



# Interfacial capacitance of an oxidised copper electrode



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## ABSTRACT

Polycrystalline copper electrodes were oxidised in 0.1 M KOH<sub>aq</sub> at –350 mV vs. Hg|HgO. The properties of such formed oxide layers were studied by means of X-ray photoelectron spectroscopy and impedance measurements. The layers are composed with Cu<sub>2</sub>O with properties of a p-type semiconductor. The impedance spectra recorded at potentials of Cu<sub>2</sub>O formation were found to meet the requirements of correct and valid impedance data. An analysis of data fitting errors allowed selection of the equivalent circuit optimal for Cu<sub>2</sub>O covered electrodes. The overall interfacial capacitance depends on the electrode potential and on the oxide thickness. Elements of the equivalent circuit describing capacitances of the double layer and of the oxide have been determined. It can be estimated that the double layer capacitance of the oxidised Cu electrode is comparable with the capacitance measured for the metallic surface at potentials of hydrogen evolution.

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## 1. Introduction

Copper is one of non-noble metals with numerous applications in various areas of technology and science. In case of many applications, such as oxygen evolution reaction or oxidation of organic compounds, the surface of Cu electrodes becomes partially oxidised or completely covered with an oxidised layer formed under the conditions applied [1–6]. The properties of such formed oxide/hydroxide layers may strongly affect general electrochemical behaviour of Cu based materials. Therefore, further development of application of Cu based electrodes at conditions of surface oxidation requires thorough knowledge about electrochemical properties of the oxidised, passive layers electrochemically formed on the electrode surface. The interfacial capacitance established at the electrode|electrolyte interface is amongst the parameters describing properties of the oxidised surface. Most of the oxides and hydroxides of non-noble and noble metals exhibit non-metallic, semiconducting or insulating properties [7–9]. Thus, a significant fraction of the overall potential drop at the oxidised metal|electrolyte interface may be located inside the oxide/hydroxide layer. Two components contribute to the overall interfacial capacitance of an oxidised electrode,  $C_{\text{total}}$ : the double layer capacitance on the electrolyte side,  $C_{\text{dl}}$ , and the capacitance of a non-metallic oxide/hydroxide. These two capacitances are usually represented as connected in series [10–13] and separate determination of their values is not always trivial. On the other hand, the knowledge of structure of the interfacial capacitance would be helpful in evaluation of potential distribution at the electrode|elec-

trolyte interface. This, in turn, would provide an important contribution in understanding of interfacial process, important in e.g. electrocatalysis, and would help in development of many devices, such as electrochemical capacitors or fuel cells.

Cu oxides, including Cu<sub>2</sub>O, possess semiconducting properties [7,14–22,23–29], as follows from the capacitance [16] and photoelectrochemical [7,15,17,24,26–30] measurements. Cu<sub>2</sub>O is a p [15,17,18,26,28–30] or n-type [15,17,18,28] semiconductor, depending on the thickness of the electrochemically formed oxides [15,17] and pH of the electrolyte [18,28]. The interfacial capacitance of a Cu electrode decreases upon oxidation, in agreement with a parallel plate capacitor model [23,31,32] (Eq. (1)):

$$C = \frac{\varepsilon_0 \varepsilon A}{d_{\text{ox}}} \quad (1)$$

where  $\varepsilon$  and  $\varepsilon_0$  is dielectric permittivity of the oxidised layer and vacuum, respectively,  $A$  is the surface area and  $d_{\text{ox}}$  is the oxidised layer thickness. However, potential influence on the capacitance is rather complex [31–34]. The double layer capacitance of Cu electrodes has been analysed extensively at potentials where the surface is oxide-free and metallic [33,35–37], less work has been done to study the double layer capacitance of the oxidised copper. In [38] the Cu oxidation in 0.1 M NaOH was studied by means of impedance spectroscopy. The double layer was modeled as a constant phase element, CPE. The value of the exponential factor determined for the double layer at –370 mV vs. Ag|AgCl in 0.1 M NaOH was 145  $\mu\text{S s}^\alpha \text{cm}^{-2}$  while the respective exponential factor was equal to 0.5 [38]. For Cu oxidised in 0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> the double layer capacitance of 25  $\mu\text{F cm}^{-2}$  was calculated on the basis of Eq. (1) with assumed series connected capacitances of the double layer and of the oxide [31].

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This paper describes results of studies on the interfacial capacitance of Cu electrodes oxidised in 0.1 M KOH<sub>aq</sub>. The oxidised layers were formed at –350 mV vs. Hg|HgO for various oxidation times. Composition of the oxidised layers was determined on the basis of X-ray photoelectron spectroscopy experiments while their electronic properties were determined by means of impedance and photocurrents measurements. An analysis of impedance spectra allowed determination of components of the interfacial capacitance of the oxidised copper|0.1 M KOH<sub>aq</sub> interface.

## 2. Experimental

The experiments were carried out with a standard three electrode system with a polycrystalline copper foil (POCh, 99.9%), Hg|HgO and Pt gauze wire or Au foil serving as working, reference and counter electrodes, respectively. Before the experiments the working electrode was polished mechanically with a diamond polishing compound (Metadi, Buehler, 9 and 1 μm). Analytical grade reagents (POCh) and water purified in a Millipore system were used for preparation of the electrolyte solutions. The electrolyte solutions were deaerated with Ar or N<sub>2</sub> (Air Products, 5 N), during the experiments the gas stream was directed above the electrolyte level. All the potentials in the text are given in respect to Hg|HgO electrode.

The oxidised layers were formed by a constant potential oxidation at –350 mV with various total polarisation times up to 1800 s. A CHI 660D potentiostat (CH Instruments) and a Metrohm Faraday cage were used in the electrochemical measurements. The measurements were carried out at 293 K (VWR 1146D thermostat). A 150 W Xe lamp with a ZXE power supply unit (Optel, Poland) were used for photocurrents measurements. X-ray photoelectron spectroscopy (XPS) analysis was carried out in Institute of Physical Chemistry of Polish Academy of Sciences, Warsaw, with an ESCA-LAB-210 apparatus (VG Scientific). Al X-ray and Ar<sup>+</sup> ion guns were used, the latter in depth profiling experiments. The rate of ion sputtering was 12.7 nm min<sup>–1</sup> for standard samples of SiO<sub>2</sub>/Si (Reference Material No. 564, Institute for Reference Materials and Measurements, European Commission-Joint Research Center). To the best of author's knowledge, no reported values of respective sputtering rates for Cu<sub>2</sub>O can be found in literature. However, for many metal oxides the rate of sputtering with Ar<sup>+</sup> is significantly smaller as compared to SiO<sub>2</sub> [39,40].

The impedance measurements of the oxidised electrodes were performed according to two procedures:

- (1) Single frequency potential scan with AC signal amplitude of 5 mV and DC potentials steps of 40 or 50 mV. The capacitance was calculated as a series element in a RC circuit.
- (2) Impedance spectroscopy measurements, EIS, at a constant polarisation potential and with AC signal frequency range of 8300 kHz–0.26 Hz with amplitude of 5 mV. The purpose of selection of such narrow frequency range was to reduce time of spectra acquisition.

The exact value of potential onset of Cu oxide formation is hard to determine, some works point to a premonolayer oxidation of Cu at potentials significantly more negative than the apparent onset of well defined oxidation peaks at voltammetric curves [6,41]. Therefore, the measurements of the capacitance of the metallic surface were carried out at potentials in hydrogen evolution region, (HER, –1400 to –1500 mV), where no surface oxidation takes place and the surface can be considered oxide-free. The capacitance measured in this region was practically potential independent and establishes a reference point for the measurements carried out for the oxidised surface and was also used for the real surface area

estimation with the assumed specific capacitance of 25 μF cm<sup>–2</sup> [42]. The spectra (3000–3 Hz, 5 mV amplitude) were recorded after 90 s of polarisation. The equivalent circuit used for HER region was composed with an ohmic resistance,  $R_{ohm}$ , connected in series with a subcircuit containing a constant phase element and a charge transfer resistance,  $R_{ct}$ , both connected in parallel [43]. The parallel resistance depicts kinetics of HER while the CPE mirrors the double layer capacitance. The impedance of CPE is defined as [44–47] (Eq. (2)):

$$Z_{CPE} = Q^{-1}(i\omega)^{-\alpha} \quad (2)$$

where  $Q$  is the preexponential factor;  $i$  is the imaginary unit; and  $\alpha$  is the exponential factor ( $0 \leq \alpha \leq 1$ , with  $\alpha = 1$  for the ideal capacitance).  $Q$  and  $\alpha$  values obtained for –1400 to –1500 mV were in the range of  $(3.32\text{--}2.96) \times 10^{-5} \Omega^{-1} s^\alpha \text{ cm}^{-2}$  and 0.972–0.985, respectively. For a simple circuit containing  $R_{ohm}$  connected in series with a subcircuit containing a parallel combination of CPE and  $R_{ct}$ , the CPE can be recalculated into the capacitance units according to the method presented in [43,48] with assumed surface distribution of time constants (Eq. (3)):

$$C_{dl} = \left( Q \left( \frac{1}{R_{ohm}} + \frac{1}{R_{ct}} \right)^{(\alpha-1)} \right)^{\left(\frac{1}{\alpha}\right)} \quad (3)$$

It was not possible to determine the value of the pseudocapitance related to the adsorbed hydrogen. The possible reasons include potential independent surface coverage with adsorbed hydrogen at such negative overpotentials [49–52] or a very low value of the coverage [53]. Estimated roughness factor of the electrodes studied was  $3.5 \pm 0.4$ , all parameters in the text are reported in respect to such estimated real surface area.

## 3. Results and discussion

### 3.1. Cyclic voltammetry characterisation of Cu electrode in 0.1 M KOH

Fig. 1 shows a cyclic voltammetry curve for a Cu electrode recorded in 0.1 M KOH<sub>aq</sub> for –350 to –1300 mV. Between ca. –725 and ca. –350 mV copper is oxidised to Cu(I) compounds with Cu<sub>2</sub>O as the most often reported oxidation product [15,54–62]. A pair of red-ox peaks denoted as A and C is attributed to formation

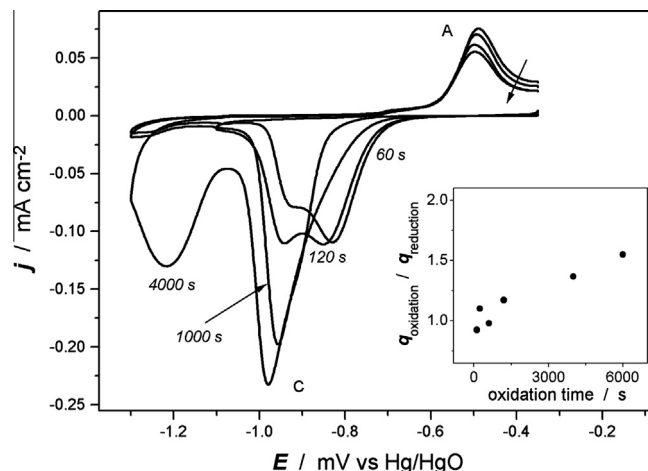


Fig. 1. Cyclic voltammetry curve for a Cu electrode in 0.1 M KOH<sub>aq</sub> recorded with 20 mV s<sup>–1</sup> after various polarisation times at –350 mV indicated on the plot. Letters denote current peaks described in the text, the arrow in peak A indicates changes in the oxidation peak with increasing number of oxidation cycles. The experiments were carried out for the same electrode with increasing oxidation time at –350 mV. Inset: the ratio between the oxidation charge at –350 mV and the cathodic charge calculated from Cu(I) reduction peaks.

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