Kinetic study of the electrocatalytic oxidation of acetaldehyde at Ni/Al layered double hydroxide modified sol-gel derived carbon ceramic electrode

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Abstract

In this research, the Ni/Al layered double hydroxide modified sol gel derived carbon ceramic (Ni/Al LDH-SGD-CC) electrode was used for electrocatalytic oxidation of acetaldehyde. The oxidation of acetaldehyde happens at the potential where Ni (III) species are generated. The modified electrode exhibited remarkable electrocatalytic activity for the oxidation of acetaldehyde under alkaline conditions; it indicated that the anodic oxidation of acetaldehyde could be catalyzed at Ni/Al LDH-SGD-CC electrode. This proves that the Ni/Al LDH bears the main role in electro-catalytic oxidation of acetaldehyde. The catalytic rate constant, charge-transfer coefficient, the number of electrons involved in the rate-determining step (n_α) and exchange current density for chemical reaction of acetaldehyde were estimated as 0.356×10^4 cm^3 mol^{-1} s^{-1}, 0.51, 1 and 2.76×10^{-8} Acm^{-2} respectively.

Keywords: Ni/Al layered double hydroxide; modified carbon ceramic electrode; electrocatalytic oxidation; acetaldehyde.

Introduction

Acetaldehyde is one of the simplest compounds containing carbonyl groups; it has received much attention as a hazardous in studies of air pollution and reactions involving small organic molecules [1,2]. Acetaldehyde oxidation features an attractive model system, which could help in understanding some basic aspects in the electrocatalysis of organic reactions [3]. It is also an intermediate of ethanol oxidation, provoking the waste of great part of the energetic content of the process and making direct ethanol fuel cell systems impracticable from both economical and technical points of view. The direct oxidation of acetaldehyde has been studied at several electrodes and supported catalysts including: Cu, Au/GC, Pt, Rh and Pt-Ru-Rh electrodeposits, Cu–PVC, Ni/Cu–PVC composite modified electrodes and supported Pt catalyst [4-10]. Although metals such as Pt, Cu are very active in the anodic oxidation of acetaldehyde; they are too expensive for practical applications. Due to its low concentration and high reactivity, the measurement of acetaldehyde is a task of considerable difficulty. Additionally, the main problem in the electrochemical measurements of acetaldehyde with metals electrodes is the formation of catalytic poisons blocking the active surface sites of the

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metal. Rasch and Iwasita found that the main reaction products of acetaldehyde oxidation are CO_2 and acetic acid, with the product yield depending sensitively on the acetaldehyde concentration. For the lowest (0.01M) acetaldehyde concentration, CO_2 was detected as the only reaction product, while for higher acetaldehyde concentrations (0.1 M and 1 M), both CO_2 and acetic acid were identified at comparable selectivities. The authors proposed that the pathway leading to CO_2 formation (in potential scans) is limited by the coverage of adsorbate species formed at low potentials [11]. Surpassing this challenge requires intensive research devoted to the design of new modified electrodes with advantages such as surface renewal, easier preparation, low cost, high stability and high performance electrochemical characteristics. Electrodes modified of sol–gel process have attracted much attention in recent times [12]. The sol–gel technology which involves preparing glassy materials at room temperature could support the immobilization of different reagents. In 1994, Lev et al [13] introduced the sol–gel derived carbon ceramic electrodes (CCEs) which are comprised of dispersion of carbon powder into the starting sol–gel solution. And, this new kind of electrode had been largely utilized to design electrochemical devices whose surfaces could be renewed by a simple polishing step [14,15]. Nowadays much attention is focused to the development of new carbon ceramic electrode modifying with inorganic supports for various electrochemical applications. Alternatively, several recent studies have used electrodes modified with inorganic catalysts, such as Ni/Al LDHs synthetic clays Materials. LDHs are layered materials with the brucite

like structure in which a partial substitution of the divalent cations has taken place; anions (and water molecules) are located in the interlayer region balancing the charge excess [16]. Among these LDHs, Ni-based LDHs which mean the divalent metal cation we can name Ni^{2+} as having received more attention because of their potential application in electrochemical biosensors. On the other hand, the Ni^{2+} cation in the host layers is electrochemically active. The unique electrocatalytic effect mediated by Ni^{2+}/Ni^{3+} redox couples in alkaline circumstance [17].

In this study, the electrocatalytic properties of the Ni/Al LDH-SGD-CC electrode toward the oxidation of acetaldehyde was investigated in alkaline solution aiming at the elucidation of the kinetics and the derivation of the rate constants.

Experimental
General
Methyltrimethoxysilane (MTMOS) was purchased from Fluka and was also used without further purification. HCl, methanol, acetaldehyde, 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-SGD-CC electrode as the 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.

Preparation of Ni/Al layered double hydroxide

The Ni/Al LDHs were prepared by hydrothermal method [18]. A series of Ni/Al LDHs with nominal Ni^{2+}/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 $NiSO_4.6H_2O$ and $Al_2(SO_4)_3.18H_2O$ (Ni^{2+}/Al^{3+}=3/1 (molar ratio)) were dissolved in deionized water (40 mL). Then aqueous solution of 0.5 mol L^{-1} Na_2CO_3 and 3 mol L^{-1} 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 in to a 50mL stainless Teflon-lined autoclave and heated at 180 °C for 8 h, then cooled to room temperature naturally. The resulting products were filtrated and washed several times with distilled water and absolute ethanol. The green solid was then collected and dried at room temperature for 12 h.

Preparation of Ni/Al LDH-SGD-CC electrode

The Ni/Al LDH-SGD-CC electrode and unmodified carbon ceramic electrode was prepared according to the procedure described by Lev and co-workers [13]. The fabrication procedure is as follows: 0.2 mL Methyltrimethoxysilane, 0.6 mL methanol and 20µl hydrochloric acid (11M) were mixed and stirred for 2 min until a homogeneous gel solution appeared, then 0.5 g graphite powder and Ni/Al LDH powder at a sufficient ratio were added and the resultant mixture was shaken for additio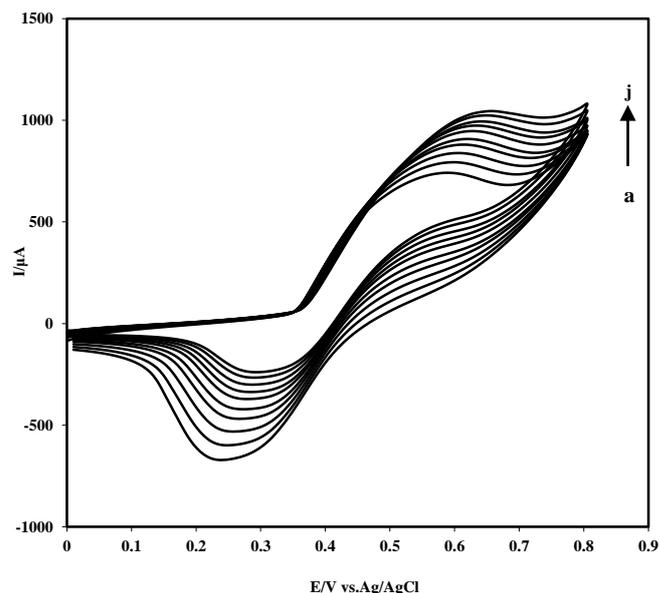nal 5 min. Then the mixture was packed into a teflon tube (5cm length and 2 mm inner diameter) and dried for 24 h at room temperature. Then the electrode was polished with polishing paper and rinsed with distilled water. The unmodified carbon ceramic electrode was constructed by the same procedure without adding Ni/Al LDH to graphite powder. The electric contact was made using a copper wire through the back of the electrode.

Results and discussion

In this experiment, for the activation of Ni/Al LDH-SGD-CC electrode, the electrode was placed in 0.1 M NaOH and the electrode potential was cycled between 0 and 700 mV (*vs*. Ag/AgCl) at a scan rate of 50 mVs^{-1} for 5 cycles in a cyclic voltammetry regime until a stable voltammogram was obtained (Figure 1A). As this figure shows, 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-SGD-CC electrode shows reproducible cyclic voltamograms. A single and well-defined redox couple has found. A pair of redox peaks which was also observed correspond to the couple Ni$^{(III)}$/ Ni$^{(II)}$ and can be described by the equation 1.

In order to reveal the electrocatalytic activity of Ni/Al LDH-SGD-CC electrode toward the oxidation of acetaldehyde, the voltammetric experiments were carried out on both modified and unmodified CCEs in the presence of acetaldehyde. Figure 1B shows the cyclic voltammograms of Ni/Al LDH-SGD-CC electrode in presence of acetaldehyde in 0.1 M NaOH solution. As shown, no oxidation response of acetaldehyde can be seen in the potential range from 0 to 0.8V on unmodified CC electrode (curve a), it indicates the

nonelectroactivity of acetaldehyde on this substrate. As for the Ni/Al LDH-SGD-CC electrode (curve b), the oxidation current remarkably increases, the anodic oxidation of acetaldehyde could be catalyzed at Ni/Al LDH-SGD-CC electrode.

Figure 1. (A) Repetitive cyclic voltammograms of Ni/Al LDH-SGD-CC electrode in 0.1M NaOH in the potential range of 0 to 700 mV. Potential sweep rate is 50mVs^{-1}. (a) First cycle and (e) end cycle. (B) Cyclic voltammograms of an unmodified carbon ceramic electrode (a) and Ni/Al LDH-SGD-CC electrode (b) in 0.1M NaOH Solution in presence of 0.05M acetaldehyde. Conditions: scan rate of 50mVs^{-1}, potential range 0 to 800 mV.

As has been reported in the literature [19,20], this behavior is typical of what had been expected for mediated oxidation of acetaldehyde which can be reported as follows:

$$LDH\text{-}Ni(II) + OH^- \rightleftharpoons LDH(OH^-)\text{-}Ni(III) + e \quad (1)$$

$$LDH(OH^-)\text{-}Ni(III) + organic\ compound \longrightarrow$$

$$LDH\text{-}Ni(II) + oxidation\ product \quad (2)$$

The relative decrease of the cathodic peak in presence of acetaldehyde is attributed to the partial consumption of nickel oxyhydroxide species for the acetaldehyde oxidation with the formation of nickel hydroxide in accordance of reaction (1). This would clearly indicate that the applied modifier in this process participates directly in the electrocatalytic oxidation of acetaldehyde. As suggested in literatures [21- 26] the oxidation of a variety of aldehydes used DME polarography in aqueous base and we found that the oxidation is preceded by a chemical step involving the reversible nucleophilic addition of hydroxide to the carbonyl group forming the electroactive gem-diolate species,

$$RCHO + OH^- \rightleftharpoons R\overset{\displaystyle O^-}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}H \xrightarrow[-2H^+]{-2e} RCO_2^- \quad (3)$$

I   II   III

II, which is oxidized in a two-electron irreversible process to the corresponding carboxylate.

Figure 2 depicts the cyclic voltammograms Ni/Al LDH-SGD-CC electrode at different concentrations of acetaldehyde.

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

It can be seen that an enhancement in concentration of acetaldehyde resulted in an increase in the anodic current at 0.63V (*vs*. Ag/AgCl). There is a good linear relationship between the oxidation peak current and the acetaldehyde concentration in the range of 0.01 to 0.1 M with a detection limit of 9.45 mmol L^{-1} (shown as the inset of this figure).

The effect of scan rate on the electro-oxidation of acetaldehyde in 0.1 M NaOH solution containing 0.05 M acetaldehyde at different scan rates was investigated by cyclic voltammetry (Figure 3A). A plot of peak height (I$_p$) versus the square root of scan rate (v$^{1/2}$), in the range of 3–100 mVs^{-1}, was constructed (inset Figure 3A). This plot was found to be linear, suggesting that, at sufficient overpotential, the process was diffusion-controlled. Also, plotting the current function against the potential sweep rate (Figure 3B) revealed negative slope confirming the electrocatalytic nature of the process.
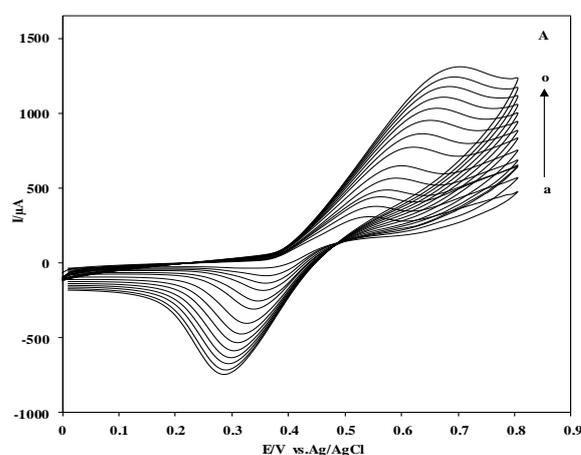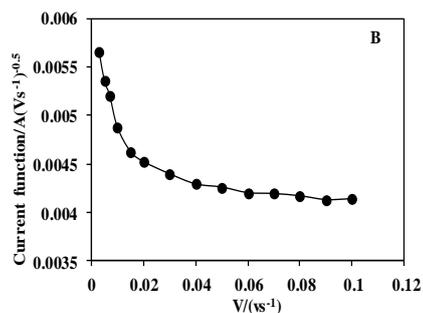
Figure 3. (A) Cyclic voltammograms of Ni/Al LDH-SGD-CC electrode in 0.1M NaOH containing 0.05 M of acetaldehyde at various potential scan rates (from inner to outer) 3-100 mVs^{-1}. Variation of the catalytic current with the square root of sweep rate (inset). (B) Current function *vs.* V for 0.1M NaOH solution in the presence of 0.05M acetaldehyde.

To obtain information on the rate-determining step, a Tafel plot was drawn (not shown), derived from data of the rising part of the current–voltage curve at a low scan rate of 5 mVs^{-1}. A slope of 115 mVdecade^{-1} is obtained indicating the one-electron transfer to be rate limiting assuming an anodic electron-transfer coefficient of α =0.51. The exchange current density (j_0) evaluated from Tafel plots is 2.76×10^{-8} Acm^2.

Chronoamperometry (CA) is also used to investigate the electro-oxidation of acetaldehyde on Ni/Al LDH-SGD-CC electrode. Chronoamperograms of Ni/Al LDH-SGD-CC electrode in the absence (curve a) and presence (Curves b–h) of acetaldehyde in 0.1 M NaOH at the oxidation potential of 650 mV (*vs.* Ag/AgCl) are presented in Figure 4A.

The inset of Figure 4A shows plots of currents sampled at fixed time as a function of acetaldehyde concentration. The response is linearly proportional to the concentration of acetaldehyde in the range of 0.01–0.07 M. Plotting of the net current with respect to the mines square roots of time presents a linear dependency (Figure 4B). This indicates that the transient current must be controlled by a diffusion process. The transient current is due to catalytic oxidation of acetaldehyde and the current increases as the acetaldehyde 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 acetaldehyde.
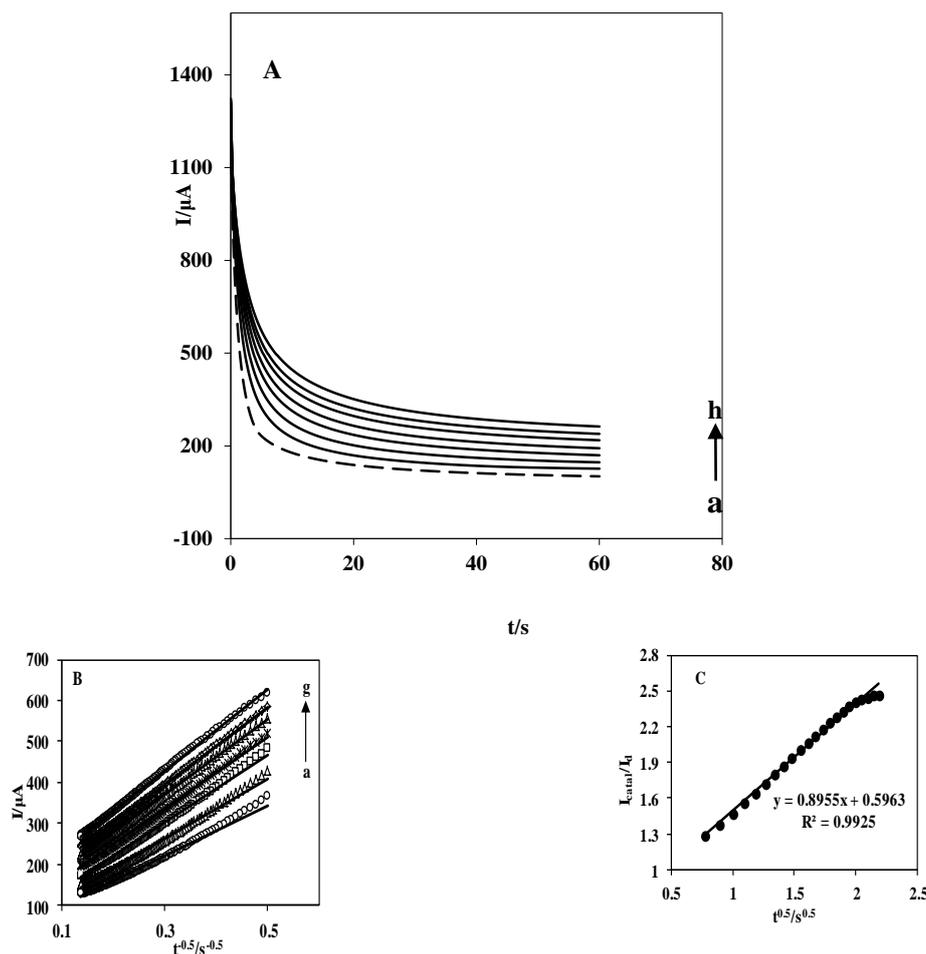
Figure 4. (A) Chronoamperograms of Ni/Al LDH-SGD-CC electrode in 0.1 M NaOH containing different concentrations of acetaldehyde: 0.0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and0.07 M acetaldehyde, from (a) to (h), respectively. Potential steps were 0.65 and 0.0 V, respectively. (B) Dependency of transient current on $t^{-1/2}$. (C) Dependency of I_{cat}/ I_d on $t^{1/2}$derived from CAs of (a) and (h) in panel (A).

CA results can also be employed to evaluate the catalytic rate constant (k) for the electrode reaction according to [27]:

$$\frac{I_{catal}}{I_d} = \lambda^{1/2}\pi^{1/2} = \pi^{1/2}(kCt)^{1/2} \qquad (1)$$

where I_{catal} is the catalytic current, I_d is the limiting current in the absence of acetaldehyde and $\lambda = kCt$ (k, C and t are the catalytic rate constant, bulk concentration of acetaldehyde and the elapsed time, respectively). Based on the slope of the I_{catal}/I_d *vs.* $t^{1/2}$ plot, the value of k for 0.07 M acetaldehyde was

calculated to be 0.356×10^4 cm^3 mol^{-1} s^{-1} (Figure 4C).

The pseudo-steady state polarization curves of the electro-oxidation of acetaldehyde on Ni/Al LDH-SGD-CC electrode at a number of acetaldehyde concentrations are presented in Figure 5. 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 550 mV (vs. Ag/AgCl) and to reach a plateau at 670 mV (vs. 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. At potentials as high as 740 mV (vs. Ag/AgCl), the decomposition (oxidation) of solvent interferes and the plateau region becomes ill defined.

According to Eq. (2), the plots of the inverse of current against the inverse of acetaldehyde concentration should be linear [27]:

$$i_f^{-1} = \left(FAk_1\Gamma\right)^{-1} + \left[\frac{k_1 + k_{-1}}{2FAk_1k_2\Gamma}\right]c_m^{-1}$$
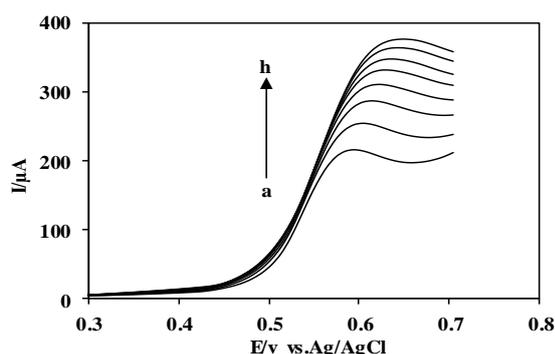
Figure 5. Pseudo-steady state polarization curves of Ni/Al LDH-SGD-CC electrode obtained from (a) to (h) 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 and 0.09M acetaldehyde, respectively.
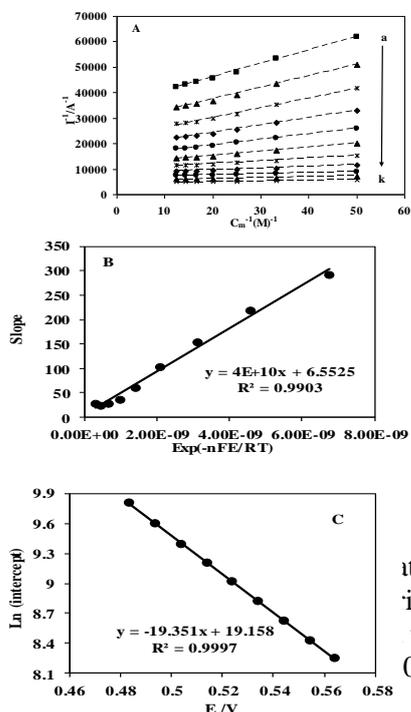
513; (e) 523; (f) 533; (g) 543; (h) 553 and (i) 564 mV (vs. Ag/AgCl) as curves (a–i). (B) Plot of the slopes (of curves in 6A) *vs.* exp (-nFE/RT). (C) Plot of the Ln (intercepts) (of curves in 6A) *vs.* applied potential.

Figure 6A 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 Figure 6B. Using this graph along with Eq. (2) reveals that the rate constant of reaction k$_2\Gamma$ and the ratio of k$^0_{-1}$/k$^0_1$ are 6.29×10^{-10} cms^{-1} and 6.09×10^{12} respectively. Figure 6C presents the variation of the intercepts of the lines in Figure 6A with the applied potential in a semi-log scale. Using this graph and Eq. (2), the magnitudes of k$^0_1\Gamma$ and the anodic transfer coefficient of 3.94×10^{-13} mol s^{-1}cm^{-2} and 0.497 have been obtained.

The modified electrode retained its initiate activity for more than 60 days when kept in air at ambient conditions. A decrease of 11% was observed in the current response of the electrode at the end of 60th day.

In addition, repetitive recording of cyclic voltamograms in acetaldehyde solution tested the reproducibility of the electrocatalytic effect of the modified CCE. It was found that the relative standard deviation (R.S.D.) of the peak currents of 30 mmol L^{-1} acetaldehyde for ten replicate determinations was 1.84%.

Table 1 compared the proposed electrode for acetaldehyde oxidation with electrodes reported in the literatures. As it shows, the proposed electrode is comparable with other electrodes such as Pt/Ru/Os and copper electrode. Despite this, the advantages

of the Ni/Al LDH-SGD-CC electrode are its good stability and reproducibility of surface renewal by simple polishing, excellent catalytic activity and simplicity of preparation.

Table 1. Comparison of acetaldehyde electrooxidation on bare and modified electrodes

Electrode	E_p(mV)	I_p(μA)	sensitivity	α	n_α	References
Pt/Ru/Os	1150	1.2×10^{-6}	-	-	-	[28]
Copper Electrode	680	500	11.532	0.63	1.2	[29]
$Pt_{80}Sn_{10}M_{10}$	800	250	-	-	-	[30]
Ni/Al LDH-SGD-CC	604	980	3.321	0.51	1.02	This work

Conclusion

This work has demonstrated a simple and efficient carbon ceramic electrodes modified by Ni/Al-LDH. The results show that, by comparison of the different responses to acetaldehyde oxidation, using Ni/Al LDH-SGD-CC electrodes is a more effective catalyst for the electrooxidation of acetaldehyde. Using the cyclic voltammetry and chronoamperometry techniques and also steady-state polarization measurements, the kinetic parameters such as charge transfer coefficient (α) and the catalytic reaction rate constant (k) for oxidation of acetaldehyde were determined. High stability, good reproducibility, rapid response, easy surface regeneration and fabrication are the important characteristics of the proposed electrode.

Acknowledgments

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