

ELECTRO-OXIDATIONS MEDIATED BY POLYANILINE*JAMES JOSEPH and DINESH CHANDRA TRIVEDI*

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The electropolymerisation of aromatic compounds at the anode surface is an interesting reaction for the synthesis of electroactive polymers. These polymers can modify the electrode surface to facilitate fast electron transfer reaction and are capable of controlling the electrode potential, so that the reaction can become selective. The application of polyaniline coated electrodes for the selective oxidations of hydroquinone and *o*-phenylenediamine are reported in this communication.

Key words: Polyaniline, electrode modification, hydroquinone, *o*-phenylenediamine

INTRODUCTION

One of the major developments in electrochemistry is the chemical or electrochemical modification of electrode surfaces. A particular group such as redox species can be attached to electrode surface by (i) chemisorption (ii) covalent bonding (iii) film deposition. Polymer films formed on the electrode surface have good adhesion and electrical properties [1]. Some of these films are electroactive and electrochromic [2-4]. These two properties combined with good stability under ambient conditions make them interesting for their potential use as chemically modified electrodes for selective reactions.

Almost all chemically modified electrodes are known for the immobilization of redox mediators on the electrode surfaces. The function of mediator [4,5] is to facilitate the electron transfer from electrode to species in the solution. If the molecular attachment scheme is such that the immobilised substance can exchange electrons with the electrode surface, the electrode displays electrochemical responses on oxidation or reduction with solution phase. In most cases, the reaction sequence can be described by electrochemical catalytic regeneration mechanism [6].

In this paper, the application of polyaniline coated electrodes for the selective oxidation of hydroquinone and *o*-phenylenediamine (OPD) is reported.

EXPERIMENTAL**Preparation of polyaniline (PA) modified electrodes**

Electrodeposition of PA from aqueous medium on platinum electrode (0.25 cm² area) was carried out from 1M Na₂SO₄ solution whose pH was adjusted to 1 by adding drops of dilute H₂SO₄, 2% by volume of the monomer was added. The deposit of PA formed on the electrode surface was dark green in colour. The deposition was carried out by passing 150 coulombs of electricity.

PA from nonaqueous bath on stainless steel substrate was deposited from double distilled acetonitrile as solvent containing 0.1M anhydrous sodium perchlorate and 1 x 10⁻² M aniline. Water content of the medium was not more than 1 x 10⁻²M. All

experiments were carried out under argon atmosphere. The conductivity of the thin film deposited by this method was 10⁻⁴ohm⁻¹cm⁻¹.

Galvanostatic polarisation studies

The galvanostatic polarisation at platinum and stainless steel anodes was carried out in 1N H₂SO₄ containing 2% by volume of the monomer. The potential of the anode vs saturated calomel electrode (SCE) was monitored using multimeter connected between working anode and reference electrode. The medium was stirred using a magnetic stirrer.

Oxidation of hydroquinone and OPD

The oxidation of 10⁻²M of hydroquinone and 10⁻²M OPD on platinum and PA coated platinum anodes was studied in 0.1M H₂SO₄ medium. In the case of hydroquinone the solution turned yellow while in the case of OPD the solution turned orange. The colour change is due to the formation of quinone.

When the oxidation of hydroquinone and OPD was carried out at current density 0.2 mA.cm⁻² and at room temperature, the current efficiencies were found to be around 90%. The solutions were extracted with ether and water layer was vacuum distilled to get concentrated solution from which quinones separate out on cooling.

The melting points of the benzoquinones obtained from hydroquinone and orthophenylenediamine were 388K and 339K respectively. 1,4 - benzoquinone was yellow in colour while 1,2 - benzoquinone is orange red in colour.

Oxidation of ortho cresol using polyaniline coated stainless steel anode obtained from nonaqueous medium

Oxidation of ortho cresol was carried out on a polyaniline coated stainless steel electrode at pH 9.0 in a divided cell. NaHCO₃ and Na₂SO₄ were used as electrolytes. 1% by volume of *o*-cresol was dissolved in NaOH to get sodium salt and added to the cell. On passing current (0.5A) (cell voltage = 6.8V) a brown colour deposit was observed at the anode and consequently current decreased with time initially for 10 minutes and increased slightly, which was evidently not due to corrosion of anode but due to formation of

porous film of poly *o*-methyl phenoxy phenylene. The films of PA obtained from aqueous and nonaqueous media are subjected to scanning electron micrograph studies.

RESULTS AND DISCUSSION

The deposition of PA on stainless steel substrate occurs at 0.680 volts vs SCE as depicted in Fig. 1. Polarisation studies indicate that hydroquinone and *o*-phenylenediamine can be selectively oxidised at lower potentials on polyaniline modified electrode (Fig.2). The hydroquinone does not change catalytic properties of electrode by adsorption or chemisorption unlike in polypyrrole modified electrode [5] indicating that orientation of PA and polypyrrole on electrode surface are different. In the case of PA, bonding takes place between nitrogen and carbon through 1,4 - position and in polypyrrole bonding occurs at 2 and 5 positions thereby — NH group remains free which can take part in surface adsorption phenomenon.

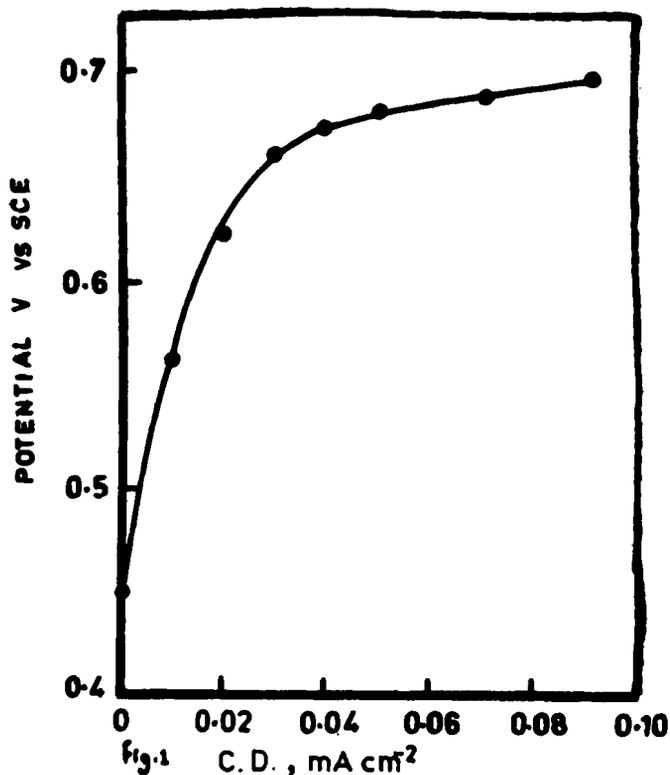


Fig. 1: Deposition of poly-aniline on Pt (galvanostatically) from pH 1 containing 2% by volume aniline

SEM studies on the film obtained from nonaqueous medium was of fibre type and nonporous (Fig. 3(a) 1131). The film obtained from the deposition of polyaniline from aqueous medium was uniform with micro crystallinity (Fig. 3(b) 1152).

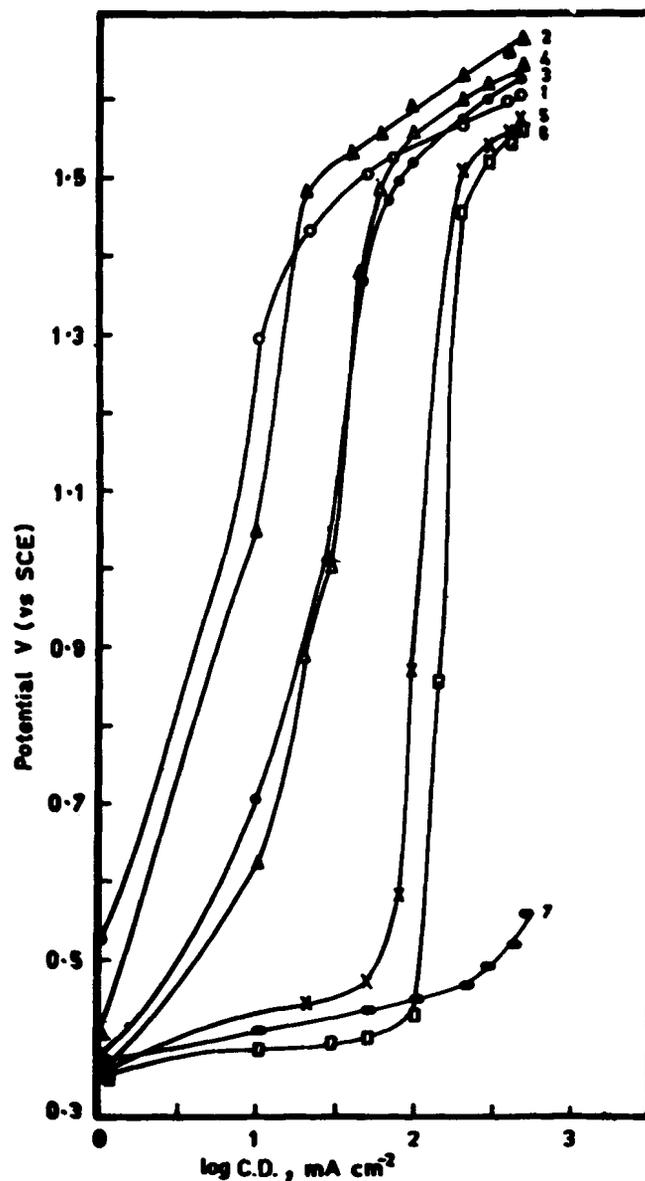


Fig.2: Tafel curves on Pt anode and PA coated Pt in 0.1M H_2SO_4 solution. Electrode area: 0.25 cm^2 ; (1) Bare Pt (2) Pt/OPD (3) PA (4) PAQ/OPD (5) Pt/hydroquinone (6) PA/hydroquinone 7. PA/OPD

Oxidation of *o*-cresol using polyaniline coated electrodes

The film obtained after oxidising *o*-cresol at pH 9 on the electrode surface was featureless. (Fig. 3(c) 1156). The conductivity of film was found to be of the order of $10^{-8} - 10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$.

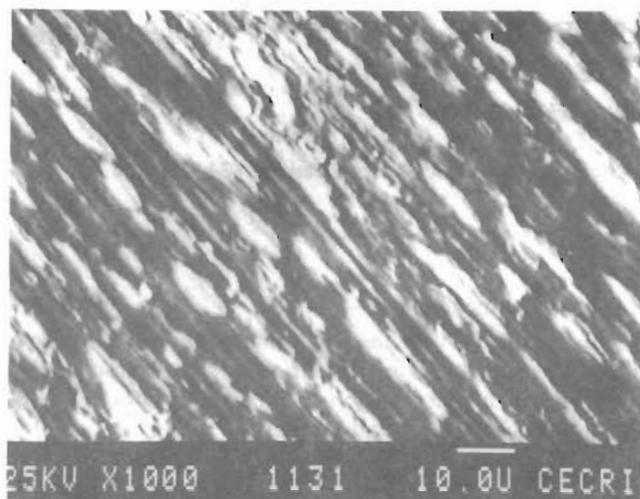
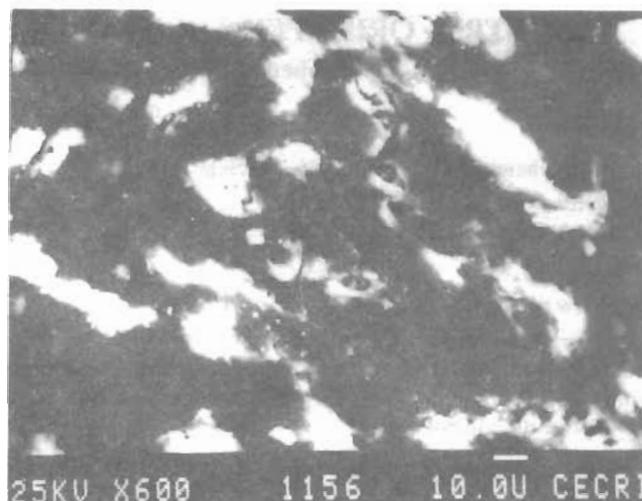
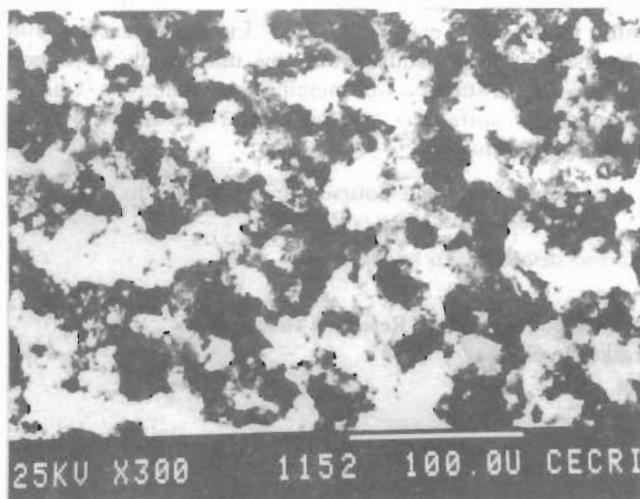


Fig.3: Scanning electron micrographs (a) 1131 P A film from non-aqueous medium



(c) 1156 P A film after oxidation of o-cresol



(b) 1152 P A film from aqueous medium (pH1)

CONCLUSION

The orientation of polyaniline on electrode was linear with head to tail coupling. It has been proved that polyaniline electrodes

can be used as chemically modified electrodes for specific synthesis.

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