

*Full Paper*

## **Electrocatalytic Oxidation of n-propanol on Ni/Al LDH Nanoparticles**

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**Abstract-** The general electrochemical behavior of n-propanol has been investigated on Ni/Al layered double hydroxide nanoparticles modified carbon ceramic electrode (Ni/Al LDH/NMCC) is characterized by cyclic voltammetry, steady state polarization and chronoamperometry in alkaline media a good redox behavior of Ni(III)/Ni(II) couple at the surface of these electrodes can be observed. The results showed that the electrocatalytic activity of the Ni/ALDH/NMCC electrode is much higher than those of unmodified carbon ceramic electrode under similar experimental conditions. The apparent catalytic rate constant (K) and transfer coefficient ( $\alpha$ ) were determined by cyclic voltammetry and were approximately  $0.314 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and 0.51, respectively. The modified electrode shows a stable and linear response in the concentration range of 0.01 to 0.1 mol L<sup>-1</sup> with a correlation coefficient of 0.9919. The modified CCEs containing Ni/Al LDH nanoparticles show good repeatability, short response time, long term stability (4 months) and excellent catalytic activity.

**Keywords-** Modified Carbon Ceramic Electrode, Electrocatalytic Oxidation, n-Propanol, Cyclic Voltammetry, Sol Gel

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### **1. INTRODUCTION**

The choice of a suitable modified material is an important factor that affects the electrocatalytic performance [1]. The development of novel electrode materials for use in the

determination of clinically, industrially and environmentally important compounds is currently an area of very active investigation [2]. Electrochemical analysis has become of growing importance in industrial process control, environmental monitoring, and different applications in medicine and biotechnology. A lot of research has been conducted in recent years on the attractive properties of nanoparticles and their electrochemical and electrocatalytic behavior [3,4]. In the last few years the use of layered double hydroxides (LDHs) to construct chemical modified electrodes (CMEs) has received great attention due to their versatility, wide range of composition, and low cost [5]. Recent reports show that electrodes modified with thin films of a redox active Ni/Al LDH can catalyze the oxidation of small organic molecules in alkaline media [6]. More recently, reported that Ni(II) sites in the lattices of LDH are electrochemically active. The behavior of the Ni/Al LDH modified electrodes will be compared with that of the structurally similar a Ni(OH)<sub>2</sub> electrodes [7]. These days Increasing interest has been focused on sol-gel derived carbon ceramic electrodes (CCEs), which are generally prepared by doping graphite powder into silicate gel matrix [8,9]. Because CCEs have advantages of low-cost, high stability, good surface-renewable repeatability, ease to prepare and modify much work has been devoted to preparing CCE modified with different electroactive species for electroanalytical applications [10-19].

Direct alcohol fuel cells (DAFCs) based on methanol as fuel have attracted enormous attention as power sources for portable electronic devices and transportation due to the much higher energy density than gaseous fuels such as hydrogen and natural gas [20,21]. However, the development of DAFCs based on methanol fuel is facing serious difficulties: (1) slow methanol electrooxidation kinetics, (2) high methanol crossover, (3) high methanol toxicity, and (4) high noble metal loading [22]. Therefore, other alcohols were considered as alternative fuels. Here, the saturated C<sub>3</sub>-alcohols (1-propanol and 2-propanol) were investigated as the fuels for DAFCs. [23]. A lot of work has been done to study the electro-oxidation of n-propanol and on based catalysts in alkaline medium [24-28]. Mechanism and kinetic of n-propanol oxidation have been studied under a wide ranges of conditions and on various electrodes including (Pd, Pt) [29,30], binary and ternary alloys [31].

In this study, a novel carbon ceramic electrode is prepared using a Ni-Al LDH nanoparticles and investigation of the electrocatalytic properties of a Ni/Al LDH/NMCC electrode toward the oxidation of n-propanol. The electrochemical behavior of n-propanol suggests that Ni/Al LDH/NMCC exhibits obvious electrocatalytic activity to the oxidation of n-propanol, since it greatly enhances the oxidation peak current of n-propanol. The results showed that the Ni/Al LDH/NMCC electrode can be used as an appropriate electrochemical sensor and a candidate as an anode for the fuel cell applications.

## 2. EXPERIMENTAL

### 2.1. Reagents and Apparatus

Methyltrimethoxysilane (MTMOS) was purchased from Fluka and used without further purification. HCl, methanol, n-propanol, high purity graphite powder and other reagents were of analytical reagent grade and provided from Merck or Fluka. All solutions were prepared with doubly distilled water. Electrochemical measurements were carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system with PGSTAT12 boards (ECO Chemie, Utrecht, and The Netherlands). The system was run on a PC using GPES 4.9 software. Ni/Al LDH/NMCC electrode as working electrode (prepared as follows) was employed for the electrochemical studies. A platinum wire was employed as counter electrode and an Ag/AgCl electrode served as the reference electrode. All experiments were performed at room temperature of  $25\pm 2$  °C.

### 2.2. Preparation of Ni/Al LDH nanoparticles

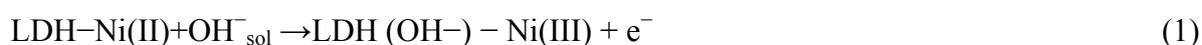
The Ni/Al LDHs nanoparticles were prepared by hydrothermal method [32]. A series of Ni/Al LDHs with nominal  $\text{Ni}^{2+}/\text{Al}^{3+}$  atomic ratio of 3/1 were prepared by hydrothermal reaction at 180°C. All of them were prepared as follows: appropriate amounts of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  ( $\text{Ni}^{2+}/\text{Al}^{3+}=3/1$  (molar ratio)) were dissolved in deionized water (40 mL). Then aqueous solution of  $0.5 \text{ mol L}^{-1} \text{Na}_2\text{CO}_3$  and  $3 \text{ mol L}^{-1} \text{NaOH}$  was added to the above solution drop by drop with vigorous stirring to adjust the pH value of the solution. After that, the suspension was transferred into a 50 mL stainless Teflon-lined autoclave and heated at 180 °C for appropriate time, then cooled to room temperature naturally. The resulting products were filtrated and washed several times with distilled water and absolute ethanol. The apple-green solid was then collected and dried at room temperature for 12 h. Nanoparticles of Ni/Al LDH were obtained.

### 2.3. Preparation of Ni/ALDH/NMCC electrodes

The unmodified and modified carbon ceramic electrodes were prepared according to the procedure described by Lev and co-workers [8]. The fabrication procedure were as follows: 0.2 mL MTMOS, 0.6 mL methanol and 20  $\mu\text{l}$  HCl ( $11 \text{ mol L}^{-1}$ ) were mixed and stirred for 2 min until a homogeneous gel solution appeared, then 0.5 g graphite powder and Ni/Al LDH nanoparticles powder at a sufficient ratio were added and the resultant mixture was shaken for additional 5 min. Then the mixture was packed into a Teflon tube (5 cm length and 2 mm inner diameter) and dried for 48 h at room temperature. Then the electrode was polished with polishing paper and rinsed with distilled water. The unmodified carbon ceramic electrode was constructed by the same procedure without adding Ni/Al LDH nanoparticles to graphite powder. The electric contact was made with a copper wire through the back of the electrode.

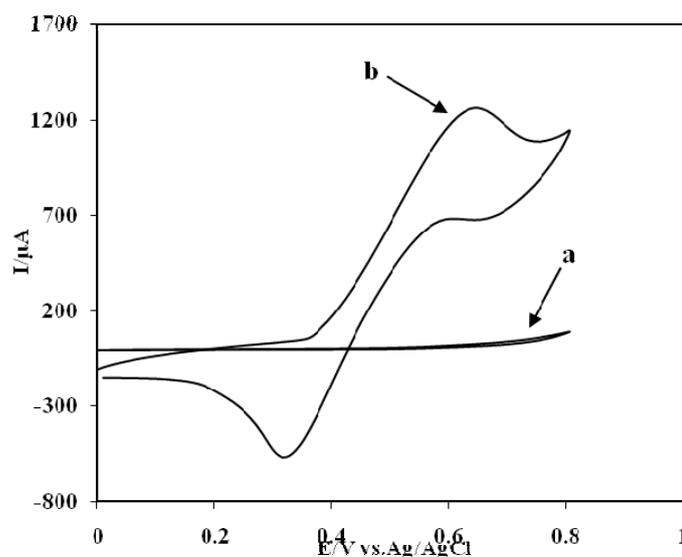
### 3. RESULTS AND DISCUSSION

In this study, Ni/Al LDH/NMCC electrode was used for electrocatalytic oxidation of n-propanol. For the activation of this electrode, the electrode was placed in 0.1 mol L<sup>-1</sup> NaOH and the electrode potential was cycled between 0 and 700 mV (*vs.* Ag/AgCl) at a scan rate of 50 mV s<sup>-1</sup> for 5 cycles in a cyclic voltammetry regime until a stable voltammogram was obtained (figure not shown). It was found that, with increase of the scan number, the currents for both anodic and cathodic peaks increase steadily for up to 5 runs. After 5 runs, the Ni/Al LDH/NMCC electrode shows reproducible cyclic voltammograms. A single and well-defined redox couple has found. A pair of redox peaks was observed which correspond to the couple Ni<sup>(III)</sup>/Ni<sup>(II)</sup> can be described by the reaction (1) [33]:



The limiting step of the process might be ascribed to the diffusion-migration of OH<sup>-</sup> ions to and from the LDH phase or to the electronic transport through the electroactive material by an electron hopping mechanism along the layered double hydroxides [34].

Fig. 1 represents the cyclic voltammograms of the present electrocatalysts in 0.1 mol L<sup>-1</sup> NaOH+0.05 mol L<sup>-1</sup> C<sub>3</sub>H<sub>7</sub>OH at a sweep rate of 50 mV s<sup>-1</sup>, at (a) unmodified carbon ceramic electrode comparing by (b) Ni/Al LDH/NMCC electrode. At the unmodified carbon ceramic electrode, no anodic current due to the oxidation of n-propanol is observed but for Ni/Al LDH/NMCC electrode a large anodic peak is observed. It was found that in comparison to unmodified carbon ceramic electrode, electrochemical behavior of n-propanol was greatly improved at Ni/Al LDH/NMCC electrode, indicating that the anodic oxidation of n-propanol could be catalyzed at Ni/Al LDH/NMCC electrode.

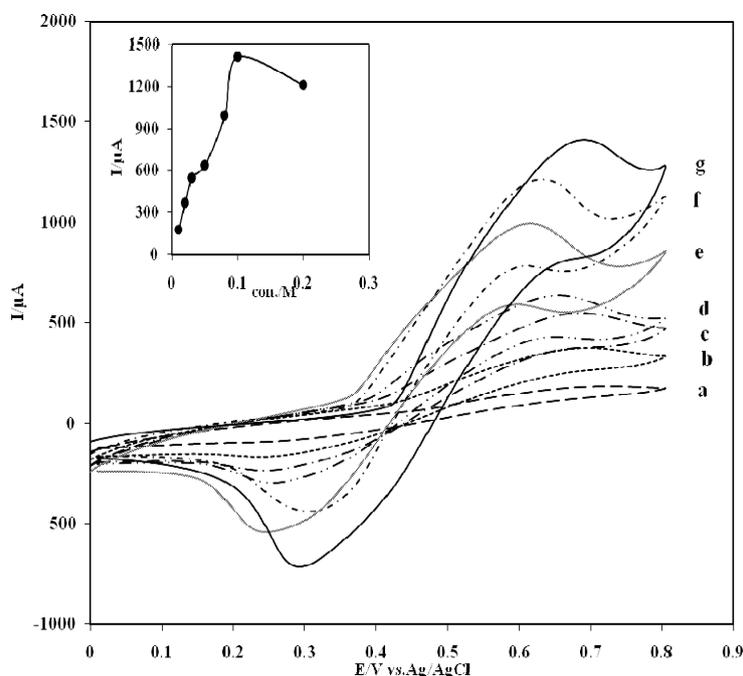


**Fig. 1.** Cyclic voltammograms of unmodified carbon ceramic electrode (a) and Ni/Al LDH/NMCC (b) electrode in 0.1 mol L<sup>-1</sup> NaOH containing 0.05 mol L<sup>-1</sup> n-propanol

The relative decrease of the cathodic peak height in presence of n-propanol is attributed to the partial consumption of nickel oxyhydroxide species for the n-propanol oxidation with the formation of nickel hydroxide in accordance of reaction (2) [35]. However this assumption is questioned by the redox behavior of  $M(OH)_2/M(OOH)$  in which the oxidation of hydroxide to oxyhydroxide is accompanied by the transport of  $H^+$  ions out of the film and not the  $OH^-$  ions transport into the film [36]. This indicates clearly that the applied modifier in this process participates directly in the electrocatalytic oxidation of n-propanol.

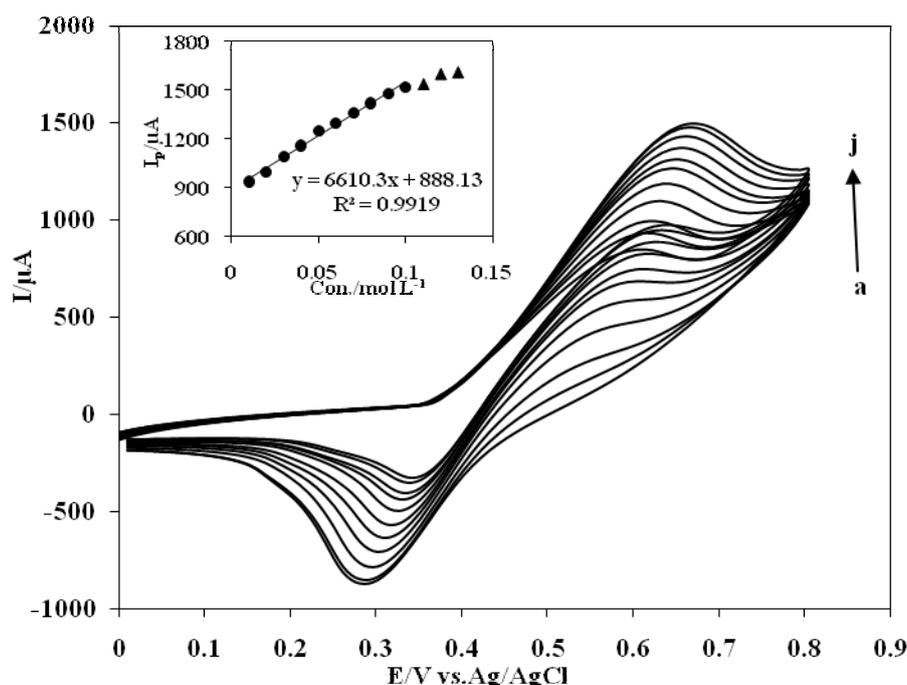


Here we present the effect of NaOH concentration on n-propanol oxidation at Ni/Al LDH/NMCC electrode (Fig. 2). It can be seen that with an increase in  $OH^-$  concentration the peak current of n-propanol oxidation increase first and then begin to decrease remarkably at a NaOH concentration of  $0.1 \text{ mol L}^{-1}$ . The results indicate that the  $OH^-$  ion participates in the oxidation of n-propanol and may also be adverse to the oxidation of n-propanol for the competitive adsorption on the active sites to n-propanol. However, at high  $OH^-$  concentration ( $>0.1 \text{ mol L}^{-1}$ ), the currents mainly come from the redox of Ni(III)/Ni(II) couple, because of the competitive adsorption on the active sites caused by  $OH^-$ . To obtain high oxidation current at lower oxidation potential,  $0.1 \text{ mol L}^{-1}$  NaOH was chosen as support electrolyte.



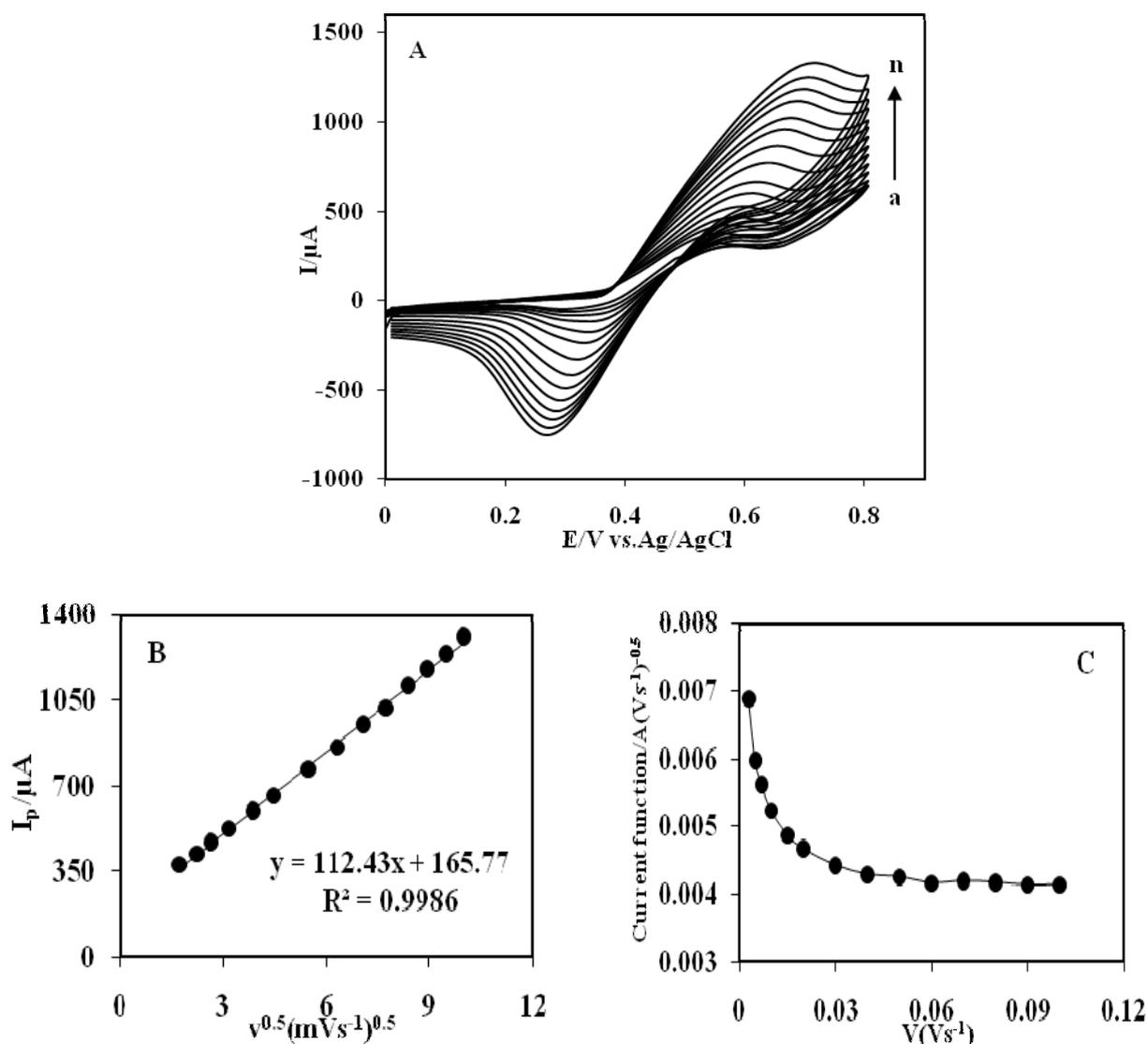
**Fig. 2.** Cyclic voltammograms of Ni/Al LDH/NMCC electrode in  $0.05 \text{ mol L}^{-1}$  n-propanol containing different concentrations of NaOH at the scan rate of  $50 \text{ mV s}^{-1}$ . The NaOH concentration is (a) 0.01, (b) 0.02, (c) 0.03, (d) 0.05, (e) 0.08, (f) 0.1, (g)  $0.2 \text{ mol L}^{-1}$ . The inset displays the peak currents vs. NaOH concentration

With the increase of n-propanol concentration, the anodic peak current gradually increased (Fig. 3). The characteristic shape of cyclic voltammogram in this potential region indicates that the signal is due to the oxidation of n-propanol. The catalytic peak current is proportional to the concentration of n-propanol in the range 0.01 mol L<sup>-1</sup> to 0.1 mol L<sup>-1</sup>. The linear regression equation is  $I (\mu\text{A}) = 6610.3 c_{\text{n-propanol}} (\text{mol L}^{-1}) + 888.13$  ( $R = 0.9919$ ).



**Fig. 3.** Cyclic voltammograms of different concentrations of n-propanol at Ni/Al-LDH/NMCC electrode in 0.1 mol L<sup>-1</sup> NaOH at a scan rate of 50 mV s<sup>-1</sup>. Concentrations of n-propanol from (a) to (j) are 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1 mol L<sup>-1</sup>, respectively

Fig. 4A shows the cyclic voltammograms of Ni/Al LDH/NMCC electrode in 0.1 mol L<sup>-1</sup> NaOH solutions containing 0.05 mol L<sup>-1</sup> n-propanol at different scan rates. The obtained results show that the catalytic effect of the mediator appeared at all testing scan rate. It can also be noted from this figure that, with an increasing scan rate, the peak potential for the catalytic oxidation of the n-propanol shifts to more positive potentials, suggesting a kinetic limitation in the reaction between the redox sites of the modifier and the n-propanol. However the electrocatalytic oxidation current of n-propanol linearly increased with the square root of potential scan rate (Fig. 4B), which demonstrates the reaction is diffusion controlled. Also, plotting the current function against the potential sweep rate (Fig. 4C) revealed negative slope confirming the electrocatalytic nature of the process.

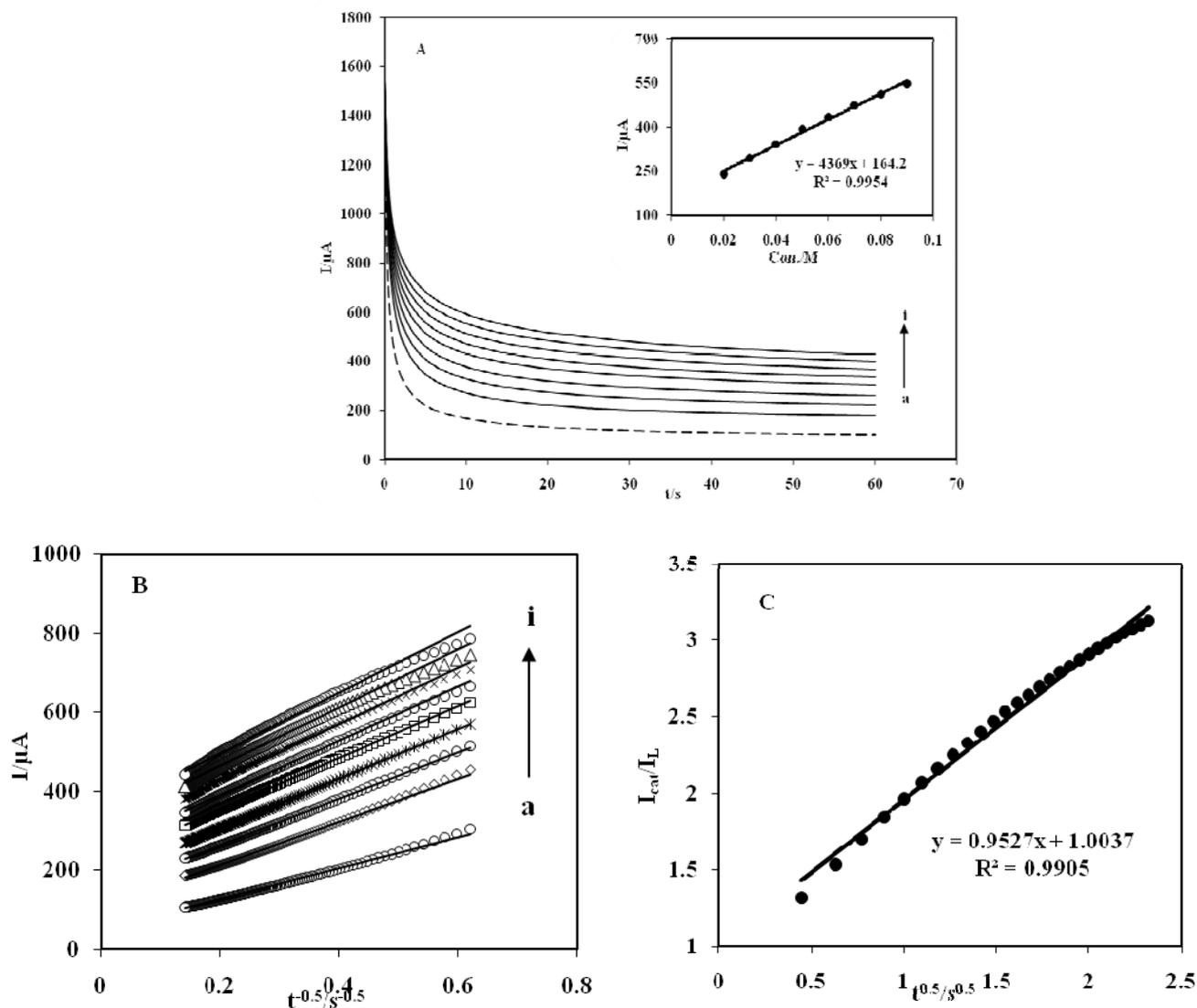


**Fig. 4.** (A) Cyclic voltammograms of Ni/Al-LDH/NMCC electrode in  $0.1 \text{ mol L}^{-1}$  NaOH containing  $0.05 \text{ mol L}^{-1}$  of n-propanol at various potential scan rates (from inner to outer)  $3\text{-}100 \text{ mV s}^{-1}$ . (B) Variation of the catalytic current with the square root of sweep rate. (C) Current function vs.  $v$  for  $0.1 \text{ mol L}^{-1}$  NaOH solution in the presence of  $0.05 \text{ mol L}^{-1}$  n-propanol

To obtain information on the rate-determining step, a Tafel plot was drawn (figure not shown), derived from data of the rising part of the current voltage curve at a low scan rate of  $5 \text{ mV s}^{-1}$ . A slope of  $113.9 \text{ Mv decade}^{-1}$  is obtained indicating the one-electron transfer to be rate limiting assuming an anodic electron transfer coefficient of  $\alpha=0.52$ . The exchange current density ( $J_0$ ) evaluated from Tafel plots is  $3.19 \times 10^{-9} \text{ Acm}^{-2}$ .

Chronoamperometry (CA) is also used to investigate the electrooxidation of n-propanol on Ni/Al LDH/NMCC electrode. Chronoamperograms of Ni/Al LDH/NMCC electrode in the

absence (curve a) and presence (Curves b–i) of n-propanol in 0.1 mol L<sup>-1</sup> NaOH at the oxidation potential of 650 mV (vs. Ag/AgCl) are presented in Fig. 5A.



**Fig. 5.** (A) Chronoamperograms of Ni/Al LDH/NMCC electrode in 0.1 mol L<sup>-1</sup> NaOH containing different concentrations of n-propanol: 0.0, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 and 0.09 mol L<sup>-1</sup>, from (a) to (i), respectively. Potential steps were 0.65 and 0.0 V, respectively. (B) Dependency of transient current on  $t^{-1/2}$ . (C) Dependency of  $I_{\text{catal}}/I_L$  on  $t^{1/2}$  derived from CAs of (a) and (g) in panel (A)

The inset of Fig. 5A shows plots of currents sampled at fixed time as a function of n-propanol concentration. The response is linearly proportional to the concentration of n-propanol in the range of 0.02 to 0.09 mol L<sup>-1</sup>. Plotting of the net current with respect to the minus square roots of time presents a linear dependency (Fig. 5B). This indicates that the

transient current must be controlled by a diffusion process. The transient current is due to catalytic oxidation of n-propanol and the current increases as the n-propanol concentration is raised. No significant cathodic current is observed when the electrolysis potential is stepped to 0 mV (*vs.* Ag/AgCl) indicating the irreversible nature of the oxidation of n-propanol. CA results can also be employed to evaluate the catalytic rate constant ( $k$ ) for the electrode reaction according to [37]:

$$I_{\text{catal}}/I_L = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kC_0t)^{1/2} \quad (1)$$

where  $I_{\text{catal}}$  is the catalytic current,  $I_L$  is the limiting current in the absence of n-propanol and  $\lambda=kCt$  ( $k$ ,  $C$  and  $t$  are the catalytic rate constant, bulk concentration of n-propanol and the elapsed time, respectively). Based on the slope of the  $I_{\text{catal}}/I_L$  *vs.*  $t^{1/2}$  plot, the value of  $k$  for 0.05 mol L<sup>-1</sup> n-propanol was calculated to be  $0.314 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (Fig. 5C).

Fig. 6. indicates pseudo-steady state current potential curves recorded for the electrocatalytic oxidation of n-propanol. Typical S-shape plots have been obtained.

The pseudo-steady state polarization curves of the electro-oxidation of n-propanol on Ni/Al LDH/NMCC electrode at a number of n-propanol concentrations are presented in Fig. 6A. The rotation rate of the electrode is maintained at 3000 rpm to avoid the interference of the mass transfer in the kinetics measurements. The oxidation process was found to begin at nearly 450 mV (*vs.* Ag/AgCl) and to reach a plateau at 745 mV (*vs.* Ag/AgCl) while the oxygen evolution starts at still higher potentials. In the course of reaction the coverage of Ni<sup>III</sup> increases and reaches a saturation (steady state) level and the oxidation current follows accordingly. According to Eq. (2) [37]:

$$i_f = \left( \frac{2FAk_1\Gamma k_2C_m}{k_1 + k_{-1} + 2k_2C_m} \right) \quad (2)$$

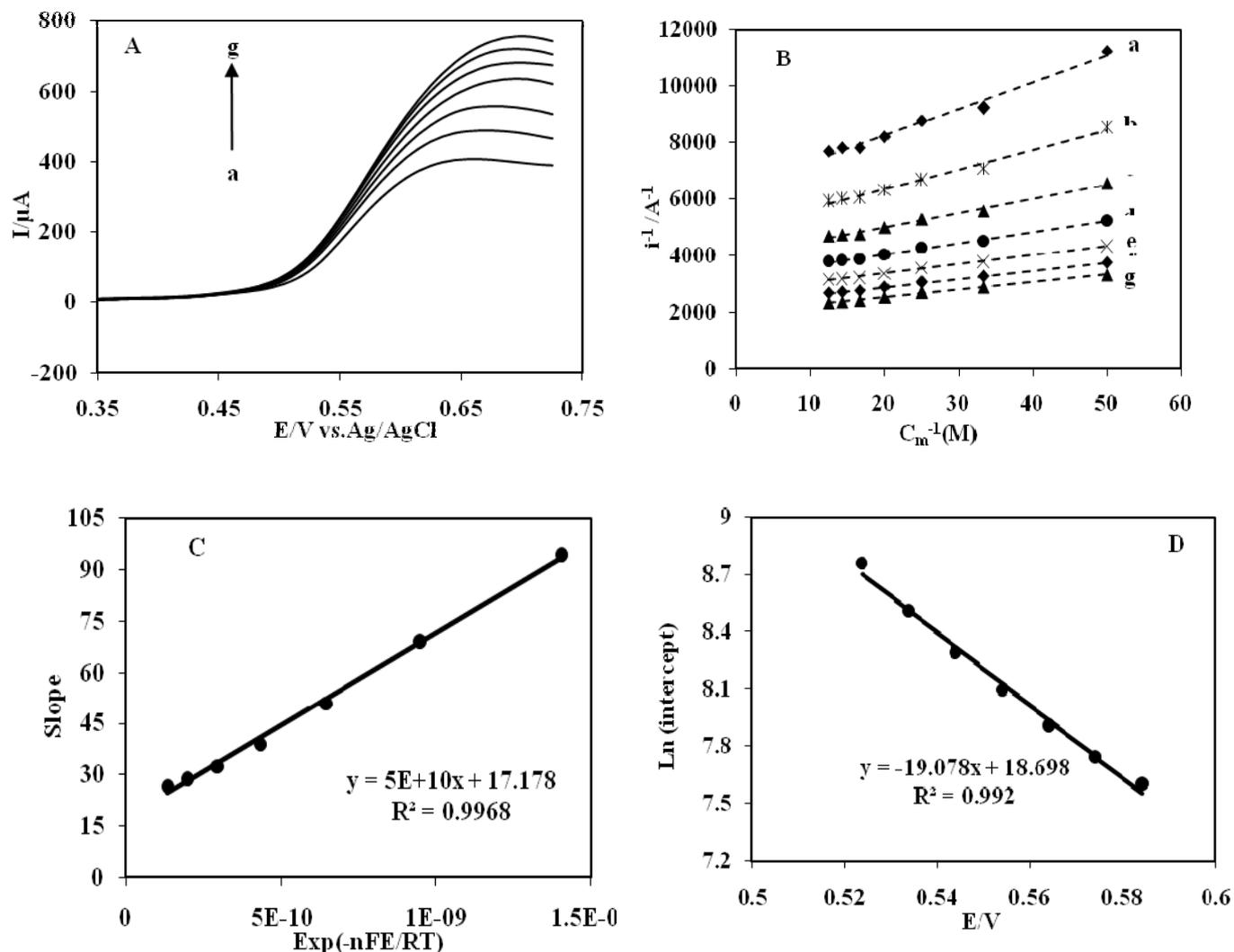
The plots of the inverse current against the inverse n-propanol concentration should be linear [38]:

$$i_f^{-1} = (FAk_1\Gamma)^{-1} + \left[ \frac{k_1 + k_{-1}}{2FAk_1k_2\Gamma} \right] C_m^{-1} \quad (3)$$

Fig. 6B. Presents the  $i^{-1}$  versus  $C_m^{-1}$  dependencies where straight lines at various potentials have been obtained. Both the intercepts and slopes of the straight lines appearing in this figure were potential dependent.

The slopes are plotted against  $\exp(-nFE/RT)$  with  $n=1$  and the graph is presented in Fig. 6C. Using this graph along with Eq. (3) reveals that the rate constant of reaction,  $k_2\Gamma$  and the ratio of  $k_{-1}/k_1$  are  $2.4 \times 10^{-9} \text{ cm s}^{-1}$  and  $2.9 \times 10^6$  respectively.

Fig. 6D presents the variation of the intercepts of the lines in Fig. 6B with the applied potential in a semi-log scale. Using this graph and Eq. (3) the magnitudes of  $k_0^0 \Gamma$  and the anodic transfer coefficient of  $6.3 \times 10^{-13} \text{ mol s}^{-1} \text{ cm}^{-2}$  and 0.49 have been obtained.



**Fig. 6.** (A) Typical pseudo-steady state polarization curves of Ni/Al LDH/NMCP electrode obtained in 0.02 (a), 0.03 (b), 0.04 (c), 0.05 (d), 0.06 (e), 0.07 (f) and 0.08 (g)  $\text{mol L}^{-1}$  n-propanol respectively. The potential sweep rate is  $5 \text{ mV s}^{-1}$ . (B) Plot of  $i^{-1}$  (from polarization curves in Fig. 6A) against  $C_m^{-1}$  at various potentials: (a) 523; (b) 533; (c) 543; (d) 553; (e) 564; (f) 574 and (g) 584 mV (vs. Ag/AgCl) as curves (a–g). (C) Plot of the slopes (of curves in 6B) vs.  $\text{exp}(-nFE/RT)$ . (D) Plot of the  $\text{Ln}(\text{intercept})$  (of curves in 6B) vs. applied potential.

#### 4. CONCLUSIONS

The modified carbon ceramic electrode containing Ni/Al-LDH nanoparticles offers some novel modifier application possibilities in the field of chemically modified electrodes. This modified electrode exhibits oxidation at lower overpotential compared with the unmodified carbon ceramic electrode. The charge transfer coefficient and the number of electrons involved in the rate determining step were calculated.

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