

## ELECTROCHEMICAL MODIFICATION OF ELECTRODE BY O-PHENYLENEDIAMINE

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[ Received: 1987 July; Accepted: 1988 April ]

The surface changes occur when either a platinum or stainless steel electrode is polarised in acetonitrile containing  $\text{LiClO}_4$  or  $\text{NaClO}_4$  and o-phenylenediamine (OPD). While an adherent yellowish brown film formation takes place on anode surface white porous, inhomogeneous deposit is found on the cathode. In this investigation it has been established that the anodically polymerised film can be used as chemically modified electrode for the oxidation of phenol and aniline. It has also been observed that for the formation of cathodic deposit, water in the electrolyte is a must. The products have been identified by I.R. spectra.

**Key words:** Chemically modified electrode, electro-oxidation, o-phenylenediamine

## INTRODUCTION

The development of the technology in the area of chemically modified electrode for the electro-organic synthesis is dependent on different methods of obtaining organic or inorganic films. It is possible to obtain an organic polymer film on metallic surface by oxidation or reduction of a compound which produces polymerizable radical or cationic species. The polymerisation of pyrrole in nonaqueous media has opened a new area of research in the field of electrochemistry [1]. The polymers obtained are both electroactive and electrochromic in nature and hence the electroactive nature of the polymers allows them to use as chemically modified electrodes [2-8].

In this paper, the surface modifications occurring on a platinum or stainless steel electrode polarisation in acetonitrile containing  $\text{LiClO}_4$  or  $\text{NaClO}_4$  and o-phenylenediamine are studied. It has been established that the anodically polymerised film can be used as chemically modified electrode (CME) for the oxidation of phenol and aniline.

## EXPERIMENTAL

## Electropolymerization

Electropolymerization studies were carried out using platinum and stainless steel electrodes in nonaqueous and aqueous media. The electrolyte consists of acetonitrile, lithium perchlorate and monomer (o-phenylenediamine (OPD)). Other solvents such as tetrahydrofuran (THF),  $\text{CH}_2\text{Cl}_2$ , dimethylformamide (DMF) and supporting electrolytes like  $(n\text{-Bu})_4\text{N}^+\text{BF}_4^-$ ,  $\text{NaClO}_4$  were also employed. All the reagents were dried over  $\text{P}_2\text{O}_5$  or anhydrous calcium chloride before use.

All the experiments were carried out under argon or nitrogen atmosphere. The ratio of monomer to supporting electrolyte was maintained at 1:10 to obtain good conductivity of the system. Wherever  $\text{LiClO}_4$  or  $\text{NaClO}_4$  or  $(n\text{-Bu})_4\text{N}^+\text{BF}_4^-$  was used the concentration of the same was maintained at 1 M. In all the cases current density was maintained between 0.01 and 0.05  $\text{kA}\cdot\text{m}^{-2}$ .

The polymer coated electrode was used as an anode to carry out oxidation studies for organic substances like phenol and aniline.

Porous, spongy and white deposit was obtained on the cathode. It was soluble in water but insoluble in almost all organic solvents such as benzene, diethyl ether, acetone and did not melt up to 573K. Elemental analysis of this deposit indicated the presence of lithium.

It was found possible to increase the thickness of the film of the cathode considerably, whereas it was difficult to increase the thickness of the anodic film more than 10  $\mu\text{m}$ . The anodic film was more adherent and difficult to peel off than the cathodic film. The conductivity of the cathodic and anodic films was measured by four probe technique.

## Doping studies

During electropolymerisation of OPD at anode, doping of anion such as  $\text{ClO}_4^-$  takes place. The level of doping was determined by leaching the perchlorate ion in double distilled water. The leached polymer was again doped with  $\text{ClO}_4^-$  ion from 1M solution of  $\text{LiClO}_4$  in acetonitrile. These experiments on leaching and doping were repeated and the level of doping in the polymer matrix was 42-50% depending on the current density and other factors like the percentage of water in electrolyte.

## Polymer modified electrode in aqueous medium

1M  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  in double distilled water containing 0.1M monomer was used as electrolyte. Polymerisation was carried out on either stainless steel or platinum electrode in divided and undivided cells at different pH values ranging from 1 to 10. At lower pH, irregular, less adherent film was obtained, while at pH 8 adherent and uniform film was obtained. Nature of the anodic film was same as that obtained from nonaqueous medium.

## Polarisation studies

Polarisation of OPD at stainless steel or Pt electrode was carried out in a H-type cell. Potential of the electrode was measured against SCE.

For galvanostatic cathodic, anodic polarisation, 1M  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  in acetonitrile or in water containing different concentrations of monomer was used as electrolyte. Galvanostatic polarisation studies of phenol and aniline at modified anode as well as

on bare stainless steel were carried out either in 1M Na<sub>2</sub>SO<sub>4</sub> or 1M LiClO<sub>4</sub> · 3H<sub>2</sub>O solution. The effect of Cu<sup>2+</sup> on the modification of electrode surface was also studied.

## RESULTS AND DISCUSSION

### Electropolymerisation

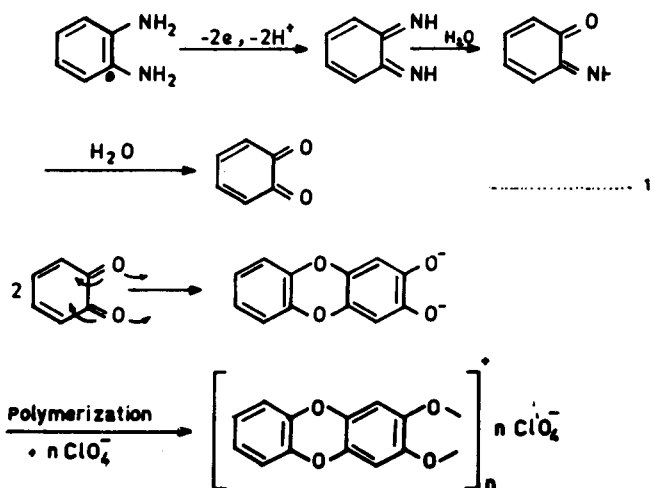
Figs. 1 to 4 show the results of galvanostatic polarisation of stainless steel and platinum in nonaqueous and aqueous media with OPD. There was no anodic and cathodic deposit under complete anhydrous condition. Little amount (min. 2%) of water was necessary for obtaining cathodic and anodic deposit. On passing the current, anode surface became yellowish brown due to the formation of an adherent polymer film, which was insoluble in water and in almost all known organic solvents like acetone, ether, alcohol, benzene, THF, acetonitrile etc. But it was found to be soluble in concentrated HCl resulting in yellowish brown coloured solution. The anodic deposit did not melt up to 573K. The elemental analysis of anodic polymer indicated the absence of nitrogen.

It has been observed that during prolonged electrolysis the acidity of the electrolyte increases due to the discharge of perchlorate ion at the anode and deposition of lithiated compound at cathode. This may be one of the reasons for restricting the polymer thickness at the anode surface.

The elemental analysis of anodic deposit showed the absence of nitrogen which was expected as in the case of aniline polymer. On evaporation of the anolyte after modification, red crystals with m.p. at 343K were obtained. It was identified as orthobenzoquinone. The tests for organic acids in anodic polymer was also negative.

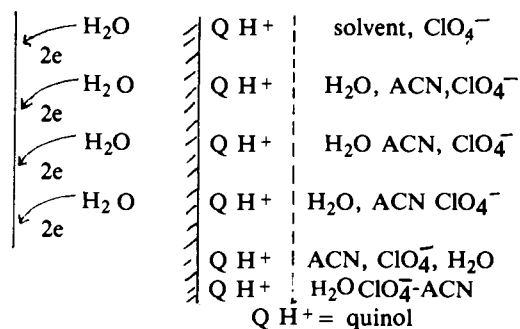
On the basis of the observations and physicochemical tests the following mechanism is proposed for the oxidative polymerisation of OPD at anode.

### ANODIC POLYMERIZATION :-

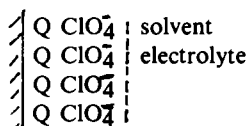


I.R. spectrum also supports the above structure of the polymer. The band in the region at 1000 cm<sup>-1</sup> to 1100 cm<sup>-1</sup> is due to perchlorate ion. The band at 1380 cm<sup>-1</sup> and 1460 cm<sup>-1</sup> have been assigned to ring oxygen. The band at 1460 cm<sup>-1</sup> may also be due to the coupling of the aromatic nuclei at ortho position. The bands at 2925 and 2910 cm<sup>-1</sup> are due to aromatic ring. A broad band at 3500 cm<sup>-1</sup> is due to the hydrogen bonded hydroxyl group.

The mechanism of the modification of anode surface can be explained in the following schematic diagram.



During polymerisation

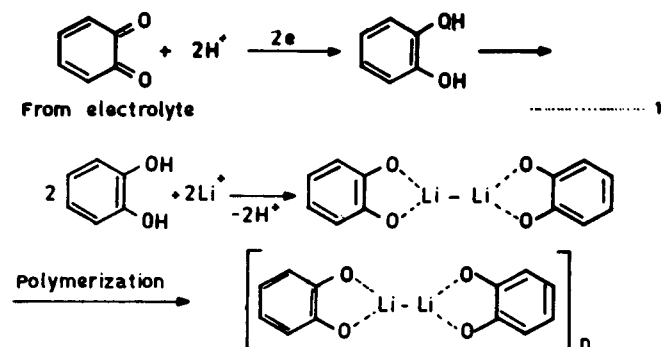


Q = quinone polymerized

The property of cathodic deposit suggests the salt-like structure. The atomic absorption spectroscopic measurements indicated the presence of 11% lithium in cathodic deposit. This confirms that cathodic deposit is a lithiated adduct.

From the above observations the following mechanism is proposed for the cathodic deposition.

### CATHODIC REACTION



I.R. spectrum of cathodic deposit also supports the above structure of the polymer. The band at  $480\text{ cm}^{-1}$  was assigned to Li-O bond. No band was observed at  $1670\text{ cm}^{-1}$  which is normally associated with hydrogen bonded  $\text{H}_2\text{O}$  molecule. This suggests that the compound obtained on cathode was not LiOH but a derivative of organic species namely quinol. Therefore the broad band between  $1300 - 1600\text{ cm}^{-1}$  may be due to organic species attached to the lithium. The band at  $2900\text{ cm}^{-1}$  is due to the aromatic ring.

The anodic curve in Fig.1 shows slight increase in current at  $0.5\text{V}$  vs SCE indicating the formation of a free radical. Again the sudden

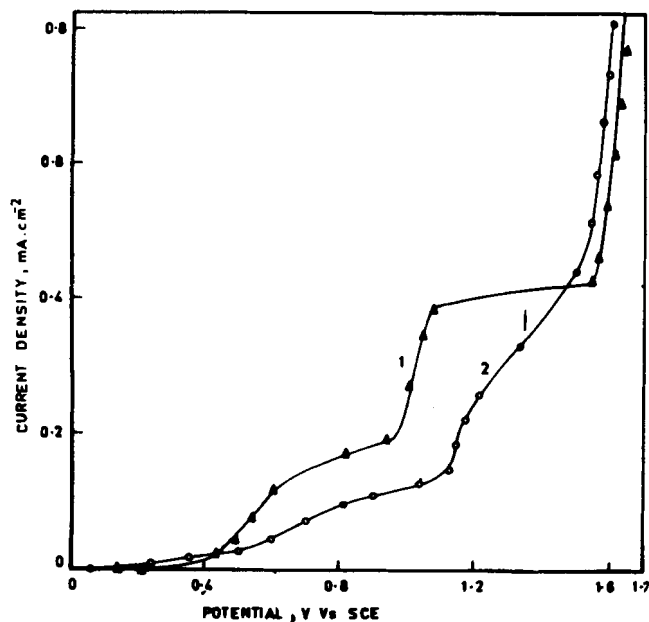


Fig.1: Galvanostatic polarisation of OPD at stainless steel electrode in nonaqueous medium.

Electrolyte  $1\text{M LiClO}_4$  in  $\text{ACN} + 0.1\text{M OPD}$ , R.E. — SCE, C.E. — S.S.

1. S.S. as anode/OPD area  $27.1\text{ cm}^2$ ; 2. S.S. as cathode/OPD area  $28.34\text{ cm}^2$

increase in current at  $0.9\text{V}$  vs SCE may be due to the polymerisation of free radical at the anode surface and simultaneous doping of polymer with perchlorate ion. Similarly in the cathodic curve there is a jump in current at  $1.15\text{V}$  vs SCE, probably indicating the formation of hydroquinone getting deposited in the form of lithium adduct.

The comparison of the results in aqueous and nonaqueous media (Figs 1 to 4) reveals an interesting observation. In aqueous medium there is a sudden rise of current at  $1.4\text{V}$  (Fig.2) and  $1.6\text{V}$  vs SCE (Fig.4) for stainless steel and Pt anodes respectively without any plateau. This indicates that the polymerisation of OPD in aqueous medium is associated with simultaneous evolution of oxygen.

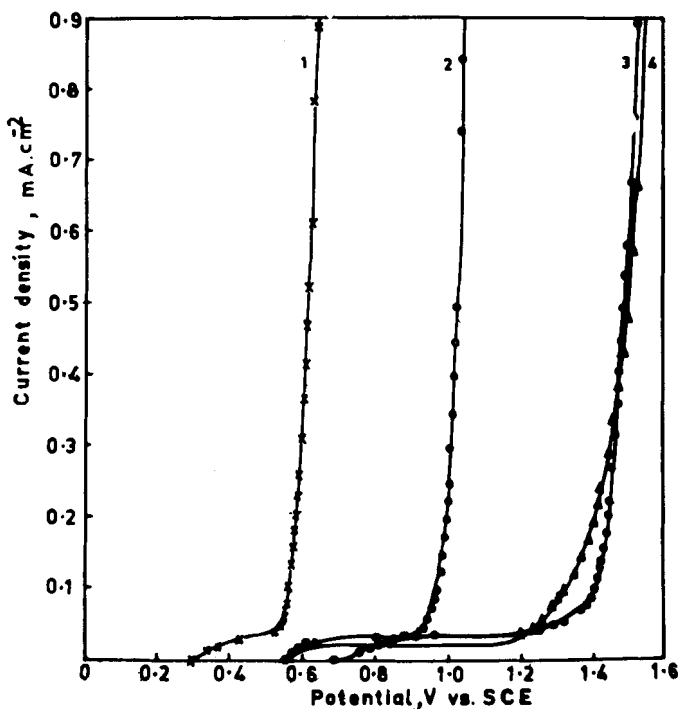


Fig.2: Galvanostatic polarisation of OPD at stainless steel in electrolyte with different pH.

Electrolyte  $1\text{M LiClO}_4 \cdot 3\text{H}_2\text{O}$  in water; C.E.: S.S.; R.E.: S C E  
1. S.S./OPD-pH = 10; 2. S.S./OPD-pH = 1; 3. S.S./OPD-pH = 6; 4. S.S./OPD-pH = 8

In the case of nonaqueous medium at least two breaks are observed in current voltage curves, thereby indicating that the polymerization takes place with free radical reaction which is the slowest step.

From Fig.2 it can be observed that although pHs 6 and 8 give almost same potential at which current rise takes place, in actual practice it has been found that the deposit obtained at pH8 is more adherent.

The resistivity of films obtained at different pH was found to be as follows:

pH - 1 =  $1.845\text{ ohm}^{-1}\text{cm}^{-1}$ ; pH - 6 =  $2.833\text{ ohm}^{-1}\text{cm}^{-1}$ ;  
pH - 8 =  $3.0\text{ ohm}^{-1}\text{cm}^{-1}$ ; and pH - 10 =  $3.4\text{ ohm}^{-1}\text{cm}^{-1}$

Fig. 5 shows the polarisation curves of stainless steel anode with OPD and with and without addition of  $\text{CuSO}_4$ . It is seen that at  $0.8\text{V}$  vs SCE there is a slight increase in current which is attributed to the presence of a little oxygen in solution. Then there is a sudden jump in current at  $1.4\text{V}$  vs SCE. Although the potential at which the jump in current is identical both in presence and absence of  $\text{CuSO}_4$ , the thickness of anodic deposit, however, increases considerably and reaches to  $20\text{ }\mu\text{m}$  in the presence of  $\text{CuSO}_4$ . This indicates that the first step in polymerisation namely the oxidation of o-phenylenediamine is initiated by  $\text{Cu}^{2+}$  ion in solution and helps in the build up of the thickness.

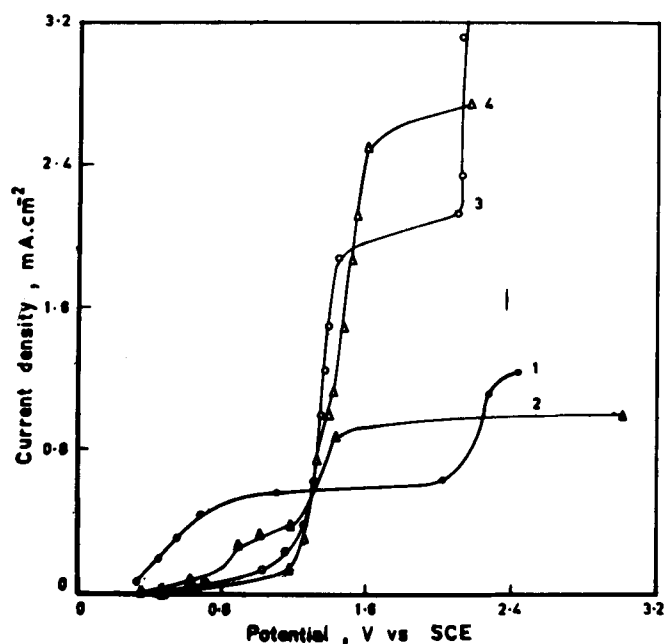


Fig. 3: Galvanostatic polarisation of OPD at Pt 1N nonaqueous medium; Electrolyte; 1M  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  in ACN; Pt as cathode; R.E.: S C E C.E.; S.S.; area of electrode =  $0.8 \text{ cm}^2$   
1. Bare Pt; 2. Pt/OPD; 3. Pt/2ml 0.1M OPD; 4. Pt/3ml 0.1M OPD;

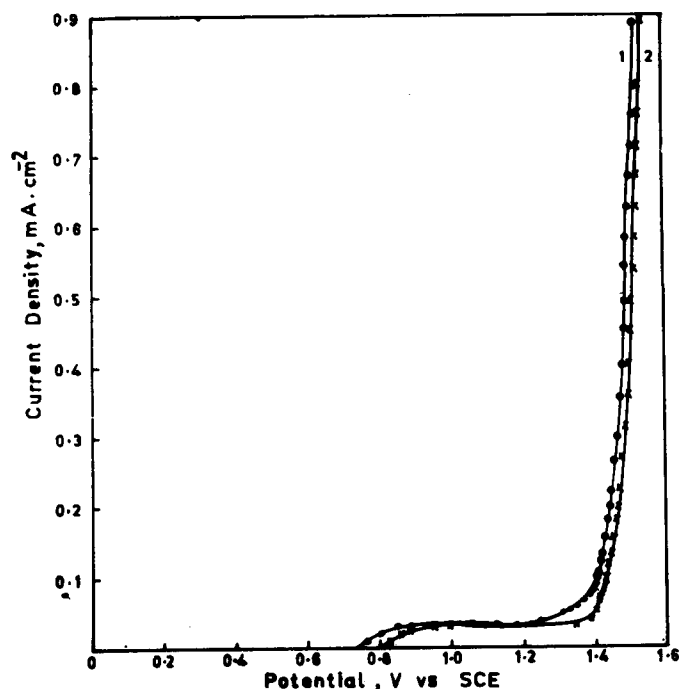


Fig. 5: Galvanostatic polarisation of OPD at stainless steel electrode in aqueous medium  
Electrolyte 1M  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  C.E.: S.S.; R.E.: S C E  
1. S.S./OPD-; 2. S.S./OPD +  $\text{CuSO}_4$

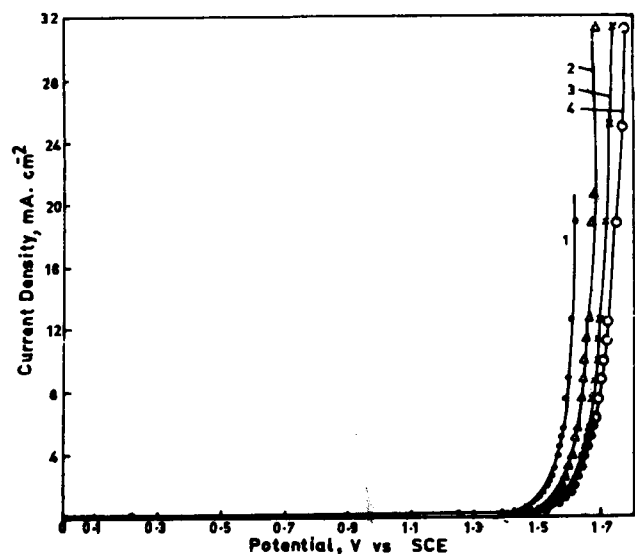


Fig. 4: Concentration polarisation — galvanostatic anodic polarisation of OPD at Pt electrode in aqueous medium.  
Electrolyte 1M  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  in water. C.E.: S.S.; R.E.: SCE: Electrode area:  $0.8 \text{ cm}^2$   
1. Bare Pt electrode; 2. Pt/1ml 0.1M OPD; 3. Pt/2ml 0.1M OPD; 4. Pt/3ml 0.1M OPD

#### Studies on modified electrodes

On the modified anode surface the oxidation studies of aniline and phenol were carried out in aqueous medium (pH = 8) (Figs. 6 & 7). When the modified electrode prepared both in presence and absence of  $\text{Cu}^{++}$  was used in the presence of depolariser like aniline or phenol, the potentials shifted to more positive values with the electrodes obtained in the absence of  $\text{Cu}^{++}$  (Fig. 6). This indicates that the oxidation at the modified surface proceeds by adsorption of organic moiety on previously modified surface. When similar studies were carried out on electrode without modified surface, it was observed that both aniline and phenol got polymerised at the anode surface giving rise to less conducting film. However, on the modified surface with yellow brown colour, the aniline got polymerised to dark bluish green film.

On polymer modified electrode the studies on oxidation of phenol and aniline in aqueous  $\text{Na}_2\text{SO}_4$  medium at pH 8 was carried out and the results are shown in Fig. 7. The products of oxidation were extracted using ether and were identified by I.R. spectrum. In the case of aniline, it gets oxidised to quinone at pH 8. But at pH 1 the same gets polymerised to a green polymer which has been identified as emeraldine. Similarly phenol also gives a quinone at pH 8. It is interesting to note that in presence of aniline the potential shifts from 1.1V to 1.65V whereas in the case of phenol the potential shifts from 1.1V to 0.9V.

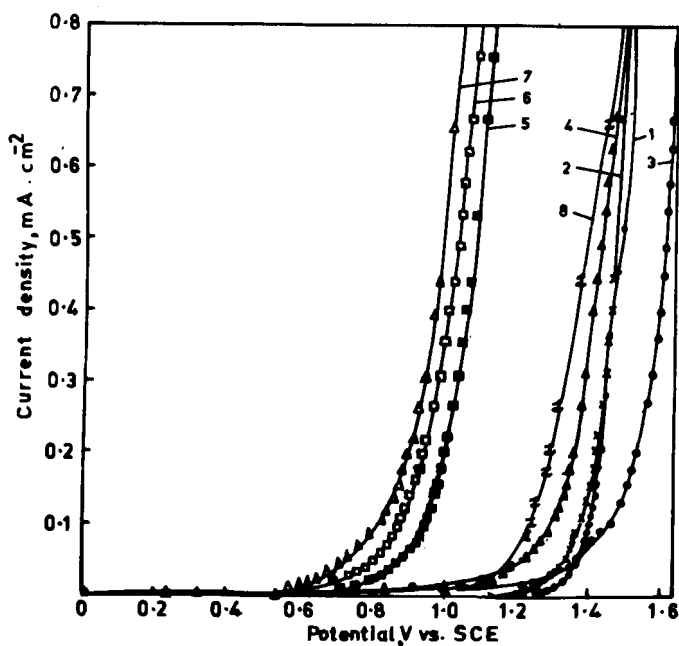


Fig.6: Galvanostatic polarisation studies of modified stainless steel electrode

Electrolyte 1M LiClO<sub>4</sub>·3H<sub>2</sub>O in water C.E.: S.S.; R.E.: S C E

1. Bare electrode I modified; 2. Bare electrode II; 3. Electrode I/Phenol; 4. Electrode II/Phenol; 5. Electrode I/ aniline at pH6; 6. Electrode II/ aniline at pH6; 7. Bare S.S./aniline; 8. Bare S.S./phenol

Electrode I = Modified electrode by adding CuSO<sub>4</sub>·5H<sub>2</sub>O in OPD

Electrode II = Modified without adding CuSO<sub>4</sub>·5H<sub>2</sub>O in OPD

Scanning electron microscopic studies were carried out on anodic and cathodic deposited polymer films and are shown in Fig.8 (a to d). The No.1721 (Fig.8a) is the photograph of anodic polymerisation of OPD on stainless steel anode in aqueous medium, which shows that the film is compact without any surface deformation. Photographs 1724 and 1725 (Fig. 8 b & c) due to polymerisation of OPD in aqueous medium on stainless steel anode in presence of Cu<sup>++</sup>, reveal that it is multilayer structure with dendritic growth. The micrograph 1727 (Fig. 8d) indicates the crystalline deposit of OPD polymerisation in nonaqueous medium.

### CONCLUSION

It is possible to achieve the anodic polymerisation of OPD on substrates like stainless steel under both aqueous and nonaqueous media. This polymer modified anode surface can be used as a

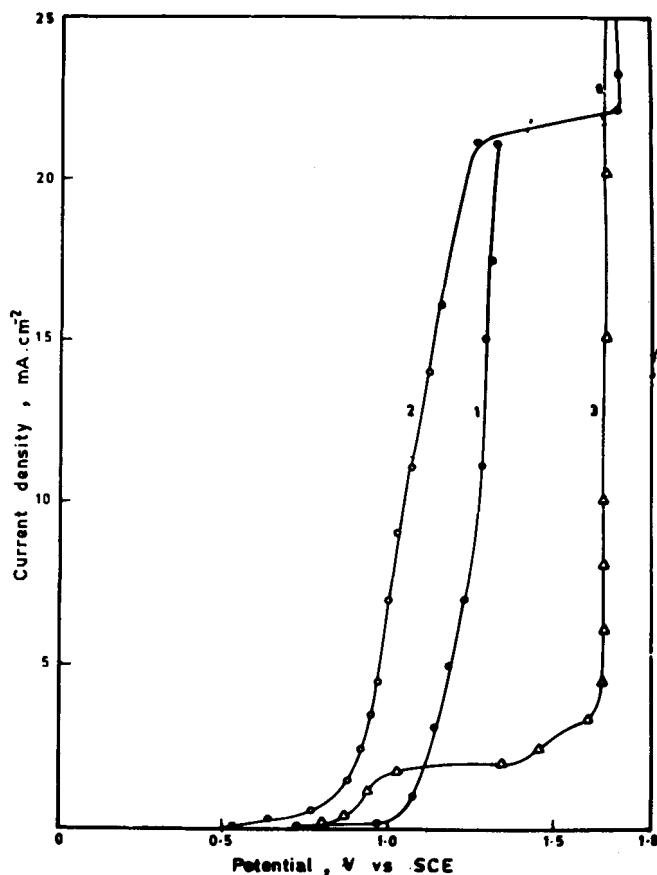


Fig.7: Galvanostatic polarisation of phenol and aniline at anodically modified stainless steel. Electrode modified in nonaqueous medium and used in aqueous medium.

Electrolyte 1M Na<sub>2</sub>SO<sub>4</sub> in water C.E. = S.S.;R.E. = SCE;pH = 8  
1. Modified electrode-phenol; 2. Modified electrode-aniline; 3. Bare electrode

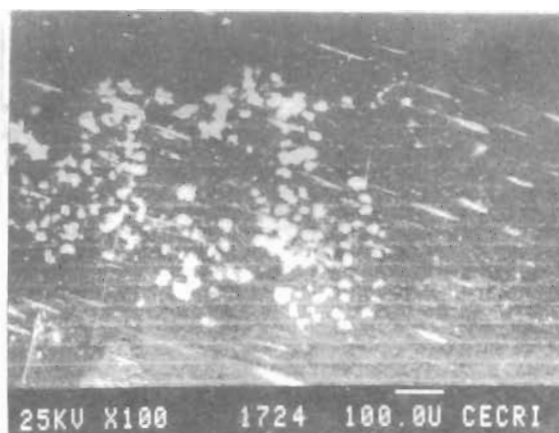
chemically modified electrode for carrying out selective oxidation studies. It has also been observed that it is possible to get a deposition on cathode during polymerisation studies under nonaqueous condition, which has not so far been reported to the knowledge of the authors. Since both cathodic and anodic deposits are conducting in nature, they can be used for making the complete polymer battery.

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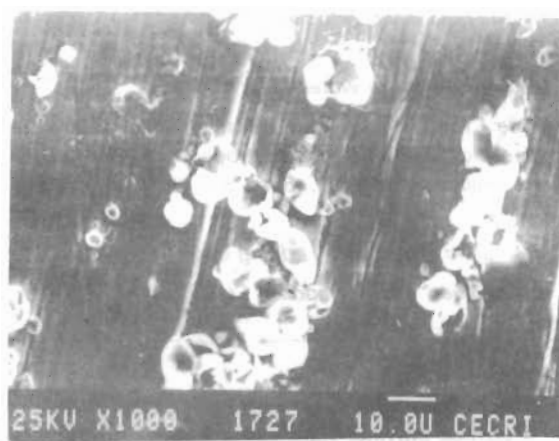
(a) aqueous medium



(b) aqueous medium in presence of  $\text{Cu}^{2+}$



(c) aqueous medium in presence of  $\text{Cu}^{2+}$



(d) nonaqueous medium

Fig.8: SEM studies on anodically polymerized OPD

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