

Full Paper

A New Kinetic-Mechanistic Approach to Elucidate Formaldehyde Electrooxidation on Ni/Al LDH Nanoparticles Modified Carbon Ceramic Electrode

Ghasem Karim-Nezhad, Ali Pashazadeh* and Sara Pashazadeh

Department of Chemistry, Payame Noor University, PO BOX 19395-3697 Tehran, Iran

* Corresponding Author, Tel.: +98 461 2349868; Fax: +98 461 2332556

E-mail: a.pashazadeh20@gmail.com

Received: 19 August 2014 / Accepted with minor revision: 6 December 2014/

Published online: 31 December 2014

Abstract- In the present study, electrocatalytic oxidation of formaldehyde was investigated on Ni/Al Layered double hydroxide nanoparticles modified carbon ceramic (Ni/Al LDH/NMCC) electrode in alkaline media (i.e. NaOH 0.1 M). The process of oxidation involved and its kinetics were established by using cyclic voltammetry, chronoamperometry as well as steady state polarization measurements. The cyclic voltammogram of the resulting modified electrode prepared under optimum conditions, shows a good redox behavior of Ni(III)/Ni(II) couple at the surface of these electrodes can be observed. A new mechanism based on the electrochemical generation of Ni(III) active sites and their subsequent consumption by the formaldehyde in question was also investigated. For Ni/Al LDH/NMCC electrode, the transfer coefficient (α), the number of electrons involved in the rate-determining step (n_α) and the catalytic rate constant (k) for modified electrode were calculated as 0.43, 1 and $0.6536 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ respectively. The modified electrode shows a stable and linear response in the concentration range of 0.01 to 0.1 mol L⁻¹ with a correlation coefficient of 0.9906.

Keywords- Formaldehyde, Kinetic, Nanoparticles, Electrocatalytic Oxidation, Cyclic Voltammetry

1. INTRODUCTION

Formaldehyde(FM), a very important commercial chemical, is one of the most toxic pollutants used as an adhesive material in pressed wood products, as preservatives in paints, coatings and cosmetics, and numerous other applications [1]. Instantly has been an increasing attention about the electrochemical behavior of aliphatic aldehydes, particularly formaldehyde, in various environmental samples. Although formaldehyde is toxic and not very suitable for fuel cells, the study of its electrochemical oxidation is important for the full understanding of methanol oxidation because formaldehyde is produced by partial oxidation of methanol [2]. Many publications have been devoted to experimental studies of the electrochemical reduction and oxidation of formaldehyde (CH_2O) at electrodes made of various materials and also finding the most suitable catalyst and catalyst support is very crucial to its application both in fuel cells and pollution remediation [3]. Mechanism and kinetic of formaldehyde oxidation have been studied under a wide ranges of conditions and on various electrodes including (Pt, Ni, Cu, etc.) [4-7], binary and ternary alloys [8,9] and nanocomposites [10,11].

Nowadays, carbon electrodes are widely used in electroanalysis due to their low background current, wide potential window, chemical inertness, low cost, and suitability for various sensing and detection applications [12-14]. Among carbon electrodes carbon ceramic electrodes (CCEs) have been a lot of attention, due to produce surface renewable, bulk modified electrodes for electroanalytical and electrocatalytic applications in aqueous media. Since the pioneering work of Lev and co workers sol-gel derived composite carbon electrodes (CCEs) [15] have been widely used to develop all kinds of carbon ceramic composite electrodes (CCEs).

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 [16]. The structure of LDHs consists of positively charged brucite-like layers, whose net charge is compensated by anions located in the interlayers, which can be easily exchanged. For this reason these compounds are also called anionic clays [17]. Several papers on the application of LDHs in chemically modified electrodes have been reported [18].

The current research was an attempt to develop and apply modified electrodes by Ni/Al LDH nanoparticles that was also aimed at inspecting the kinetics of electrochemical processes oxidation of Formaldehyde.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

Formaldehyde and other reagents were of analytical grade supplied by Merck (Darmstadt, Germany) and were used without further purification. 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 ± 2 °C.

2.2. Preparation of Ni/Al LDH nanoparticles

In a typical experiment, 15 mmol of sodium sulfate were dissolved in 25 mL of 0.2 M solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ni/Al molar ratio of 2). A clear green solution was obtained after stirring for 5 min. Then 10 mL of 5 M NaOH was added all at once under stirring inducing a pH increase from 3.1 to 13.5, leading to a clear blue solution. Afterward, the solution was transferred into a 40 mL capacity Teflon-lined stainless steel autoclave (autogenous pressure) 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 [19]. Nanoparticles of Ni/Al LDH were obtained.

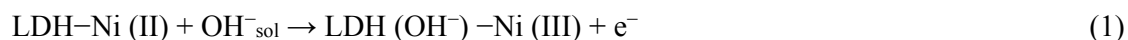
2.3. Preparation of Ni/Al LDH/NMCC electrode

The Ni/Al LDH/NMCC electrode and unmodified carbon ceramic electrode was prepared according to the procedure described by Lev and co-workers [20]. The fabrication procedure were as follows: 0.2 mL MTMOS, 0.6 mL methanol and 20 μl HCl (11 M) 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 (5cm 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

Repetitive cyclic voltammograms (CVs) of Ni/Al LDH/NMCC electrode in 0.1 M NaOH solution in the range of 0 to 700 mV (vs. Ag/AgCl) at a scan rate of 50 mVs^{-1} have been shown in Fig. 1A. As this figure shows, with increase of the scan number, the currents for both anodic and cathodic peaks increase slightly for up to 5 runs. After 5 runs, the Ni/Al

LDH/NMCC electrode shows reproducible cyclic voltamograms. A single and well defined redox couple has found. A pair of redox peaks was observed which correspond to the couple Ni (III)/Ni (II) can be described by the following reaction [21]:



The Ni/Al LDH/NMCC electrode was used for electrocatalytic oxidation of formaldehyde. Fig. 1B presents the CVs of 0.050 M formaldehyde at (a) unmodified carbon ceramic electrode and (b) at Ni/Al LDH/NMCC electrode at 0.1 M NaOH solution. At the unmodified carbon ceramic electrode, no anodic current due to the oxidation of formaldehyde 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 formaldehyde was greatly improved at Ni/Al LDH/NMCC electrode, indicating that the anodic oxidation of formaldehyde could be catalyzed at Ni/Al LDH/NMCC electrode. One may propose a possible mechanism for electrocatalytic oxidation of formaldehyde at the surface of Ni/Al LDH/NMCC electrode is as follow:

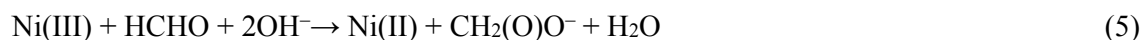
In aqueous solution, formaldehyde is almost completely hydrated, giving methylene glycol $\text{CH}_2(\text{OH})_2$.



With an equilibrium constant of the order of 10^3 [22]. Due to its pK_a of ca. 12.8, the methylene glycol exists predominantly in its ionized form in 0.1 M NaOH:



When $\text{CH}_2(\text{OH})\text{O}^-$ diffuses from the bulk solution to the electrode surface, the methylene glycol ion is quickly oxidized to $\text{CH}_2(\text{O})\text{O}^-$ by the Ni(III) species on the electrode. These results showed that the modified electrode has a high ability for formaldehyde oxidation and the following mechanism can be proposed for the mediated electrooxidation of formaldehyde at the surface of this modified electrode:



The Ni (III) species on the electrode surface are consumed faster and more easily because of the catalytic oxidation of HCHO, producing an anodic current that is dependent on the HCHO concentration [23].

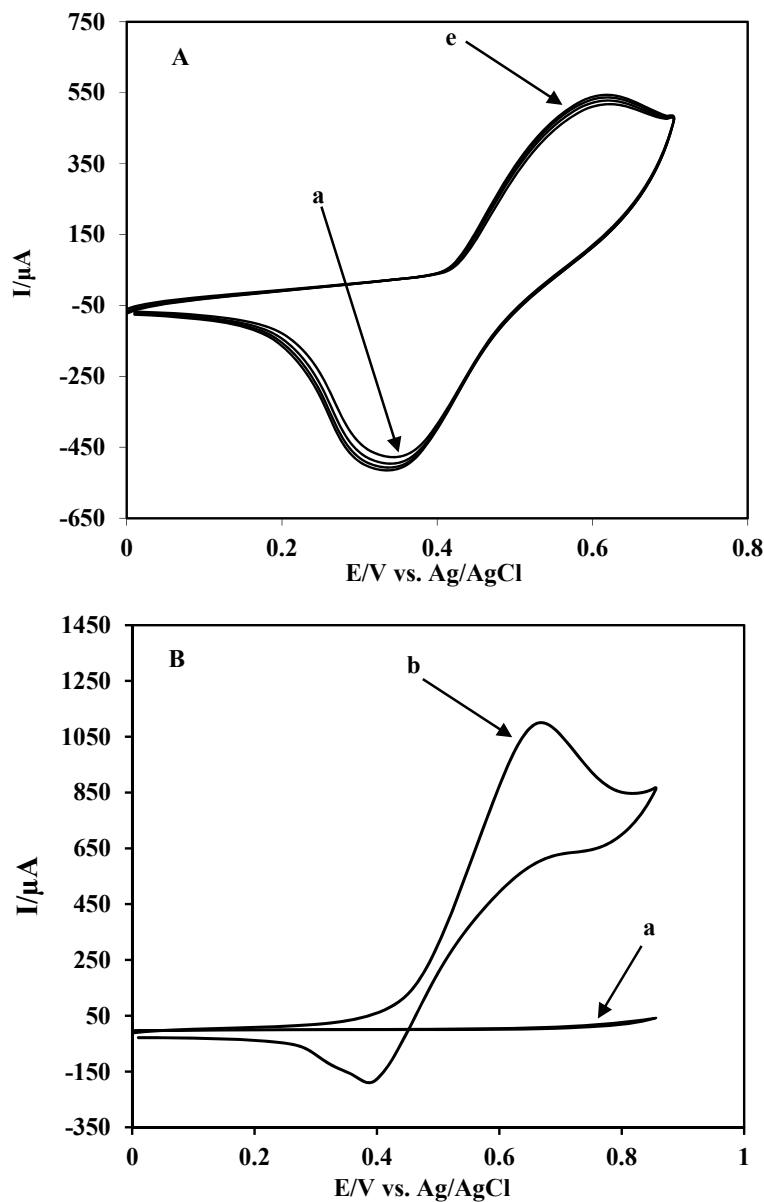


Fig. 1. (A) Repetitive cyclic voltammograms of Ni/Al LDH/NMCC electrode in 0.1 M NaOH in the potential range of 0 to 700 mV. Potential sweep rate is 50 mVs^{-1} . (a) First cycle and (e) end cycle. (B) Cyclic voltammograms of an unmodified carbon ceramic (a) and Ni/Al LDH/NMCC (b) electrode in 0.1 M NaOH solution in presence of 0.05 M formaldehyde; Conditions: scan rate of 50 mVs^{-1} , potential range 0 to 850 mV

Fig. 2 shows the effect of formaldehyde concentration on the cyclic voltammograms of the Ni/Al LDH/NMCC electrode. As can be seen from Fig.2, the height of the anodic peak increases with increasing formaldehyde concentration. The calibration curve obtained from these voltammograms is shown as the inset of this figure. There is a good linear relationship

between the oxidation peak current and the formaldehyde concentration in the range of 0.01 to 0.1 M.

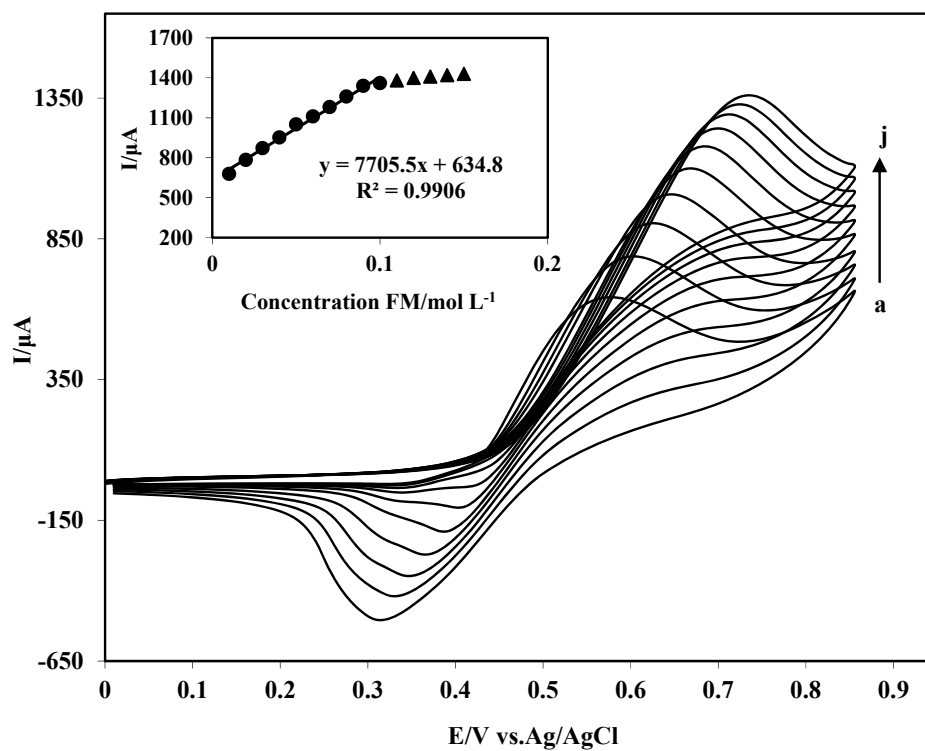


Fig. 2. CVs of different concentrations of formaldehyde at Ni/Al LDH/NMCC electrode in 0.1 M NaOH at a scan rate of 50 mV s^{-1} . Concentrations of formaldehyde from (a) to (j) are 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1 M, respectively

In order to test the effects of scan rate on the cyclic voltammograms of Ni/Al LDH/NMCC electrode in the presence of 0.050 M formaldehyde recorded in 0.1 M NaOH solution at different scan rates (Fig. 3A). As can be seen, the anodic peaks potential shifted to more positive potentials with increasing of potential scan rate. However the electrocatalytic oxidation current of formaldehyde linearly increased with the square root of potential scan rate (Fig. 3A), which demonstrates the reaction is diffusion controlled. Also, plotting the current function against the potential sweep rate (Fig. 3B) revealed negative slope confirming the electrocatalytic nature of the process.

To obtain information on the rate-determining step, a Tafel plot was drawn (Not show), derived from data of the rising part of the current–voltage curve at a low scan rate of 5 mVs^{-1} . A slope of $136.9 \text{ mVdecade}^{-1}$ is obtained indicating the one-electron transfer to be rate limiting assuming an anodic electron-transfer coefficient of $\alpha=0.43$. The results obtained from the two different methods were in good agreement. The exchange current density (j_0) evaluated from Tafel plots is $3.3 \times 10^{-9} \text{ Acm}^{-2}$.

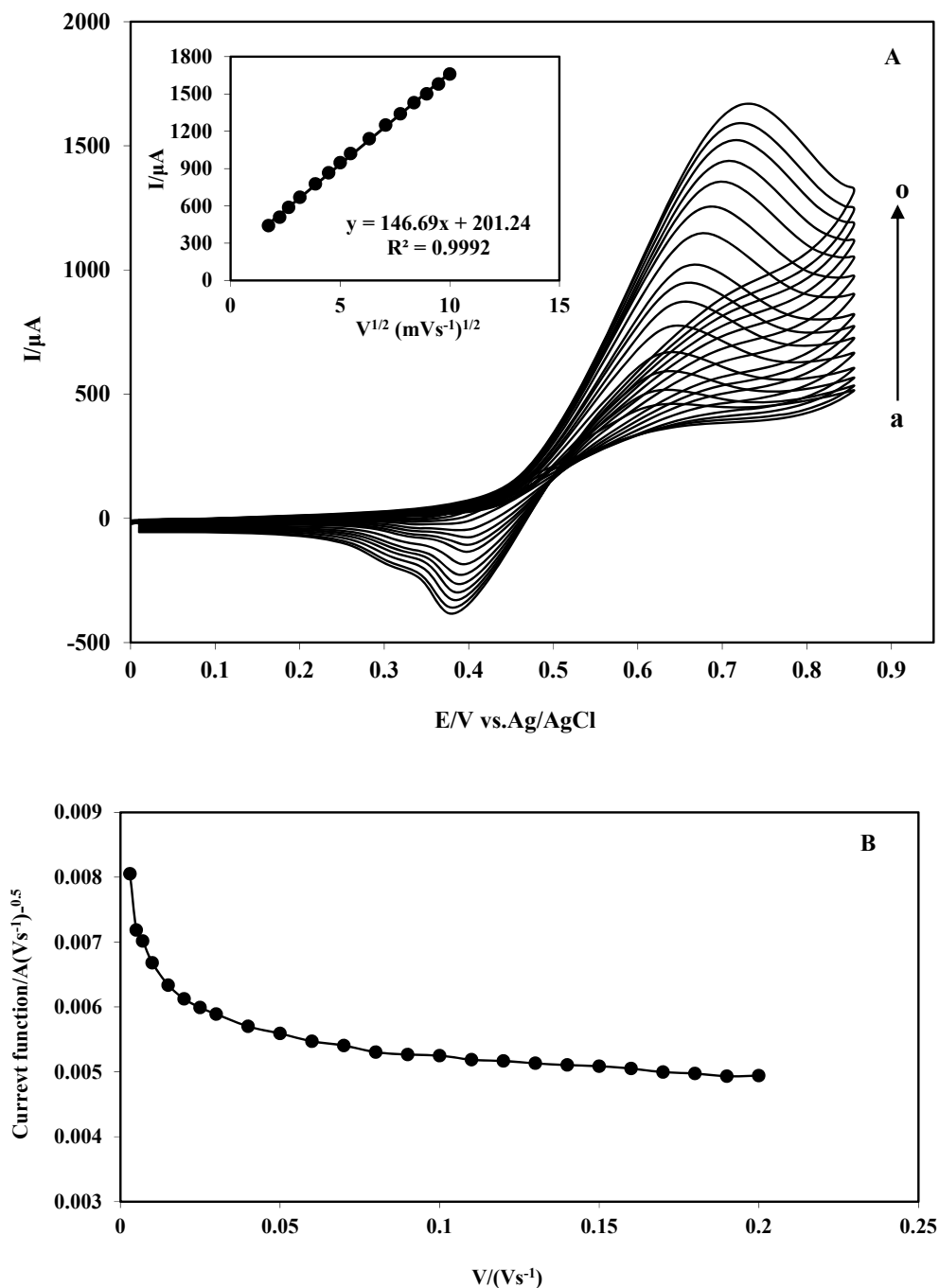


Fig. 3. (A) Cyclic voltammograms of Ni/Al LDH/NMCC electrode in 0.1 M NaOH containing 50 mM of formaldehyde at various potential scan rates (from inner to outer) 3-100 mVs^{-1} . Variation of the catalytic current with the square root of sweep rate (inset). (B) Current function vs. ν for 0.1 M NaOH solution in the presence of 0.05 M formaldehyde

The chronoamperometry, as well as the other electrochemical methods, was employed for the investigation on Ni/Al LDH/NMCC electrode. Fig. 4 shows the chronoamperometric measurements of formaldehyde. Figure represents the current-time profiles obtained by

setting the working electrode potential at 650 mV for the various concentrations of formaldehyde. Good linear dependencies have been observed. Plotting of net currents with respect of the mines square roots of time presents linear dependencies (Fig. 4A). Therefore, a diffusion-controlled process is dominated during the electrocatalytic oxidation of formaldehyde. The level of the Cottrell current, measured for 60 s, increased by increasing the formaldehyde concentration. Calibration curve was recorded in the 0.1 M NaOH solution, containing the formaldehyde concentration in the range of 0.0-0.06 M (Fig. 4A) that was linearly proportional to the formaldehyde concentration. The plot of I versus $t^{-1/2}$, for a Ni/Al LDH/NMCC electrode in the presence of formaldehyde, showed a straight line (inset Fig. 4B).

Chronoamperometry studies can be done to evaluate the catalytic rate constant, the catalytic current (I_{catal}) is dominated by the rate of electrocatalyzed oxidation of formaldehyde. So, the rate constant for the chemical reaction between formaldehyde and oxidized form of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ is determined according to the method described in the literature [24]:

$$\frac{I_{\text{catal}}}{I_{\text{L}}} = \gamma^{1/2} \left(\pi^{1/2} \text{erf}(\gamma^{1/2}) + \frac{\exp(-\gamma)}{\gamma^{1/2}} \right) \quad (1)$$

Where I_{catal} and I_{L} are the currents of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ in the presence and absence of formaldehyde, respectively. While, $\gamma = kC_0t$ (C_0 is the bulk concentration of formaldehyde); k is the catalytic rate constant ($\text{M}^{-1}\text{S}^{-1}$); t is time elapsed per second and $\text{erf}(\gamma^{1/2})$ is the argument of error function. During experiment, it is assumed that formaldehyde is present in large excess rather than $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$ and in addition, where γ exceed 2, the error function is almost equal to 1 and the above equation can be considered as follows:

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

The slopes of the $I_{\text{catal}}/I_{\text{L}}$ versus $t^{1/2}$ was determined for 0.060M formaldehyde and k was calculated to be 0.6536×10^4 ($\text{M}^{-1} \text{s}^{-1}$) (Fig. 4C).

The pseudo-steady state polarization curves of the electro-oxidation of formaldehyde on Ni/Al LDH/NMCC electrode at a number of formaldehyde concentrations are presented in Fig. 5A. 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 350 mV/Ag/AgCl and to reach a plateau at 583.3 mV/Ag/AgCl while the oxygen evolution starts at still higher potentials. In the course of reaction the coverage of Ni^{III} increases and reaches a saturation (steady state) level and the oxidation current follows accordingly.

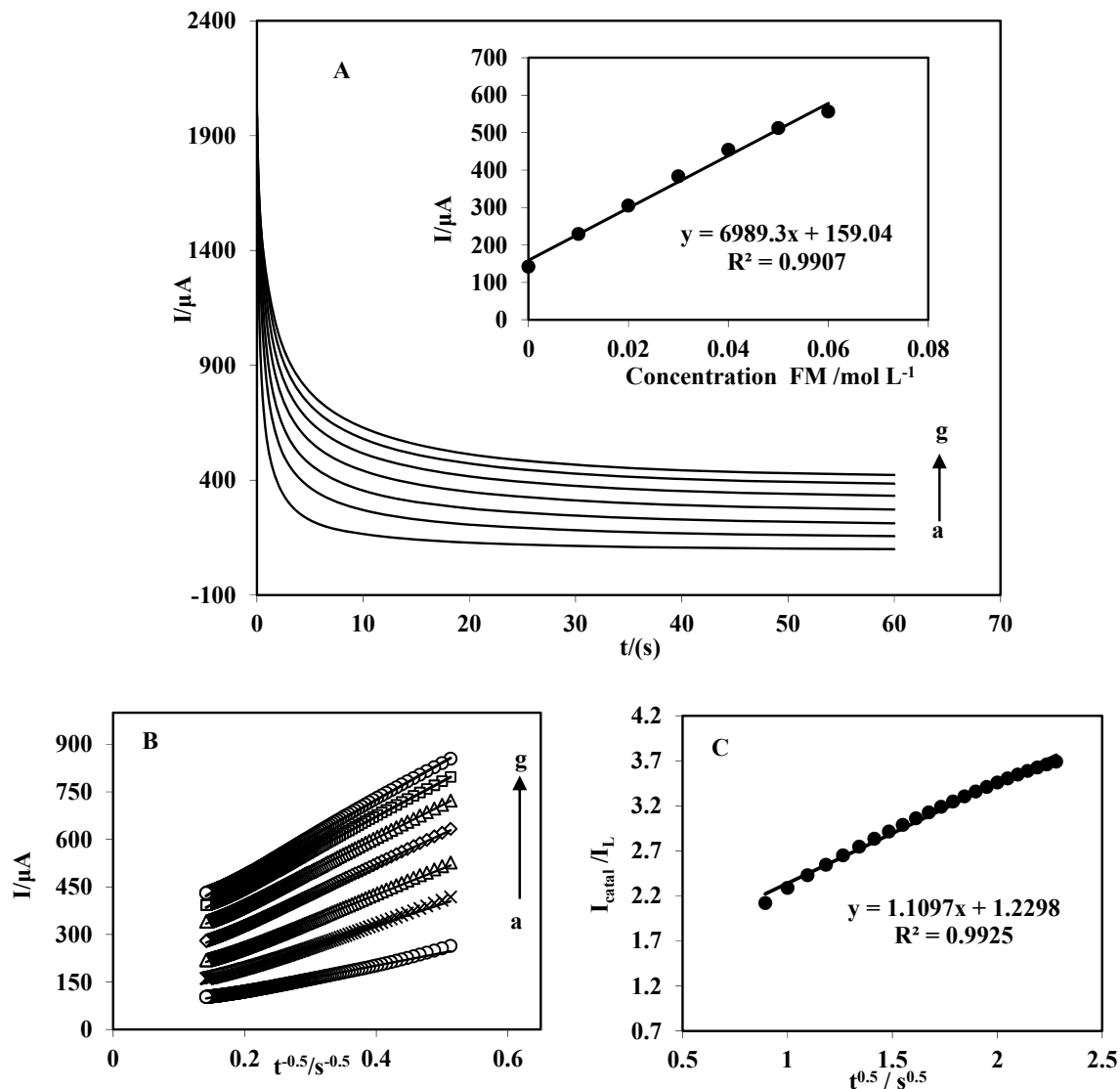


Fig. 4. (A) Chronoamperograms of Ni/Al LDH/NMCC electrode in 0.1 M NaOH with different concentrations of formaldehyde of 0.0, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 M formaldehyde, from (a) to (g), respectively. Potential steps were 0.65 and 0.0 V, respectively. (B) Dependency of transient current on $t^{-1/2}$. (C) Dependency of I_{cat}/I_L on $t^{1/2}$ derived from CAs of (a) and (g) in panel (A)

According to Eq. (3):

$$i_f = \left(\frac{2FAk_1\Gamma k_2 C_m}{k_1 + k_{-1} + 2k_2 C_m} \right) \tag{3}$$

The plots of the inverse current against the inverse formaldehyde concentration should be linear [24]:

$$i_f^{-1} = (FAk_1\Gamma)^{-1} + \left[\frac{k_1 + k_{-1}}{2FAk_1k_2\Gamma} \right] C_m^{-1} \quad (4)$$

Fig. 5B 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.

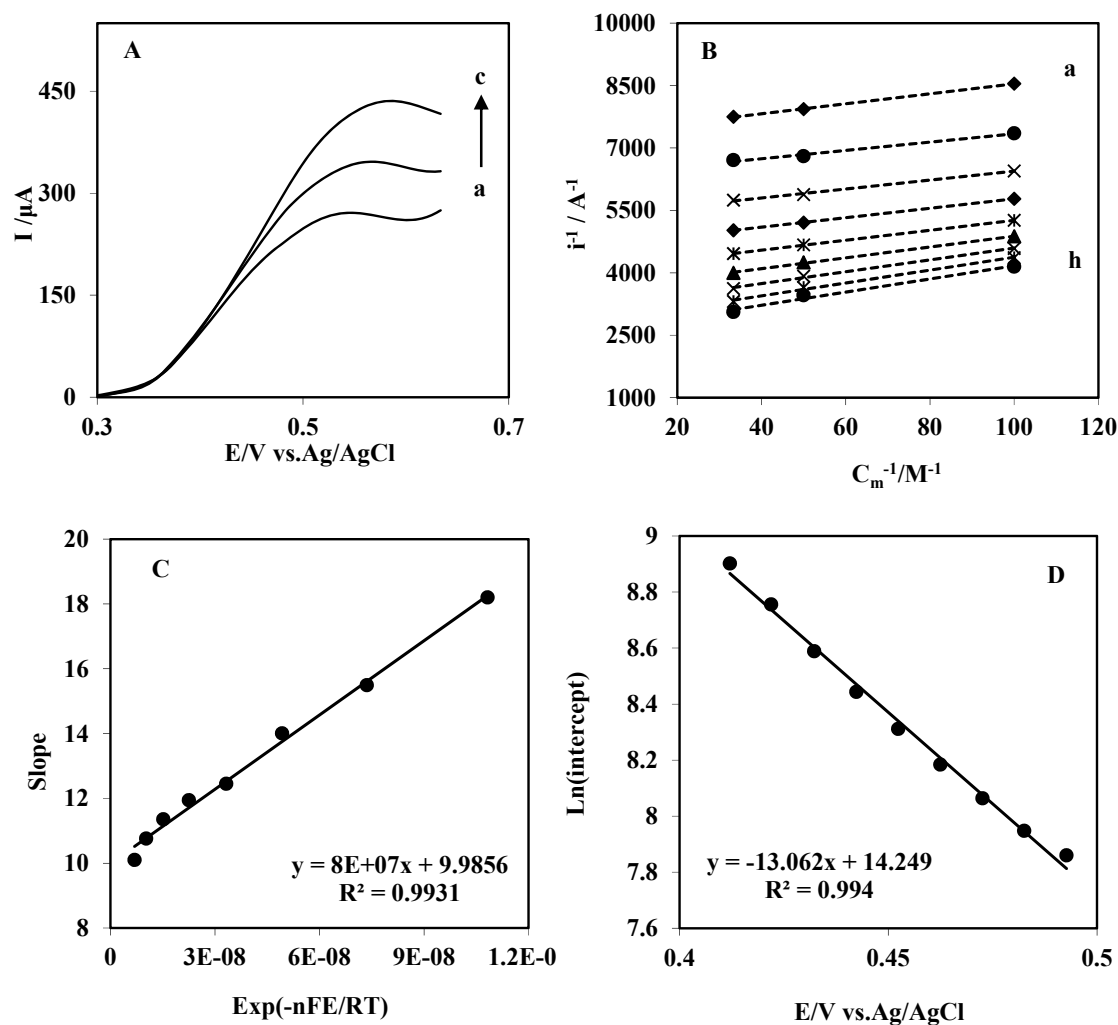


Fig. 5. (A) Pseudo-steady state polarization curves of Ni/Al LDH/NMCC electrode obtained in 0.01 (a), 0.02 (b) and 0.03M formaldehyde (c), respectively. The potential sweep rate is 5 mVs^{-1} . (B) Plot of i^{-1} (from polarization curves in Figure 5A) against C_m^{-1} at various potentials: (a) 412.1; (b) 422; (c) 432.3; (d) 442.4; (e) 452.4; (f) 462.5; (g) 472.6; (h) 482.6 and (i) 492.7 mV/Ag/AgCl as curves (a–i). (C) Plot of the slopes (of curves in 5B) vs. $\text{exp}(-nFE/RT)$. (D) Plot of the $\text{Ln}(\text{intercept})$ (of curves in 5B) vs. applied potential

The slopes are plotted against $\exp(-nFE/RT)$ with $n=1$ and the graph is presented in Fig. 5C Using this graph along with Eq. (4) reveals that the rate constant of reaction, $k_2 \Gamma$ and the ratio of k_{-1}/k_1 are $4.17 \times 10^{-9} \text{ cm s}^{-1}$ and 8.09×10^6 respectively.

Fig. 5D presents the variation of the intercepts of the lines in Fig. 5B with the applied potential in a semi-log scale. Using this graph and Eq. (4) the magnitudes of $k_1 \Gamma$ and the anodic transfer coefficient of $5.35 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$ and 0.34 have been obtained.

4. CONCLUSION

For the first time, the electrooxidation of formaldehyde was successfully performed using the carbon ceramic electrode modified with Ni/Al LDH nanoparticles. The modified electrode shows excellent and persistent electrocatalytic activity toward oxidation of formaldehyde high conductivity and good stability in aqueous solution compared to many of the previously reported electrodes. The relatively high sensitivity of the modified electrode toward the analyte species suggests its potential utility as an appropriate electrochemical sensor for formaldehyde.

REFERENCES

- [1] O. Nikitina, S. Shleev, G. Gayda, O. Demkiv, M. Gonchar, L. Gorton, E. Csoregi, and M. Nistor, *Sensor. Actuators B* 125 (2007) 1.
- [2] G. Samjeske, A. Miki, and M. Osawa, *J. Phys. Chem. C* 111 (2007) 15074.
- [3] L. I. Skvortsova, and T. P. Aleksandrova, *J. Anal. Chem.* 59 (2004) 847.
- [4] M. C. Santos, and L. O. S. Bulhoes, *Electrochimica. Acta* 49 (2004) 1893.
- [5] P. Olivi, L. O. S. Bulhoes, J. M. Leger, F. Hahn, B. Beden, and C. Lamy, *Electrochimica. Acta* 41 (1996) 927.
- [6] S. M. Golabi, and A. Nozad, *Electroanalysis* 16 (2004) 199.
- [7] G. Karim-Nezhad, P. SeyedDorrajji, and B. ZareDizajdizi, *J. Anal. Bioanal. Electrochem.* 3 (2011) 1.
- [8] J. B. Raoof, A. Mrani, R. Ojani, and F. Monfared, *J. Electroanal. Chem.* 633 (2009) 153.
- [9] K. Nishimura, K. I. Machida, and M. Enyo, *J. Electroanal. Chem. Inter. Electrochem.* 251 (1988) 117.
- [10] G. Y. Gao, D. J. Guo, and H. L. Li, *J. Power Sourc.* 162 (2006) 1094.
- [11] V. Selvaraj, M. Alagar, and K. Sathish Kumar, *Appl. Catal. B: Environ* 75 (2007) 129.
- [12] P. T. Kissinger, and W. R. Heineman, *Laboratory Techniques in Electroanalytical Chemistry*, second ed, Dekker, New York (1996).
- [13] J. Wang, *Electroanal. Chem*, second ed., Wiley, New York (2000).
- [14] R. L. McCreery, and A. J. Bard (Ed.), *Electroana. Chem*, vol.18, Dekker, New York (1991).

- [15] J. Wang, V. A. Pamidi, and D. S. Park, *J. Anal. Chem.* 68 (1996) 2705.
- [16] Y. Wang, D. Zhang, W. Peng, L. Liu, and M. Li, *Electrochim. Acta* 56 (2011) 5754.
- [17] L. Guadagnini, A. Mignani, E. Scavetta, and D. Tonelli, *Electrochim. Acta* 55 (2010) 1217.
- [18] P. Wang, and G. Zhu, *Electrochem. Commun.* 4 (2002) 36.
- [19] V. Prevot, N. Caperaa, C. Taviot-Gue'ho, and C. Forano, *Crys. Grow. Desig.* 9 (2009) 3646.
- [20] M. Tsionsky, G. Gun, V. Glezer, and O. Lev, *J. Anal. Chem.* 66 (1994) 1747.
- [21] E. Scavetta, L. Guadagnini, A. Mignani, and D. Tonelli, *Electroanalysis* 20 (2008) 2199.
- [22] A. Ciszewski, and G. Milczarek, *J. Electroanal. Chem* 469 (1999) 18.
- [23] J. B. Raoof, M. A. Karimi, S. R. Hosseini, and S. Mangelizade, *Int. J. Hydrogen Energy.* 36 (2011) 13281.
- [24] M. Hasanzadeh, G. Karimnezhad, M. G. Mahjani, M. Jafarian, N. Shadjou, B. Khalilzadeh, and L. A. Saghatforoush, *Catalys. Commun.* 10 (2008) 295.