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DOI

[10.1016/0003-2670\(94\)00394-2](https://doi.org/10.1016/0003-2670(94)00394-2)

Publication date

1995

Published in

Analytica Chimica Acta

[Link to publication](#)

Citation for published version (APA):

Huang, X., Pot, J. J., & Kok, W. T. (1995). Electrochemical characteristics of conductive carbon cement as matrix for chemically modified electrodes. *Analytica Chimica Acta*, 300, 5-14. [https://doi.org/10.1016/0003-2670\(94\)00394-2](https://doi.org/10.1016/0003-2670(94)00394-2)

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Analytica Chimica Acta 300 (1995) 5–14

ANALYTICA
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Electrochemical characteristics of conductive carbon cement as matrix for chemically modified electrodes

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Received 18 March 1994; revised manuscript received 1 August 1994

Abstract

Conductive carbon cement (CCC) was evaluated as matrix material for the preparation of electrodes bulk-modified with electrocatalysts. For pure CCC electrodes the background current characteristics were examined. In acidic or neutral phosphate buffers the useful electrode potential range was from -0.3 to $+1.0$ V vs. SCE, while in 0.1 mol l^{-1} NaOH it was from -0.3 to $+0.7$ V. The electrochemical reversibility of CCC electrodes was examined by measuring the standard rate constants for the reduction of hexacyanoferrate(III) and the oxidation of hydroquinone, using cyclic voltammetry (CV) and rotating disk experiments. The reversibility of a CCC electrode was comparable with that of a freshly polished glassy carbon electrode and better than that of carbon paste electrodes. CCC was used as matrix for the preparation of electrodes bulk-modified with cuprous oxide and cobalt phthalocyanine (CoPC). With a Cu_2O -CCC electrode the oxidation potential of glucose, which shows sluggish kinetics at unmodified carbon electrodes, was strongly reduced. The kinetics of the mediated glucose oxidation has been studied with a rotating disk electrode. It was shown that at glucose concentrations higher than approximately 1 mmol l^{-1} the electrochemical regeneration of the catalyst becomes rate-determining. The Cu_2O -CCC modified electrode has been applied with a constant potential in flow-injection analysis for the determination of glucose. The long-term stability of the electrode was studied; repeated injections of a glucose solution during a period of 6 h yielded a relative standard deviation of the peak height of 1.8% ($n=57$). In CV experiments the electrocatalytic activity of CoPC was shown for the oxidation of various compounds such as penicillamine, hydrazine and bile acids. Application of the CoPC-CCC electrode for the detection of bile acids in flow-through detection with a constant or pulsed potential failed, due to a rapid deactivation of the electrode.

Keywords: Cyclic voltammetry; Chemically modified electrodes; Conductive carbon cement; Cuprous oxide; Cobalt phthalocyanine; Carbohydrates; Bile acids

1. Introduction

Carbon is the most widely used electrode material for amperometric detection in flowing solutions, for instance in flow injection analysis (FIA) and liquid chromatography (LC) [1]. Apart from the well known glassy carbon, various carbon composite materials have been used for this purpose. These materials consist of

a mixture of a carbon material with an insulator, such as carbon paste [2], graphite/silicone rubber [3], carbon powder/epoxy resin [4,5], graphite/PTFE [6], reticulated vitreous carbon/epoxy resin [7,8], graphite/polythene [9,10], graphite/Kel-F [11–20] or carbon powder/polystyrene [21–25]. The reason to use these carbon composite materials instead of glassy carbon was usually either to facilitate the construction or the renewal of the electrode, or to obtain improved

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signal-to-noise ratios. More recently, however, the incorporation of electrocatalysts in the composite materials has been studied.

One of the problems encountered in electrochemical detection with carbon electrodes is the low reversibility of the electrochemical reaction of many organic compounds, necessitating the application of high overpotentials for detection. Several techniques have been developed to improve the reversibility of carbon electrodes by pretreatment of the electrode surface, for instance by polishing, heat treatment or electrochemical activation [26]. With these techniques a non-selective improvement of the electrode kinetics can be realised. A more selective improvement of the electrode reversibility can be obtained by modification of the electrode surface with an electrocatalyst, mediating in the electron transfer between the electrode and certain types of compounds in the solution. One of the approaches for this modification is to apply a monomolecular layer or a three-dimensional film containing the electrocatalyst on the surface of the carbon electrode [27–31]. However, it is often difficult to prepare a homogeneous, mechanically stable film with an electrocatalyst.

Another approach to electrode modification is to prepare bulk-modified electrode materials. For this, a solid electrocatalyst is mixed with a carbon composite matrix such as carbon paste or carbon powder/epoxy resin [32–36]. It has been shown that bulk modification is flexible and easy to perform. When the electrode surface has become inactive by, e.g., poisoning of the catalyst by impurities, a fresh surface layer containing the catalyst is easily obtained by polishing.

In previous work [37] we have shown that conductive carbon cement (CCC) can be used as matrix material to prepare an electrode bulk-modified with cobalt phthalocyanine (CoPC). The modified CCC electrode was used for the detection of cysteine compounds in body fluids after separation by LC. CCC, a mixture of carbon particles with a polyacrylic resin, is readily available and easy to use for the preparation of modified electrodes. The CCC matrix was shown to have a high mechanical stability and compatibility with organic modifiers in the solution. This resulted in a better reproducibility and a longer lifetime of the electrode than with a carbon paste matrix.

For the functioning of bulk-modified electrodes, the electrochemical characteristics of the matrix material

are of importance. The useful potential range of a modified electrode is limited by the solvent decomposition on the matrix. Furthermore, at some stage in the mediated electrochemical process, electron transfer with the conducting matrix particles has to take place. In the work presented here, modified and unmodified CCC electrodes have been studied. Charge transfer rates for common analytes on unmodified CCC have been compared with those on carbon paste and glassy carbon electrodes. The kinetics of the oxidation of glucose on a CCC electrode modified with cuprous oxide has been studied in detail, using rotating disk electrode (RDE) experiments and FIA. Some applications of CoPC-modified CCC electrodes will also be presented.

2. Experimental

2.1. Apparatus

Cyclic voltammetry (CV) experiments were conducted using a computerized Autolab electrochemical analyzer (ECO Chemie, Utrecht) with a platinum auxiliary electrode and a SCE reference electrode. RDE experiments were carried out with a 626 Polarecord and a 663 VA Stand (Metrohm, Herisau). For FIA a peristaltic pump (Gilson) was used, with a Rheodyne 7010 injection valve with a 30 μ l sample loop. For amperometric detection a Model 1049A programmable electrochemical detector (Hewlett Packard) was operated in the constant potential mode with a Metrohm wall-jet electrochemical cell containing a Ag/AgCl reference electrode and a glassy carbon counter electrode.

The working electrodes in CV, RDE, and FIA experiments were standard Metrohm glassy carbon disk electrodes (3 mm diameter, mounted in PTFE) and carbon paste electrode bases (PTFE body, 3 mm diameter cavity). The latter were packed with either carbon paste or conductive carbon cement, with or without modifiers.

2.2. Chemicals and solutions

Cobalt phthalocyanine (Aldrich) and cuprous oxide (Fluka) were used as received. Carbon paste was from Metrohm (E287) and conductive carbon cement (CCC) from Gerhard Neubauer (Münster). Bile acid sodium salts were purchased from Fluka (deoxycholic,

chenodeoxycholic, ursodeoxycholic, glycocholic, taurocholic and taurodeoxycholic acid) or Sigma (cholic, taurochenodeoxycholic, tauroursodeoxycholic, glycodeoxycholic and glycochenodeoxycholic acid). Other chemicals used were A.R. grade. The standard solutions of analytes were prepared daily. Solutions were deaerated with helium before use.

2.3. Preparation of the electrodes

Glassy carbon electrodes were polished with 0.05 μm alumina particles (Buehler) on a polishing pad (Buehler) and ultrasonicated for 2 min. Modified carbon paste electrodes were prepared by mixing 5% CoPC (w/w) or 20% Cu_2O (w/w) with carbon paste and pressing the mixture into the cavity of the electrode body. The excess of carbon paste was removed by polishing on a piece of clean smooth paper.

To prepare modified CCC electrodes, CCC was mixed with 5% CoPC (w/w) or 20% Cu_2O (w/w) in the following way. About 300 mg of CCC was transferred into a 1 ml glass vial with a stirrer inside, and the desired amount of modifier was added. Then 300 μl of acetone was added. When necessary, a few μl of CCC thinner was added. Mixing was achieved on a magnetic stirrer while acetone was allowed to evaporate until a thick paste formed. The vial was closed until use. First, pure CCC was packed in the cavity of carbon paste electrode body and allowed to dry. The excess of CCC was polished off with dry emery paper (grade 2/0, Oakey) and the surface layer of CCC was removed with an acetone-soaked tissue. At this stage, modified CCC paste was packed into the resulting shallow cavity and allowed to dry overnight. The excess of the dried mixture was first polished off with dry emery paper (grade 2/0), then subsequently with 3 μm and 0.3 μm imperial micro finishing film sheets (3M). The final polish was achieved with 0.05 μm alumina particles on a Buehler pad and ultrasonication for 2 min in subboiled water. A fresh surface of the electrode could be obtained in two ways. One way was to repeat the polishing procedure beginning with a 3 μm polishing sheet. The second method was by removing the top layer with an acetone-soaked tissue and repacking with modified CCC. Unmodified CCC electrodes were prepared in the same fashion. After preparation the electrodes were washed with sub-boiled water and dried with compressed air before use.

2.4. Kinetic data analysis

Heterogeneous rate constants k^0 were evaluated from the peak separation ΔE_p in CV according to the method of Nicholson [38]. From the peak separation a value of the parameter ψ was obtained which is related to k^0 by [39]:

$$\psi = \frac{(D_0/D_R)^{\alpha/2} \cdot k^0}{[D_0 \pi \nu (nF/RT)]^{1/2}} \quad (1)$$

where ν is the scan rate, D_0 and D_R are the diffusion coefficients of the oxidized and reduced forms of the substrate, respectively, and the other symbols have their usual meaning. The value of k^0 for the hexacyanoferrate couple was also determined by RDE experiments using the Koutecky-Levich equation, which can be written as:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (2)$$

where i is the current measured, i_k the kinetic current representing the kinetic control process and i_d the diffusion current. The diffusion current for a RDE is given by:

$$i_d = nFA \cdot D_0^{2/3} \cdot \nu^{-1/6} \cdot \omega^{1/2} \cdot c_0 \quad (3)$$

where A is the electrode surface area, D_0 is the diffusion coefficient of the substrate, ν the hydrodynamic viscosity of the solution, ω the rotation rate of the electrode and c_0 the substrate concentration. From the intercept of the Koutecky-Levich plot (i^{-1} vs. $\omega^{-1/2}$), i_k was obtained and the forward rate constant k_f calculated according to:

$$i_k = nFA \cdot k_f \cdot c_0 \quad (4)$$

Since the forward rate constant at a certain potential is given by:

$$k_f = k^0 \cdot \exp\left[\frac{-\alpha nF(E-E_0)}{RT}\right] \quad (5)$$

k^0 could be evaluated from a plot of $\ln k_f$ vs. E .

It has been recognized [40] that in mediated electrocatalysis three current-controlling factors should be taken into account: (1) the mass transport of the analyte to the electrode surface, as manifest in the limiting current i_d ; (2) the rate of electron transfer between the analyte and the active sites of the mediator; (3) the

self-electron exchange rate of the mediator at the applied potential. The rate for the chemical step in an oxidative mediated electrode process can be expressed as:

$$i_{\text{ch}} = nFA \cdot k_{\text{ch}} \cdot \Gamma_{\text{ox}} \cdot c_e \quad (6)$$

where k_{ch} is the rate constant for the electron transfer, Γ_{ox} the surface concentration of the active form of the mediator, and c_e the analyte concentration at the electrode surface. The kinetic equation for the reactivation of the mediator reaction can be expressed as:

$$i_s = nFA \cdot k_s \cdot \Gamma_{\text{red}} \quad (7)$$

where k_s is the self-exchange rate constant and Γ_{red} the surface concentration of the inactive form of the mediator. The sum of the surface concentrations of the mediator in the oxidized and reduced form is a constant:

$$\Gamma_{\text{ox}} + \Gamma_{\text{red}} = \Gamma \quad (8)$$

In the steady state, the currents calculated from Eqs. 6 and 7 are equal, and an expression for the kinetic current i_k can be found by combining Eqs. 6–8 [41–43]:

$$\frac{1}{i_k} = \frac{1}{nFAk_{\text{ch}}\Gamma c_e} + \frac{1}{nFAk_s\Gamma} \quad (9)$$

In mediated electrocatalytic measurements the Koutecky-Levich approach is not valid. Plots of $1/i$ vs. $1/\omega^{1/2}$ are curved, and observed slopes do not represent the convective diffusion in the solution. Still, when the kinetics of the electrode reactions are relatively slow, the intercepts of such plots at high rotation speed give a good indication of the kinetic current, with c_e equal to the bulk analyte concentration c_0 . By measuring i_k for different analyte concentrations and the construction of a plot of $1/i_k$ vs. $1/c_0$, the values of k_{ch} and k_s can be obtained from the slope and the intercept, respectively.

3. Results and discussion

3.1. Background current characteristics of CCC

In 0.1 mol l⁻¹ phosphate buffer of pH 7.0, with cyclic voltammetry no peaks were observed in a potential range from -0.3 to +1.2 V, except for a higher background at the positive end. However, when the

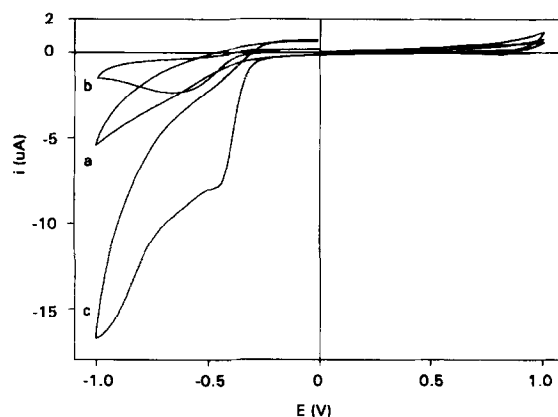


Fig. 1. Cyclic voltammetric background signals with (a) polished GC and (b) CCC electrode in degassed 0.1 mol l⁻¹ phosphate buffer (pH 7.0), and (c) CCC electrode in air saturated buffer. Scan rate: 10 mV s⁻¹.

potential was extended to more negative values, a wave appeared which decreased somewhat in successive scans (see Fig. 1). A similar phenomenon in the negative scan was observed with 0.1 mol l⁻¹ phosphate buffer of pH 2.0 and with 0.1 mol l⁻¹ NaOH. The nature of this wave is difficult to establish, since its onset-potential (-0.3 V) is in the range of oxygen reduction. Although it could be characteristic for the CCC electrode surface, a contribution of traces of oxygen trapped in the CCC material can not be excluded. Carbon electrodes normally show a high cathodic background current. For example, similar cathodic residual waves characterize carbon electrodes [2,44], while the applied potential range has a dramatic influence on the background characteristics of carbon-epoxy electrodes [4]. This effect was not observed with CCC electrodes. High cathodic residual currents generally make carbon electrodes unsuitable for reductive detection, for which mercury electrodes are preferably used. The useful electrochemical window for bare CCC electrodes, as determined by CV techniques, can be estimated as -0.3 to +1.0 V vs. SCE in a phosphate buffer of pH 2.0 or 7.0 and -0.3 to +0.7 V in 0.1 mol l⁻¹ NaOH. Since the main goal of the development of electrocatalytic CMEs is to reduce the overpotential of electrode reactions, this potential range can fulfil the requirements.

3.2. Reversibility of electrode reactions on CCC

The reduction of hexacyanoferrate(III) was studied as a well known example of an outer-sphere, one-electron

tron process. Data obtained in CV experiments with different carbon materials are given in Table 1. The cathodic peak current with CCC electrodes was proportional to the square root of the scan rate from 5 to 200 mV s^{-1} , which is characteristic for a diffusion controlled process. At higher scan rates, this relationship tailed off and an increase of the peak separation and a decrease of the i_a/i_c ratio were observed. The standard rate constant k^0 for the hexacyanoferrate redox couple was evaluated from the peak separation ΔE_p . Rates of electron transfer for the CCC electrodes and conventionally polished glassy carbon electrodes were similar. It must be noted, however, that the reversibility of glassy carbon electrodes strongly depends on the history and treatment of the surface. For this same electrochemical process standard rate constants from 10^{-4} to $7 \times 10^{-2} \text{ cm s}^{-1}$ have been reported [26,45,46]. The lower k^0 values obtained with the carbon paste electrodes may be caused by the influence of a thin film of pasting oil on the carbon surface [47]. The formal potential $E^{\circ'}$, taken as the average of the oxidation and reduction peak potentials, was the same for all electrode materials. The value found (+0.23 V vs. SCE) is in agreement with literature data [46–48].

A slight aging-effect of the CCC electrode was observed as has been found with carbon paste [47] and pretreated glassy carbon electrodes [26,45]. In a series of 30 CV scans, the signal was almost constant after a few scans. Subsequently the electrode was taken out and washed with water, and another CV scan was conducted. Compared with the original first scan, the peak separation increased by 10 mV and cathodic current decreased by 4%. No obvious memory effect was observed when a blank solution was measured with a CCC electrode which was first used in a solution of hexacyanoferrate(III).

To further explore the electrode kinetics, RDE experiments were also carried out. Voltammograms were

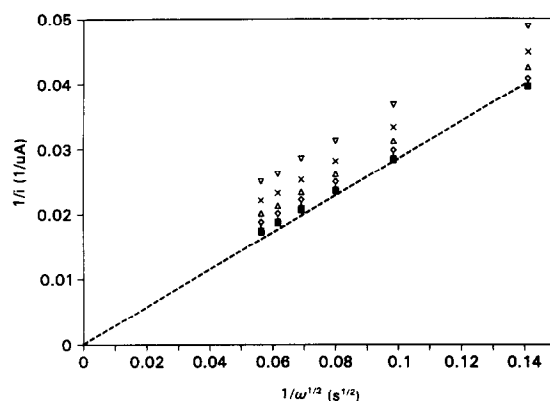


Fig. 2. Koutecky-Levich plots for the reduction of hexacyanoferrate(III) obtained with a CCC electrode at different potentials. (v) +0.05 V; (x) 0.0 V; (Δ) -0.05 V; (\diamond) -0.10 V; (+) -0.15 V; (\blacksquare) -0.20 V; (-----) theoretical diffusion current.

recorded at several rotation rates and Koutecky-Levich plots were constructed (Fig. 2). The slopes of the plots are in good agreement with the theoretical value calculated from the Levich equation (Eq. 3) using a value for D of $0.763 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. From the intercepts rate constants at different potentials could be calculated. The standard rate constant at $E^{\circ'} = 0.275 \text{ V vs. Ag/AgCl/sat. KCl}$ can be estimated as $4.3 \pm 0.5 \times 10^{-3} \text{ s}^{-1}$, which is in reasonable agreement with the value obtained by CV experiments.

Fig. 3a shows cyclic voltammograms of hydroquinone at several scan rates v with the CCC electrode. The relationship between i_p and $v^{1/2}$ was linear between 5 and 100 mV s^{-1} . At higher scan rates this relationship tailed off which suggested that the electron transfer became the rate determining process (Fig. 3b). This was confirmed by a shift of E_p to more positive values and a decrease of i_c/i_a with increasing v . After a few scans at the same scan rate, the peak separation remained unchanged, while the anodic peak current decreased by 1.6%, possibly due to the adsorption of oxidation products at the electrode surface. Table 2 lists

Table 1
Cyclic voltammetric reduction of hexacyanoferrate(III)

Electrode material	n^a	$E_{p,c}$ (V)	ΔE_p (V)	i_c (μA)	k^0 ($10^{-3} \text{ cm s}^{-1}$)
CCC	9	0.185 ± 0.004	0.088 ± 0.007	5.3 ± 0.2	3.3 ± 0.3
Glassy carbon	3	0.183 ± 0.003	0.090 ± 0.003	5.0 ± 0.1	2.5 ± 0.1
Carbon paste	5	0.120 ± 0.035	0.208 ± 0.044	4.6 ± 0.2	0.3 ± 0.1

Solution: $10^{-3} \text{ mol l}^{-1} \text{ K}_3\text{Fe}(\text{CN})_6$ in $1 \text{ mol l}^{-1} \text{ KCl}$. Scan rate 10 mV s^{-1} . Potentials against SCE.

^a Number of different electrodes tested.

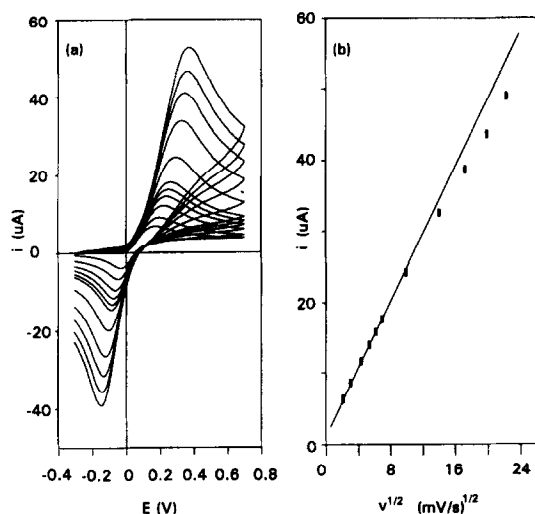


Fig. 3. (a) Cyclic voltammograms of the oxidation of 10^{-3} mol l^{-1} hydroquinone in 0.1 mol l^{-1} phosphate buffer (pH 7.0) with a CCC electrode at different scan rates. (b) Dependency of the peak current on the scan rate.

the results of the CV experiments on the oxidation of hydroquinone with CCC, glassy carbon and carbon paste electrodes. The standard rate constant k^0 was evaluated with Nicholson's method using a value for D of 0.661×10^{-5} cm 2 s $^{-1}$ [49]. It is seen that also for this anodic oxidation process, the electrode reversibility of CCC was better than that of carbon paste.

An explanation for the reversibility difference between CCC and carbon paste electrodes may be found in the surface topology of the materials. With carbon paste electrodes the carbon platelets are oriented parallel to the surface, forming a relatively compressed material, covered by a thin layer of pasting oil which hinders electron transfer [47]. In the case of CCC electrodes, scanning electron microscopy shows no preferential alignment of the carbon particles but rather a random distribution. More carbon with edge orientation is exposed to the solution, on which electron transfer occurs more readily than on basal plane orientation carbon [50].

3.3. Oxidation of glucose on Cu $_2$ O modified CCC

Metal oxide modified electrodes for the catalysis of redox processes have drawn considerable attention of electroanalytical chemists (e.g., [51]), yet only a few applications in flowing solutions have been described [33,35,52]. Following the work of Xie and Huber

[52], who developed carbon paste electrodes bulk modified with cuprous oxide, we have modified the CCC matrix with Cu $_2$ O for the determination of carbohydrates.

In cyclic voltammetry in blank sodium hydroxide solutions, in the first anodic scan with a freshly prepared Cu $_2$ O–CCC electrode, an irreversible peak is observed with a peak potential of +0.20 V. In later scans this peak did not show. The anodic peak may be related to the oxidation of Cu(I) to Cu(II) on the electrode surface. Its area corresponds to approximately 6.9×10^{-9} mol Cu cm $^{-2}$.

Cyclic voltammograms of glucose on Cu $_2$ O modified CCC in 0.1 mol l^{-1} NaOH show one irreversible anodic wave at +0.55 V (Fig. 4). The height of this peak remained stable in successive scans within 5%. The anodic process on Cu $_2$ O–CCC was not influenced by the hydroxide concentration above a certain value (≥ 0.1 mol l^{-1}), as has also been observed by others [52]. The appearance of only one anodic wave in CV indicates that the oxidation reaction is different from that on gold electrodes, where two waves are observed at -0.53 and $+0.15$ V [53,54], attributed to the oxidation of the aldehyde group and the alcohols groups of glucose, respectively. Similar CV behaviour has been observed with copper electrodes and various other copper containing CMEs in alkaline solutions [55–58]. Both Cu(II) and Cu(III) have been suggested to act as an electron transfer mediator for the oxidation of aldehyde groups [59]. However, since the oxidation of carbohydrates occurs at or near the oxidation wave of the Cu(III)/Cu(II) redox couple, although the actual mechanism of glucose oxidation remains uncer-

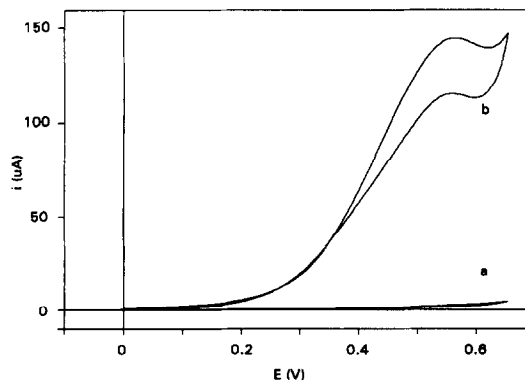


Fig. 4. Cyclic voltammograms of 5×10^{-3} mol l^{-1} glucose in 0.1 mol l^{-1} NaOH with (a) bare CCC and (b) Cu $_2$ O–CCC electrodes. Scan rate: 50 mV s $^{-1}$.

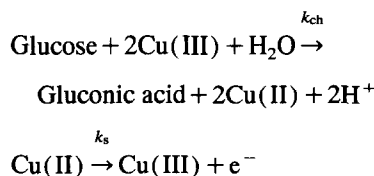
Table 2
Cyclic voltammetric oxidation of hydroquinone

Electrode material	n^a	$E_{p,a}$ (V)	ΔE_p (V)	i_a (μA)	k^0 ($10^{-4} \text{ cm s}^{-1}$)
CCC	5	0.162 ± 0.027	0.193 ± 0.037	9.1 ± 0.6	3.7 ± 0.3
Glassy carbon	5	0.181 ± 0.026	0.228 ± 0.042	9.4 ± 0.3	2.4 ± 0.1
Carbon paste	5	0.251 ± 0.024	0.355 ± 0.043	9.9 ± 0.6	0.5 ± 0.1

Solution: $10^{-3} \text{ mol l}^{-1}$ hydroquinone in 0.1 mol l^{-1} phosphate buffer (pH 7.0). Scan rate 10 mV s^{-1} . Potentials against SCE.

^a Number of different electrodes tested.

tain, it is generally accepted that Cu(III) actively participates in the catalytic oxidation of the carbohydrates. Therefore, the following general scheme of the mediated electrocatalytic oxidation of glucose may be representative:



In RDE experiments it was found that the oxidation current for glucose, measured at $+0.60 \text{ V}$, hardly depended on the rotation rate of the electrode. Plots of $1/i$ vs. $1/\omega^{1/2}$ yielded straight lines, but with slopes much lower than calculated from the Koutecky-Levich equation (Eqs. 2 and 3). Such behaviour is expected for mediated electrode processes when the electrode kinetics are relatively slow. From the intercepts of the plots obtained, the kinetic current i_k was estimated for different glucose concentrations. Interestingly, the kinetic current was not proportional to the glucose concentration c_0 . This was already predicted in Eq. 9 with c_e equal to c_0 for slow electrode process. In Fig. 5, $1/i_k$ is plotted against $1/c_0$. The data points were obtained

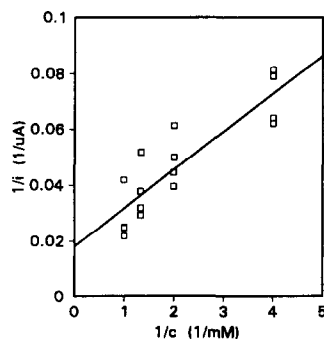


Fig. 5. Dependency of the kinetic current in RDE experiments on the glucose concentration with Cu_2O -CCC electrodes.

in 4 series of measurements, with polishing of the electrode in between. Before rotation rates were varied, a few pre-scans were carried out to obtain a stable baseline. Although the experimental scatter in the plot is rather large, it is clear that an intercept exists. From the slope of the plot a value for $k_{\text{ch}}\Gamma$ of $5.4 \pm 0.8 \times 10^{-3} \text{ cm s}^{-1}$ is found, and from the intercept a value for $k_s\Gamma$ of $4.1 \pm 1.1 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$. Combination of these two values gives, as k_s/k_{ch} , a 'saturation concentration' for glucose of 0.76 mmol l^{-1} . Below this concentration the catalytic oxidation of glucose controls the overall process, while at higher glucose concentrations the regeneration of the mediator is rate determining. For the latter process a heterogeneous rate constant can be calculated, with the surface concentration of the catalyst as determined earlier, of 0.6 s^{-1} .

The characteristics of the Cu_2O -CCC electrode were further examined in flow-injection (FIA) experiments. Fig. 6 shows the hydrodynamic voltammogram for glucose oxidation. A maximum sensitivity is obtained at $+0.50 - +0.55 \text{ V}$, which is in agreement with the results of the CV experiments. The decrease of the sensitivity at higher potentials seems to be a common

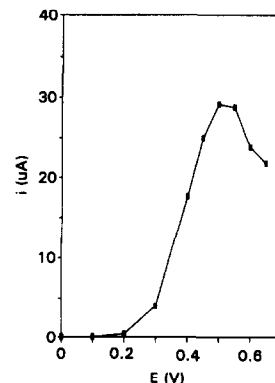


Fig. 6. Hydrodynamic voltammogram of $10^{-3} \text{ mol l}^{-1}$ glucose with a Cu_2O -CCC electrode. Carrier: 0.1 mol l^{-1} NaOH; flow rate: 1 ml min^{-1} .

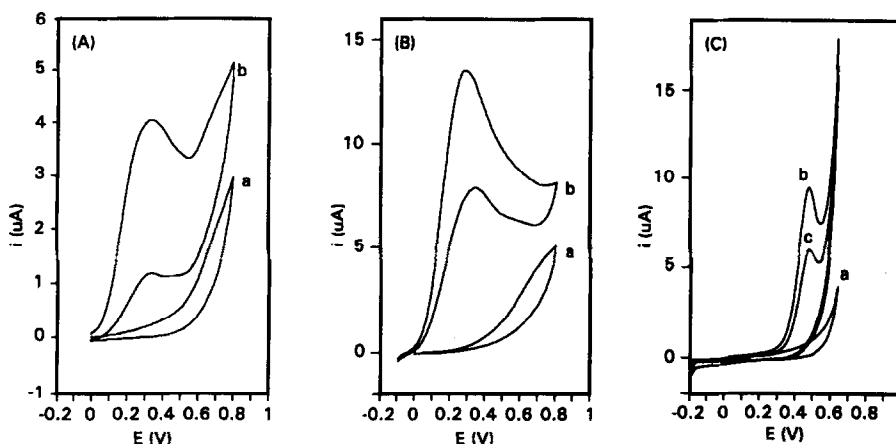


Fig. 7. Cyclic voltammetry with CoPC–CCC electrodes. (A) 10^{-3} mol l^{-1} penicillamine in 0.1 mol l^{-1} phosphate buffer (pH 7.0) with (a) bare CCC and (b) CoPC–CCC electrodes. (B) 0.5×10^{-3} mol l^{-1} hydrazine in 0.1 mol l^{-1} phosphate buffer (pH 7.0) with (a) bare CCC and (b) CoPC–CCC electrodes. (C) 10^{-3} mol l^{-1} cholate in 0.1 M NaOH with (a) bare CCC, (b) CoPC–CCC electrode for the first scan and (c) the second scan. Scan rate: 10 (A, B) or 20 (C) $mV s^{-1}$.

characteristic of electrocatalytic CMEs, related to the deactivation of the catalyst. The original activity of the electrode could be restored by applying a lower potential again.

When the flow rate of the solution was varied (from 0.2 to 2 ml/min), it was found that the area of the glucose peak obtained, expressed in coulombs, was inversely proportional to the flow rate. This supports the conclusion from the RDE experiments that the overall process is controlled by the electrode kinetics and not by the mass transport to the electrode surface. The decrease of the peak area with the flow rate then reflects the decrease of the residence time of the sample plug in the flow-through cell.

The peak heights in FIA were linear with the glucose concentration in the range from 10^{-6} to 10^{-3} mol l^{-1} . At higher concentrations the sensitivity decreased. Again, there is a striking agreement with the RDE experiments, where a ‘saturation concentration’ of 0.76 mmol l^{-1} of glucose was found. At higher concentrations the electrochemical regeneration of the catalyst becomes the limiting factor for the current.

The stability of electrode was tested in FIA experiments using a constant detection potential of +0.60 V. Within a period of 6 h, the relative standard deviation of the peak height for the repeated injection of a 10^{-3} mol l^{-1} glucose solution was +1.8% ($n=57$).

3.4. CoPC modified CCC

CoPC modified electrodes show effective oxidation of some small [60–62] and larger molecular com-

pounds [63–65], which normally exhibit a sluggish reaction at carbon electrodes. As shown in Fig. 7, in cyclic voltammetry CoPC exhibits electrocatalytic behaviour towards different compounds. Compared to pure CCC, the overpotentials for the oxidation of penicillamine and hydrazine in phosphate buffer (pH 7) were strongly reduced with CoPC–CCC electrodes, with anodic peak potentials of +0.34 and +0.28 V vs. Ag/AgCl, respectively. In previous work we have already shown that CoPC–CCC electrodes can be used for the detection of sulfhydryl compounds in flowing solutions [37]. The long-term stability of the CoPC–CCC electrode was shown to be much better than an analogous electrode with a carbon paste matrix.

In the literature a method has been described for the determination of bile acids by LC with pulsed amperometric detection [66]. Various bile acids, with molecular structures including one to three hydroxy groups, could be oxidized at a gold electrode. Since it has been shown before that electrode modification can replace the pulsed potential mode for detection, we have tested the use of CoPC–CCC electrodes with bile acids. In cyclic voltammetry, we found that CoPC catalyzed the oxidation of bile acids in 0.1 mol l^{-1} NaOH. For various bile acids (see Experimental section) anodic peak potentials between +0.54 and +0.59 V were observed. However, in two respects the behaviour of the electrode towards bile acids was different from that with, e.g., penicillamine. First, the anodic current in the backward scan was absent. Secondly, the anodic

response strongly decreased after the first scan with a freshly polished electrode (Fig. 7c). Attempts to detect bile acids in a flowing solution with CoPC–CCC electrodes, at a constant or pulsed potential, failed. A rapid decrease of the electrode activity was observed in all cases.

4. Conclusions

CCC compares favourable to carbon paste in respect to available potential range and electrochemical reversibility for different oxidizable compounds. However, the main advantage of this matrix material for bulk-modification of electrodes over carbon paste is its mechanical stability. This makes the application of CCC electrodes in flow-through detection feasible. A highly reproducible sensitivity can be obtained. Compared to other solid matrix materials described in the literature, such as epoxy resins, CCC electrodes are easy to prepare and to renew.

As has been shown for the cuprous oxide electrodes, the results of CV and RDE batch experiments are easily translated to optimized conditions for detection in FIA, LC or capillary electrophoresis. For instance, the flow rate effect and the decrease of the sensitivity at high analyte concentrations as observed in FIA could be explained on the basis of kinetic data obtained with a RDE. From the limited set of examples with CoPC electrodes it appears that the observation of a catalytic effect in CV does not guarantee that a chemically modified electrode can be used in flow-through detection. An indication of the long-term stability in flow is given by the stability of CV signals in successive scans.

The use of modified CCC electrodes for detection in liquid chromatography and capillary electrophoresis is now further investigated in our laboratory.

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