

*Full Paper*

## **Electro-Catalytic Oxidation of Formaldehyde and Acetaldehyde on Copper Chloride Modified Copper Electrode**

**Ghasem Karim-Nezhad\*, Parisa Seyed Dorraji, Behruz Zare Dizajdizi**

*Chemistry Department, Payame Noor University, 19395-4697 Tehran, I. R. of Iran*

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

E-Mail: [g.knezhad@gmail.com](mailto:g.knezhad@gmail.com)

*Received: 13 October 2010 / Accepted: 13 February 2011 / Published online: 28 February 2011*

---

**Abstract-** The electrocatalytic oxidation of formaldehyde and acetaldehyde on copper chloride modified copper electrode in alkaline solution was investigated. The process of oxidation and the kinetics have been investigated using cyclic voltammetry, chronoamperometry, and steady-state polarization measurements. The results show that the (ClCu)<sub>2</sub>O film on the electrode behaves as an efficient catalyst for the electrooxidation of two species in alkaline medium. The CV changes observed indicate that the modified electrode has a good catalytic activity for the oxidation of formaldehyde and acetaldehyde. The transfer coefficient ( $\alpha$ ), the number of electrons involved in the rate-determining step ( $n_\alpha$ ) and the catalytic rate constant ( $k$ ) for modified electrode were calculated.

**Keywords-** Electrocatalytic Activity, Modified Electrode, Formaldehyde, Acetaldehyde, Alkaline Media

---

### **1. INTRODUCTION**

Formaldehyde is water soluble and biodegradable. Formaldehyde occurs naturally in the atmosphere through a variety of biological and chemical processes. As a result of various metabolic processes, formaldehyde is naturally present in the human body at very low concentrations. It is also produced incidentally in the course of natural processes and human

activities that involve the combustion of organic materials, such as bush fires and fuel. As a metabolic intermediate, formaldehyde is present at low levels in most living organisms. It is emitted by bacteria, algae, plankton, and vegetation as well. The anodic oxidation of formaldehyde on various metals was investigated mostly in connection with fuel cells. Formaldehyde, as one of the intermediate products of methanol oxidation, can be activated to decompose to smaller fragments, protons, electrons and CO<sub>2</sub> at high efficiency. More recent data shows that formaldehyde fuel cells are attractive alternatives for proton exchange membrane (PEM) fuel cells applications [1–8]. The fact that it is one of the most widely used reduction agents in electroless Cu plating has simulated CH<sub>2</sub>O oxidation studies on polycrystalline Cu surface. The mechanism of electrooxidation of organic species, such as formaldehyde, involves the coupling of the electron transfer reaction with a dissociative chemisorptions step; therefore the kinetic of the latter process is greatly affected by catalytic properties.

Acetaldehyde is a compound that is frequently used as a model for the electrochemical behavior of aldehydes [9,10]. Acetaldehyde is also an intermediate of ethanol oxidation, and therefore, in order to elucidate the mechanism of the oxidation reaction leading to CO<sub>2</sub>, it is worth to undertake studies using this molecule as model. In alkaline medium (0.1M NaOH), acetaldehyde can undergo two kinds of chemical reactions: The first one is the Cannizzaro reaction which yields a carboxylate and an alcohol and the other is aldolization that acetaldehyde was converted to acetate, 3-hydroxybutanal and 3-hydroxybutanoate in alkaline medium [11-13]. Electrochemical oxidation of acetaldehyde continues to be interesting topics because it arouses great investigations in different catalytic application areas. It is an intermediate product in ethanol electrooxidation and in the degradation of lots of polluting organic compounds. Although platinum is known to be the best electrocatalyst [14-20], it is known that its activity is improved by the modification of its surface with transition metals such as Ru, Sn, Mo, etc. Wieckowski et al. reported that Pt alloyed with osmium can also constitute a promising catalyst for the electrochemical oxidation of small molecules [21–23]. When depositing Ru and Os in submonolayer amounts on Pt (1 1 1) single crystals, they showed that these electrodes exhibited higher surface activity at lower potentials. In recent years multi-electron oxidation processes, C–C bond cleavage and the generation of lower molecular weight products from organic substrates on copper-based electrodes in alkaline solutions have received considerable attention [24,25].

The present study was an attempt at continuing our recent studies on the development and application of the modified electrodes which were aimed at inspecting the kinetics and mechanisms of electrochemical processes [26,27]. This paper will focus on the electro-oxidation of formaldehyde and acetaldehyde on copper chloride modified copper (CCMC) electrode.

## 2. EXPERIMENTAL

### 2.1. Reagents and instrumentation

All chemicals were obtained from Merck, of the highest grade available and used without further purification. All solutions and subsequent dilutions were prepared daily, using doubly distilled water. Electrochemical data, cyclic voltammetry (CV) and chronoamperometry were carried out using an Autolab potentiostat PGSTAT 12 (Eco Chemie Utrecht, Netherlands) equipped with GPES 4.9 software. The cell used was equipped with modified copper electrode as the working electrode, a platinum wire as an auxiliary electrode and with an Ag/AgCl/saturated KCl (from Metrohm) as a reference electrode. All potentials in the text are quoted versus this reference electrode. A personal computer was used for data storage and processing.

### 2.2. Preparation of copper chloride modified copper (CCMC) electrode

Prior to modification, the base copper electrode was polished to a mirror finish using alumina slurry with 0.05  $\mu\text{m}$ . After each polishing, the electrode rinsed thoroughly with acetone and then with doubly distilled water, in order to remove any adsorbed substance on the surface.

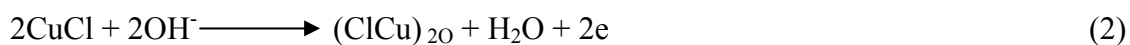
Film of oxy copper chloride was formed on the copper surface by the method previously reported [27]. Briefly, the copper electrode was placed in 0.1 M  $\text{CuCl}_2$  solution for 20 s.

In this step, a layer of copper (I) chloride was formed at the surface of copper electrode as following reaction:



Subsequently, the electrode was conditioned in 0.10 M NaOH solution, and the modification was completed under the regime of cyclic voltammetry where 5 consecutive cycles in the range of  $-250$  to  $-1000$  mV (vs. Ag/AgCl) with a potential sweep rate of  $50 \text{ mVs}^{-1}$  were applied until a featureless voltammogram was obtained.

It seems that a film of oxy copper chloride  $(\text{ClCu})_2\text{O}$ , as shown in the following reaction, is formed at the surface of electrode during the cyclic voltammetry step:

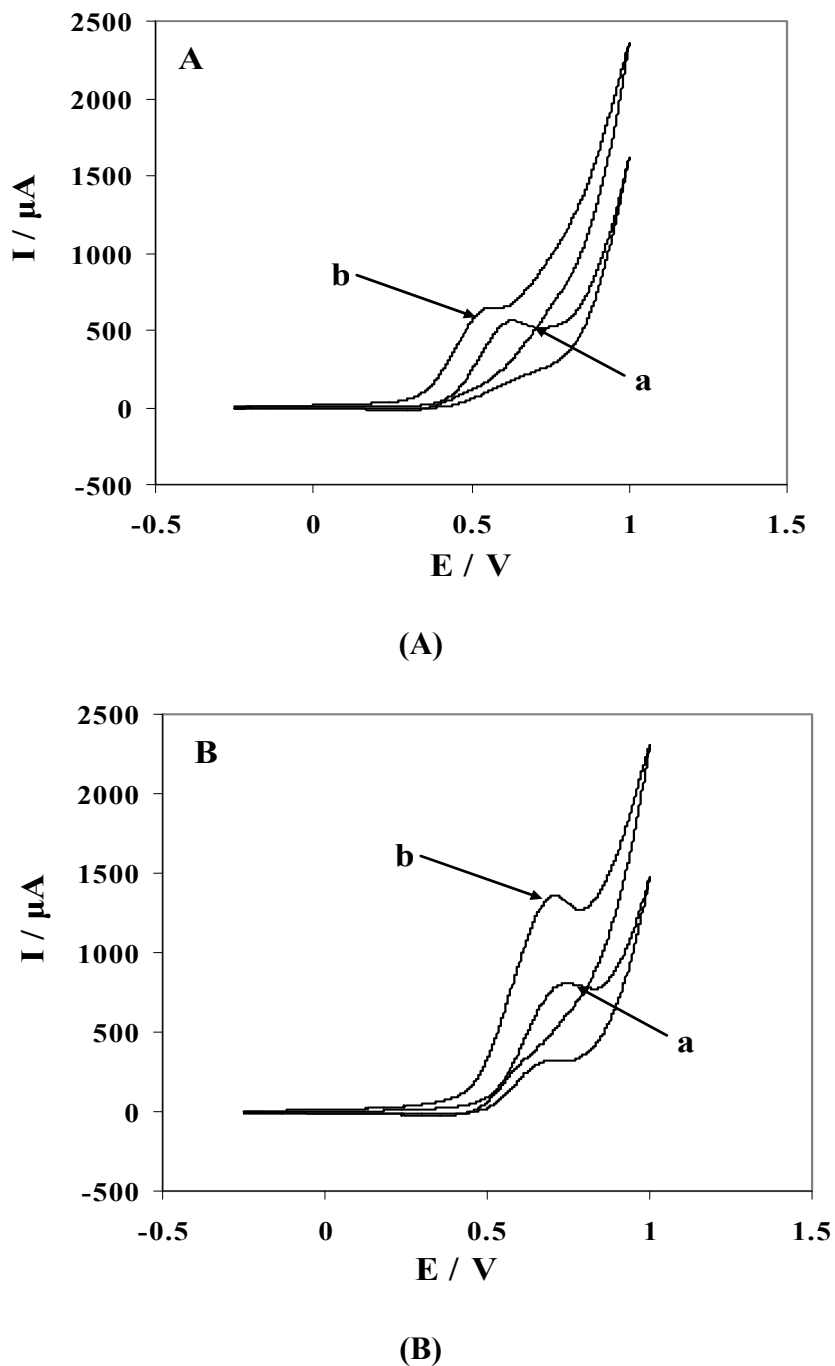


## 3. RESULTS AND DISCUSSION

### 3.1. Cyclic voltammograms of formaldehyde and acetaldehyde at CCMC electrode

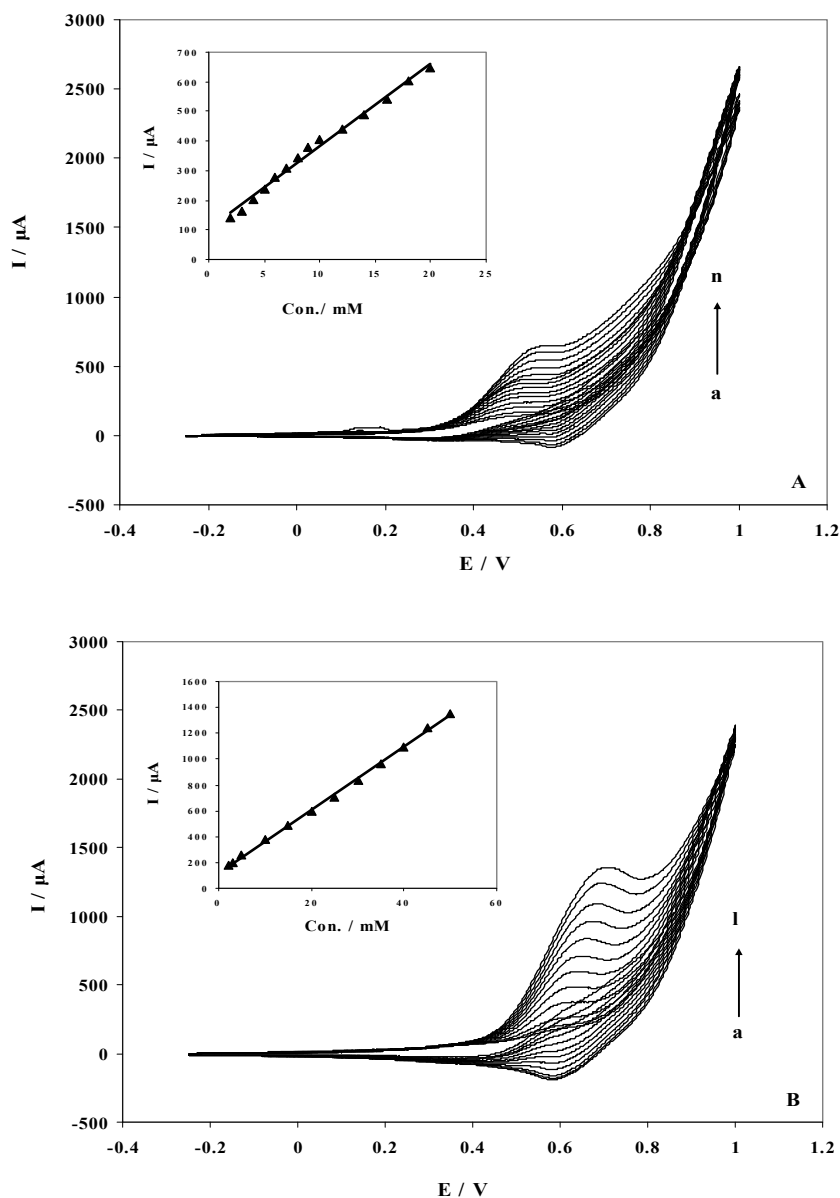
The cyclic voltammogram curves of 20 mM formaldehyde (A) and 50 mM acetaldehyde (B) oxidation on the (a) bare copper electrode and (b) CCMC electrode in the solution of 0.1 M NaOH are presented in Fig. 1. As can be seen, at the bare electrode, a small anodic current due to the oxidation of formaldehyde or acetaldehyde is observed but no cathodic peak is found, which indicates an irreversible heterogeneous charge transfer in this system.

Compared to curves (a), the visible differences found for curves (b) were a low peak potential and a high current. These differences demonstrate that for CCMC electrode oxidation of HCHO and CH<sub>3</sub>CHO become easier.



**Fig. 1.** CVs of formaldehyde and acetaldehyde at the bare electrode (a) and the copper chloride modified copper electrode (b) in 0.1M NaOH solution at the scan rate of 50  $\text{mVs}^{-1}$  (A) 20 mM formaldehyde; (B) 50 mM acetaldehyde

The CV changes observed indicate that the CCMC electrode has a good catalytic activity for the oxidation of formaldehyde and acetaldehyde. This proves that the copper chloride layer formed on the surface of the copper electrode bears the main role in electro-catalytic oxidation of HCHO and CH<sub>3</sub>CHO on the surface of CCMC electrode.



**Fig. 2.** (A) Cyclic voltammograms of CCMC electrode in 0.1 M NaOH in the presence of different concentrations of formaldehyde: 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18 and 20 mM. Inset A: plot of peak current vs. formaldehyde concentrations. (B) Cyclic voltammograms of CCMC electrode electrode in 0.1 M NaOH in the presence of different concentrations of acetaldehyde: 2, 3, 5, 10, 15, 20, 25, 30, 25, 40, 45 and 50 mM. Inset B: plot of peak current vs. acetaldehyde concentrations

Surface photographs of CCMC electrode (studied by SEM) showed that considerable amounts of microcrystals have been formed on the copper surface during the modification. Also Surface elemental analysis of the modified electrode (studied by energy dispersive x-ray (EDX) technique) showed that a layer of  $(\text{ClCu})_2\text{O}$  was formed at the surface of the electrode in the modification step [27].

As the measurement depended on the formation layer of  $(\text{ClCu})_2\text{O}$  at the surface of the electrode, the effect of the solution concentration of  $\text{CuCl}_2$  was examined. The results showed (not shown here) that the solution concentration of  $\text{CuCl}_2$  was closely related to the peak potential but hardly to the peak current. The peak potential decreased with  $\text{CuCl}_2$  concentration increasing in the range of 0.001-1 M. When  $\text{CuCl}_2$  concentration was in the range of 0.1- 1 M, the peak potential achieved a minimum value and was nearly unchanged. Accordingly, 0.1 M  $\text{CuCl}_2$  concentration was selected as optimum level in subsequent studies. The effect of the modification time was also studied and 20 s was chosen as optimal.

Fig. 2A and B shows cyclic voltammograms of CCMC electrode in 0.1 M NaOH solution in the presence of different concentrations of formaldehyde / acetaldehyde. As can be seen from Fig. 2, any increase in the concentration of formaldehyde (in the range of 2 to 20 mM) / acetaldehyde (in the range of 2 to 50 mM) cause a good proportional linear enhancement of the anodic peak currents (Fig. 2, insets).

### 3.2. Kinetics of formaldehyde and acetaldehyde at CCMC electrode

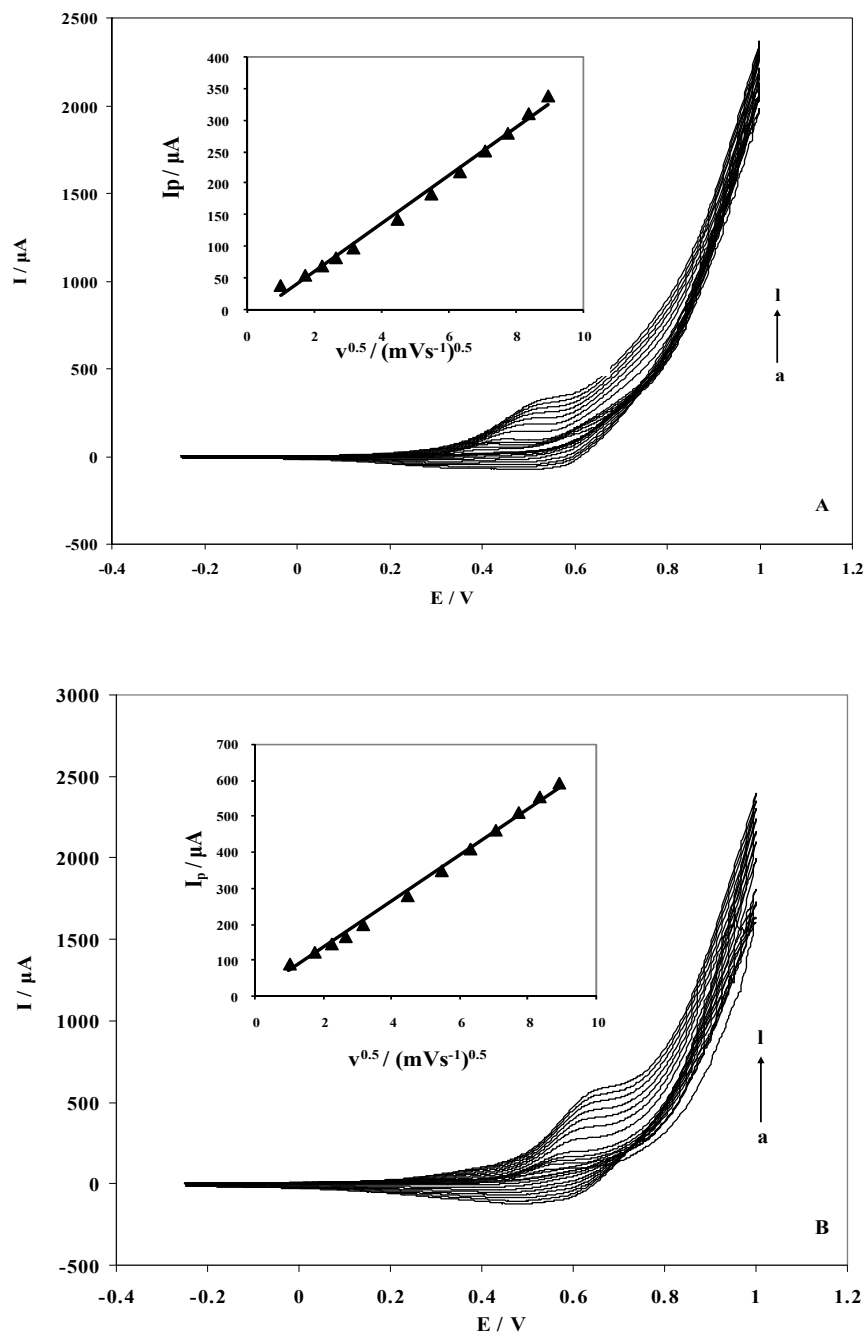
Fig. 3 shows the CVs of CCMC electrode in 0.1 M NaOH solution containing 8 mM formaldehyde (A) and 20 mM acetaldehyde (B) at different scan rates. The oxidation peak potentials of the two species were observed to shift positively with an increase in the scan rate. In addition, a linear relationship between the oxidation peak current for the oxidation of formaldehyde / acetaldehyde and the square root of scan rate in the scan rate range from 1 to 80  $\text{mVs}^{-1}$  were obtained (Fig. 3, insets) The linear regression equations for formaldehyde and acetaldehyde were  $I_{\text{pa}} (\mu\text{A}) = -14.897 + 38.108v^{1/2} (\text{mVs}^{-1})^{1/2}$  and  $I_{\text{pa}} (\mu\text{A}) = 5.0119 + 64.591 v^{1/2} (\text{mVs}^{-1})^{1/2}$ , with the correlation coefficient, 0.9931 and 0.9967, respectively. Therefore, the contribution of diffusion played a more important role in the electrode process. Also, plots of the scan rate normalized current ( $I_p/v^{1/2}$ ) vs. scan rate (Fig. 4) also exhibited the characteristic shape of a typical EC' catalytic process [28].

For determination of the transfer coefficient ( $\alpha$ ) and the number of electrons involved in the rate-determining ( $n_\alpha$ ), Tafel plots were drawn (Fig. 5) using the data from the rising part of the current voltage curve at a scan rate of 3  $\text{mVs}^{-1}$ . The results are given in Table 1.

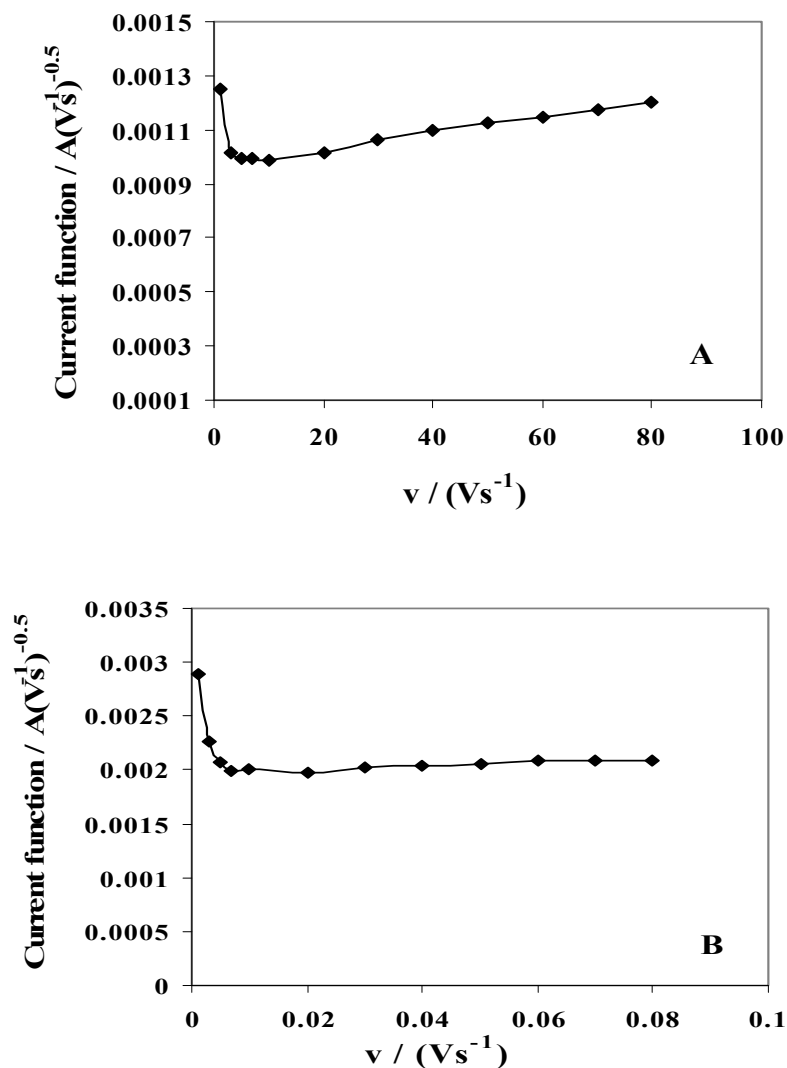
The Tafel slope,  $b$ , can be obtained by another method. The peak potential,  $E_p$ , is proportional to  $\log v$  as can be seen in Fig. 6. The Tafel slope may be estimated according to the equation for the totally irreversible diffusion-controlled process [28]:

$$E_p = \frac{b}{2} \log v + \text{constant} \quad (3)$$

Tafel slope obtained based on Eq.(3) are 177.636 and 128.002 mVdecade<sup>-1</sup> respectively for formaldehyde and acetaldehyde oxidation at CCMC electrode. These results are close to that obtained from the rising part of voltammogram recorded at the 3 mVs<sup>-1</sup>.



**Fig. 3.** Effect of scan rate on HCHO (A) and CH<sub>3</sub>CHO (B) oxidation obtained from forward CV scan upon 0.1 M NaOH+8 mM HCHO and 0.1 M NaOH+20 mM CH<sub>3</sub>CHO using CCMC electrode. Scan rates from down to up are 1, 3, 5, 7, 10, 20, 30, 40, 50, 60, 70 and 80 mVs<sup>-1</sup>, respectively. The insets show the dependence of the anodic peak currents on the square root of scan rates

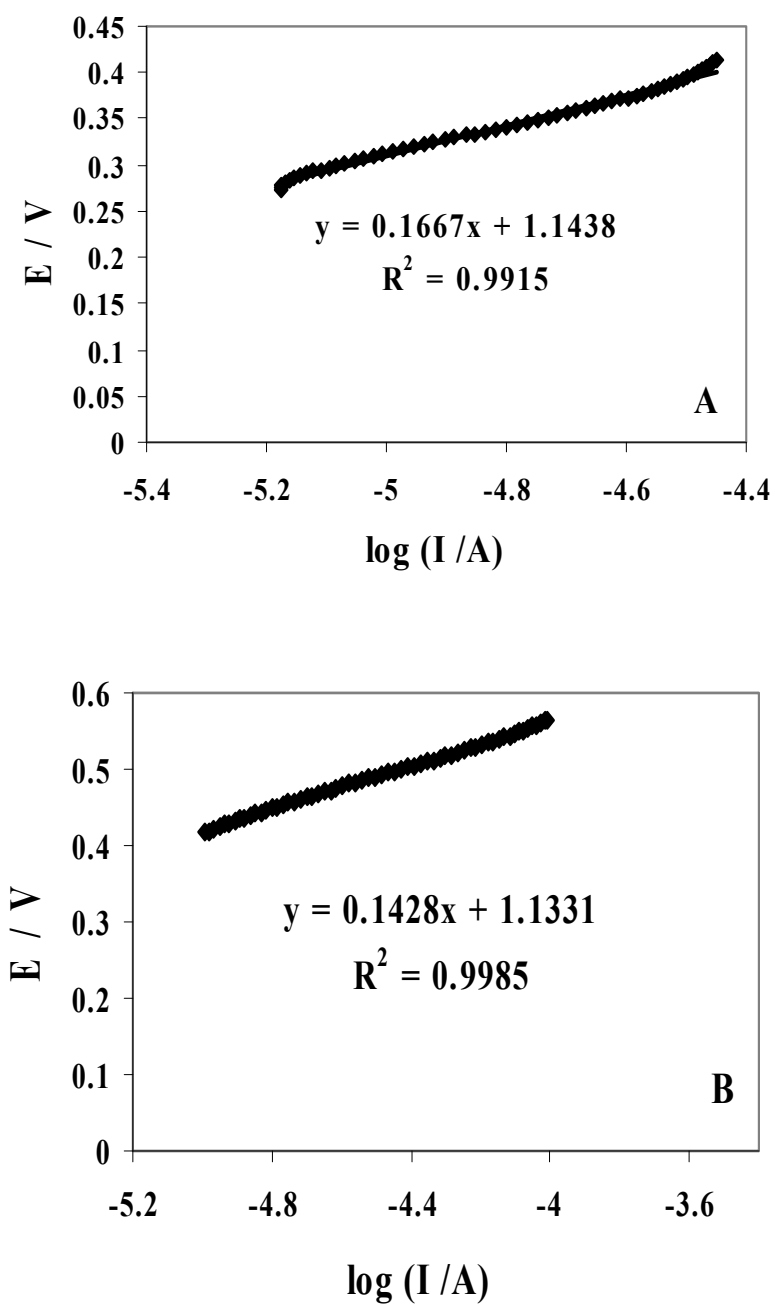


**Fig. 4.** Current function vs.  $v$  for 0.1M NaOH solution in the presence of 8 mM formaldehyde (A) and 20 mM acetaldehyde

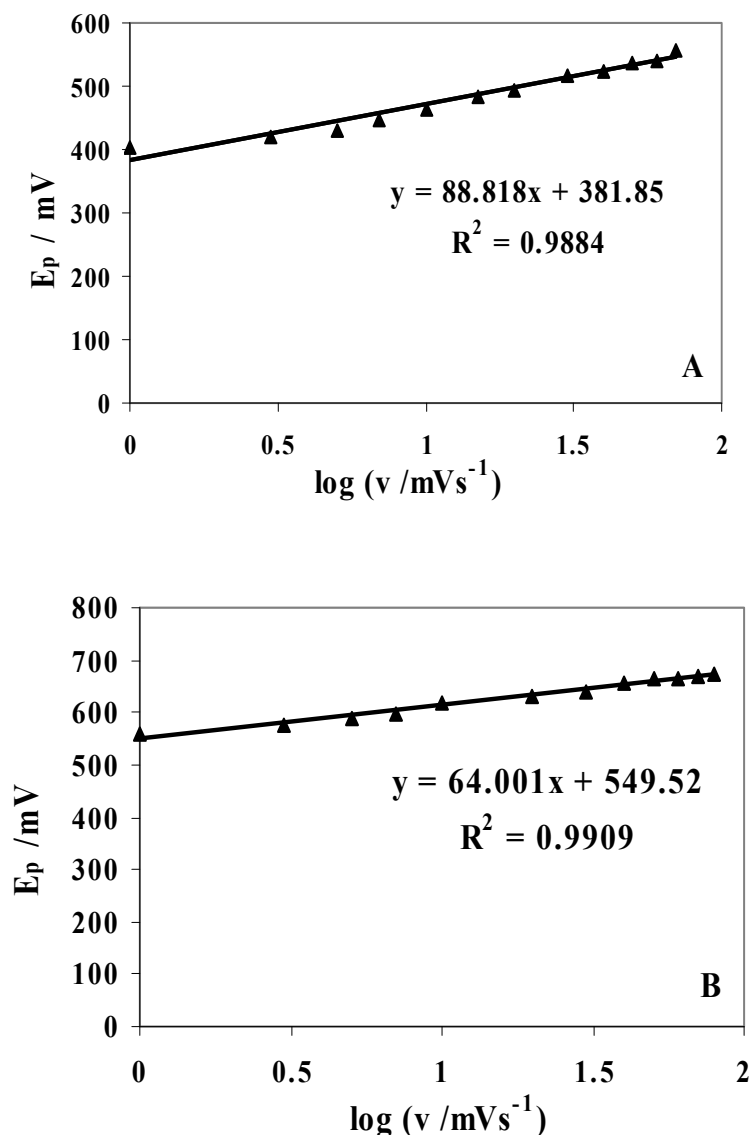
**Table 1.** Kinetic parameters of formaldehyde and acetaldehyde oxidation at CCMC electrode

Tafel slope	$\alpha$	$n_a$
formaldehyde		
0.1667	0.35	0.69 $\approx$ 1
acetaldehyde		
0.1428	0.41	0.83 $\approx$ 1





**Fig. 5.** Tafel plot derived from the rising part of voltammogram recorded at a scan rate  $3 \text{ mV s}^{-1}$  for formaldehyde (A) and acetaldehyde (B)

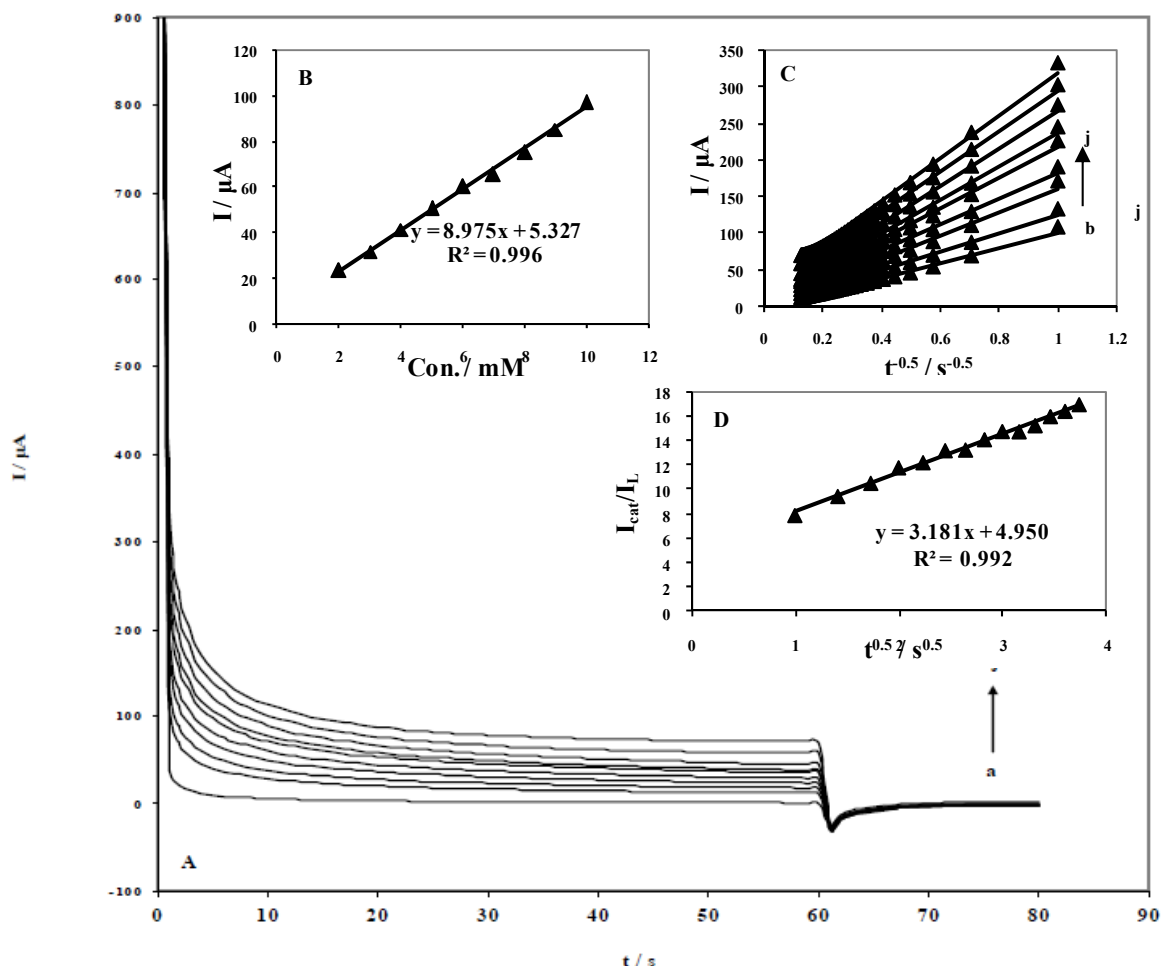


**Fig. 6.** plots of  $E_p$  vs. logarithm  $v$  from cyclic voltammograms recorded for CCMC electrode in 0.1M NaOH containing 8 mM formaldehyde (A) and 20 mM acetaldehyde (B) at potential sweep rates of 1 to 80  $\text{mVs}^{-1}$

### 3.3. Chronoamperometric studies

The electrocatalytic oxidation of formaldehyde at the modified electrodes was studied by chronoamperometry. Double-step chronoamperograms were recorded by setting the working electrode potentials to desired values and used to measure the catalytic rate constant on the modified surfaces. Fig. 7A shows double-step chronoamperograms for the copper chloride modified electrode in the absence and presence of different concentrations of formaldehyde. The applied potential steps were 560 and 0.00 mV. The current is negligible when the potential is stepped down to 0.00 mV, indicating that the electrocatalytic oxidation processes

are irreversible. Fig. 7B, show the plot of sampled current at a fixed time interval of 15 s with respect to the concentration of formaldehyde in the range of 2 to 10 mM. Good linear dependencies have been observed. Plotting of net currents with respect of the minus square roots of time, present linear dependencies (Fig. 7C). Therefore, a diffusion-controlled process is dominated during the electrocatalytic oxidation of formaldehyde.



**Fig. 7.** (A) Double steps chronoamperograms of CCMC electrode in 0.1 M NaOH solution containing formaldehyde with different concentrations of: (a)–(j): 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 mM, respectively. Potential steps were 560 mV for oxidation and 0.00 mV for reduction. (B): Dependency of sampled current at fixed time of 15 s to the concentration of formaldehyde. (C): Dependency of transient current on  $t^{-0.5}$ . (D): Dependency of  $I_{cat}/I_d$  on  $t^{0.5}$  derived from the data of chronoamperograms related to concentrations of 0 and 8mM

The ratio of the transient current in the presence of formaldehyde to the limiting current in its absence follows [28]:

$$\frac{I_{catal}}{I_d} = \lambda^{1/2} \left[ \pi^{1/2} \operatorname{erf}(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}} \right] \quad (4)$$

where  $I_{catal}$  is the catalytic current in the presence of formaldehyde,  $I_d$  the limiting current in the absence of formaldehyde and  $\lambda = kCt$  ( $k$ ,  $C$  and  $t$  are the catalytic rate constant, bulk concentration of formaldehyde and the elapsed time, respectively) is the argument of the error function. For  $\lambda > 1.5$ ,  $\text{erf}(\lambda^{1/2})$  almost equals unity and Eq. (4) reduces to:

$$\frac{I_{catal}}{I_d} = \lambda^{1/2} \pi^{1/2} = \pi^{1/2} (kCt)^{1/2} \quad (5)$$

From the slope of the  $I_{catal}/I_d$  vs.  $t^{1/2}$  plot, the value of  $k$  for 8 mM formaldehyde was calculated to be  $4.03 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (Fig. 7D).

Similar chronoamperograms were collected for acetaldehyde. The value of and  $k$  for 20 mM acetaldehyde obtained according to the method described in the above calculated to be  $3.62 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

#### 4. CONCLUSION

A copper chloride modified copper electrode was checked for electrooxidation of formaldehyde and acetaldehyde in alkaline media. The electrode showed electrocatalytic oxidation of these species. With the use of cyclic voltammetry and chronoamperometry techniques, the kinetic parameters of these species, such as charge-transfer coefficient, the number of electrons involved in the rate-determining step and catalytic reaction rate constant were determined.

#### REFERENCES

- [1] M. I. Manzanares, A. G. Pavese, and V. M. Solis, *J. Electroanal. Chem.* 310 (1991) 159.
- [2] K. Nishimura, K. Kunimatsu, K. Machida, and M. Enyo, *J. Electroanal. Chem.* 260 (1989) 181.
- [3] H. Yang, T. H. Lu, K. H. Xue, S. G. Sun, G. Q. Lu, and S. P. Chen, *J. Mol. Catal. A* 144 (1999) 315.
- [4] R. Ramanauskas, I. Jurgaitiene, and A. Vaskelis, *Electrochim. Acta* 42 (1997) 191.
- [5] A. Pavese, and V. Solis, *J. Electroanal. Chem.* 301 (1991) 117.
- [6] H. M. Villullas, F. I. Mattos-Costa, P. A. P. Nascente, and L. O. S. Bulhoes, *Electrochim. Acta* 49 (2004) 3909.
- [7] M. C. Santos, and L. O. S. Bulhoes, *Electrochim. Acta* 49 (2004) 1893.
- [8] S. Park, Y. Xie, and M. J. Weaver, *Langmuir* 18 (2002) 5792.
- [9] J. Silva-Chong, E. Mendez, J. L. Rodriguez, M. C. Arevalo, and E. Pastor, *Electrochim. Acta* 47 (2002) 1441.
- [10] E. Mendez, J. L. Rodriguez, M. C. Arevalo, and E. Pastor, *Langmuir* 18 (2002) 763.

- [11] J. D. Robert, and M. C. Caserio, *Basic Principles of Organic Chemistry*; Benjamin: New York (1965).
- [12] W. Ji, Y. Chen, and H. H. Kung, *Appl. Catal. A: Gen.* 161 (1997) 93.
- [13] A. S. Y. Lee, and C. C. Kung, *J. Chin. Chem. Soc.* 45 (1998) 509.
- [14] B. I. Podlovchenko, O. A. Petry, A. N. Frumkin, and H. Lal, *J. Electroanal. Chem.* 2 (1966) 12.
- [15] B. Bittins-Cattaneo, S. Wilhelm, E. Cattaneo, H. W. Buschmann, and W. Vielstich, *Ber. Bunsenges. Phys. Chem.* 92 (1988) 1210.
- [16] L. W. H. Leung, and S. C. Chang, *J. Electroanal. Chem.* 266 (1989) 317.
- [17] T. Iwasita, and B. Rasch, *Electrochim. Acta* 35 (1990) 989.
- [18] S. C. Chang, L. W. H. Leung and M. J. Weaver, *J. Phys. Chem.* 94 (1990) 6013.
- [19] F. Cases, J. L. Vasquez, J. M. Perez, A. Aldaz, and J. Clavilier, *J. Electroanal. Chem.* 281 (1990) 283.
- [20] K. Ikeda, K. Hashimoto, and A. Fujishima, *J. Electroanal. Chem.* 437 (1997) 241.
- [21] G. Tremiliosi-Filho, H. Kim, W. Chrzanowski, A. Wieckowski, B. Grzybowska, and P. Kulesza, *J. Electroanal. Chem.* 467 (1999) 143.
- [22] A. Crown, I. R. Moraes, and A. Wieckowski, *J. Electroanal. Chem.* 500 (2001) 333.
- [23] P. Waszczuk, C. Q. Lu, A. Wieckowski, C. Lu, C. Rice, and R. I. Masel, *Electrochim. Acta* 47 (2002) 3637.
- [24] L. A. Colon, R. Dadoo, and R. N. Zare, *Anal. Chem.* 65 (1993) 476.
- [25] S. Mannino, M. Rossi, and S. Ratti, *Electroanalysis* 3 (1991) 711.
- [26] G. Karim-Nezhad, R. Jafarloo, and P. Seyed Dorraji, *Electrochim. Acta* 54 (2009) 5721.
- [27] G. Karim-Nezhad, and P. Seyed Dorraji, *Electrochim. Acta* 55 (2010) 3414.
- [28] A. J. Bard, and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, Wiley, New York (1980).