Electrochemical Oxidation of Saccharose on Copper (Hydr)oxide-Modified Electrode in Alkaline Media

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Abstract: A stable copper (hydr)oxide-modified electrode was prepared in 0.5 mol/L NaOH solution by cyclic voltammetry in the range of –250 to 1 000 mV. It can be used for electrochemical studies in the range of –250 to 1 000 mV without interfering peaks because there is no oxidation of copper. During an anodic potential sweep, the electro-oxidation of saccharose on Cu occurred by the formation of Cu^{III} and this reaction also occurred in the early stages of the reversed cycle until it is stopped by the negative potentials. A mechanism based on the electro-chemical generation of Cu^{III} active sites and their subsequent consumption by saccharose was proposed, and the rate law and kinetic parameters were obtained. The charge transfer resistance from theoretical and impedance studies was used to verify the mechanism. Under chronoamperometry regimes, the reaction followed Cottrellian behavior. The transfer of up to 21 electrons was observed in further investigations of the electro-oxidation of saccharose on a (hydr)oxide Cu rotating disk electrode.

Key words: saccharose; copper (hydr)oxide; equivalent circuit; electrocatalytic oxidation; mechanism

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Carbohydrates that comprise more than 80% of available biomass are the most abundant compounds. The electrochemical detection of carbohydrates, which is important in many medical, biological, and industrial applications, is simple, selective, and cheap [1,2], and is an alternative to spectroscopic methods used in high performance liquid chromatography (HPLC) and flow injection analysis (FIA) experiments. Many comprehensive investigations have been carried out during the past decades on the electrocatalytic oxidation of alcohols, poly-alcohols, and carbohydrates on different catalytic metal electrodes that were aimed at the development of sensors and fuel cells [3,4], but only a few of these have studied saccharose electro-oxidation [5].

The electro-oxidation of carbohydrates have been studied on a variety of metallic [3,6–10], metal oxide [11–13], and metal complex [14] electrodes. Luo et al. [15] employed cyclic voltammetry, hydrodynamic voltammetry, coulometry, and NMR to characterize the oxidation of glucose and related polyalcohols on a copper electrode. Studies by Miller [16] have defined the oxidation states of Cu in alkaline solutions by assigning five peaks to three major single-electron processes involving Cu/Cu^I, Cu^I/Cu^{II}, and Cu^{II}/Cu^{III} transitions in the cyclic voltammogram of a copper electrode. De Chialvo and co-workers [17] showed that

there are soluble species associated with different oxidation states of Cu, which makes a study involving the electro-oxidation and electroreduction of Cu in alkaline media very complex. They suggested the presence of Cu, Cu_{ads}, Cu_{ads}OH, Cu₂O, and Cu_{2ads}O on the surface of Cu^I, while in solution, some other species were postulated to be present.

It can be suggested that the formation of a stable layer of copper (hydr)oxide on the surface of a copper electrode can protect the electrode from corrosion so that there are no oxidation peaks of copper in this case. This idea was applied in this work to study the electro-oxidation of saccharose with the aim to elucidate its mechanism and derive the kinetic parameters of the process.

1 Experimental

Sodium hydroxide and saccharose used were analytical grade from Merck. They were used without further purification. All solutions were prepared with doubly distilled water.

Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising a EG&G Model 273A potentiostat/galvanostat and Solartron Model 1255 frequency re-

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sponse analyzer. The system was controlled by a PC using M270, M352, M398, and Zplot/Zview commercial softwares and a GPIB interface. The frequency range of 100 kHz to 15 MHz and modulation amplitude of 5 mV were employed for impedance measurements. A rotating electrode system (EG&G model 1636) was also employed. A saturated Ag/AgCl electrode and a Pt wire were used as the reference and counter electrodes, respectively. Cylindrical copper bars with the purity of 99.9% were fitted into Teflon that exposed circular areas of copper of diameters 5 and 4 mm to prepare the rotating disk and working electrodes, respectively. The surface of the electrode was mechanically polished with 2500 grit sand paper and then with 0.05 μm α -alumina powder prior to all experiments. The polished surfaces were rinsed with doubly distilled water prior to use. All measurements were carried out at (298 ± 2) K.

2 Results and discussion

Figure 1(a) presents a cyclic voltammogram of copper in 0.5 mol/L NaOH solution in the range of -900 to $1\,000$ mV vs. Ag/AgCl recorded at a potential sweep rate of 10 mV/s. The voltammogram is similar to the ones reported in the literature [18,19,20] and consists of well defined peaks in both the anodic and cathodic half cycles. On comparing our results with those in the literature, the peaks can be readily assigned. Peak Ia is due to the Cu/Cu^I redox couple in reac-

Fig. 1. Cyclic voltammograms of copper electrode in 0.5 mol/L NaOH solution, scanning at 10 mV/s in the positive direction from an initial potential of -900 to $1\,000$ mV (a) and -250 to $1\,000$ mV (b) in the absence (1) and presence (2) of 0.02 mol/L saccharose.

tions (1) and (2), in which Cu is converted to Cu₂O in alkaline solution [21]:

Peak IIa involves the transitions Cu/Cu^{II} and Cu^I/Cu^{II} in the following electrode processes [22]:

Peak IIIa is due to the formation of soluble compounds in the redox reaction

and the dissolution equilibrium [19]:

Three reduction waves observed in the course of the cathodic scans were assigned to the reduction of Cu^{III} to Cu^{II} (peak IIIc), Cu^{II} to Cu^I (IIc), and Cu^I to Cu (peak Ia) [19]. Also, an anodic peak, IVa, just before the onset of the anodic decomposition edge of the solvent was observed. This peak was assigned to Cu^{III} species formed by reactions (8) and (9) at high hydroxide concentration [21,22]:

Figure 1(b) presents the voltammograms started at different cathodic potential limits. The oxidation peaks of copper were present in all potential ranges, which made this electrode difficult to use in many electrochemical studies. If a (hydr)oxide layer was stabilized on the copper electrode, it can protect the electrode from corrosion so that the interfering peaks due to the oxidation of copper would not appear.

Figure 2 shows repeated cyclic voltammograms recorded for the copper electrode under the above conditions in the potential range of -250 to $1\,000$ mV. In the first cycle the oxidation peaks of copper were present but in the following

Fig. 2. Repeated cyclic voltammograms of a copper electrode in the potential range of -250 to $1\,000$ mV in 0.5 mol/L NaOH. Potential sweep rate was 100 mV/s.

cycles, they have disappeared and a clean potential domain spanning nearly 1000 mV was obtained. This indicated that an irreversible electrochemical transformation had taken place during the first cycle and a stable layer of hydr(oxide) was formed on the surface of the electrode that protected the electrode from corrosion. After this, this electrode can be used for electrochemical studies in the potential range of -250 to $1\,000$ mV without any interference by the peaks from the oxidation of the underlying copper. The surface coverage of the copper hydr(oxide) layer (Γ) was calculated using the equation [23]:

$$\Gamma = \frac{Q}{nFA} \quad (10)$$

where Q was the charge obtained by integrating the area under the anodic wave of the cyclic voltammogram and other symbols have their usual meanings. The surface coverage of the copper hydr(oxide) layer on the modified electrode was found to be 1.18×10^{-7} mol/cm².

Marioli et al. [21] have suggested a different route for the oxidation of carbohydrates on copper oxide from a remarkable diminution of the copper(II) oxide peak observed upon adding the substrate. The electro-oxidation of saccharose occurs not only in the anodic but also continues into the initial stages of the cathodic half cycle (Fig. 1(2)). Assuming that saccharose molecules adsorb on Cu^{II} sites at these potentials and oxidized Cu^{II} to Cu^{III} sites, the number of Cu^{II} sites available to the sugar would decrease in the course of an anodic potential sweep. The decrease would be further accentuated by the persistent (poisonous) adsorption of the intermediates. The anodic current would thus pass through a maximum as the potential is anodically swept. In the reverse half cycle, the electro-oxidation of saccharose continues and its corresponding current goes through a maximum due to the regeneration of Cu^{II} surface species that are the active sites for the adsorption of saccharose. Thus, the rate of saccharose/intermediates oxidation, as reflected by the anodic current in the cathodic half cycle, drops as the unfavorable cathodic potentials are approached.

Figure 3 presents the effect of saccharose concentration on the cyclic voltammograms of the modified copper electrode. Increasing the concentration causes a proportional enhancement of the irreversible oxidation peak of saccharose, which is shown in the inset.

On the basis of our results, the following mechanism and kinetics can be proposed for the electro-oxidation of saccharose on the copper (hydr)oxide modified electrode. The redox transition of the copper species,

is followed by the oxidation of saccharose:

Fig. 3. Cyclic voltammograms of copper (hydr)oxide-modified electrode in 0.5 mol/L NaOH solution in the presence of different concentrations of saccharose. (1) 0; (2) 0.005 mol/L; (3) 0.01 mol/L; (4) 0.02 mol/L; (5) 0.03 mol/L; (6) 0.04 mol/L. The potential sweep rate is 10 mV/s. Inset: dependence of the anodic current electro-oxidation on saccharose concentration.

The intermediate is further oxidized to the product, glycolic acid, and formic acid [5], through similar mediated electro-oxidation process:

In the above sequence of reactions, k_1 and k_{-1} are potential dependent and have the form:

$$k_1(E) = k_1^0 \exp[\alpha nF(E - E_0)/RT] \quad (14)$$

$$k_{-1}(E) = k_{-1}^0 \exp[(\alpha - 1)nF(E - E_0)/RT] \quad (15)$$

where k^0 is the chemical rate constants measured at $(E - E_0)$ vs. $\text{Ag}/\text{AgCl} = 0$, and α is the anodic symmetry factor. The rate laws for reactions (11) and (12) have the following forms:

$$v_{(11)} = k_1 \Gamma \theta_{\text{II}} - k_{-1} \Gamma \theta_{\text{III}} \quad (16)$$

$$v_{(12)} = k_2 \Gamma \theta_{\text{III}} C_s \quad (17)$$

where the θ is the fractional coverages of different copper valance states, and C_s is the bulk concentration of saccharose. With only the 2 and 3 valance states of copper,

$$\theta_{\text{II}} + \theta_{\text{III}} = 1 \quad (18)$$

The rates of change of their coverages are:

$$\frac{d\theta_{\text{II}}}{dt} = -\frac{d\theta_{\text{III}}}{dt} = -k_1 \theta_{\text{II}} + k_{-1} \theta_{\text{III}} + k_2 \theta_{\text{III}} C_s + k_3 \theta_{\text{III}} C_i \quad (19)$$

$$\frac{dC_i}{dt} = k_2 \theta_{\text{III}} C_s - k_3 \theta_{\text{III}} C_i \quad (20)$$

where C_i is the concentration of the oxidation reaction intermediate. Assuming that the steady state approximation is valid,

$$\frac{d\theta_{\text{II}}}{dt} = -\frac{d\theta_{\text{III}}}{dt} = 0 \quad (21)$$

$$\frac{dC_i}{dt} = 0 \quad (22)$$

The values of the coverages are therefore

$$\theta_{\text{II}} = (k_{-1} + 2k_2 C_s) / (k_1 + k_{-1} + 2k_2 C_s) \quad (23)$$

$$\theta_{\text{III}} = k_1 / (k_1 + k_{-1} + 2k_2 C_s) \quad (24)$$

Subsequently:

$$v_{(11)} = (2k_1 \Gamma k_2 C_s) / (k_1 + k_{-1} + 2k_2 C_s) \quad (25)$$

On the basis of this rate equation, the Faradic current will be

$$i_f = (2FAk_1 \Gamma k_2 C_s) / (k_1 + k_{-1} + 2k_2 C_s) \quad (26)$$

and the corresponding charge transfer resistance is

$$R_{ct} = (di_f / dE)^{-1} = (k_1 + k_{-1} + 2k_2 C_s) / [2FA\Gamma k_2 C_s k_1 (2\alpha F k_2 C_s / RT + k_{-1} F / RT)] \quad (27)$$

Eq. (27) can be used for the calculation of the rate constants and for testing the validity of the kinetics and mechanism. This will be taken up after the chronoamperometry and impedance measurement have been discussed.

Figure 4(a) presents the double-step chronoamperograms that were recorded by setting the working electrode poten-

Fig. 4. (a) Double-step chronoamperograms of copper (hydr)oxide modified electrode in 0.5 mol/L NaOH solution containing saccharose of different concentrations. (1) 0; (2) 0.005 mol/L; (3) 0.01 mol/L; (4) 0.02 mol/L; (5) 0.03 mol/L. Potential steps were 730 mV for oxidation and 0 mV for reduction. (b) The plot of net current of the chronoamperogram of copper (hydr)oxide-modified electrode in 0.5 mol/L saccharose (obtained by subtracting the background current using the point-by-point subtracting method) vs. $t^{0.5}$. (c) Dependence of I_{catal}/I_d on $t^{0.5}$ derived from the data of chronoamperograms of (1) and (2) in (a).

tials to desired values in the absence and in the presence of saccharose in 0.5 mol/L NaOH solution. The applied potential steps were 730 and 0 mV vs. Ag/AgCl, respectively. The plotting of the net current with respect to minus square root of time gave a linear plot, Fig. 4(b), which indicated the dominance of a diffusion controlled process. The transition current was obviously due to the oxidation of saccharose by Cu^{III} species, which was substantiated by the results on increasing the concentration of saccharose. Also, as the electrolysis potential was stepped down to 0 mV vs. Ag/AgCl, no significant current was obtained, which indicated the irreversibility of the process. Chronoamperometry can also be used for the evaluation of the catalytic rate constant, according to [24], by

$$I_{\text{catal}}/I_d = \lambda^{0.5} [\pi^{0.5} \text{erf}(\lambda^{0.5}) + \exp(-\lambda)/\lambda^{0.5}] \quad (28)$$

The argument of the error function, λ , equals $k'C_s t$ with k' , and C_s and t are the apparent rate constant of saccharose consumption, the bulk concentration of saccharose and the time of measuring I_{catal} . For $\lambda > 1.5$, $\text{erf}(\lambda^{0.5})$ almost equals unity and the above equation reduces to:

$$I_{\text{catal}}/I_d = \pi^{0.5} \lambda^{0.5} \quad (29)$$

From the slope of the I_{catal}/I_d vs. $t^{0.5}$ plot, the value of k' was calculated to be $4.3 \times 10^6 \text{ cm}^3/(\text{mol}\cdot\text{s})$. This is shown in Fig. 4(c). It should be pointed out that k' is either k_2 or k_3 , whichever is smaller.

Figure 5 illustrates the Nyquist diagrams of the copper (hydr)oxide-modified electrodes recorded at 730 mV vs. Ag/AgCl dc-offset for concentrations of 0.005–0.05 mol/L saccharose in 0.5 mol/L NaOH solution. The Nyquist diagrams consist of two slightly depressed capacitive semicircles at the high and low frequencies. The depressed semicircle in the high frequency region is related to the adsorption of (hydr)oxide copper layer on the electrode surface. The low frequency semicircle is related to the combination

Fig. 5. Nyquist diagrams of copper (hydr)oxide-modified electrode in the 0.005 (1), 0.01 (2), 0.02 (3), 0.03 (4), 0.04 (5), and 0.05 mol/L (6) saccharose in 0.5 mol/L NaOH solution. Direct current potential is 730 mV.

of charge transfer resistance and the double layer capacitance.

The equivalent circuit compatible with these results is presented in Scheme 1. In this electrical equivalent circuit, R_s , Q_{dl} , and R_{ct} represent solution resistance, a constant phase element corresponding to the double-layer capacitance, and the charge-transfer resistance associated with the oxidation of the saccharose, respectively. The charge-transfer resistance of the electrode reaction is the only circuit element that has a simple physical meaning, which describes how fast the rate of charge transfer during electrocatalytic oxidation changes with the electrode potential or bulk concentration of saccharose in solution. Q_{ad} and R_{ad} are electrical elements related to the adsorption of (hydr)oxide copper layer. In order to obtain a satisfactory fit of the Nyquist diagrams, it was necessary to replace the double-layer capacitance with a constant phase element in the equivalent circuit. The most widely accepted explanation for the presence of this distributed element and the appearance of depressed semi-circles in the Nyquist plots is microscopic roughness, which cause an inhomogeneous distribution in the solution resistance and in the double-layer capacitance [25]. It should be added that the diffusion process observed during the oxidation process (Fig. 4(b)) would have ap-

Scheme 1. Equivalent circuits of the Nyquist diagrams in Fig. 5.

peared at very low frequencies with a high time constant. It did not appear in the sweeping frequency range in the Nyquist diagrams.

To corroborate the equivalent circuit, the experimental data were fitted to the equivalent circuit and the circuit elements were obtained. Table 1 shows the values of the equivalent circuit elements obtained by fitting the experimental results for different concentrations of saccharose. The goodness of the fit can be judged by the estimated relative errors presented in parentheses. In Table 1, Q and n are the CPE impedance coefficient and exponent, respectively. As can be seen from Table 1, increasing the saccharose concentration decreased the diameters of the second semi-circles whereas there were no corresponding changes in the first semicircles.

Table 1 Values of the equivalent circuit elements obtained by fitting the experimental results for saccharose in the Nyquist plots in Fig. 5 and relative errors

$C_0/(\text{mol/L})$	R_s/Ω	R_{ad}/Ω	$Q_{ad}/(10^4 \text{ F})$	R_{ct}/Ω	$Q_{dl}/(10^3 \text{ F})$	n_1	n_2
0.005	17.87 (0.34%)	27.56 (1.02%)	2.99 (0.81%)	320.7 (1.31%)	2.23 (1.45%)	0.87 (0.85%)	0.54 (1.28%)
0.01	19.54 (0.43%)	25.76 (0.94%)	2.58 (1.54%)	189.6 (0.77%)	3.25 (2.18%)	0.84 (2.17%)	0.47 (1.62%)
0.02	22.99 (0.52%)	25.72 (2.21%)	2.51 (1.97%)	89.55 (0.87%)	2.91 (1.05%)	0.82 (2.77%)	0.52 (2.92%)
0.03	23.21 (0.61%)	29.61 (1.59%)	2.82 (2.04%)	47.89 (3.75%)	2.79 (1.94%)	0.79 (2.84%)	0.59 (1.59%)
0.04	22.48 (0.54%)	33.54 (2.55%)	2.64 (1.54%)	30.02 (1.67%)	2.40 (2.55%)	0.78 (2.05%)	0.69 (1.88%)
0.05	21.47 (0.67%)	34.82 (2.68%)	2.61 (1.69%)	25.24 (1.91%)	2.07 (3.43%)	0.77 (2.27%)	0.73 (2.43%)

The saccharose concentration dependency of R_{ct} is presented in Fig. 6, where an initial sharp drop changed to a very slow drop as the concentration of saccharose was increased. The results were fitted to Eq. (27) to estimate the values of the rate constant. From the fitted equation and assuming $\alpha = 1$, the values of the rate constants were $k_1 = 2.2 \times 10^{-8} \text{ s}^{-1}$ and $k_2 = 2.8 \times 10^5 \text{ cm}^3/(\text{mol}\cdot\text{s})$.

In order to evaluate the performance of the copper (hydr)oxide-modified copper electrode as an amperometric sensor for carbohydrate detection, we studied the electro-oxidation ability of saccharose in alkaline solution. A typical hydrodynamic chronoamperometric response was obtained by the progressive addition of saccharose to 10 ml of a 0.5 mol/L NaOH solution under continuous stirring at 300 r/min. The electrode response time was fast for the different saccharose concentrations, giving stable currents in a few seconds. The anodic current for the different concentrations of saccharose were recorded to get the typical analyti-

cal curve. The limits of detection (LOD) and quantitation (LOQ) of the procedure were calculated according to the $3\text{S.D./}m$ and $10\text{S.D./}m$ criteria, respectively, where S.D. is

Fig. 6. Dependence of R_{ct} on saccharose concentration derived from the Nyquist diagrams (•) in Fig. 5, which were compared with theoretical equation (—).

the standard deviation of the intercept and m is the slope of the calibration curves [26]. In this curve (illustrated in Fig. 7), the anodic current at the sensor ranged from 4.995×10^{-4} to 5.928×10^{-3} mol/L with a detection limit of 1.407×10^{-4} mol/L and a quantitation limit of 4.693×10^{-4} mol/L.

Fig. 7. Chronoamperometric response of the copper-modified electrode in 0.5 mol/L NaOH for successive addition 10 μ L of 0.5 mol/L saccharose solution. The inset is the relationship of the current response of the sensor with the saccharose concentration. Applied working potential 0.73 V vs. Ag/AgCl.

Using the method described, it is possible to determine both the number of electrons transferred (n) and the apparent heterogeneous electron transfer rate constant (k), by using Koutecky-Levich plots (Eq. (30) [27]) for each carbohydrate.

$$1/I = 1/I_k + 1/I_d = (nkFAC_0^*)^{-1} + (0.62nFAC_0^*D_0^{2/3}\nu^{-1/6}\omega^{1/2})^{-1} \quad (30)$$

Figure 8 shows the voltammograms of 0.008 mol/L saccharose at rotating copper (hydr)oxide-modified electrode in

Fig. 8. Rotating voltammogram of 0.008 mol/L saccharose at copper (hydr)oxide-modified electrode in 0.5 mol/L NaOH with $\omega = 250$ (1), 500 (2), 1000 (3), 2000 (4), and 4000 r/min (5). The potential sweep rate is 10 mV/s. Inset: Plot of $1/I$ versus $\omega^{-0.5}$.

0.5 mol/L NaOH with different rotation speeds. As expected a linear relationship was observed between $1/I$ and $\omega^{-0.5}$. Values of the kinematic viscosity (ν) and diffusion coefficient (D_0) were obtained from the literature [28]. The number of electrons transferred for one molecule of saccharose was found to be 21.7 ± 2.1 . According to the literature, the number of transferred electrons during the carbohydrate oxidation is very high due to the formation of different intermediates, which are also oxidized at the highly catalytic copper hydroxide surface. The rate constant was calculated and was around 2.3×10^{-3} cm/s.

3 Conclusions

This work presented the preparation of copper (hydr)oxide-modified copper electrode in 0.5 mol/L NaOH solution by cycling the potential in the range of -250 to $1\,000$ mV. This layer protected the electrode from corrosion and thus there were no interfering oxidation peaks of copper. The modified electrode was successfully used for studying the electrocatalytic oxidation of saccharose. The electrode was electro-catalytically active around 0.7 mV vs. Ag/AgCl and the electro-oxidation occurred through a mediated electron transfer mechanism. Using cyclic voltammetry, chronoamperometry, impedance spectroscopy, and rotating disk electrode experiment, the kinetic parameters of saccharose oxidation were determined.

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