

Electrochemical Behavior of 1, 4-Butanediol at Nickel Oxide-Polyaniline Composite Film

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Summary: The composite film comprising nickel oxide dispersed in polyaniline was used to investigate the electro-oxidation of 1,4-butanediol in alkaline media. The composite film was electrochemically deposited using nickel sulphate and aniline solution. Surface coverage of the film in alkaline medium at different scan rates was indicated to involve a few hundred monolayers. Chronoamperometric and chronopotentiometric responses indicated that electro-oxidation of 1, 4-butanediol initiates from the very start of the anodic scan.

Introduction

The electrochemical and catalytic properties of conventional nickel oxide were well documented for sugars, aliphatic alcohols and amines [1-2]. The kinetics of dehydration of 1,4-butanediol to tetrahydrofuran using a strong acid cation exchange resin as catalyst had been discussed. Effects of various parameters have been investigated in detail. The initial rate varied linearly with reaction temperature. The rate data showed exponential dependence on initial substrate concentration. A mechanism had been proposed to explain the reaction behaviour. Contributions of film diffusion and intraparticle diffusion were found to be negligible in the range of parameters studied [3]. Reactor performance under integral conditions was predicted successfully using the proposed rate model [3].

Nickel oxide (NiOx) and polyaniline (PAni) were electrocodeposited from NiSO₄ and aniline through cyclic voltammetric scans to afford PAni-NiOx composite film at controlled pH environment. The electrochemical activities of the film were investigated by cyclic voltammetry in 0.1 M NaOH and 0.1 M H₂SO₄, respectively. Typical redox couples of PAni in 0.1 M H₂SO₄ appeared at approximately 0.2 and 0.4 V vs. saturated calomel electrode, Ni(II)/Ni(III) redox couple was observed at approximately 0.4 V vs. SCE in 0.1 M NaOH. The morphologies and elemental components of the films were inspected by scanning electron microscopy and energy dispersive X-ray diffraction. The stability of nickel oxide in the films was found to be enhanced against acidic environments. Electrochemical

catalytic behavior of NiOx within the composite film was conserved and demonstrated by catalytic oxidation of methanol and ethanol [4].

Many low hydrocarbon gases were oxidized using the electrocatalytic characteristics of the transition metals, which were adapted to get the right type of oxides in basic media. The height of forward scan had increased with increase in concentration of analyte in the medium. The reaction mechanism and the kinetics of the reaction were also proposed [5].

Electro-oxidation of 1,4-butanediol was studied using electro-catalytic properties of composite material [6]. The use of technology in the field of biology had introduced the intermixing of nano-sized objects with living material. The composite carbon anode was fabricated in the presence of oxides of Ni and biomolecule using voltammetric techniques. Advanced analytical and spectroscopic techniques were employed to study the symmetrical and geometrical shapes of the composite materials formed. The newly formed anode material showed best redox results with the organic nitrogenous compounds [7].

The voltammetric behavior of carbon electrodes coated by a nickel macrocyclic complex-based film in alkaline aqueous solution had been described. The modified electrodes were prepared by anodic oxidation of nickel porphyrin and nickel cyclam complexes by repeated potential scans in 0.1 M NaOH aqueous solution. The modified films acted as efficient materials for the electrocatalytic

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oxidation of alcohols and phenol derivatives in aqueous sodium hydroxide [8].

The $\text{CH}_3\text{-O-C-(CH}_3)_3$ in water was anodically oxidized at transition metal anode to check its properties. During the experiments, the physical parameters were varied and their consequences on the analyte oxidation were measured. The analyte was oxidized at 350 mV in 1.0 M potassium hydroxide. Similarly, studies were also carried out by changing the reaction media from one molar sodium sulphate in one molar potassium chloride. The changes occurring at the anode were measured by using advanced electroanalytical methods [9].

The typical organic reducing agent was used to prepare the combinations of two transition metal electrodes. The electroanalytical and spectroscopic methods were used to study the anodic behavior of the alloy anode using closed chain alcohols. The voltammetric parameters were computed for various sweep rates and for different values of concentrations of the analyte. The better results were shown by the anodic alloy toward the electrochemical studies [10].

Simple chemical and electrochemical methods were employed to get the pure metal from the composite anode of two metals. The effects of change in heat system on the characteristics of the pure metal obtained were studied. The stability of primary metal-OH at lesser values of degree Celsius, and the stability of secondary-OH at elevated values of degree Celsius were reported. Electrochemical techniques were used for coatings of material at the anodes. Effect of change in anodic and cathodic current values on the structural and morphological behavior of the anode was discussed [11].

The role of structural, morphological and composite nature of Ni anodes by using electrophysical methods in basic media was established. Two methods were employed simultaneously. The physical method had shown its independency on the reaction taking place at cathode between the 500-700 nm. While on the other hand this method had shown its direct dependency on the reaction taking place at the anode. The exact amount of the gas released at the anode could be determined using physical method. The morphological properties of the anodes could be anticipated by using this method. The overcrowding produced by various oxides of the metal was also studied. By using different surface treatments the release of gases both at anode and cathodes was discussed [12].

A new composition of a sequence was projected about the one way stream of mixture of

transition metals and their peroxides. The anode used was a pure transition metal thin sheet, and cathode used was the oxygen compound of transition metal. The anodes and the cathodes used in this sequence were dipped in highly saturated solution of zinc oxide in potassium hydroxide media. No separator was present in the system. The transition metal hydroxide was converted into peroxide at anode and the positive metal ions were converted to pure metal and deposited at cathode and vice versa. The laboratory results were remarkable with 90% and 86% energy competence in one thousand turns [13]. Many other nickel based electrodes have also been studied for various electrochemical reactions [14-23]

The present work relates to nickel oxide-polyaniline at carbon disc electrode. The chronoamperometric and chronopotentiometric responses for the oxidation of 1,4-butanediol at composite film were also studied. The voltammetric outcomes showed noticeable response toward the oxidation of the aliphatic primary diol.

Results and Discussion

Immobilization of Nickel Salt Redox Species at Carbon Disc Electrode

The nickel oxide based polyaniline film was electrochemically deposited at carbon disc electrode [6]. Fig. 1 shows the cyclic voltammetric behavior of nickel oxide based polyaniline film at carbon disc electrode in 1.0 M sodium hydroxide. The linear behavior between anodic peak current and square root of scan rate is suggestive of the process to be diffusion controlled in terms of hydroxide. Surface coverage (T^*) of redox species of composite film has been previously determined (5) from peak current at 0.1 Vs^{-1} using the following equation (5):

$$T^* = i_p 4RT / n^2 F^2 v A$$

$$T^* = 8.4 \times 10^{-7} \text{ moles cm}^{-2}$$

Electrocatalytic Studies of Composite Films

1, 4-Butanediol was oxidized on nickel oxide-polyaniline composite film at different sweep rates (Fig. 2). An increase in current density was observed with increasing scan rate. But after the sweep rate of 0.1 Vs^{-1} the oxidation peak shifted toward more positive potential. The slight shift in reduction peak toward more negative potentials was also observed. Fig. 2 (A and B) show the dependence of anodic and cathodic peak currents of 8.4 mM 1,4-butanediol on square root of scan rate. Characteristics of cyclic voltammetric parameters are shown in Table-1.

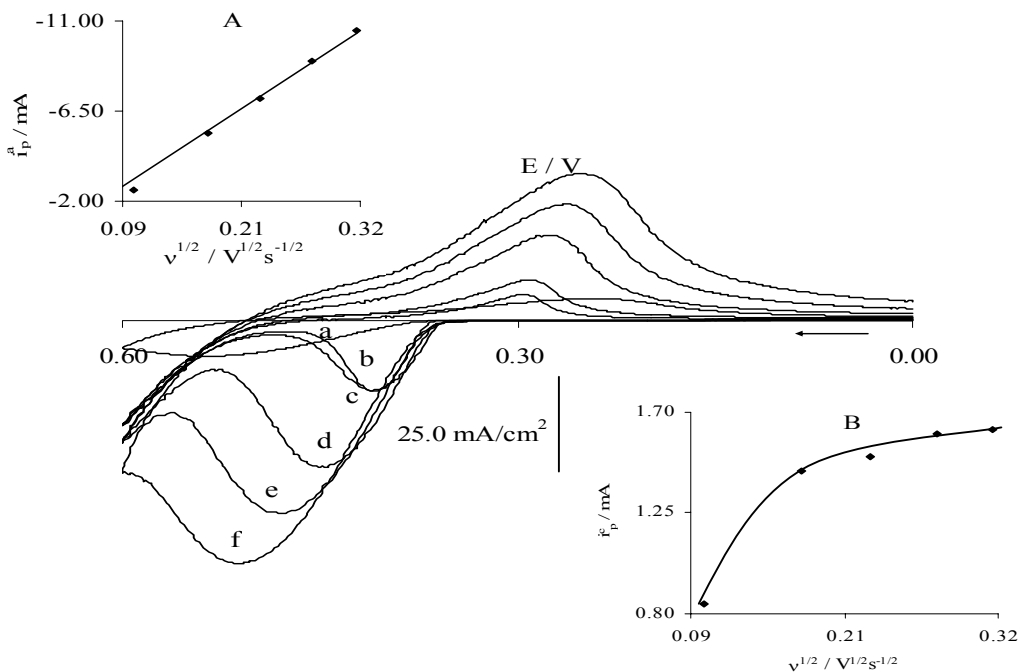


Fig. 1: Cyclic voltammetric behavior of nickel oxide-polyaniline in 1.0 M sodium hydroxide solution at different scan rates, (a) 0.005, (b) 0.01, (c) 0.03, (d) 0.05, (e) 0.075, (f) 0.1 and (g) 0.2 Vs⁻¹. Dependence of anodic (A) and cathodic (B) peak currents on the square root of scan rate.

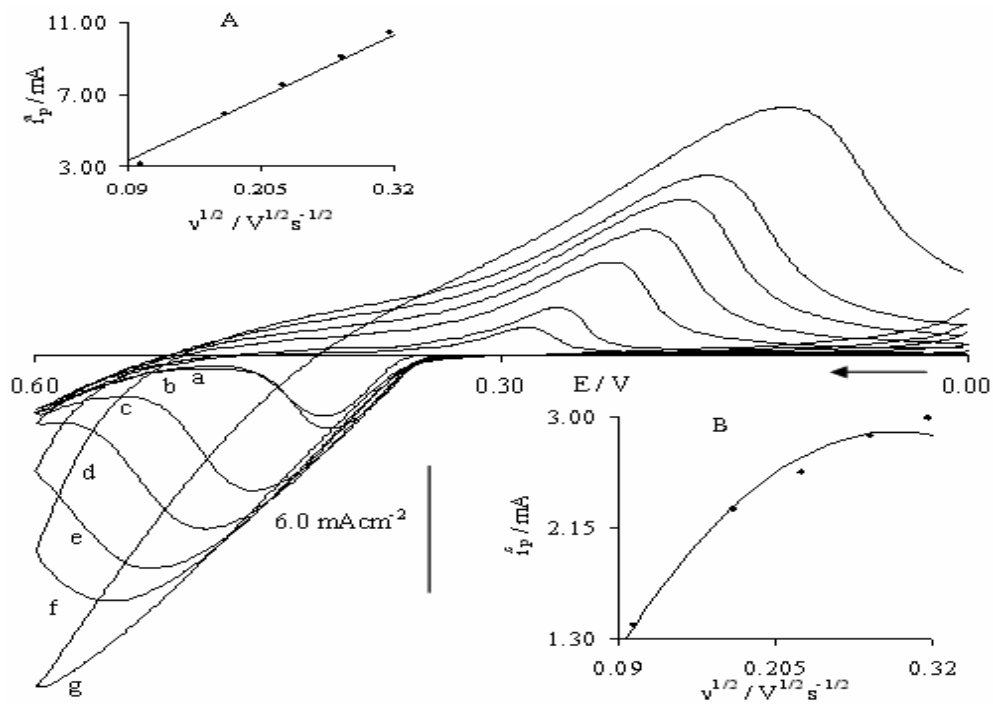


Fig. 2: Cyclic voltammograms for the oxidation of 8.4 mM 1, 4-butanediol in 1.0 M sodium hydroxide solution at different scan rates (a) 0.005, (b) 0.01, (c) 0.03, (d) 0.05, (e) 0.075, (f) 0.1, and (g) 0.2 Vs⁻¹. Dependence of anodic (A) and cathodic (B) peak currents on the square root of scan rate.

Table-1: Dependence of anodic and cathodic peak currents on scan rate. Cyclic voltammetry of 8.4 mM 1,4-butanediol in 1.0 M sodium hydroxide solution at nickel oxide polyaniline composite film at carbon disc (0.01256 cm^2) electrode versus saturated calomel electrode.

ν Vs^{-1}	$\ln \nu$ (Vs^{-1})	$\nu^{1/2}$ $\text{Vs}^{-1/2}$	E_p^a V	$E_{p/2}^a$ V	i_p^a mA	E_p^c V	$E_{p/2}^c$ V	i_p^c mA
0.010	-4.605	0.100	0.412	0.374	3.214	0.264	0.296	1.410
0.030	-3.506	0.173	0.460	0.392	5.966	0.232	0.282	2.298
0.050	-2.995	0.223	0.490	0.406	7.573	0.210	0.268	2.574
0.075	-2.590	0.273	0.518	0.424	9.119	0.190	0.256	2.856
0.100	-2.302	0.316	0.550	0.436	10.53	0.174	0.248	2.994

Pulse voltammetric techniques were also employed for the oxidation of different concentrations of 1,4-butanediol in 1.0 M sodium hydroxide solution. Normal pulse voltammetric experiments showed the involvement of adsorption phenomenon during the oxidation of 1,4-butanediol. Differential pulse voltammograms for the oxidation of different concentrations of 1,4-butanediol are shown in Fig. 3. The potential time transient behavior of nickel oxide polyaniline composite film in 1.0 M sodium hydroxide with and without 8.4 mM 1,4-butanediol is shown in Fig. 4. This behavior was recorded using current step, $50 \mu\text{A}$. Similarly, the current time behavior of nickel oxide-polyaniline in 1.0 M sodium hydroxide with and without 1,4-butanediol was recorded; showing an increase in current density just from the beginning as shown in Fig. 5.

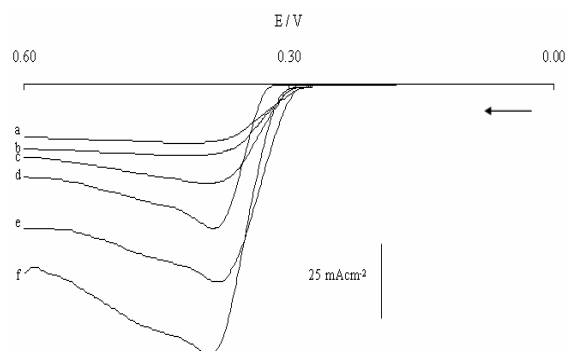


Fig. 3: Differential pulse voltammograms of different concentrations of 1,4-butanediol in 1.0 M sodium hydroxide solution on nickel oxide-polyaniline composite film at carbon disc electrode. Scan rate: 0.005 Vs^{-1} , Pulse height: 0.075 V , Pulse width: 0.05 s , Scan increment: 0.002 Vs^{-1} , Drop time: 0.4 s . Potential in volts versus saturated calomel electrode. (a) without analyte (b) 0.026, (c) 0.1, (d) 0.143 (e) 1.83 and (f) 2.8 mM.

Experimental

Electrochemical oxidation of 1,4-butanediol in alkaline media was carried out at nickel oxide-

polyaniline film deposited at carbon disc (0.01256 cm^2) electrode using cyclic and pulse voltammetric techniques.

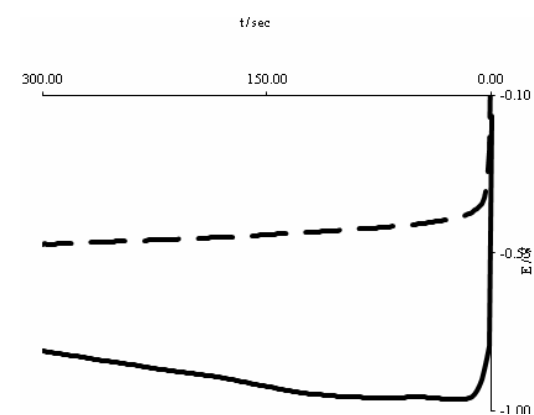


Fig. 4: Chronopotentiograms of nickel oxide-polyaniline composite film in 1.0 M sodium hydroxide in the absence (dotted line) and presence (solid line) of 8.4 mM 1,4-butanediol in the solution. I_{step} was $50 \mu\text{A}$.

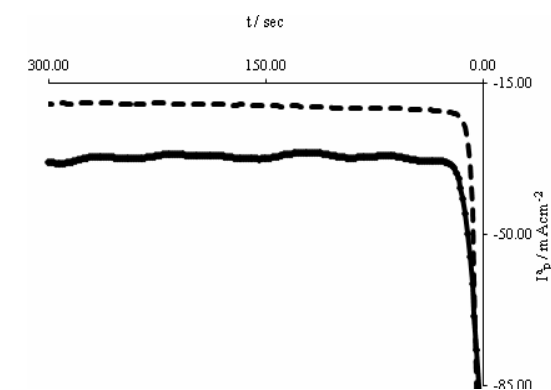


Fig. 5: Chronoamperograms of nickel oxide-polyaniline composite film in 1.0 M sodium hydroxide in the absence (dotted line) and presence (solid line) of 8.4 mM 1,4-butanediol in the solution. E_{step} was 0.6 V .

Chemicals and Materials

Sodium hydroxide used in this work was a reagent grade Merck product and used without further purification. 1,4-Butanediol was a gift from Dr. M. Sarwar. Nickel sulphate was from W. Canning, UK and aniline was from Fluka. Aniline was doubly distilled prior to use. Aniline 0.05 M in aqueous nickel sulphate 0.2 M was used for development of composite film on carbon disc electrode. γ -Alumina (0.5 microns) was from Gamry instruments. These chemicals were reagent grade and except for aniline all were used without further purification.

Deposition of Nickel Oxide Polyaniline Composite Film at Carbon Disc Electrode

Electrochemical deposition of the composite film was carried out using 0.2 M nickel sulphate and 0.005 M aniline. Cyclic voltammetry with 25 consecutive scans was performed between -0.3 V to 1.2 V versus saturated calomel electrode, at potential sweep rate, 0.05 Vs⁻¹ [6].

Electrochemical Studies of 1,4-butanediol

1,4-Butanediol (8.4 mM) was electrochemically oxidized at various sweep rates between 0.0V to 0.6 V. Different concentrations of 1,4-butanediol were also oxidized using pulse voltammetric technique. Chronoampermetric and chronopotentiometric experiments were performed as well.

Instrumentation and Technique

Electrochemical coatings of nickel oxide-polyaniline composite film were carried out using eDAQ EA161 potentiostat, ED410 data acquisition system with ES260EChem software and ED210 e-corder coupled to a PIV microprocessor. Electrochemical studies of 1,4-butanediol were carried out using EG&G, Princeton Applied Research Corp, VersaStat II potentiostat. 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 nickel oxide polyaniline (0.1256 cm²) coated carbon disc electrodes as working electrode, a platinum wire as counter electrode and saturated calomel reference electrode. All experiments were carried out at room temperature.

Conclusion

The electrooxidation of a diol (1,4-butanediol) was investigated using composite film of

polyaniline and nickel oxide electrochemically deposited at carbon disc electrode. The pronounced increase in current density for the electrooxidation of 1,4-butanediol was observed using cyclic voltammetric technique. However, pulse voltammetry is suggestive of the involvement of adsorption phenomenon at the electrode surface.

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