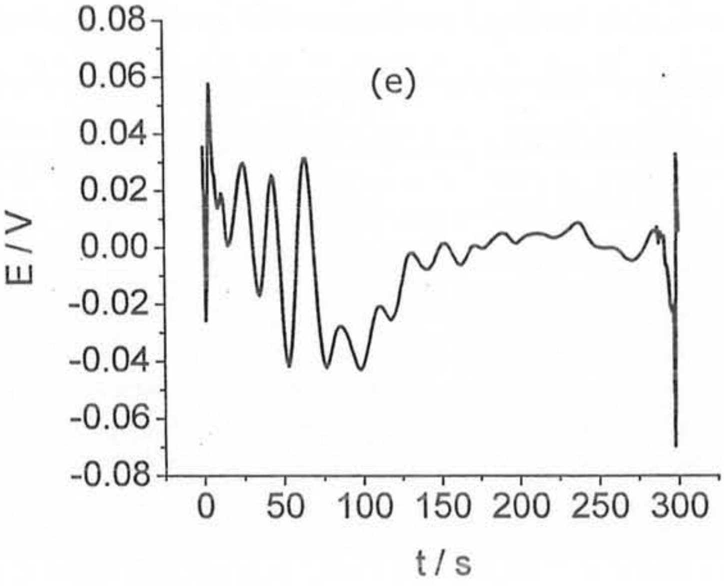


**Fig. 4.1** Variation in Potential during the electrochemical deposition of $PbO_2$ at a current density of 10 mA/cm$^2$ on (a) Ti for 15 minutes (b) Pd, (c) Pt (d) W and (e) Au for 5 minutes. Pt wire was used as cathode.

## 4. 2 Morphological studies:

### 4.2.1 X-Ray Diffraction pattern of $PbO_2$

Generally $PbO_2$ exists in two crystalline forms $\alpha$-$PbO_2$ (orthorhombic) and $\beta$-$PbO_2$ (tetragonal). The structure of $\alpha$-$PbO_2$ is more compact than that of the more porous $\beta$-$PbO_2$ having better contact between the particles. Porous structured $PbO_2$ should have more electrochemical activity (Petersson et.al. 1998). It is given in the literature (Chen et.al. 2010) that $\beta$-$PbO_2$ is obtained from the acidic deposition solution, while alkaline deposition solution gives $\alpha$-$PbO_2$ as a major product. In order to characterize the structure and crystallite size of the electrodeposited lead dioxide, X-ray diffraction technique was used. X-ray diffraction revealed that $\beta$-$PbO_2$ is the dominated product of the galvanostatic electrodeposition. XRD pattern of $PbO_2$ electrodeposited on Pd substrate at a constant current density of 10 mA $cm^{-2}$ for 5 minutes is shown in the **Fig. 4.2.**

The characteristic peaks observed at 25.2°, 32.1° and 49.0° were because of $\beta$-$PbO_2$. The $\alpha$-$PbO_2$ is identified from the peak at 28.5° which is absent in the present case and only the peaks of $\beta$-$PbO_2$ have been observed. The average crystallite size of the modified $PbO_2$ was calculated by applying the Debye-Scherrer formula

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is the crystallite thickness, K is the shape factor (0.89), $\lambda$ is the wave length of X-ray used (1.54 A°), $\beta$ is full width half maximum (FWHM) and $\theta$ is the Bragg angle. The crystallite size was found in the range of 10 ± 3 nm. However, it can not be taken as a reliable size as the modified lead dioxide contains four to five chemicals. To assess the changes in the crystal structure of $PbO_2$ on adding the different binding/ stabilizing agents a detailed sequential studies of the XRD patterns is required. This will be helpful to see the shifts in the characteristic peaks of the $PbO_2$, if occurs so, on adding different impurities in the $PbO_2$. Further the probable decrease in the crystalline structure of the lead dioxide on these additions could be related to the conductivity and electrochemical changes. The study may probably be helpful to tune the 'modified crystal picture' for the preparation of $PbO_2$ based materials for desired properties.

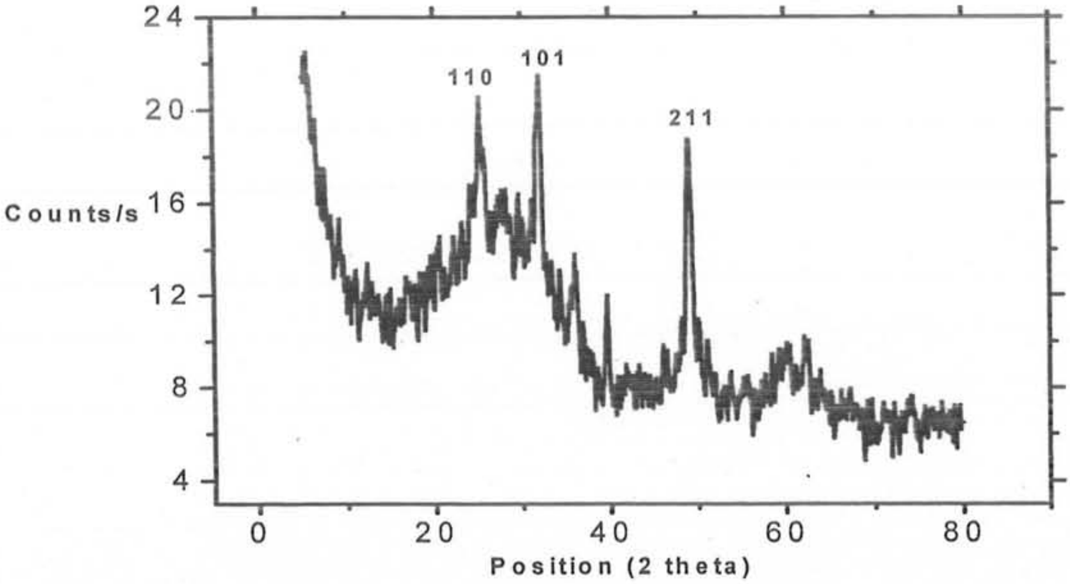


**Fig. 4.2** XRD pattern of $PbO_2$ electrodeposited on Pd substrate at a constant current density of 10 mA $cm^{-2}$ for 5 minutes from deposition solution containing 0.1M $Pb(NO_3)_2$, 0.2M $HClO_4$, 0.1M KF and 1 wt % Polyvinyl pyrrolidone (PVP).

### 4.2.2 Atomic Force Microscopy (AFM) of the modified $PbO_2$

In order to study the surface morphology of the electrodeposited modified $PbO_2$ on Pd substrate, atomic force microscopy (AFM) technique was employed. The AFM technique provides a three-dimensional surface profile and in this respect it is advantageous over the scanning electron microscopy (SEM) which provides a two-dimensional image of the sample. In principle, AFM can provide higher resolution than SEM. However, AFM cannot scan images as fast as SEM, requiring several minutes for a typical scan, while SEM is capable of scanning at near real-time, although at relatively low quality (Lapshin 2004, Lapshin 2007).

**Fig. 4.3a** shows the 3-dimensional AFM image of $PbO_2$ electrodeposited on Pd substrate with film area of 15 μm × 15 μm and average thickness of 638.4 nm. The crests and troughs are visible from the image which show uneven deposition and multilayer formation of $PbO_2$ on the substrate surface. The crests are brighter than the troughs in the image. **Fig. 4.3b** is the 2 dimensional atomic force micrograph of the same area, which shows the particle nature of the electrodeposited $PbO_2$. The black spots in this image show the substrate region without deposition.

**Fig. 4.3c** shows the 3-dimensional AFM image of $PbO_2$ electrodeposited on Pd substrate with an area of 5 μm × 5 μm and average thickness of 239.4 nm. The crests and troughs are more pronounced in this case. The 2-dimensional image of the same area in **Fig. 4.3d** shows the trough as a cavity with the black spots of undeposited substrate. This figure also shows the pronounced peanut like particles of the electrodeposited $PbO_2$.

The uneven deposition with multilayer formation of the electrochemically deposited $PbO_2$, its particle nature and some regions of the metal substrate without deposition are clearer from the 3-dimensional and 2-dimensional micrographs of the deposited $PbO_2$ with resolutions of 2 μm and 0.5 μm in the figures 4.3e to 4.3h.

From all the AFM images following general conclusions can be made.

i) The $PbO_2$ in presence of different stabilizing agents was successfully deposited on different metal substrates.

ii) The deposition is significantly inhomogeneous showing the roughness of the substrate surface.

iii) Some areas (about 2 to5 % of total substrate surface) remained undeposited indicating the resistance offered to the current or it may be physical hindrance of the surface against the material to be deposited.

iv) The high resolution images depict that the emerged particle shape (peanut like) is same throughout but the size differs in the range of 0.1um to 1um as a rough estimate. The exact crystallite size can not be reliably quoted on the basis of information at hand.

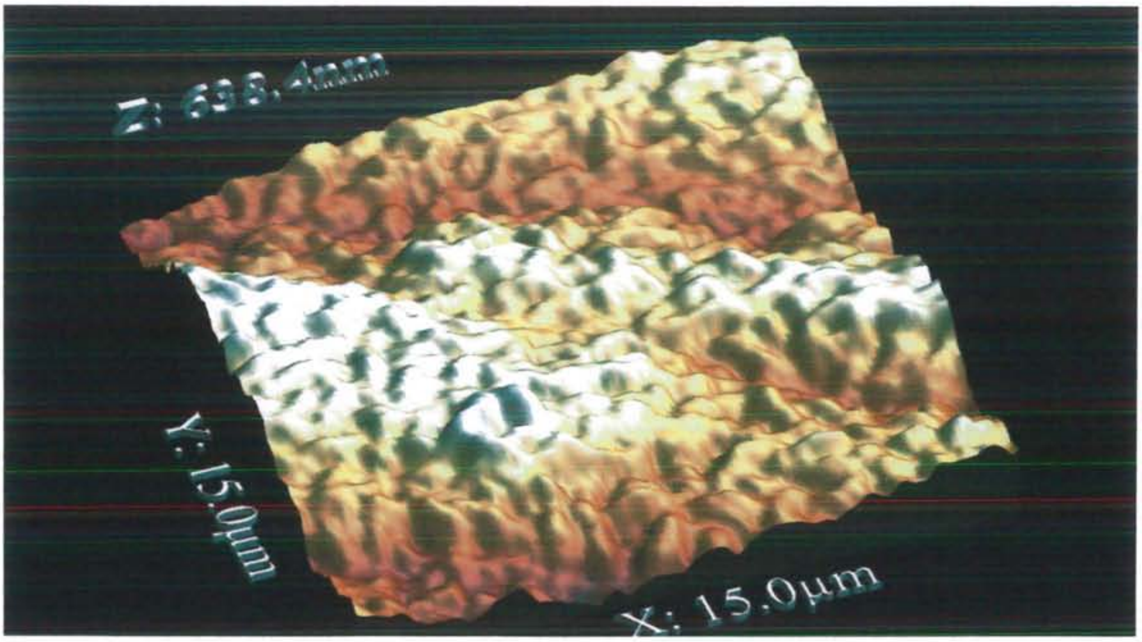


**Fig. 4.1a** 3 dimensional atomic force micrograph of $PbO_2$ electrodeposited on Pd with an area of 15 μm ×15 μm.

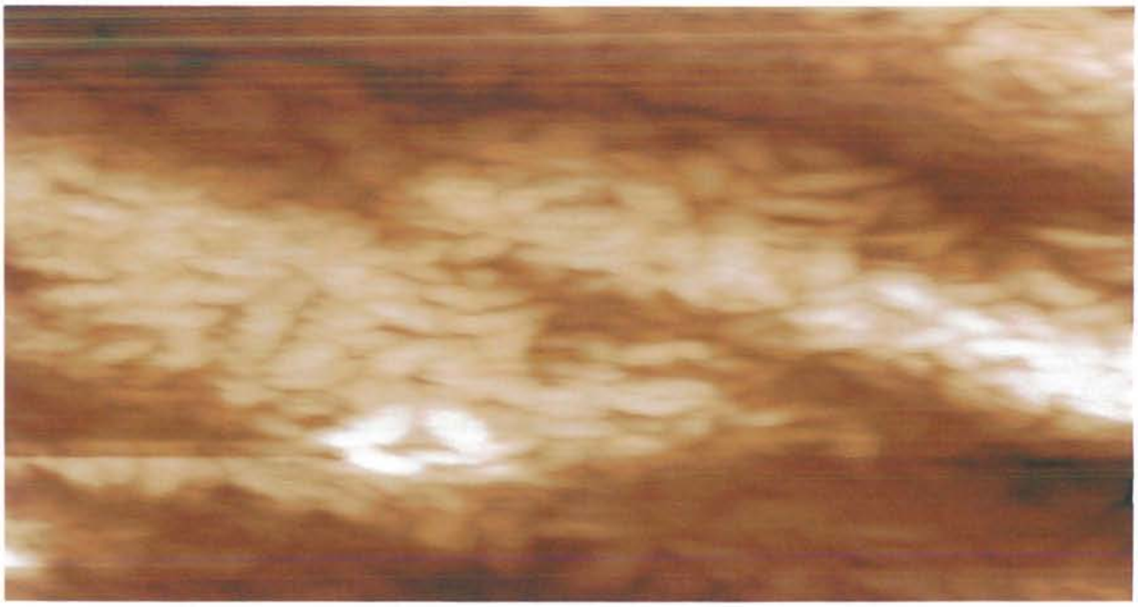
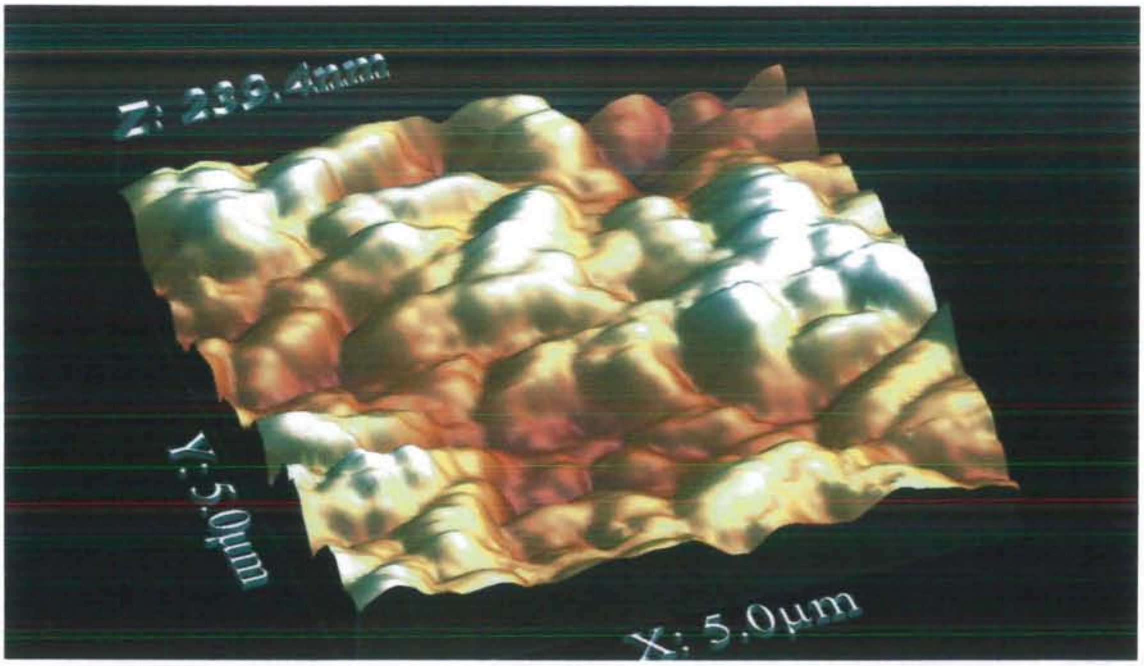


**Fig. 4.2b** 2 dimensional atomic force micrograph of $PbO_2$ electrodeposited on Pd with an area of 15 μm × 15 μm.



**4.3c** 3-D AFM image of $PbO_2$ electrodeposited on Pd substrate with an area of 5 µm × 5 µm

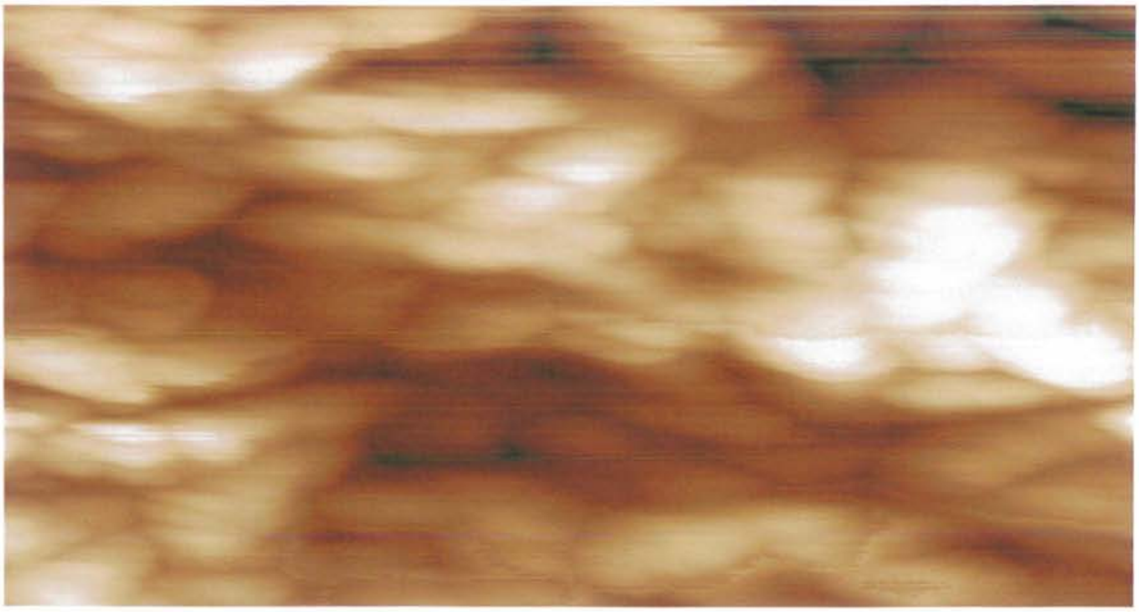


**Fig. 4.3d** 2-D AFM image of $PbO_2$ electrodeposited on Pd substrate with an area of 5 µm × 5 µm.

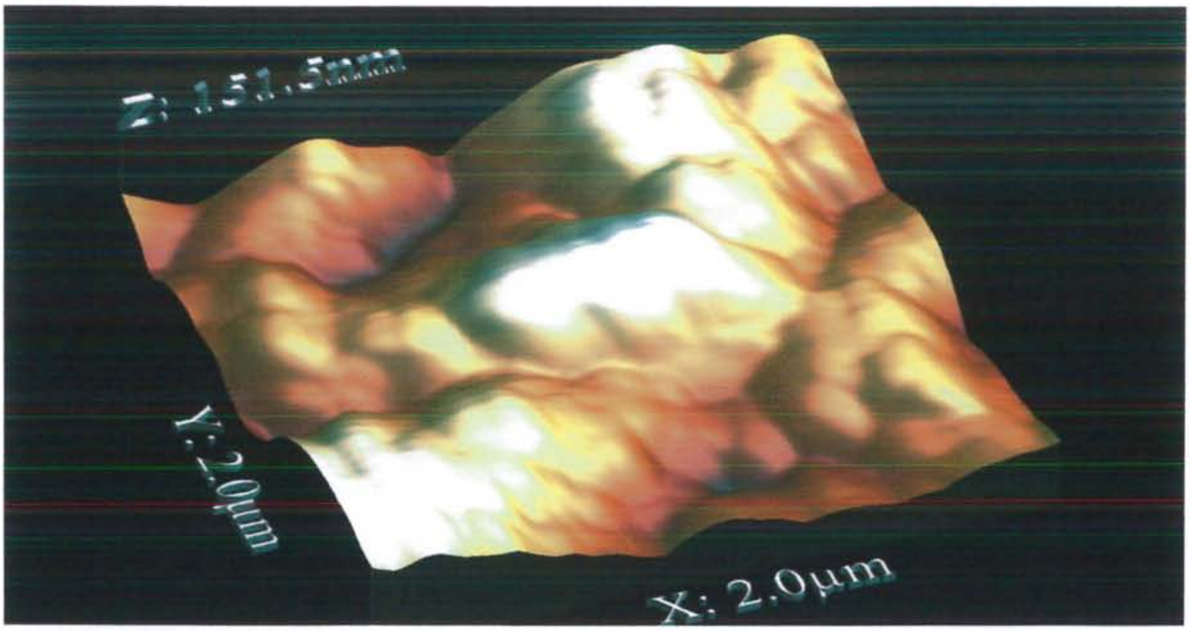


**Fig. 4.3e** 3-D AFM image of $PbO_2$ electrodeposited on Pd substrate with an area of 2 µm × 2 µm.

**Fig. 4.3f** 2-D AFM image of $PbO_2$ electrodeposited on Pd substrate with an area of 2 µm × 2 µm.

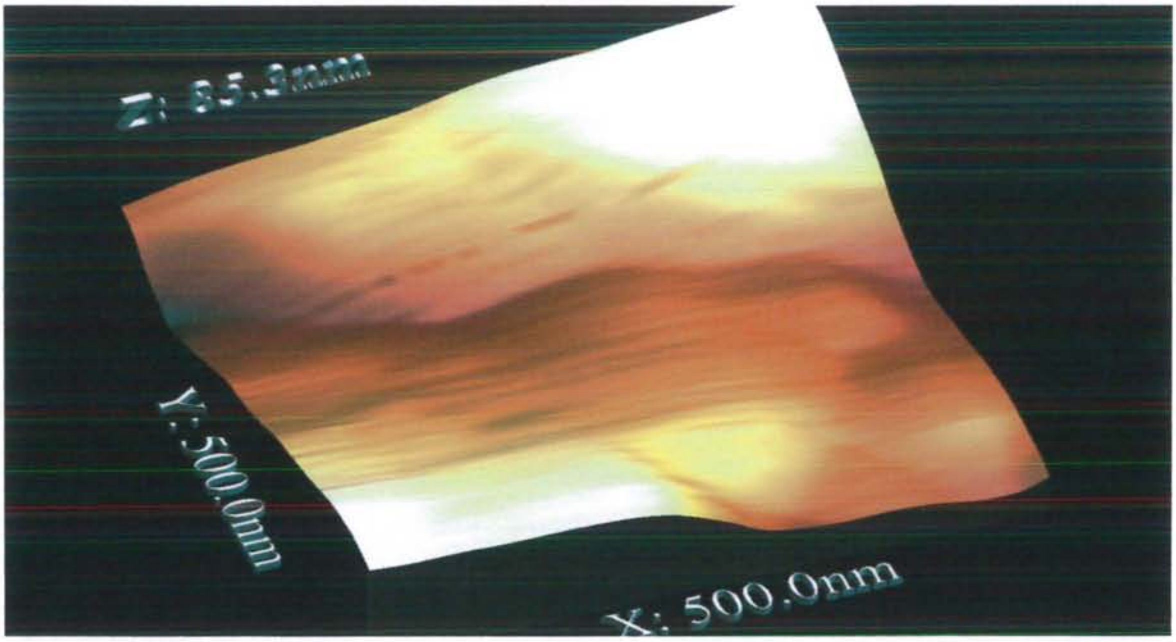


**Fig. 4.3g** 3-D AFM image of $PbO_2$ electrodeposited on Pd substrate with an area of 0.5 μm × 0.5 μm

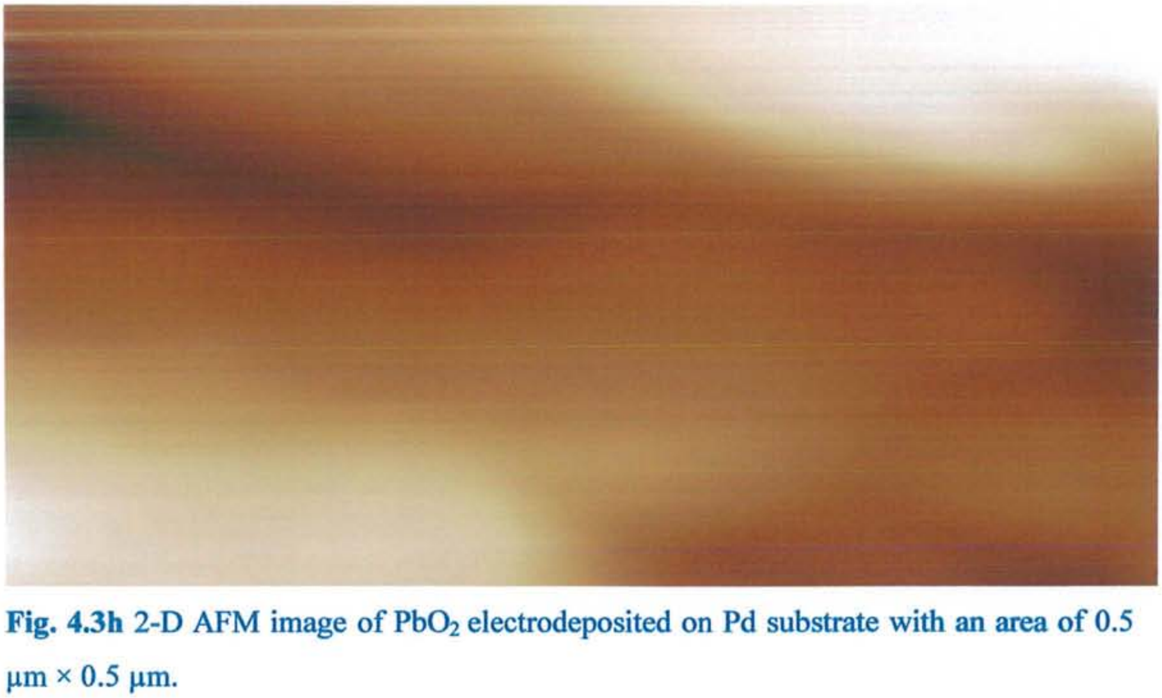


**Fig. 4.3h** 2-D AFM image of $PbO_2$ electrodeposited on Pd substrate with an area of 0.5 μm × 0.5 μm.

**Fig. 4.3** AFM images of electrodeposited $PbO_2$ electrode, 3-dimensional **(a, c, e, g)** and 2-dimensional (b, d, f, h) on Pd substrate with different resolutions of 15, 5, 2 and 0.5 μm.

## 4.3 Potential window in aqueous and non-aqueous media and $O_2$ evolution at bare and electrodeposited $PbO_2$ metals

The advantage of wide working potential range for an electrode is helpful to study greater number of compounds on it. The optimized modified electrodes were subjected for working potential analysis both in aqueous and non-aqueous media. The optimized $PbO_2$ modified electrode was obtained by depositing $PbO_2$ in presence of PVP, $HClO_4$ and $F^-$ ions. The analysis showed that the modified $PbO_2$ electrode has high potential range than the pure $PbO_2$ and other conventional electrodes. **Table 4.1** shows the working potential window of the modified $PbO_2$ electrode in aqueous Britton Robinson buffer medium and non-aqueous acetonitrile + 0.1M TBAP medium. The SCE was taken as reference in presence of auxiliary electrode of Pt wire. It is clear that the potential window has been increased significantly. The presented results are showing only the electroinactivity of the employed working electrode in the scanned potential region. To claim its optimum use the factors such as stability time, smooth horizontal scan with no charging currents and numbers of cycles are still needed to be addressed.

The oxygen evolution potential values on bare metals and $PbO_2$ electrodeposited on these metal substrates are given in **Table 4.1** below. It is clear that the oxygen evolution potential on bare Ti and $PbO_2$ deposited on Ti is the same. However this potential has been increased with the electrodeposited $PbO_2$ as compared to that on the rest of the bare metal electrodes. **Fig. 4.2** presents the cyclic voltammograms of the pure Au and modified $PbO_2$ deposited Au. The cathodic peak at about 0.7V is still inconclusive.

**Table 4.1** Potential windows in aqueous and non aqueous media and $O_2$ evolution data for pure metal substrates and modified $PbO_2$ electrodes on the metals. The SCE and Pt wire as reference and counter electrodes were used respectively.

| S.No. | Nature of working electrode | Potential window in aqueous medium (V) | Potential window in non-aqueous medium (V) | $O_2$ evolution potential in aqueous medium (V) |
|---|---|---|---|---|
| 1 | Ti | - | - | 1.37 |
| | $PbO_2$/Ti | -2 to 2.5 | -2 to 2.5 | 1.37 |
| 2 | Pd | - | - | 1.37 |
| | $PbO_2$/Pd | -2 to 0 &<br>0.8 to 2.5 | -2 to 2.5 | 1.40 |
| 3 | Pt | -0.5 to +1.5 (acidic)<br>-1 to 0.8 (basic) | - | 1.37 |
| | $PbO_2$/Pt | -2 to 0 &<br>0.8 to 2.5 | -2 to 2.5 | 1.41 |
| 4 | W | - | - | 1.60 |
| | $PbO_2$/W | -2 to 0 &<br>0.8 to 2.5 | -2 to 2.5 | 1.62 |
| 5 | Au | -0.65 to0.8 (acidic)<br>-1.5 to +0.45(basic) | - | 1.62 |
| | $PbO_2$/Au | -2 to 0 &<br>0.7 to 2.5 | -2 to 2.5 | 1.65 |

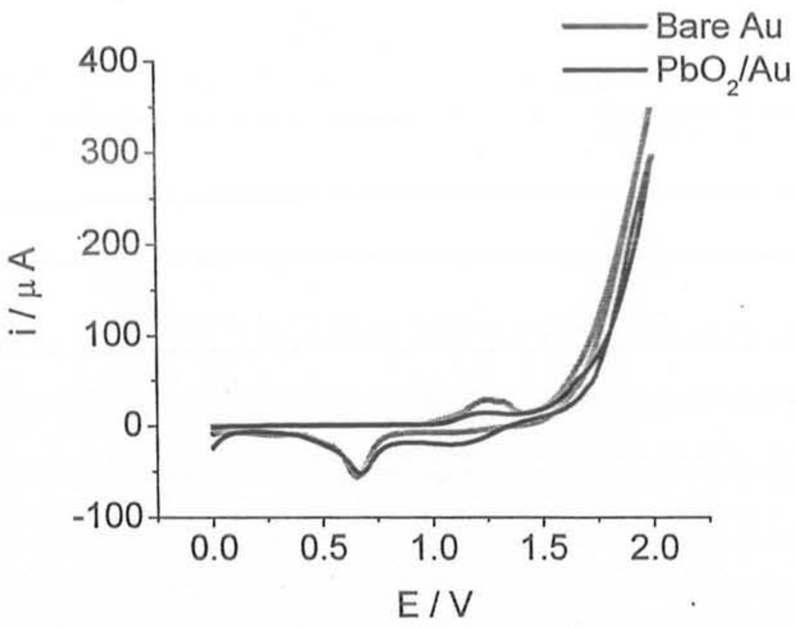


**Fig. 4.4** $O_2$ evolution on bare Au and $PbO_2/Au$ used as working electrodes vs. SCE as reference electrode and Pt wire as counter electrode.

## 4.4 Testing of the developed $PbO_2$ electrodes for some typical redox systems using Cyclic Voltammetry (CV) technique

In order to study the stability and electrochemical activity of the pure and modified $PbO_2$ electrodeposited on different substrates, cyclic voltammetric response of typical redox systems such as Ferrocene, 1,3-Dinitrobenzene and Phenol was investigated.

### 4.4.1 CV analysis of Ferrocene:

*Cyclic voltammetry of Ferrocene on Bare Ti as working electrode*

The voltammetric behavior of ferrocene was recorded in acetonitrile, first on bare titanium as working electrode and is presented in **Fig. 4.5**. In order to ensure the electrochemical inactivity of the medium (Acetonitrile + 0.1M TBAP), a blank run of the potential window is also shown in the figure.

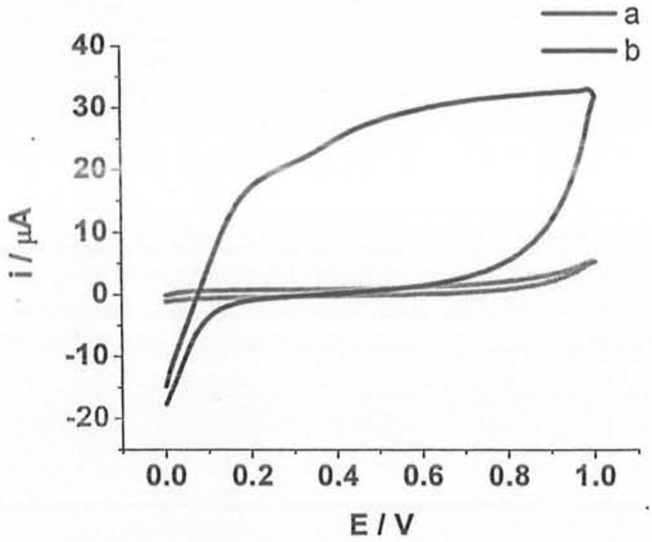


**Fig. 4.5** Cyclic voltammograms of (a) blank 0.1M TBAP + Acetonitrile (b) 2mM Ferrocene in 0.1M TBAP (tetrabutyl ammonium perchlorate) + Acetonitrile on bare Ti as working electrode vs SCE as reference electrode and Pt wire as counter electrode at a scan rate of 50 mV/s.

It is clear from the figure that no peak is observed for ferrocene on bare titanium as working electrode. It means that bare titanium is inactive for ferrocene. Similarly bare

Ti used as working electrode does not show any activity for other redox systems used i.e. 1,3-dinitrobenzene and phenol.

### *Voltammetric behavior of Ferrocene on $PbO_2$ electrodeposited Ti*

If pure $PbO_2$ obtained from deposition solution consisting of only 0.1M $Pb(NO_3)_2$ or $PbO_2$ electrodeposited from a solution consisting 0.1M $Pb(NO_3)_2$ + 0.05% nafion in 50% ethanol, on titanium substrate is used as working electrode, again no redox peak is obtained for ferrocene as shown in **Fig. 4.6A** and **4.6B.** But if $PbO_2$ electrodeposited on Ti substrate from acidic deposition solution containing 0.1M $Pb(NO_3)_2$ + 0.1 M KF + 0.2 M $HClO_4$ and 1 wt % of polyvinyl pyrrolidone (PVP), is used as working electrode, distinct oxidation and reduction peaks are observed for ferrocene as shown in the **Fig. 4.6C.**

The voltammogram for ferrocene in the **Fig. 4.6C** illustrates that in the forward scan as the voltage becomes more positive, an anodic peak current ($i_{pa}$) is observed at the anodic peak potential ($E_{pa}$). The anodic or oxidation peak indicates that ferrocene $Fe(C_5H_5)_2$ (neutral reduced form) is converted to its oxidized form ferrocenium $Fe(C_2H_5)_2^+$ according to reaction

$$Fe(C_5H_5)_2 \rightleftharpoons Fe(C_2H_5)_2^+ + e^-$$

During the reverse scan, the voltage becomes less positive and consequently, reduction of $Fe(C_2H_5)_2^+$ occurs and a cathodic peak current ($i_{pc}$) at the cathodic peak potential ($E_{pc}$) is obtained (Tsierkezos 2007).

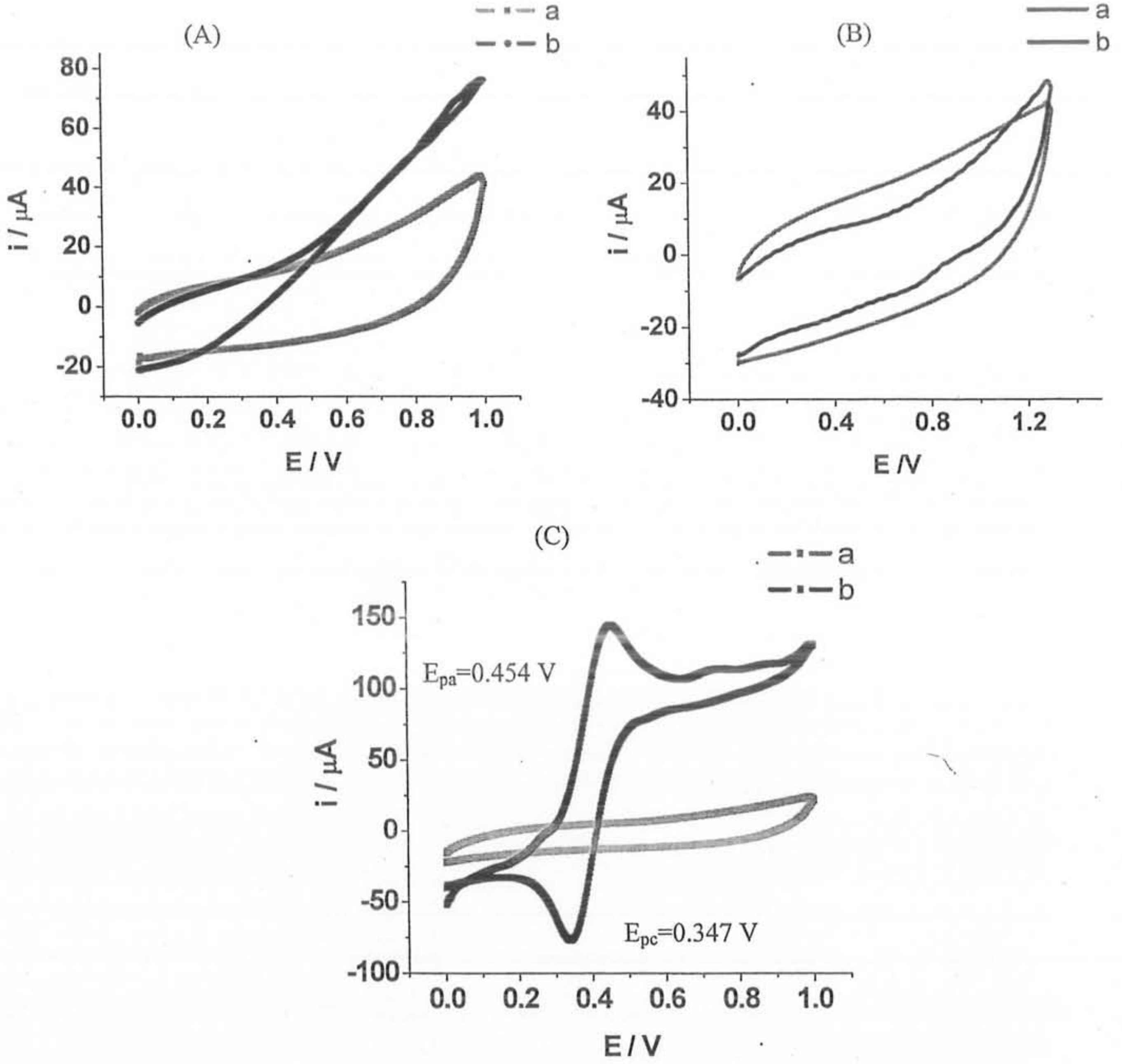


**Fig. 4.6** Cyclic voltammograms of (a) Acetonitrile + 0.1M TBAP (blank) (b) 2mM Ferrocene in Acetonitrile + 0.1M TBAP, at $PbO_2$ deposited on Ti substrate from (A) 0.1M $Pb(NO_3)_2$ solution and (B) 0.1M $Pb(NO_3)_2$ solution in 50% ethanol and 0.05% nafion and (C) 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs SCE at scan rate of 50mV/s.

### *Voltammetric behavior of Ferrocene on $PbO_2$ electrodeposited on Pd and Pt*

Pure $PbO_2$ deposited on Ti substrate was inactive for ferrocene, however, changing substrate from Ti to Pd or Pt, $PbO_2$ deposited from 0.1M $Pb(NO_3)_2$ gives characteristics peaks for ferrocene. Thus Pd and Pt are better substrates as compared to Ti. Like Ti, $PbO_2$ deposited from nafion solution is inactive for ferrocene and PVP + $F^-$ modified $PbO_2$ electrode is active for ferrocene. These results are shown in **Fig. 4.7** and **Fig. 4.8.**

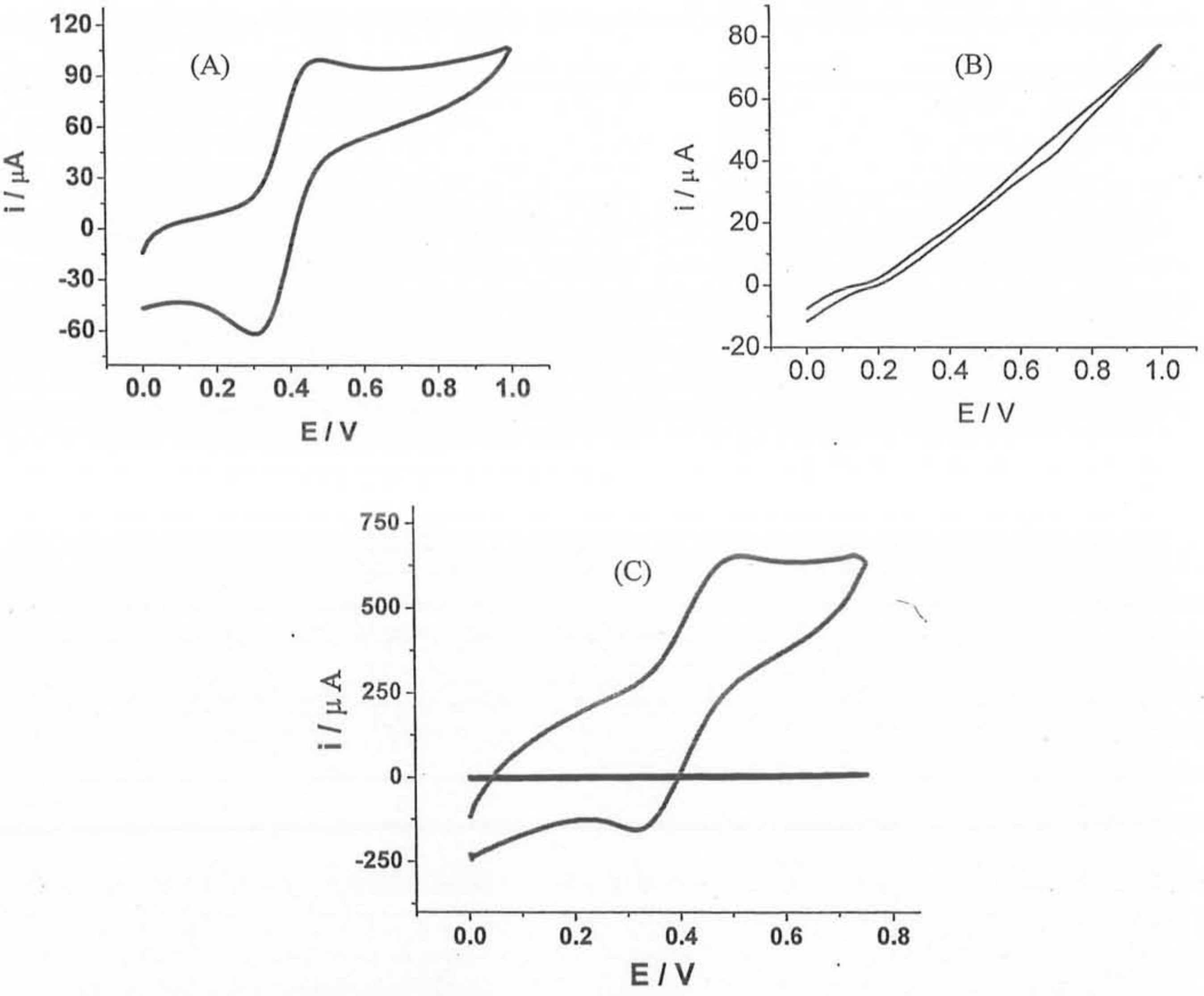


**Fig. 4.7** Cyclic voltammograms of 2mM Ferrocene in Acetonitrile + 0.1M TBAP, at $PbO_2$ deposited on Pd substrate from (A) 0.1M $Pb(NO_3)_2$ solution and (B) 0.1M $Pb(NO_3)_2$ solution in 50% ethanol and 0.05% nafion and (C) 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 50 mV/s.

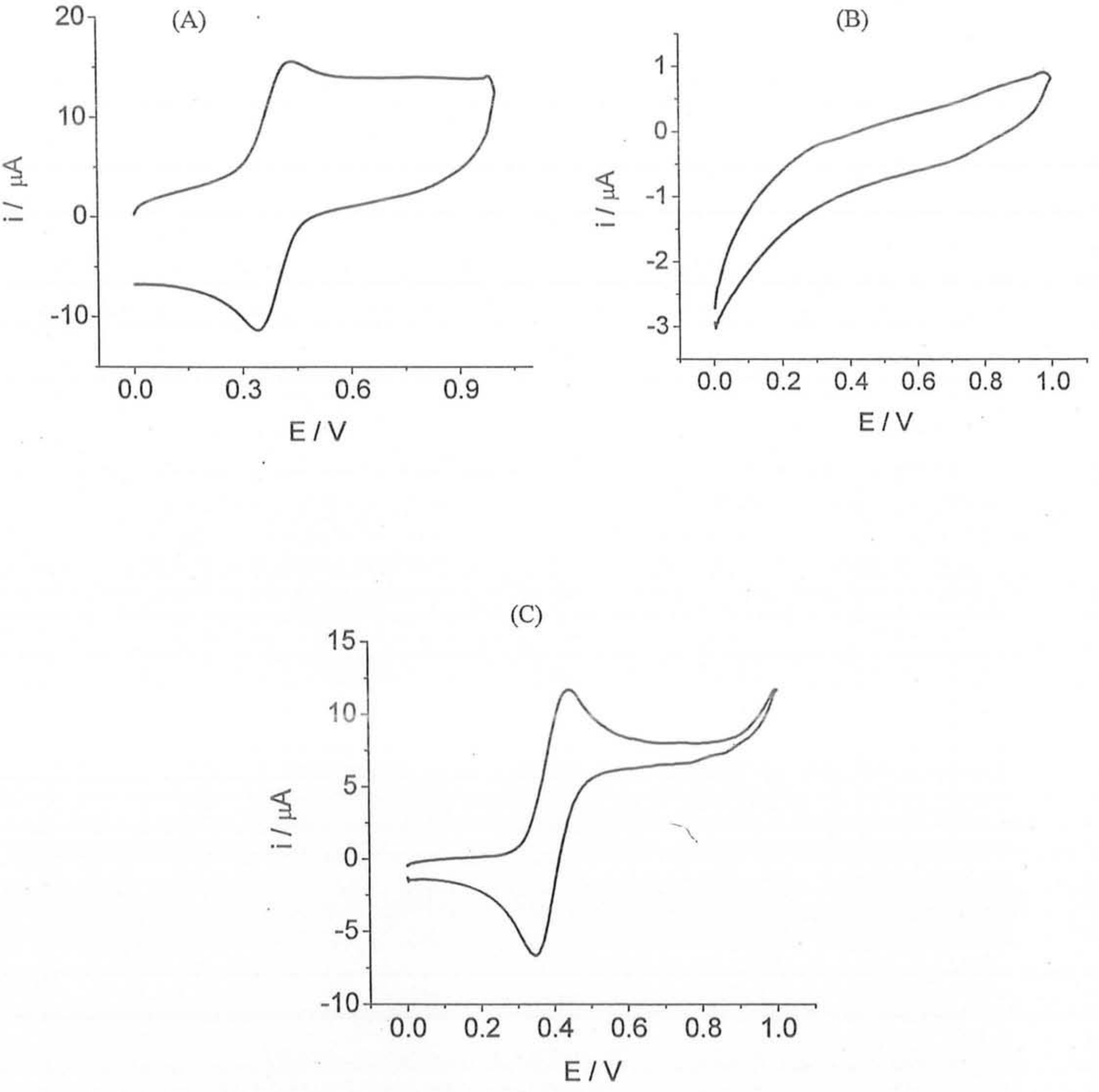


**Fig. 4.8** Cyclic voltammograms of 2mM Ferrocene in Acetonitrile + 0.1M TBAP, at $PbO_2$ deposited on Pt substrate from (A) 0.1M $Pb(NO_3)_2$ solution, (B) 0.1M $Pb(NO_3)_2$ solution in 50% ethanol and 0.05% nafion and (C) 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 50 mV/s.

***Voltammetric behavior of Ferrocene on $PbO_2$ electrodeposited on Tungsten and Gold***

$PbO_2$ deposited on W and Au substrates from all the three types of deposition solutions is active for ferrocene. In the case of W and Au substrates, $PbO_2$ deposited from nafion solution also gives characteristic peaks for ferrocene, which was not the case with other substrates. In this regard W and Au are better substrates than Ti, Pd or Pt. The results are shown for Au substrate in the **Fig. 4.9.** The activity of pure and modified $PbO_2$ electrodeposited on different substrates for ferrocene is summarized in **table 4.2.**

**Table 4.2** The activity of pure and modified $PbO_2$ electrodeposited on different metal substrates for ferrocene.

| **S.No.** | **Substrate** | **Pure $PbO_2$** | **$PbO_2$ + Nafion + 50 % ethanol** | **$PbO_2$ + PVP + $F^-$ + 0.2M $HClO_4$** |
|---|---|---|---|---|
| 1 | Ti | × | × | √ |
| 2 | Pd | √ | × | √ |
| 3 | Pt | √ | × | √ |
| 4 | W | √ | √ | √ |
| 5 | Au | √ | √ | √ |

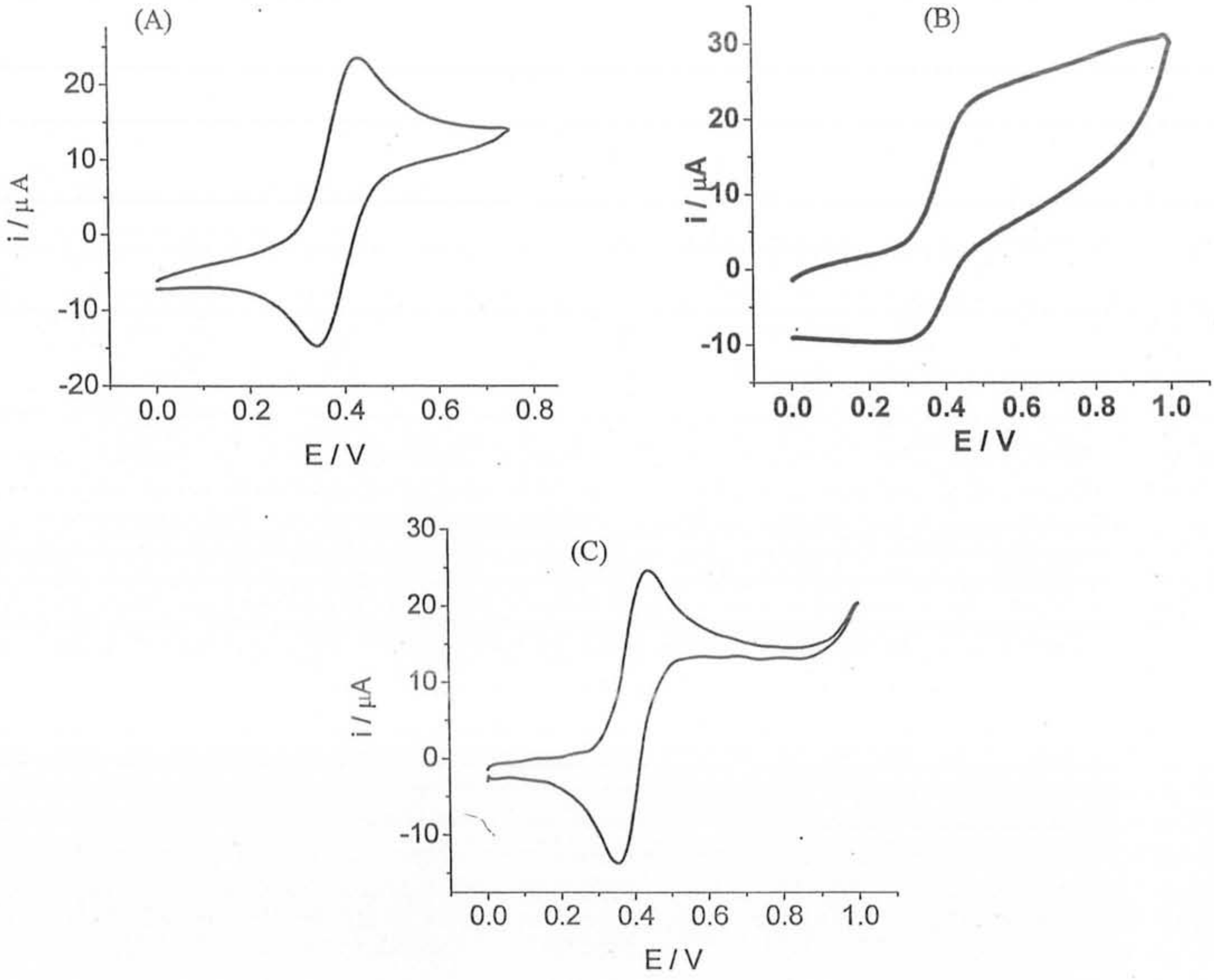


**Fig. 4.9** Cyclic voltammograms of 2mM Ferrocene in Acetonitrile + 0.1M TBAP, on $PbO_2$ deposited on Au substrate from (A) 0.1M $Pb(NO_3)_2$ solution, (B) 0.1M $Pb(NO_3)_2$ solution in 50% ethanol and 0.05% nafion and (C) 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 50mV/s.

***Effect of number of Cycles and Scan rate***

The effect of number of cycles and scan rate on the cyclic voltammogram of 2 mM ferrocene is shown in the **Fig. 4.10**. It is clear that with repeated cycles, there occurs a small decrease in the peak current response. This may be due to the little rearrangement or deterioration of the active sites of $PbO_2$ with cycling. However, with the increasing scan rate, increase in the peak current values was observed. The observed behaviour is as per expectation and in accordance to that of conventional commercial electrodes.

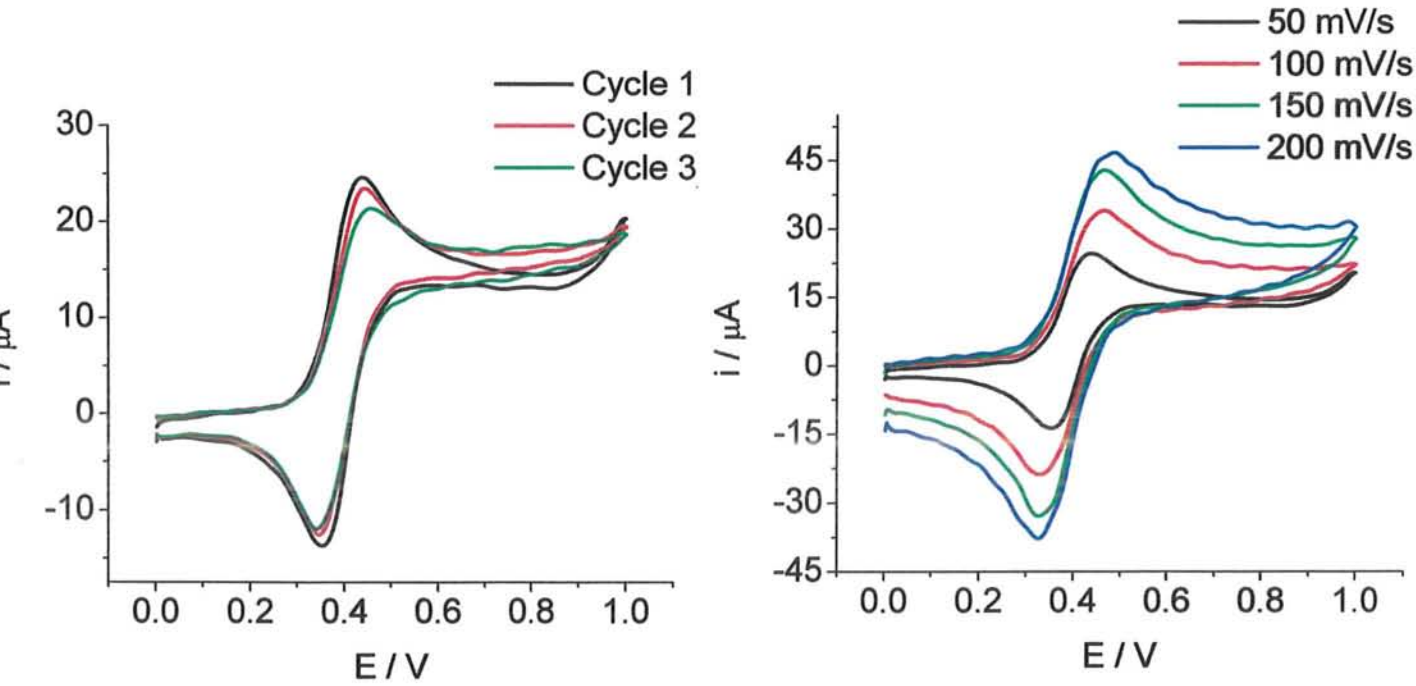
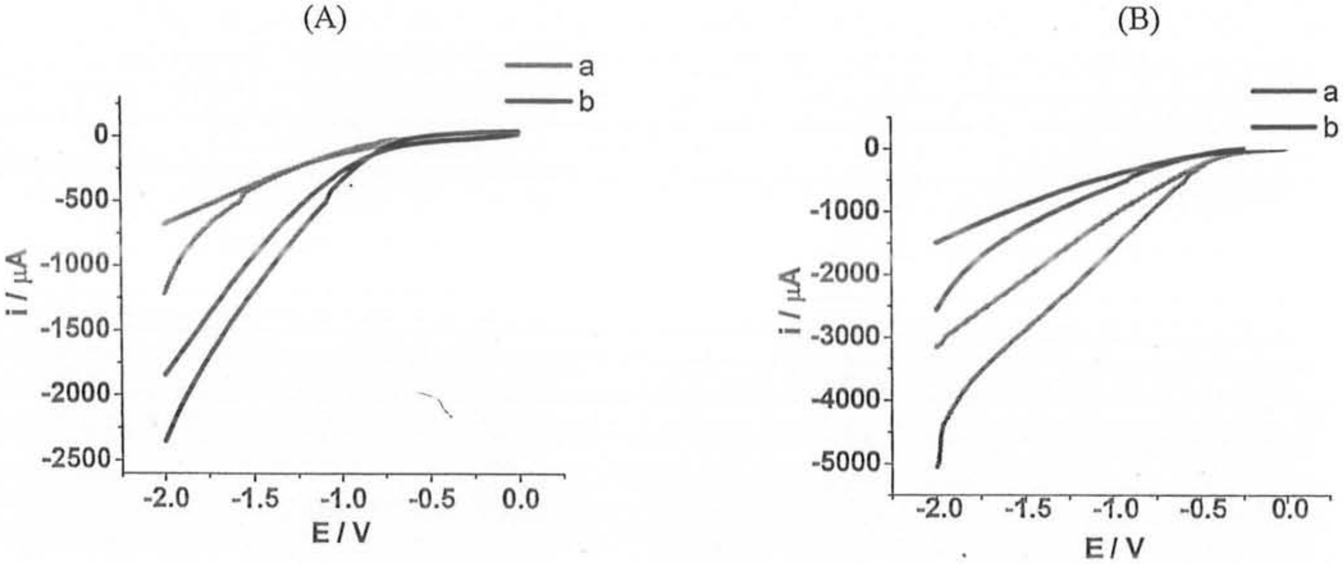


**Fig. 4.10** Cyclic voltammograms of 2mM Ferrocene in Acetonitrile + 0.1M TBAP and (A) the effect of number of cycles (B) scan rate, at $PbO_2$ deposited on Au substrate from 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 50 mV/s.

### 4.4.2 CV analysis of 1,3-Dinitrobenzene:

To further ascertain the electrochemical activity of pure and modified $PbO_2$ electrodes voltammetric behaviour of 1,3-dinitrobenzene on these electrodes was investigated. Unlike ferrocene, pure as well as modified $PbO_2$ electrodeposited on Ti gave no response for 1,3-dinitrobenzene.These results are shown in **Fig. 4.11.** Similar results are obtained if we use the substrates such as Pd, Pt and W except Au. The possible reasons could be the working ability of the modified electrodes in the negative potential region, the responsive ability of the redox couple and the changes in the surface morphology of the working electrodes.



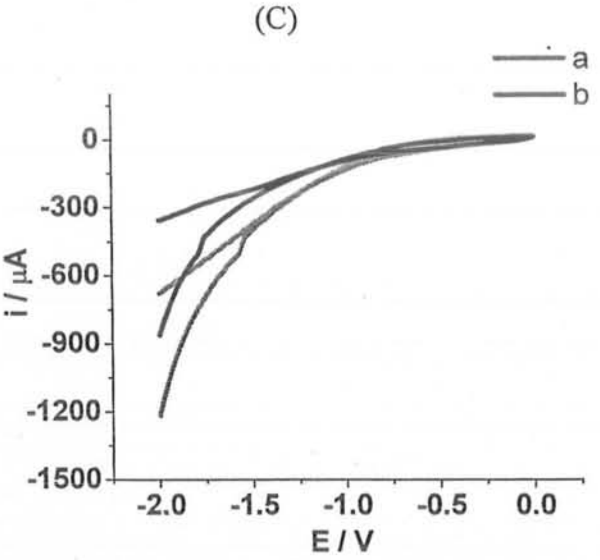


**Fig. 4.11** Cyclic voltammograms of (a) Acetonitrile + 0.1M TBAP (b) 6mM 1,3-dinitrobenzene in Acetonitrile + 0.1M TBAP, on $PbO_2$ deposited on Ti substrate from (A) 0.1M $Pb(NO_3)_2$ solution and (B) 0.1M $Pb(NO_3)_2$ solution in 50% ethanol and 0.05% nafion and (C) 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 50 mV/s.

Only modified $PbO_2$ electrode deposited from solution containing 0.1M $Pb(NO_3)_2$, 0.1 M KF, 0.2 M $HClO_4$ and 1 wt % PVP on Au substrate show electrochemical activity for 1,3-dinitrobenzene. The cyclic voltammogram for 6 mM 1,3-dinitrobenzene in acetonitrile and 0.1M tetra butyl ammonium perchlorate (TBAP) as supporting electrolyte is shown in the **Fig. 4.12.** This behaviour indicates that the appropriate surface for the electron transfer to occur and observable requires the compatibility of the substrate with the deposition solution. The Au showed this compatibility in present case. The chemistry behind this needs further investigations.

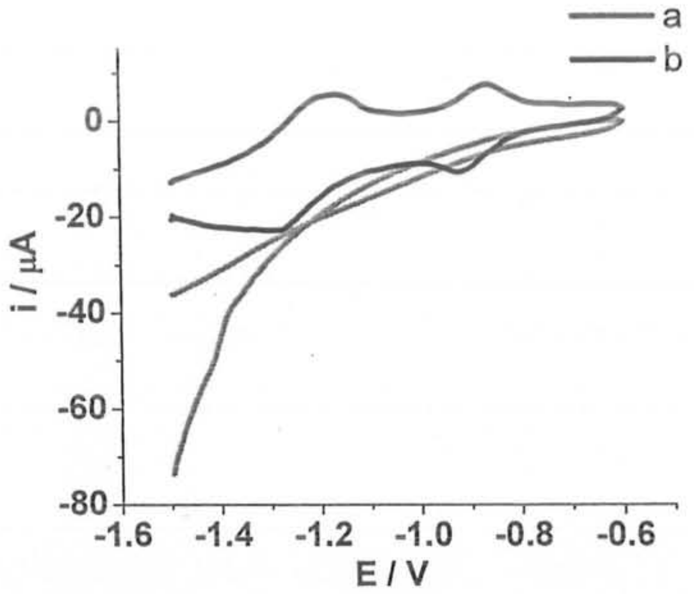


**Fig. 4.12** Cyclic voltammogram of (a) Acetonitrile+0.1M TBAP (b) 6mM 1,3-dinitrobenzene in Acetonitrile + 0.1M TBAP, on $PbO_2$ deposited on Au substrate from 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 200mV/s.

*Effect of number of Cycles and Scan rate*

The effect of number of cycles and scan rate on the cyclic voltammogram of 6 mM 1,3-dinitrobenzene is shown in the **Fig. 4.13.** It is clear that with repeated cycles almost no change in the peak current values is observed. The peak currents are essentially constant for several cycles. It means that no passivation of the electrode takes place during repeated cycling processes. These results indicate that there were no chemical reactions coupled with the electron transfer; consequently, the oxidized forms are stable in the time frame of the experiment and the charge-transfer process is reversible. As expected, the increasing scan rate increases the peak current values.

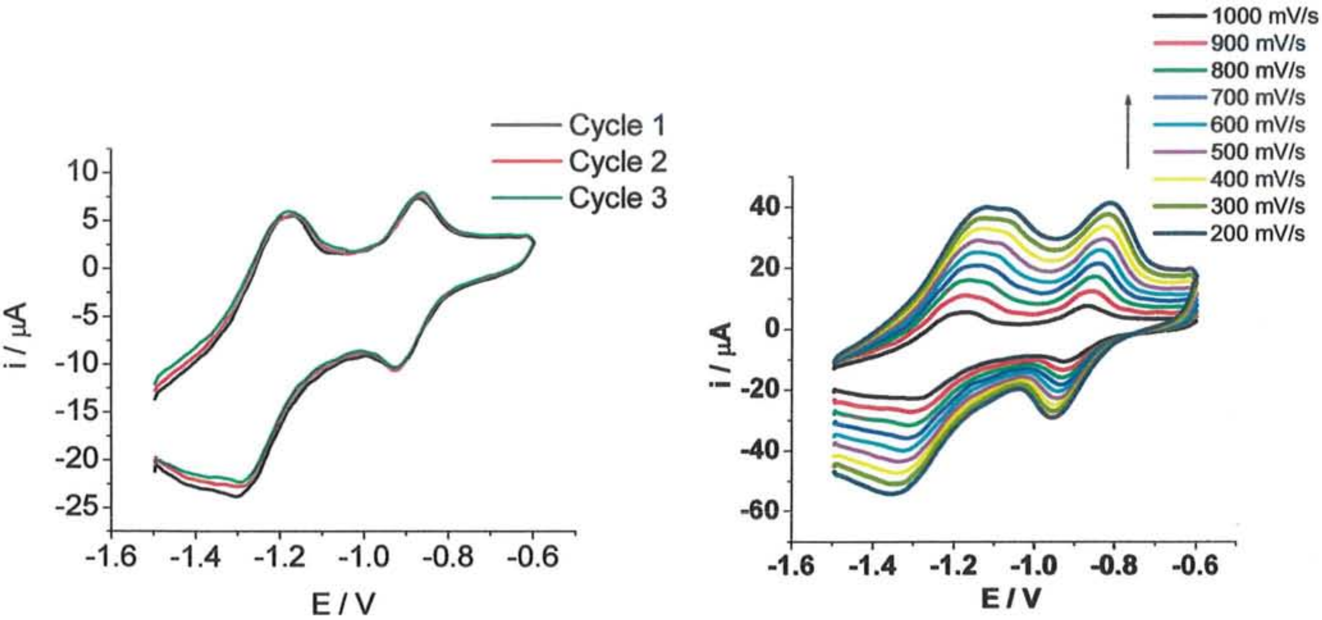


**Fig. 4.13** Cyclic voltammograms of 6mM 1,3-dinitrobenzene in Acetonitrile + 0.1M TBAP and the effect of number of cycles and scan rate, at $PbO_2$ deposited on Au substrate from 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 50 mV/s.

### 4.4.3 CV analysis of Phenol:

The third redox system studied for the electrochemical activity of pure and modified $PbO_2$ was the persistent organic pollutant phenol in portable and waste water. This compound was dissolved in Britton-Robinson buffer and the pH was adjusted to 2 as at this pH phenol shows best redox activity on glassy carbon used as working electrode. However, redox behavior of phenol was checked at pH values such as 4, 6, 8 and 10 as well. First blank run of the buffer and then the analyte phenol was taken on pure $PbO_2$. No peak was observed for phenol and therefore the pure $PbO_2$ remained inactive for phenol. Then the activity of the nafion added $PbO_2$ was checked and the result was the same as pure $PbO_2$. $F^-$ modified electrode was also inactive for phenol as is clear from the **Fig. 4.14**, however it showed a reduction peak for the blank buffer medium, which may be due to the reduction of some species in the Britton Robinson buffer. This peak was not observed, when glassy carbon is used as working electrode. Same results were obtained, when the deposition was carried out on other electrodes such as Pd, Pt, W and even Au.

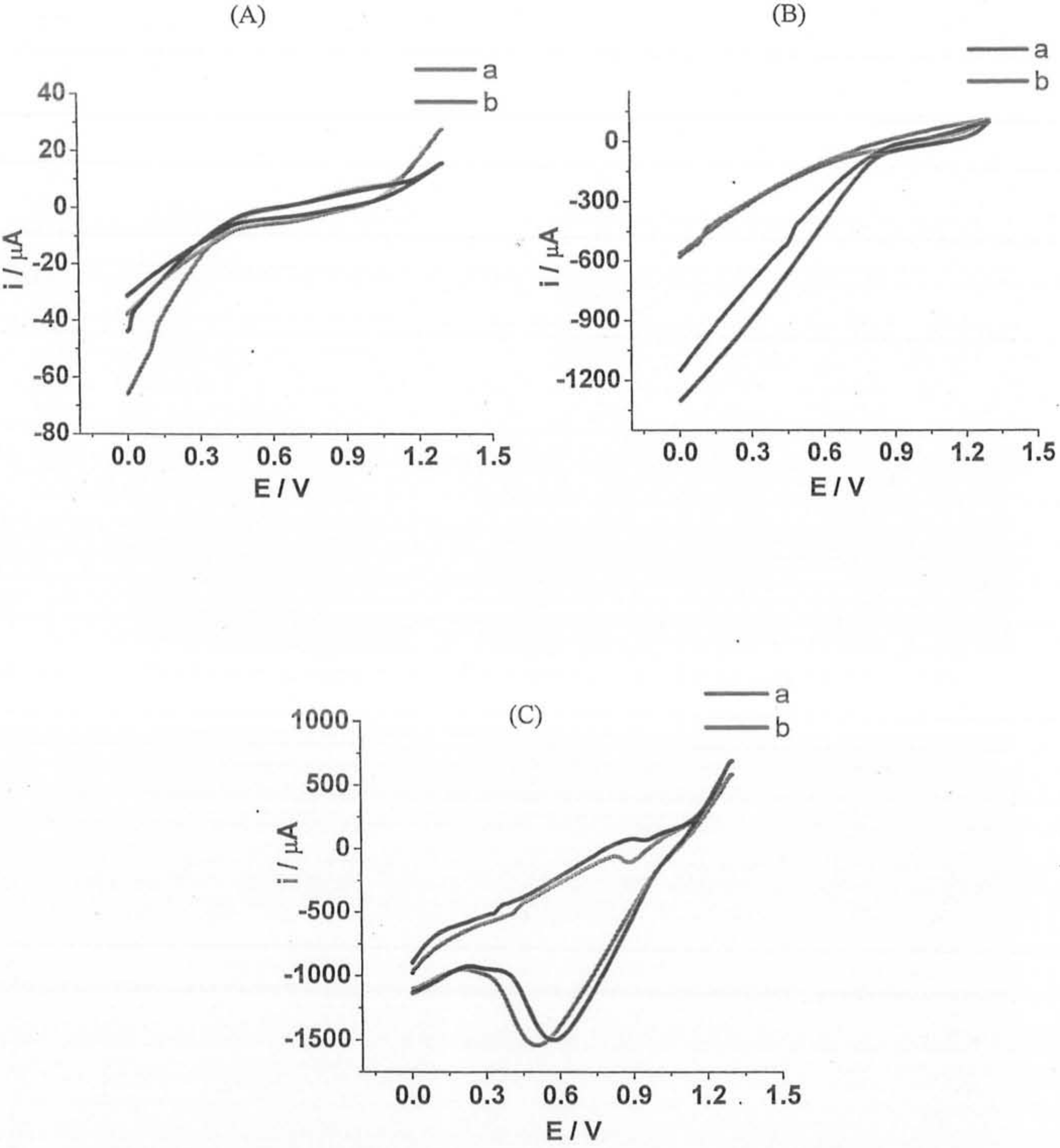


**Fig. 4.14** Cyclic voltammogram of (a) Blank Britton-Robenson buffer pH 2 (b) 0.5mM phenol + Britton-Robenson buffer pH 2 at $PbO_2$ deposited on Ti substrate from (A) 0.1M $Pb(NO_3)_2$ solution and (B) 0.1M $Pb(NO_3)_2$ solution in 50% ethanol + 0.05% nafion and (C) 0.1M $Pb(NO_3)_2$ solution in 0.1M KF, 0.2M $HClO_4$ and 1 wt % PVP vs. SCE at scan rate of 50mV/s.

For phenol analysis simple phenol was checked from 0.1mM concentration to 20 mM at pH values of 2, 4, 6, 8 and 10. Apart from simple phenol, other phenols like 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, nitro phenol and amino phenols were also run in Britton-Robinson buffer. 4-chlorophenol was also studied in DMSO plus tetra butyl ammonium perchlorate and in $Na_2SO_4$ solution. The observed results were not presentable.

***Quantitative data for selected redox systems on the bare and $F^-$ modified $PbO_2$ deposited metals***

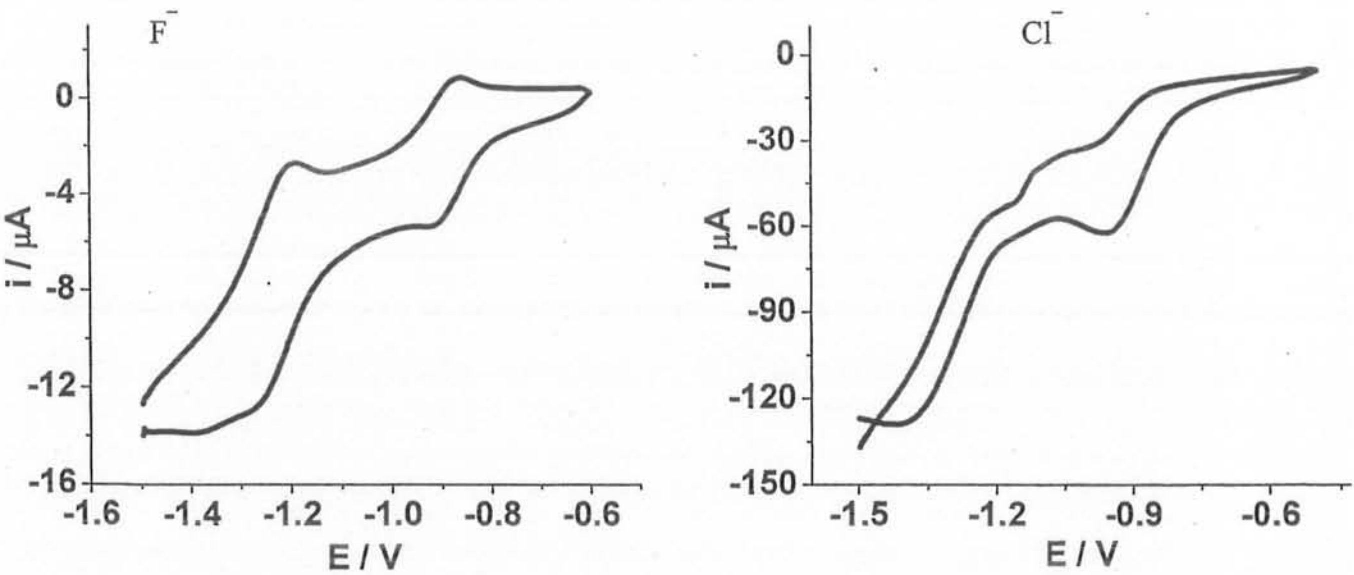
The electrochemical activity data of the selected redox systems such as ferrocene, 1,3-dinitrobenzene and phenol on the bare metals and $F^-$ modified $PbO_2$ electrode deposited on these metal substrates is given in **Tale 4.3**. It is clear that bare Ti, Pt and W substrates used as working electrodes were not active for all the three compounds. Bare Ti does not give any single peak for any compound. Bare Pt and W give only oxidation peaks for ferrocene and the reduction peak is missing. Bare W also gives two peaks for 1,3-dinitrobenzene, the two peaks are missing. Bare Pd gives peaks for ferrocene and phenol and for dinitrobenzene, the two peaks are missing. Whereas bare Au electrode was active for all of these compounds. $PbO_2$ electrodeposited on Ti, Pd, Pt and W is active for ferrocene only. $PbO_2$/Au is active for ferrocene and 1,3-dinitrobenzene and not for phenol.

**Table 4.3** CV data for the bare and modified $PbO_2$ deposited electrodes on the metals in acetonitrile and BRB solutions. SCE and Pt wire were used as reference and counter electrodes respectively.

| S.No | Nature of electrode material used | Peak positions of selected Compounds (V) | | |
|---|---|---|---|---|
| | | Acetonitrile + TBAP | | BRB |
| | | Ferrocene (FC) | 1,3-DNB | Phenol |
| 1 | Ti | - | - | - |
| | $PbO_2$/Ti | 0.454 / 0.347 | - | - |
| 2 | Pd | 0.442 / 0.37 | -0.753 / -1.058 | 1.023 |
| | $PbO_2$/Pd | 0.52 / 0.313 | - | - |
| 3 | Pt | 0.483 | - | - |
| | $PbO_2$/Pt | 0.469 / 0.344 | - | - |
| 4 | W | 0.464 | -0.807 / -0.941 | - |
| | $PbO_2$/W | 0.459 / 0.385 | - | - |
| 5 | Au | 0.422 / 0.351 | -1.165 / -0.843 /<br>- 0.929 / -1.0319 | 0.989 |
| | $PbO_2$/Au | 0.435 / 0.359 | -1.2 / -0.875<br>-0.931 / -1.295 | - |

## 4.5 Effect of Halides on the activity of $PbO_2$ electrode deposited on Au substrate

Since F$^-$ modified electrode deposited on Au substrate show activity for the redox behavior of 1,3-dinitrobenzene, next we wanted to study the effect of other halides on the activity of $PbO_2$ electrode. For this purpose, instead of 0.1 M F,$^-$ we added Cl,$^-$ Br$^-$ and I$^-$ one by one into the deposition solution containing 0.1M $Pb(NO_3)_2$, 0.2M $HClO_4$ and 1 wt % PVP. With all of these halides, a decrease in the number of peaks for 1,3-dinitrobenzene was noted and in the absence of halides no single peak was observed for the compound. All of these differently modified electrodes with any of halides are active for ferrocene and inactive for phenol. The results for the effect of different halides on the activity of lead dioxide electrode for 1,3-dinitrare are shown in the **Fig. 4.15.** Also it was noted that in the absence of F$^-$ weak binding for $PbO_2$ deposition takes place in which case the deposited $PbO_2$ is easily removed from the electrode surface after just single run. In the presence of F$^-$ the electrode after several runs is reactivated just by rinsing its surface with distilled water and acetone. Thus F$^-$ is the best among halides to increase the binding stability and activity of $PbO_2$ electrode.



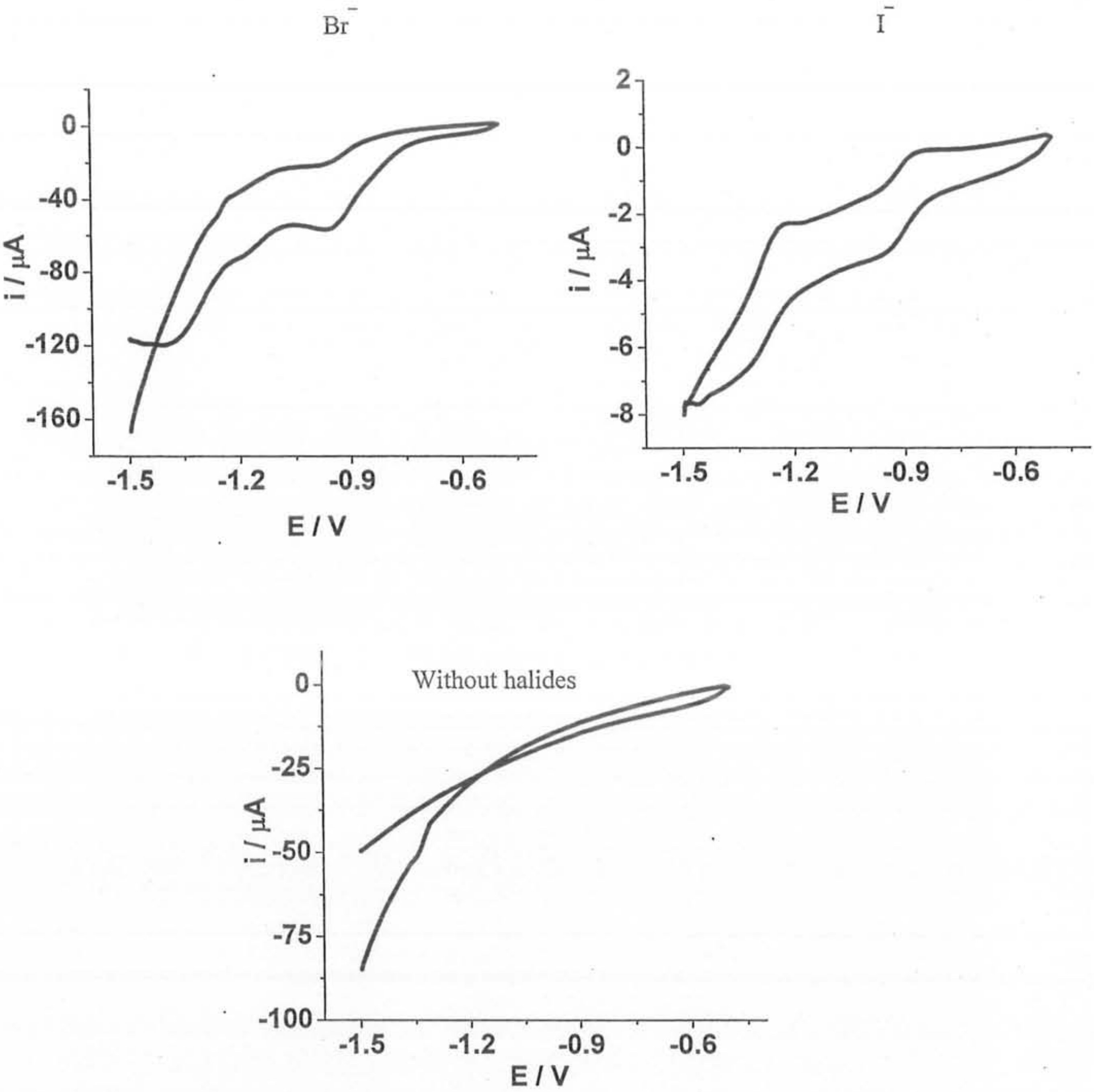
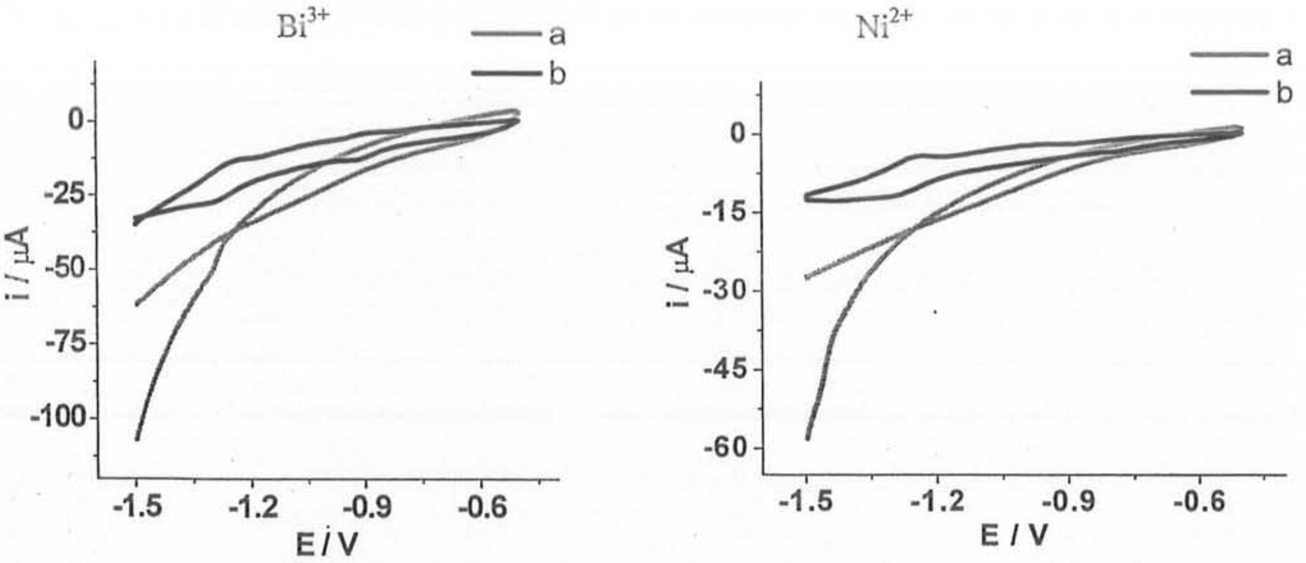


**Fig. 4.15** Cyclic voltammograms of 6mM 1,3-dinitrobenzene on modified $PbO_2$ electrode: electrodeposited from solutions containing 0.1 M $Pb(NO_3)_2$, 0.2 M $HClO_4$ and 1 wt % PVP with $F^-$, $Cl^-$, $Br^-$, $I^-$ and without any halide vs. SCE.

## 4.6 Effect of Metal ions on the activity of $F^-$ modified $PbO_2$ electrode deposited on Au substrate

After it was found that among halides, fluoride is the best one to enhance the stability and electrochemical activity of $PbO_2$ electrode; next the effect of some metal ions like $Bi^{3+}$, $Ni^{2+}$ and $Ag^+$ on the fluoride modified electrode was studied. These metal ions were added one by one into the deposition solution containing $Pb(NO_3)_2$, $F^-$, $HClO_4$ and PVP and their effect was evaluated by studying the deposited electrode for 1,3-dinitrobenzene. It was observed that in the presence of these metals no peak was observed for 1,3-dinitrobenzene **(Fig. 4.16)** as well as phenol, although such modified electrodes were active for ferrocene and the deposition was strong enough. It can be concluded that these metal ions decreased the activity of the $F^-$ modified $PbO_2$ electrode, however, the adsorption of $PbO_2$ was strong and not weakened especially in the presence of $Ni^{2+}$. As mentioned in the section 4.1 of this chapter the work on this aspect is limited and demands precise empirical studies to reach a solid result.



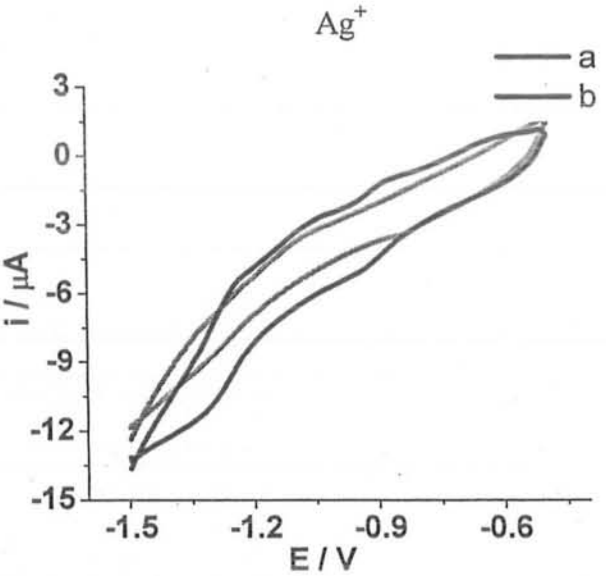


**Fig. 4.16** Cyclic voltammograms of 6mM 1,3-dinitrobenzene on modified $PbO_2$ electrode electrodeposited from solutions containing 0.1 M $Pb(NO_3)_2$, 0.1 M KF, 0.2 M $HClO_4$ and 1 wt % PVP with $Bi^{3+}$, $Ni^{2+}$ and $Ag^+$ vs. SCE.

## 4.7 References

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# Conclusions

In the current study lead dioxide ($PbO_2$) was electrochemically deposited on different metal substrates (Ti, Au, Pd, Pt and W) and characterized for its ability as electrode material. The optimized conditions for the galvanostatic deposition of $PbO_2$ are 0.1M $Pb(NO_3)_2$ solution, 10 mA/cm$^2$ current density and 5 minutes deposition time for all the substrates except Ti for which it was 15 minutes. X-ray diffraction revealed that β-$PbO_2$ having tetragonal symmetry is the dominated product of the galvanostatic electrodeposition. AFM technique showed the inhomogeneous deposition of $PbO_2$ with multilayer formation. The results are also indicative of poor surface pretreatment. The results showed that the working potential window in aqueous and non-aqueous media and the oxygen evolution potential values of the modified $PbO_2$ are higher than those of the corresponding metal substrates. Au was found the most suitable substrate among the metals used for the electrochemical deposition of $PbO_2$. Among halides, $F^-$ is excellent to enhance the stability and electrochemical activity of $PbO_2$. The observed results of metal ion dopants such as $Bi^{3+}$, $Ni^{2+}$ and $Ag^+$ are contrary to the reported literature and demand more work on this aspect. However, the overall findings of the present work show that the developed new electrode showed improvement in potential window, increase in oxygen evolution potential and chemical and electrochemical stability in both the aqueous and organic media. The preliminary findings are encouraging and demand for more work in this very area of cost effective electrode development.