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Electro-oxidation of Cyclohexanol on a Copper Electrode Modified by Copper-dimethylglyoxime Complex Formed by Electrochemical Synthesis

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Copper-dimethylglyoxime complex (CuDMG) modified Copper electrode (Cu/CuDMG) showed a catalytic activity towards cyclohexanol oxidation in NaOH solution. The modified electrode prepared by the dimethylglyoxime anodic deposition on Cu electrode in the solution contained 0.20 M NH_4Cl + NH_4OH (pH 9.50) and 1×10^{-4} M dimethylglyoxime. The modified electrode conditioned by potential recycling in a potential range of −900 ~ 900 mV *vs*. Ag/AgCl by cyclic voltammetry in alkaline medium (1 M NaOH). The results show that the CuDMG film on the electrode behaves as an efficient catalyst for the electro-oxidation of cyclohexanol in alkaline medium *via* Cu (III) species formed on the electrode.

Key Words: Cyclohexanol, Electrocatalysis, Copper dimethylglyoxime, Alkaline media

Introduction

A detailed knowledge of the electrochemical behavior of organic compounds bears primary importance for development of appropriate sensors and for advanced electrochemical synthesis.[1-3] Numerous studies deal with electrocatalytical oxidation of organic substance should have the following properties (i) The energy of adsorption of substrate molecules and/or intermediate species formed on the catalyst surface should be sufficiently high to constantly decrease the activation energy of the dehydrogenation step, constantly but it should be sufficiently low for intermediate and final products to be desorbed easily, and (ii) the energy realized by formation of water molecular as one of the reaction products should be sufficient to compensate for the energy needed energy for the desorption of dehydrogenated organic intermediates from the metal surface. Copper electrode is the most active and the most often used for electrocatalysts.[4-12]

The literature on electrochemical oxidation of alcohols can roughly be grouped into three sets: fuel cells, hydrogenous and homogenous catalysis.[13-16] The inorganic community's investigation of the electrooxidation of alcohols primarily consisted of homogenous systems. The alcohol substrates are typically either cyclic alcohol such as the reaction stops after $2e^-$ oxidation to the ketone or primary alcohols. Thus competition between $2e^-$ oxidation to the aldehyde and $4e^-$ oxidation to carboxylic acid becomes possible. Alcohols can also undergo $6e^-$ oxidation to CO_2; rarely appear in the homogeneous studies.[15-16]

Adipic acid as an oxidation product of cyclohexanol, cyclohexen or cyclohexanon, has been widely used not only as an important intermediate in manufacturing of nylon, but also a plasticizer and a food additive. Since cyclohexanol is an important material used in producing adipic acid, it worths to study the reaction mechanism of electro-oxidation of cyclohexanol.[17-19]

Recently, we conducted the electrochemical oxidation of cyclohexanol on a copper electrode.[20] In the present work, the copper electrode is electrochemically modified with dimethylglyoxime and the efficiency of the electrode, towards the electrocatalytic oxidation of cyclohexanol in alkaline medium, is investigated.

Experimental Details

All used chemicals were analytical grade from Merck (Darmstadt, Germany) and were used without further purification. All solutions were prepared with doubly distilled water. Electrochemical measurements carried out in a conventional three-electrode cell powered by an electrochemical system comprising an AUTOLAB system with PGSTAT12 boards (Eco Chemie, Utrecht, The Netherlands). The system was run on a PC using GPES 4.9 software. A saturated Ag/AgCl (from Metrohm) and platinum wire were reference and counter electrodes, respectively. All potentials were measured with respect to the Ag/AgCl and positioned, by means of a Luggin capillary, as close to the working electrode as possible. Cylindrical copper bars with the purity of 99.9% were fitted into Teflon exposing circular areas having 4 mm diameters (surface area is 0.126 cm^2) to prepare stationary and working electrodes, respectively. The copper surfaces polished with sand paper and 0.05 μm alumina to a mirror finish and were subsequently rinsed with distilled water. Films of DMG were formed on the Cu electrode with surface area 0.126 cm^2 by the method previously reported by Bobrowski.[21] The modified electrodes were prepared by cyclic the potential of the working electrode in the range of −900 to 900 mV Ag/AgCl at a scan rate of 100 mV/s for 70 cycles. The surface concentration of DMG film which were controlling by the number of cycles applied in the deposition process is electrochemically evaluated in 0.1 M NaOH solution.

Prior to the modification, the Cu electrode polished with 0.05 μm alumina suspension on a polishing micro-cloth and rinsed thoroughly with doubly distilled water. All experiments were performed at ambient temperature 22 ± 3 ºC.

Results and Discussion

Fig. 1 (image a), shows the structure of the copper surface immediately after polishing with sand paper and 0.05 μm alumina. As seen in this image the surface is almost smooth and uniform. The image b in Fig. 1 shows the structures of the Cu/CuDMG electrode after formation of film on Cu electrode. In these conditions some cracks appear on the film. Therefore the obtained film shows irregular shapes and is not uniform. On the whole, Cu surface has an approximately smooth morphology, while relatively no uniform and irregular shapes of DMG film with have an average size of 10 μm are formed on Cu surface.

The electrocatalytic activity of Cu/CuDMG electrode for cyclohexanol oxidation was evaluated by cyclic voltammetry and compared with copper electrode. Fig. 2A shows the CVs of electro-oxidation of cyclohexanol on Cu and Cu/CuDMG electrodes in the presence and absence of cyclohexanol in 0.1 M NaOH solution. At Cu/CuDMG electrode, oxidation of cyclohexanol resulted in a typical electrocatalytic response. In the presence of the cyclohexanol, it was observed that the anodic current increased drastically. In the presence of cyclohexanol

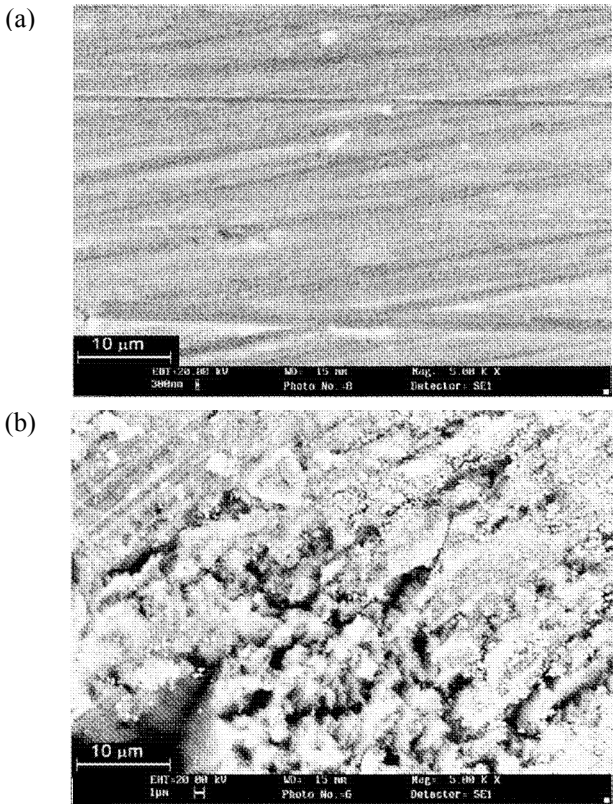

Figure 1. SEM images of Cu electrode surface immediately after polishing (a), SEM images of Cu/CuDMG electrode after formation of film on Cu electrode.

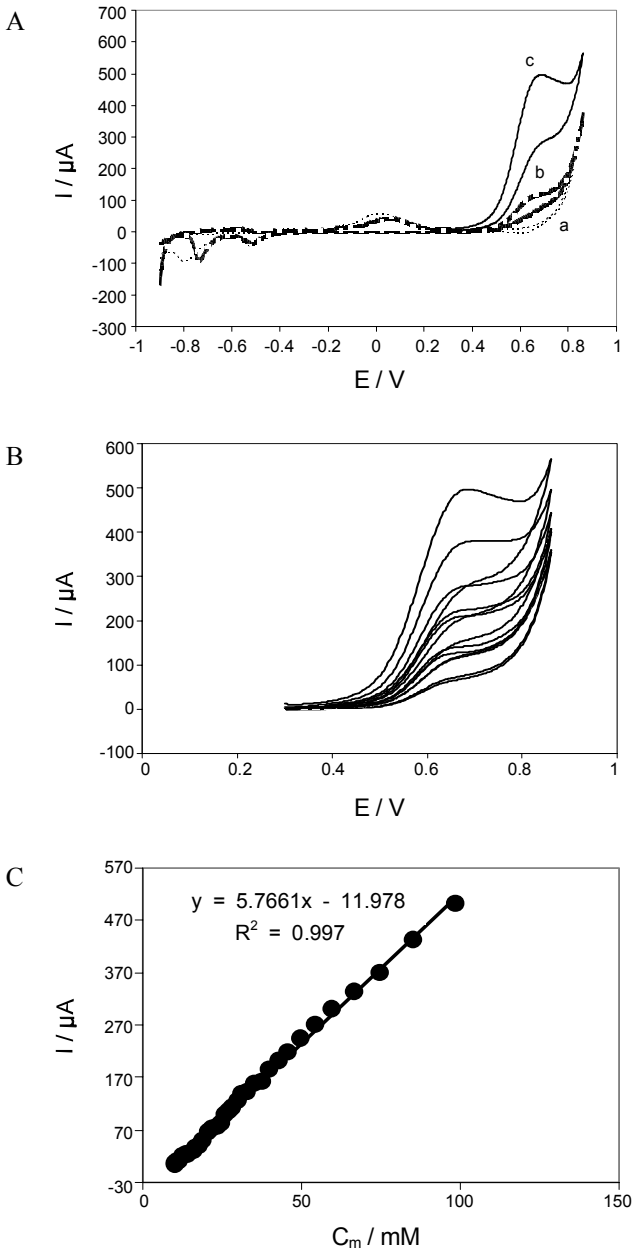

Figure 2. A: Cyclic voltammograms (CVs) of Cu electrode (b) and Cu/CuDMG electrode (c) in the absence (a) and the presence (b and c) of 0.2 M cyclohexanol in 0.1 M NaOH solution at a potential sweep rate of 10 mV/s. B: Cyclic voltammograms of Cu/CuDMG electrode in 0.1 M NaOH solution in the presence of different concentrations of cyclohexanol in Cu/CuDMG electrode. From inner to the outer: 0.03 (a) 0.08 (b), 0.1 (c), 0.15 (d), 0.2 (e), and 0.25 M (f), respectively. The potential sweep rate is 10 mV/s. C: Dependency of peak current on the concentration of cyclohexanol in the range of 0.01 - 0.1 M.

the ratio i_{pa}/i_{pc} was 74.16. In absence of it the ratio decreased to 29.01. The result indicates that cyclohexanol is oxidized by active Cu (III) moiety through a cyclic mediation redox process.[20] The Cu^{2+}/Cu^{3+} redox couple acts as a catalyst for the oxidation of cyclohexanol in basic solutions. It can be clearly seen in Fig. 2A which was recorded in 0.1 M NaOH/0.2 M cyclohexanol on Cu electrode (curve b) and Cu/CuDMG electrode (curve c), respectively. Furthermore, the current of

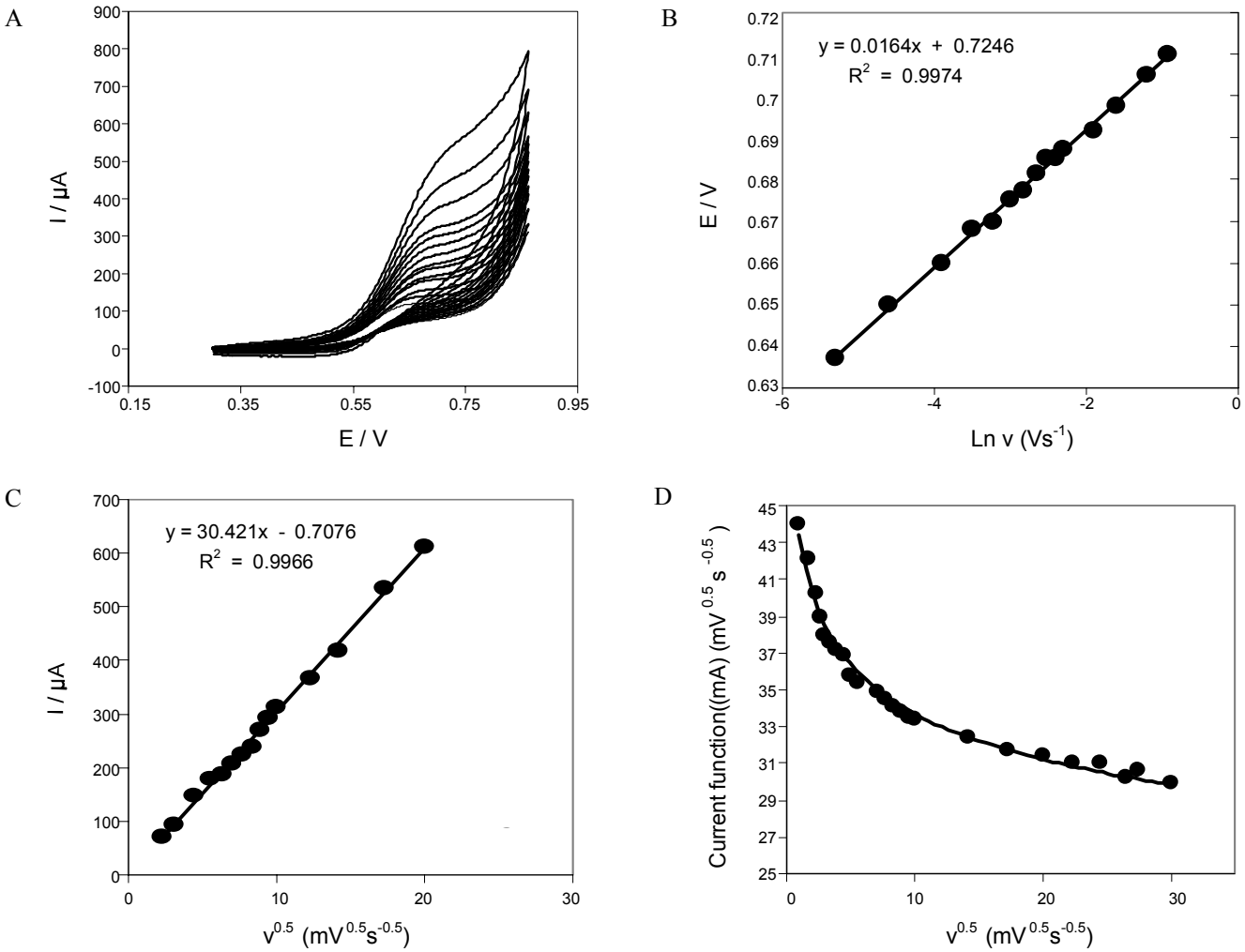

Figure 3. A: Cyclic voltammograms of the Cu/CuDMG electrode in 0.1 M NaOH solution in the presence of cyclohexanol in various potential sweep rates of 2, 5, 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 and 300 mV/s. B: Dependence of the peak potential on Ln ν for the oxidation of cyclohexanol at Cu/CuDMG electrode obtained from the data of panel (B). C: Dependence of anodic peak current during the forward sweep on the square roots of potential sweep rate. D: Current function *vs*. ν 0.5 for 0.1 M NaOH solutions in the presence of 0.1 M cyclohexanol.

the Cu/CuDMG electrode is much higher than Cu electrode. For example, at the potential 0.7 V, the Cu/CuDMG electrode presents a current of about 500 µA, nearly five times higher than that of the Cu electrode (~100 µA). On the basis of the observation we presume that the Cu/CuDMG electrode shows significantly greater electrocatalytic activity towards cyclohexanol oxidation than Cu electrode.

Fig. 2B shows the effect of cyclohexanol concentration on the anodic peak current at Cu/CuDMG electrode in 0.1 M NaOH. It is clearly observed that as the cyclohexanol concentration increases, the peak height increases linearly with cyclohexanol concentration up to 0.25 M. It can be assumed that the increase is due to the presence of a diffusion controlled process that appears to play an important role at low cyclohexanol concentrations. While the cyclohexanol concentration exceeds it limits, the rate of the whole oxidation process which seems to be limited by that of the catalytic process in origin and its rate depends on the reaction between cyclohexanol and CuDMG species, which is present in the film.

In the high range of concentrations this dependency is signifying the dominance of the diffusion controlled processes (linear). This dependency observed in the range of 0.03 - 0.25 M.

Fig. 2B shows that upon increasing cyclohexanol concentration its irreversible oxidation develops in the region of the electrochemical formation of Cu^{III}. Thus, it is likely that the electro-generated Cu^{III} species is the active moiety which efficiently speeds up the oxidation of cyclohexanol. Any increase in the concentration of cyclohexanol causes a proportional almost linear enhancement of the anodic wave, Fig. 2C. It is worth to emphasis that the anodic formation of Cu^{III} seems to be an irreversible process, Fig. 2 and the regeneration of the surface happens through a chemical redox reaction. The involvement of the catalytically active Cu^{III} species, in the early stages of the reverse cathodic sweep is supported by the anodic response of cyclohexanol oxidation, Fig. 2 (curve c).

Fig. 3A illustrates cyclic voltammograms of 0.08 M cyclohexanol using the Cu/CuDMG electrode recorded at different potential sweep rates. Fig. 3B indicates anodic peak currents increased linearly with the square root of the potential sweep rate. It indicates a mass transfer-controlling process of oxidation

Table 1. Values of the electrocatalytic reaction rate constants k (obtained from choronoamperometry), $k_2\Gamma$, $k^o_1\Gamma$ and α (obtained from polarization curves) for Cu and Cu/CuDMG.

Electrode	k^a / cm^3 mol^{-1} s^{-1}	$k_2\Gamma^b$ / cm s^{-1}	$k^o_1\Gamma^c$ / mol s^{-1} cm^{-2}	α
Cu	5.06×10^5	8.74×10^{-12}	1.91×10^{-13}	0.63
Cu/CuDMG	3.36×10^6	1.41×10^{-10}	6.44×10^{-15}	0.57

[a]It should be pointed out that k is either k_2(E) or k_3(E) whichever is smaller which indicated in reactions of 4 and 5. k evaluated from Eq.(4) by choronoamperometry technique. [b]$k_2\Gamma$ was evaluated from $v_2 = k_2\Gamma\theta C_m$ ref [20] where Γ is the total number of adsorption sites per unit area of the electrode surface, θ's represent the fractional surface coverage's of copper of different valence states and C_m is the bulk concentration of cyclohexanol. [c]$k^o_1\Gamma$ was evaluated from $k_2(E) = k^o_1 \exp\left[\frac{\alpha nFE}{RT}\right]$ ref [20].

via diffusion. In addition the value of the electron-transfer coefficient for the reaction can be obtained from the following equation:[22]

$$E_p = \left(\frac{RT}{2\alpha F}\right)\ln v + constant \quad (1)$$

This is valid for a totally irreversible diffusion-controlled process. Using the dependency of anodic peak potential on the neperian logarithm of the potential sweep rate (Fig. 3C), the value of the electron-transfer coefficient was obtained as 0.59. Tafel slope is 41.99. On the basis of the slopes of the linear dependency of the anodic peak currents on the square root of the potential sweep rates (Fig. 3B), and the Randles-Sevcik equation:[23]

$$I = (2.99\times10^5)\alpha^{1/2}n^{3/2}AC^*D^{1/2}v^{1/2} \quad (2)$$

Where I_p is the peak current, A is the electrode surface area, D is the diffusion coefficient and C^* is the bulk concentration of cyclohexanol. The diffusion of coefficient for cyclohexanol was calculated to be 8.92×10^{-6} cm^2 s^{-1}. Plotting the current function (peak current divided by the square root of the potential sweep rate) against the square root of the potential sweep rate (Fig. 3D) revealed negative slope confirming the electrocatalytic nature of the process, too.

The redox transition of copper species present in the film is:

$$Cu^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu^{III} + e \quad (3)$$

and cyclohexanol is oxidized on the modified surface *via* the following reaction:

$$Cu^{III} + (C_6H_{12}O)_{ads}(Cyclohexanol) \xrightarrow{k_2(E)} intermediate + Cu^{II} \quad (4)$$

where the intermediate in the product is oxidized strongly through a similar electrooxidation process:

$$Cu^{III} + intermediate \xrightarrow{k_3(E)} Product + Cu^{II} \quad (5)$$

The electro-catalytic activity of the Cu/CuDMG and Cu electrodes towards cyclohexanol oxidation is further evaluated with chronoamperometry in 0.1 M NaOH solution. For this order, 700 mV potential steps are applied to the Cu/CuDMG electrode and Cu electrode in 0.1 M NaOH containing different concentrations of cyclohexanol. The corresponding chronoamperometric data are presented in Fig. 4A. The observations showed two noticeable points: (I) the current in the presence of cyclohexanol is much higher than that recorded in the absence of cyclohexanol for both Cu/CuDMG and Cu electrodes. (II) The current densities recorded on Cu/CuDMG electrode are significantly higher than that of Cu electrode. (III) While the cyclohexanol concentration is increasing for both of the two electrodes the current increases.

The rate constants of the reactions of cyclohexanol and the ensued intermediates with the redox sites of the Cu/CuDMG electrode can be derived from the chronoamperograms according to:[24]

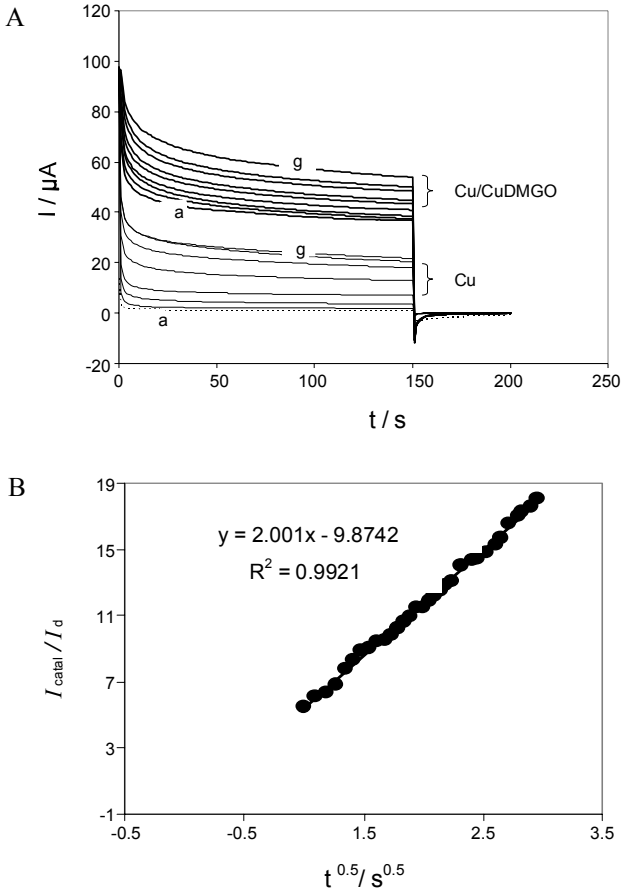

Figure 4. A: Double step chronoamperograms of Cu and Cu/Cu DMG electrode (dashed lines) in 0.1 M NaOH solution with different cyclohexanol concentrations of 0 (a), 0.03 (b), 0.07 (c), 0.1 (d), 0.15 M (e), 0.2 (f), and 0.22 M (g). Potential steps were 700 mV for oxidation and 0.00 mV for reduction. B: Dependence of I_{catal}/I_d on $t^{0.5}$ derived from the data of chronoamperograms of a and f in part A for Cu/CuDMG electrode.

$$\frac{I_{catal}}{I_d} = \lambda^{1/2}\left[\pi^{1/2}\mathrm{erf}(\lambda^{1/2}) + \frac{\exp(-\lambda)}{\lambda^{1/2}}\right] \quad (6)$$

where I_{catal} is the catalytic current in the presence of cyclohexanol, I_d the limiting current in the absence of cyclohexanol and $\lambda = k\,C_m\,t$ (k, C and t are the catalytic rate constant, bulk concentration of cyclohexanol and the elapsed time, respectively) is the argument of the error function. For $\lambda > 1.5$, erf ($\lambda^{0.5}$) almost equals unity and Eq. (6) reduces to:

$$\frac{I_{catal}}{I_d} = \lambda^{1/2}\pi^{1/2} = \pi^{1/2}(kCt)^{1/2} \quad (7)$$

From the slope of the I_{catal}/I_d *vs*. square root of time plot the value of k at a given concentration of cyclohexanol is derived. Fig. 4B indicates dependency of I_{catal}/I_d on $t^{0.5}$ derived from the data of chronoamperograms of a and f in Fig. 4A for Cu/CuDMG electrode. The mean value of k in the concentration range of 0.03 - 0.22 M was found to be 3.36×10^6 cm^3 mol^{-1} s^{-1}. It should be pointed out that k is either k_2(E) or k_3(E) whichhever is smaller. This result was compared with Cu electrode[20] that indicated in Table 1.

The pseudo-steady state polarization curves of the anodic oxidation of cyclohexanol on Cu and Cu/CuDMG electrodes in the absence and presence of 0.08 M cyclohexanol are presented in Fig. 5A. It is observed from Fig. 5A that current of cyclohexanol oxidation on Cu/CuDMG electrode is 2500 nA, more than three times higher than Cu electrode 1000 nA; for both of the two electrodes anodic currents in the presence of cyclohexanol are much higher than those in the absence of cyclohexanol. These observations are consistent with the results of CVs.

The pseudo-steady state polarization curves of the electro-oxidation of cyclohexanol on Cu/CuDMG electrode at a number of cyclohexanol concentrations are presented in Fig. 5B. Potentiodynamic polarization curve for Cu/CuDMG electrode in 0.1 M NaOH in the presence of 0 - 0.25 M cyclohexanol recorded using a potential sweep rate of 0.25 mV/ s. 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 600 mV Ag/AgCl and to reach a plateau at 710 mV Ag/AgCl. In the course of reaction the coverage of Cu^{III} increases and reaches a saturation (steady state) level and the oxidation current follows accordingly. According to Eq. (8):[20]

$$i_f = \left(\frac{2FAk_2\Gamma k_2 C_m}{k_1 + k_{-1} + 2k_2 C_m}\right) \quad (8)$$

The plots of the inverse current against the inverse cyclohexanol concentration should be linear:[20]

$$i_f^{-1} = \left(FAk_1\Gamma\right)^{-1} + \left[\frac{k_1 + k_{-1}}{2FAk_1k_2\Gamma}\right]C_m^{-1} \quad (9)$$

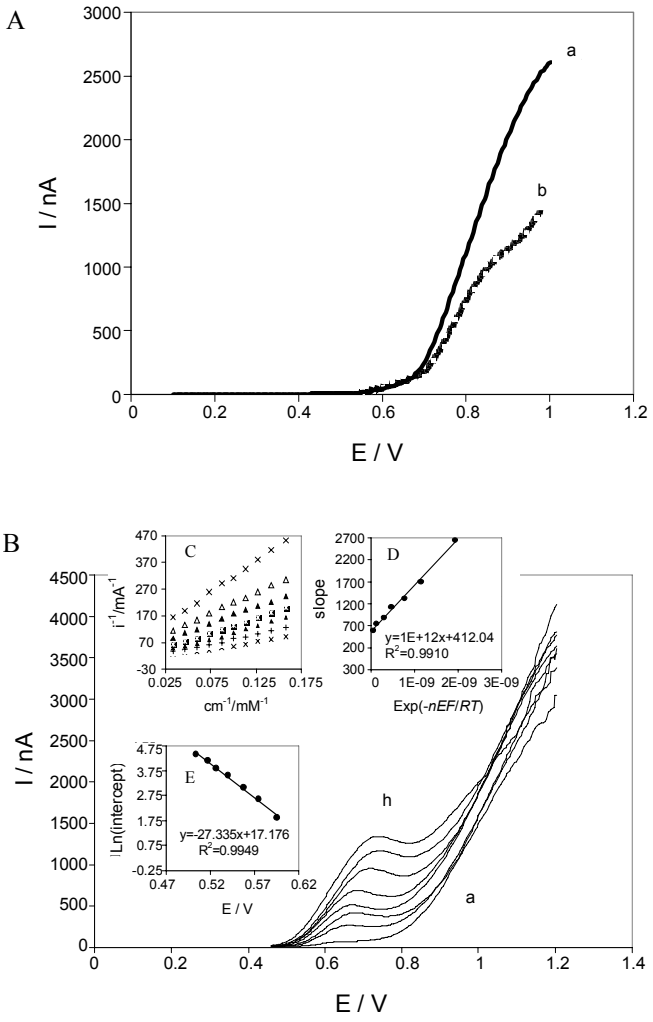

Figure 5. A: The pseudo-steady state polarization curves recorded on the Cu/CuDMG (a) and Cu (b) electrodes in the presence of 0.08 M cyclohexanol. B: Typical pseudo-steady state polarization curves of Cu/CuDMG electrode obtained in 0 (a), 0.03 (b), 0.07 (c), 0.1 (d), 0.15 M (e), 0.2 (f), 0.22 (g), and 0.25 M (g), cyclohexanol, respectively. C: Plot of i^{-1} (from polarization curves in Fig. 5B) against C_m^{-1} at various potentials: (a) 570, (b) 590, (c) 616, (d) 635, (e) 629, (f) 644, (g) 658 and (h) 673 mV as curves (a-h). D: Plot of the slopes (of curves in A) *vs*. exp (*-nFE/RT*). E: Plot of the ln (intercepts) (of curves in A) *vs*. applied potentially.

Fig. 5C 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 are potential dependent. The slopes are plotted against exp (*-nFE/RT*) with n = 1 and the graph is presented in Fig. 5D. Using this graph along with Eq. (9) reveals that the rate constant of reaction 4,[20] $k_2\Gamma$ and the ratio of k^0_{-1}/k^0_1 are 1.41×10^{-10} cm s^{-1} and 4.82×10^{12}, respectively. Fig. 5E presents the variation of the intercepts of the lines in Fig. 5C with the applied potential in a semi-log scale. Using this graph and Eq. (9) the magnitudes of $k^0_1\Gamma$ and the anodic transfer coefficient of 6.44×10^{-15} mol s^{-1} cm^{-2} and 0.57 have been obtained. From the above findings the value of $k^0_{-1}\Gamma$ was worked out to be 3.104×10^{-2} mol s^{-1} cm^{-2}. This result was compared with Cu electrode[20] that is indicated in the Table 1.

Conclusion

The Cu/CuDMG electro activity detection of towards cyclohexanol oxidation has been performed by cyclic, linear voltammetric measurements and chronoamperometric methods. Its electrocatalytic activity compared with a Cu electrode. The results show that the Cu/CuDMG electrode exhibit high electrocatalytic activity towards cyclohexanol oxidation. The magnitudes of the rate constants and anodic transfer coefficients of the electro-oxidation reaction have been obtained.

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