

## Dispersed Nickel Oxide Films for Electro-oxidation of 1, 4-Butanediol

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**Summary:** 1, 4-Butanediol was oxidized using electro-catalytic properties of composite material of nickel oxide and polyaniline. The formation of composite film of nickel oxide and polyaniline was carried out from aqueous nickel sulphate solution containing aniline using cyclic voltammetry at carbon disc electrode. The fine dispersion of polyaniline within the nickel oxide matrix enhanced the catalytic properties of modified electrode towards the electro-oxidation of 1, 4-butanediol. The results indicated that in 1.0 M sodium hydroxide solution, the anodic peak current increased with the concentration of 1, 4-butanediol.

### Introduction

The potentiodynamic response of the nickel/alkaline aqueous solution inter-face in the region of the hydrated Ni(OH)<sub>2</sub> to NiOOH electrochemical reaction revealed that both species undergo phase transformations [1]. The anodic product from the Ni(OH)<sub>2</sub> species involves the formation of three species energetically different which are detected during the electro-reduction process. Under well-defined perturbation conditions, a reasonable set of kinetic parameters pertaining to the anodic process was obtained which was formally interpreted through a consecutive three-step mechanism of reaction involving a charge transfer, a chemical reaction, and a charge transfer and a proton transfer process. Side reactions involved water take in account to various aging processes of the reaction products.

Using a glassy carbon electrode modified with nickel oxide by a novel route, the electro-catalysis of a number of sugars and aliphatic alcohols was reported [2]. Kinetic parameters were computed and compared with the reported data. The mechanism of oxidation of these organic compounds was discussed.

The nickel hydroxide-modified nickel electrode was prepared [3] electrochemically using cyclic voltammetry. It exhibited better catalytic response toward electrochemical oxidation of methane in 1.0 M sodium hydroxide solution.

The electrochemical modification of the nickel electrode surface with nitrophenyl groups was

performed [4] by the diazonium reduction method. The barrier properties of nitrophenyl-modified nickel surfaces were characterized using Fe(CN)<sub>6</sub><sup>3-/4-</sup> as the redox probe. Electrochemical measurements were carried out in 0.1 M potassium hydroxide containing 5 mM K<sub>3</sub>Fe(CN)<sub>6</sub> using cyclic voltammetry and the rotating disk electrode technique. The nitrophenyl groups were strongly bonded to the nickel surface since they withstood sonication in acetonitrile. The results of the X-ray photoelectron spectroscopy analysis confirmed the irreversible attachment of nitrophenyl groups onto the nickel electrode surface.

Nickel hydroxide modified nickel electrodes prepared [5] by cycling the potential of a nickel electrode in alkaline solution exhibited better electro-catalytic activity for the oxidation of methane in alkaline media. In the presence of methane the oxidation-peak-current of nickel hydroxide increased while that of the reverse process decreased. This is attributed to the mediation of nickel species, probably  $\beta$ -NiOOH phase, in the process of electro-catalysis. The mechanism of methane oxidation was also discussed in terms of the formation of intermediates normally encountered in small organics electro-oxidation. It was suggested that in the further oxidation of the intermediates, ions in the solution or anion vacancies in the solid phase of nickel hydroxide were probably involved.

The oxygen evolution reaction [6] was investigated at 60 °C in 15 wt% sodium hydroxide solution on nickel electrodes. Different surface

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treatments such as sandblasting and/or chemical pickling were employed. Fresh and aged electrodes were subjected to electrochemical measurements. The galvanostatic electrochemical ageing was performed for twenty one days, applying an anodic current equal to  $150\text{mAcm}^{-2}$ . From the Tafel plots for the oxygen evolution reaction, two well-defined Tafel slopes were observed for all the electrodes (sandblasted nickel, pickled nickel and sandblasted/pickled nickel), before and after the electrochemical aging. This behavior was due to the transformation of  $\text{Ni}(\text{OH})_2$  to  $\beta\text{-NiOOH}$ , which was the *right type of oxide* for the oxygen evolution reaction. The kinetic parameters obtained on the electrodes with different surface finishing showed that the sandblasted/pickled treated nickel substrate lost its electro-catalytic properties for the oxygen evolution reaction early during the experiment.

Electro-less cobalt [7] on the surface of spherical nickel hydroxide was used as a surface modifying method of active material for positive electrodes of rechargeable alkaline batteries. Cyclic voltammetric studies showed that the electrodes exhibited higher oxygen over-potential and more reversibility than those with pure nickel hydroxide or nickel hydroxide having 5 weight percent cobalt as a conductor.

Hybrid films of polyaniline and manganese oxide [8] were obtained through potentiodynamic deposition from solutions of aniline and manganese sulphate at pH 5.6. The hybrid films demonstrated characteristic redox behaviors of polyaniline in acidic aqueous solution. Characterization of the hybrid films by X-ray diffraction indicated the amorphous nature of manganese oxide in the films in which manganese existed in oxidation states of +2, +3, and +4, based on X-ray photoelectron spectroscopy measurement. Hybrid film of polyaniline and manganese oxide, PM 120 obtained from the solution of 0.1 M aniline and 120 mM  $\text{Mn}^{+2}$  displayed a well opened nanofibrous structure which showed 44% increase in specific capacitance from that of polyaniline ( $408\text{ Fg}^{-1}$ ) to  $588\text{ Fg}^{-1}$ , measured at  $1.0\text{ mAcm}^{-2}$  in 1.0 M sodium nitrate (pH 1). The hybrid film possessed more than 90% of its capacitance after 1000 charging-discharging cycles, with a coulombic efficiency of 98%. The specific capacitance of a symmetric capacitor using PM 120 as the electrode was  $112\text{ Fg}^{-1}$ .

Electro-active polyaniline films have been made in aqueous solutions at pH 2-12 by means of potential cycling. Fewer polyaniline hydrolysis products were formed when electropolymerization of

aniline was conducted in neutral or slightly basic solutions, providing a synthetic route for polyaniline with little degradation. Fourier transformation Infrared spectra of polyaniline [9] made in solutions of different pH displayed main vibrational bands of the polymer, including the characteristic peak of protonated states of polyaniline. Scanning electron microscope images of films made in neutral or basic solutions showed three-dimensional distributions, quite different from those made in slightly acidic solutions.

The composite material of polyaniline/nickel oxide/sodium dodecylbenzenesulfonate was synthesized [10] in sodium dodecylbenzenesulfonate micelles. The composite material has satisfactory conductivity and thermostability, and the particle length, width, and thickness are about 200-500  $\mu\text{m}$ , 3-5  $\mu\text{m}$ , and 40-96 nm, respectively.

The electro-oxidation of primary and secondary alcohols with single -OH group on bare nickel electrode is well-documented. The purpose of the present work is to investigate the electrochemical oxidation of a diol (1, 4-butanediol) using the composite film of nickel oxide and polyaniline.

## Results and Discussion

Fig. 1 shows twenty five consecutive cyclic voltammograms for electrochemical deposition of composite film of nickel oxide-polyaniline on carbon disc electrode from the solution containing 0.2 M nickel sulphate and 5.0 mM aniline at the scan rate of  $0.05\text{ Vs}^{-1}$ . The potential range was -0.3 to 1.2 V. An oxidation peak appeared at around 0.9 V. After the first scan the current density gradually decreases indicating the deposition of polymeric film of aniline at the electrode surface. This has partially blocked the electrode surface and thus hindered the mass transport process. However after successive scans the current density showed gradual increase thereby indicating the slow oxidation of nickel on account of partial blockage of electrode surface by polyaniline film. Similarly, nickel oxide film was electrochemically deposited on carbon disc electrode from 0.2 M nickel sulphate solution between 0.2 to 1.3 V at the scan rate of  $0.05\text{ Vs}^{-1}$  (Fig. 2). First scan is almost parallel to the abscissa showing no significant current. However, a gradual increase in oxidation current density was observed in subsequent scans thereby manifesting the enhancement in thickness of deposited material resulting from the oxidation of nickel.

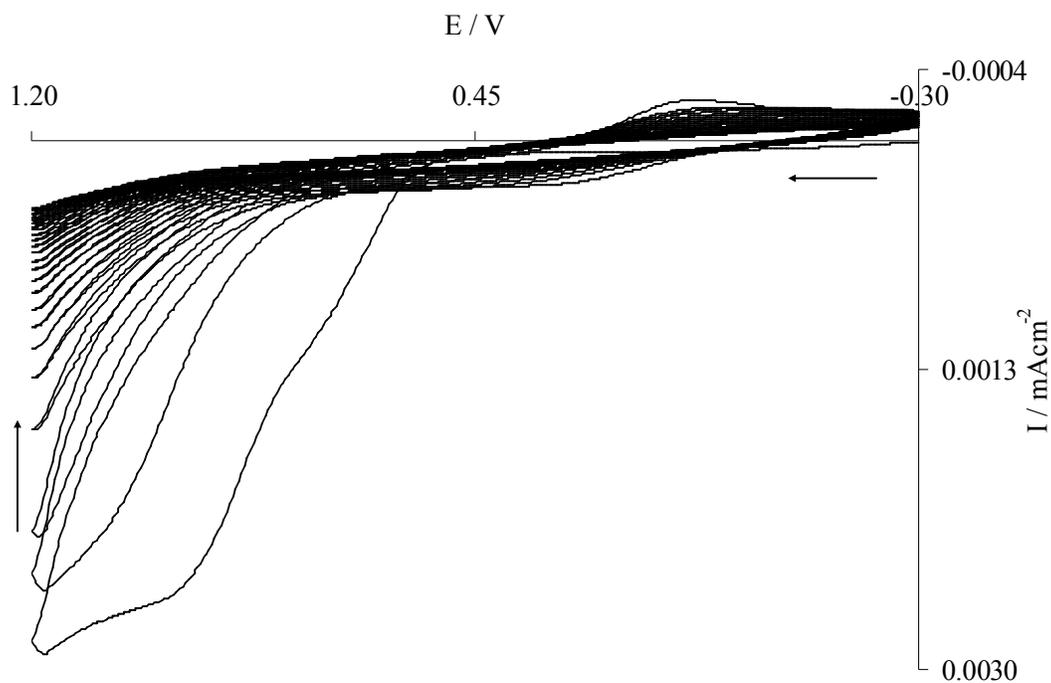


Fig. 1: Cyclic voltammograms (twenty five consecutive scans) for electrochemical deposition of nickel oxide-polyaniline composite film at carbon disc (0.1256 cm<sup>2</sup>) electrode from a solution containing 0.2M nickel sulphate and 5mM aniline at pH 7.3. Scan rate = 0.05 Vs<sup>-1</sup>

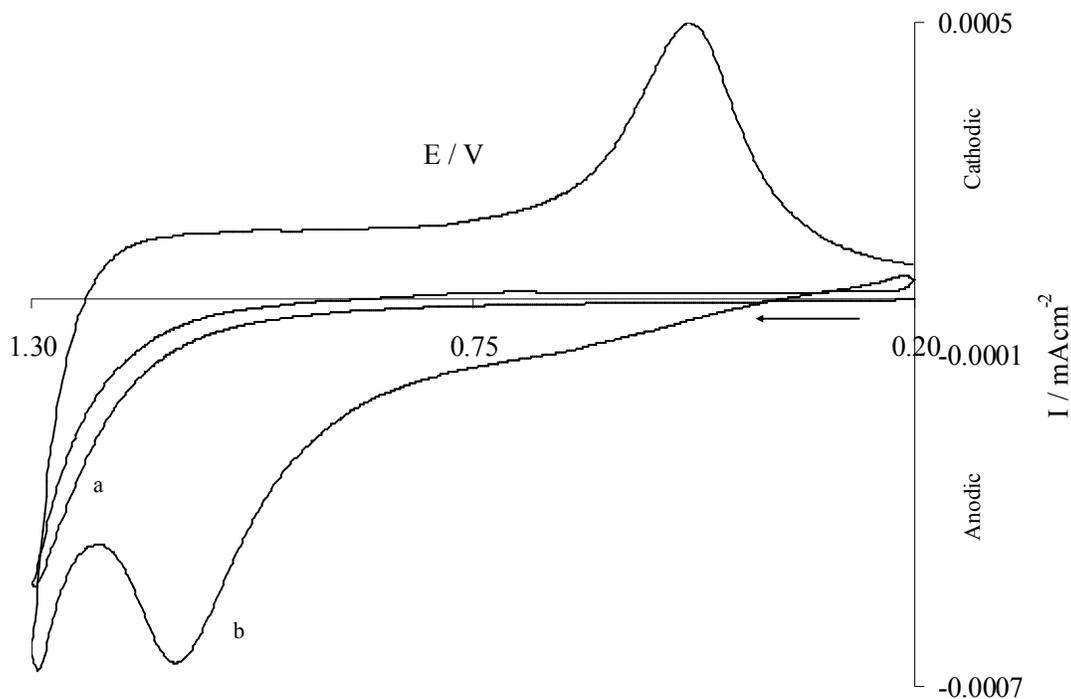


Fig. 2: Cyclic voltammograms for electrochemical deposition of nickel oxide on carbon disc (0.1256 cm<sup>2</sup>) electrode from aqueous 0.2M nickel sulphate at pH 7.3. Scan rate = 0.05 Vs<sup>-1</sup>. (a) 1<sup>st</sup> scan and (b) 25<sup>th</sup> scan

Fig. 3 illustrates the comparison of nickel oxide film and nickel oxide-polyaniline composite film in 0.1 M sodium hydroxide solution. It is evident that the oxidation current density of nickel oxide coated film is higher than that of composite film, shown as in-set. The stability of nickel oxide and nickel oxide-polyaniline composite films were compared in 0.1M sodium hydroxide after immersion

in the solutions of sulphuric acid of pH (from 1 to 4). It is well known [9] that polyaniline films are unstable at pH higher than 10, and nickel oxide loses its catalytic activity in acidic media [9]. However, the composite film of nickel oxide and polyaniline is relatively much stable at lower pH than nickel oxide film (Fig.4).

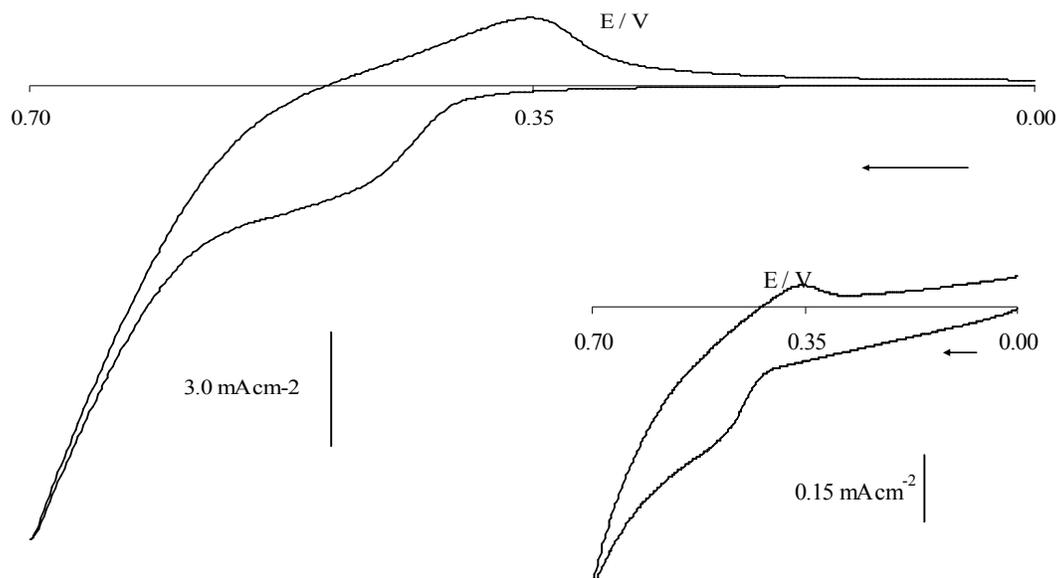


Fig. 3: Cyclic voltammograms for nickel oxide and nickel oxide-polyaniline composite film (lower right) at carbon disc electrode in 0.1M sodium hydroxide solution. Scan rate =  $0.05 \text{ Vs}^{-1}$

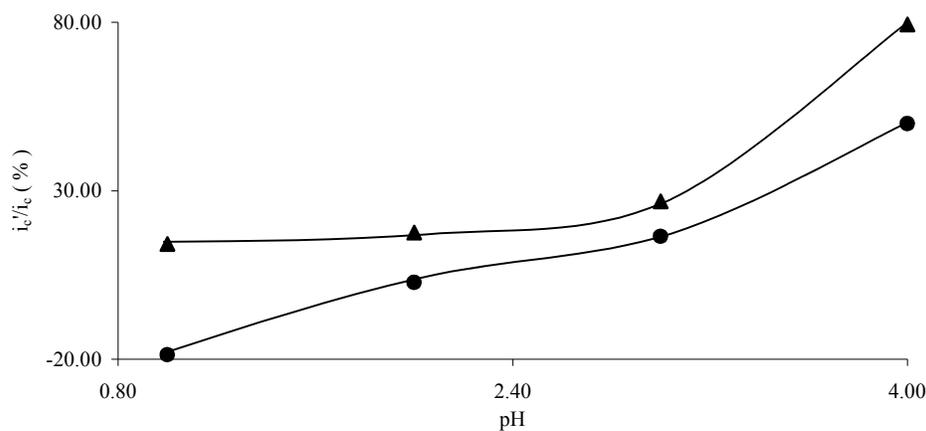


Fig. 4: Normalized % cathodic current density obtained after 20 scans in 0.1 M sodium hydroxide for (a) nickel oxide (solid line) and (b) the nickel oxide-polyaniline composite (dashed line) after the electrodes were immersed for three hours in sulphuric acid solutions (pH from 1 to 4). Currents obtained before,  $i_c$ , and after,  $i'_c$ , acid immersion. Peak currents were obtained at 0.2V and 0.25V vs. saturated calomel electrode for nickel oxide and nickel oxide-polyaniline composite films, respectively.

*Electro-catalytic Studies of Composite Films*

The electro-catalytic properties of nickel oxide-polyaniline composite film at carbon disc electrode were studied for the oxidation of 1, 4-butanediol as an analyte, and compared with those at bare nickel electrode. Fig. 5 shows that pronounced current density is exhibited by composite films in 1.0 M sodium hydroxide solution compared to bare nickel electrode. Similarly, cyclic voltammogram of 0.1mM 1, 4-butanediol in 1.0M sodium hydroxide shows substantially increased current density at composite film electrode as compared to that on bare nickel electrode (Fig. 6). The comparison of cyclic voltammograms at different concentrations of 1, 4-butanediol in 1.0 M sodium hydroxide solutions is illustrated by Fig. 7. The characteristics of cyclic voltammetric oxidation of 1, 4-butanediol are summarized in Table-1. Furthermore, the electro-oxidation of ethanol and 1, 4-butanediol (both 0.056M) in 1.0 M sodium hydroxide were carried out, showing the considerable increase in current density of 1, 4-butanediol as compared to ethanol (Fig. 8).

Table-1: Cyclic voltammetry of 1, 4-butanediol in 1.0M sodium hydroxide. Scan rate 0.05 Vs<sup>-1</sup>. Dependence of anodic peak potential on concentration of 1, 4-butanediol

C	Log (C)	E <sub>p</sub> <sup>a</sup>	E <sub>p/2</sub> <sup>a</sup>	i <sub>p</sub> <sup>a</sup>	E <sub>p</sub> <sup>a</sup> -E <sub>p/2</sub> <sup>a</sup>	i <sub>p</sub> <sup>a</sup> /C	I <sub>p</sub> <sup>a</sup>
mM	(mM)	V	V	mA	V	mA/mM	mAcm <sup>-2</sup>
0.000	0.000	0.554	0.449	8.00	0.105	0.000	63.694
0.026	-1.571	0.574	0.454	7.91	0.120	295.075	62.962
0.067	-1.170	0.498	0.430	12.82	0.068	189.645	102.070
0.100	-1.000	0.486	0.421	7.581	0.065	75.810	60.358
0.143	-0.844	0.552	0.446	17.65	0.106	123.427	140.526
0.336	-0.473	0.562	0.454	15.89	0.108	47.292	126.513
0.829	-0.081	0.498	0.432	11.65	0.066	14.053	92.755
1.300	0.114	0.511	0.440	12.12	0.071	9.323	96.497
1.830	0.262	0.550	0.448	18.37	0.102	10.038	146.258

Working electrode: Nickel oxide-polyaniline composite film electrode (0.1256 cm<sup>2</sup>), Reference electrode: Saturated calomel electrode.

Note: C = Concentration, E<sub>p</sub><sup>a</sup> = Anodic peak potential, E<sub>p/2</sub><sup>a</sup> = Anodic half peak potential, i<sub>p</sub><sup>a</sup> = Anodic peak current, i<sub>p</sub><sup>a</sup>/C = Sensitivity, I<sub>p</sub><sup>a</sup> = Anodic peak current density.

**Experimental**

Electrochemical deposition of composite film of nickel oxide and polyaniline was carried out at carbon disc electrode (0.1256 cm<sup>2</sup>) and its stability was checked in acidic and basic solutions. Furthermore, electro-catalytic activity of the composite film was investigated by carrying out electro-oxidation of 1, 4-butanediol.

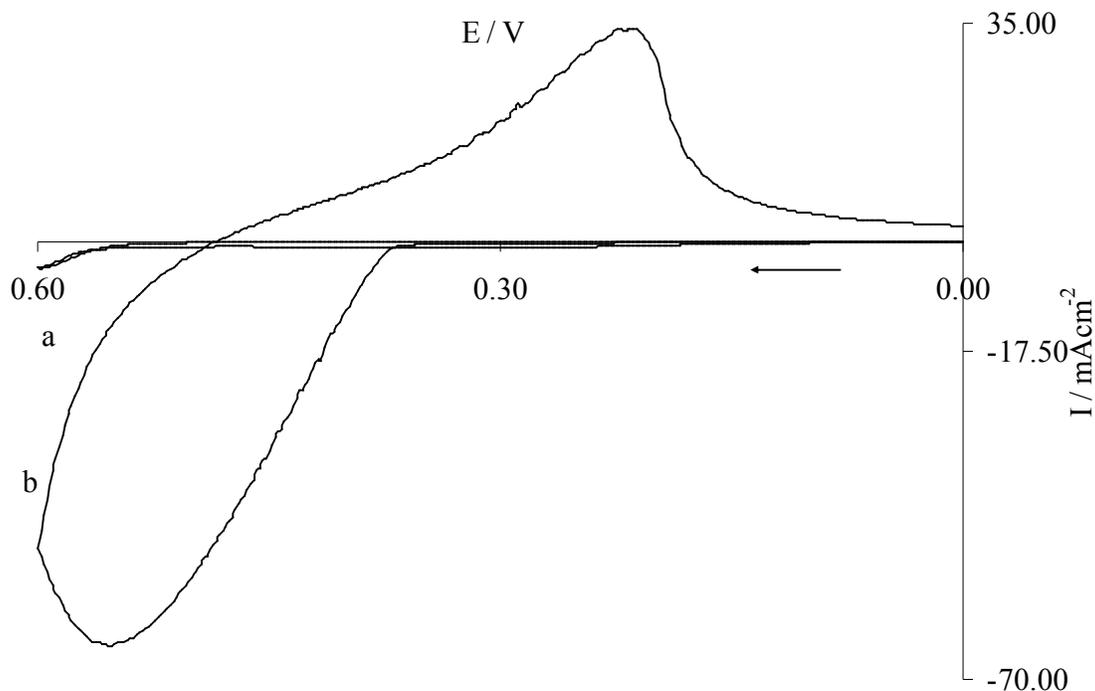


Fig. 5: Cyclic voltammograms of 1.0M sodium hydroxide solution on (a) bare nickel electrode, and (b) on nickel oxide-polyaniline composite film (b) electro-deposited by cyclic voltammetry at carbon disc (0.1256 cm<sup>2</sup>). Scan rate = 0.05 Vs<sup>-1</sup>

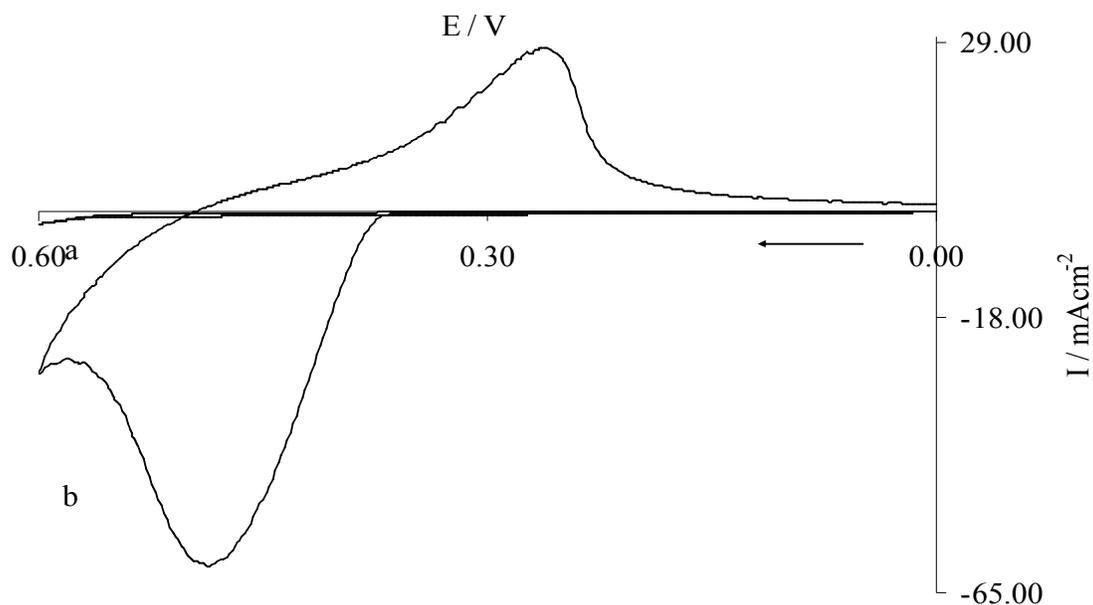


Fig. 6: Cyclic voltammograms of 0.1 mM 1, 4-butanediol in 1.0M sodium hydroxide solution, at (a) bare nickel electrode, and (b) nickel oxide-polyaniline composite film at carbon disc electrode (0.1256 cm<sup>2</sup>)

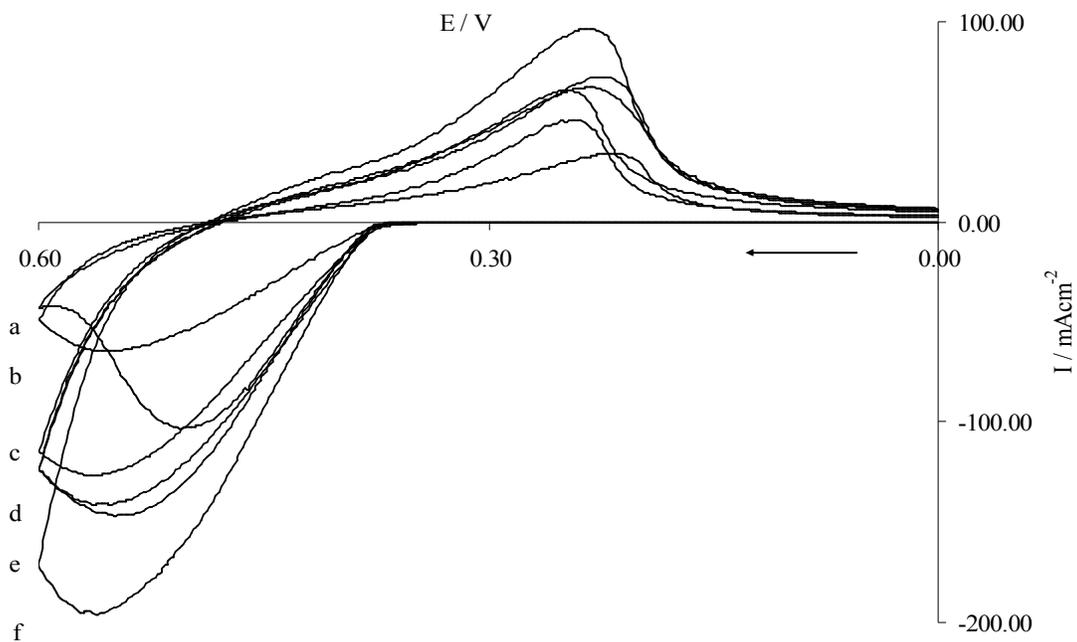


Fig. 7: Cyclic voltammograms in 1.0 M sodium hydroxide solution without (a) 1, 4-butanediol, and with different concentrations of 1,4-butanediol: (b) 0.067, (c) 0.143, (d) 0.336, (e) 1.83 and (f) 4.17 mM at nickel oxide-polyaniline composite films on carbon disc (0.1256 cm<sup>2</sup>). Scan rate = 0.05 Vs<sup>-1</sup>

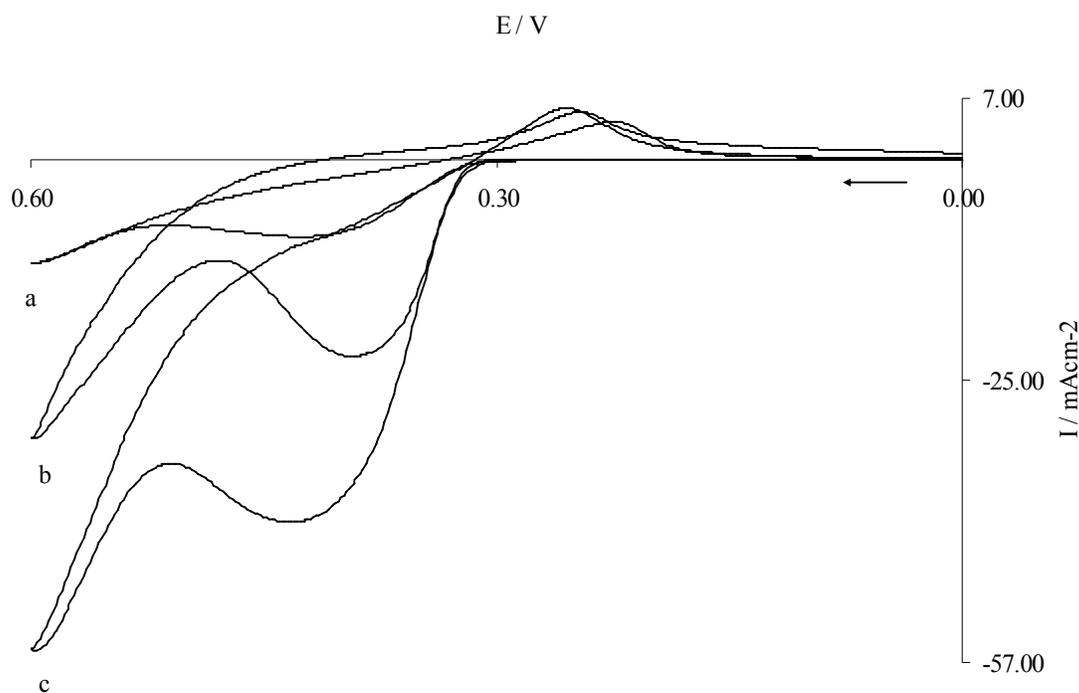


Fig. 8: Cyclic voltammograms of (a) 1.0 M sodium hydroxide solution, (b) 0.056M Ethanol in 1.0 M NaOH and (c) 0.056M 1, 4-butanediol in 1.0 M NaOH at nickel oxide-polyaniline composite film electrode ( $0.1256 \text{ cm}^2$ ). Scan rate =  $0.05 \text{ Vs}^{-1}$ .

#### Chemicals and Materials

Specification of chemicals and materials used were as follows:

1. Nickel Sulphate	$\text{NiSO}_4$	W Canning
2. Aniline	$\text{C}_6\text{H}_7\text{N}$	Fluka (98% HPLC)
3. Sodium Hydroxide	$\text{NaOH}$	E-Merck
4. Sulphuric Acid	$\text{H}_2\text{SO}_4$	E-Merck
5. Ethanol	$\text{C}_2\text{H}_5\text{OH}$	E-Merck
6. 1, 4-butanediol	$\text{C}_4\text{H}_{10}\text{O}_2$	
7. $\gamma$ -alumina (0.05 micron)	$\gamma\text{-Al}_2\text{O}_3$	Gamry Instruments

These chemicals were of analytical grade and were used without further purification. Polishing of the bare nickel electrode was done by abrading on silicon carbide paper of grit numbers 600 and 800 successively, followed by polishing at nylon-texture synthetic cloth pad soaked with slurry of  $\gamma$ -alumina powder (0.05 micron) in water.

#### Deposition of Nickel Oxide and Nickel Oxide-Polyaniline Composite Film at Carbon Disc Electrode

Electrochemical deposition of the composite film was carried out using 0.2M solution of nickel sulphate and 0.005M aniline in water. Cyclic voltammetry with 25 consecutive scans were performed between -0.3 to 1.2 V at  $0.05 \text{ Vs}^{-1}$  versus saturated calomel electrode (Fig 1). Similarly, nickel oxide film was deposited through cyclic voltammetry using 0.2 M solution of nickel sulphate between 0.2 to 1.2 V at scan rate  $0.05 \text{ Vs}^{-1}$  (Fig. 2). Neutral pH of the solution was maintained at 7 by adding sodium hydroxide solution.

#### Electrochemical Studies of Coated Films

The stability of coated films was checked by recording cyclic voltammograms (20 scans) in 0.1 M NaOH solution before and after immersion in sulphuric acid (pH from 1 to 4) for three hours. Electrocatalytic activity of the films was investigated by carrying out voltammetry using different concentrations of 1, 4-butanediol in alkaline media at the scan rate of  $0.05 \text{ Vs}^{-1}$ . For comparison some voltammograms were recorded using bare nickel electrode.

### Instrumentation and Technique

Electrochemical coating of nickel oxide and nickel oxide-polyaniline composite was carried out using eDAQ potentiostat. Data were acquired using eDAQ electrochemistry research software on a dedicated PIV microprocessor coupled to the potentiostat. Electro-catalytic studies of 1, 4-butanediol were carried out using VersaStatII potentiostat (EG&G, Princeton Applied Research Corp). Data were acquired using M270 electrochemistry research software on a dedicated PII microprocessor coupled to the potentiostat. All experiments were performed in a three electrode cell containing bare nickel disc (0.366 cm<sup>2</sup>), nickel oxide (0.1256 cm<sup>2</sup>) and nickel oxide polyaniline (0.1256 cm<sup>2</sup>) coated carbon disc electrodes as working electrodes, a platinum wire as counter electrode and a saturated calomel reference electrode. All experiments were carried out at room temperature.

### Conclusions

Composite films of nickel oxide+ polyaniline deposited from the same solution at carbon disc electrodes showed prominent anodic and cathodic peaks in 1.0M sodium hydroxide solution ascribed to Ni(II) and Ni(III) redox couple. The composite film electrode exhibited better catalytic response towards the electro-oxidation of 1, 4-butanediol compared to bare nickel electrode.

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