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The interfacial capacitance of an oxidised polycrystalline gold electrode in an aqueous HClO₄ electrolyte

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ABSTRACT

The interfacial capacitance of a polycrystalline gold electrode electrochemically oxidised in an aqueous 0.1 M HClO₄ electrolyte has been investigated by means of the electrochemical impedance spectroscopy. From 1.3 to 3 monolayers of Au atoms were oxidised under constant potential conditions and for various oxidation times. The capacitance of the oxidised layers was analysed as a function of the electrode potential and the extent of the surface oxidation. It was found that the interfacial capacitance decreases upon surface oxidation. The components of the interfacial capacitance of the oxidised layer: the double layer capacitance and the capacitance of the oxidised layer; have been separated. The capacitance of the double layer of the oxidised surface was found to be comparable to the capacitance measured for the metallic surface.

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1. Introduction

Gold is a good example of an electrode which, in the absence of redox couples in the electrolyte, can be considered as ideally polarisable in a wide range of potentials, in so called "the double layer charging" region [1]. Numerous papers are devoted to the studies on the double layer capacitance, C_{dl}, in this potential range [e.g. 2–11], but only few papers [2,3,8,12–15] deal with the results of the measurements of the interfacial capacitance in potential range of Au surface oxidation. It was found that oxidation of Au leads to a significant decrease of the total interfacial capacitance at the interface between the electrode and the electrolyte, C_{int} [2,3,13–15]. The C_{int} of non-metallic oxides should contain contributions from two capacitances: the one of the double layer of the oxidised layer|electrolyte interface, C_{dlO}, and an additional one, related to non-metallic properties of the oxide/hydroxide, C_{ox}. These two capacitances are usually represented as connected in series [13,16–18] (Eq. (1)):

$$C_{int}^{-1} = C_{dlO}^{-1} + C_{ox}^{-1}. \tag{1}$$

For the thick oxidised layers one obtains $C_{ox} \ll C_{dlO}$ and $C_{int} \approx C_{ox}$.

In case of pure dielectric behaviour of the oxidised layer the C_{ox} can be represented as a capacitance of a parallel plate capacitor. For a semiconducting oxide the C_{ox} is identified as the potential dependent capacitance related to the space charge layer, C_{sc}, formed inside the oxide/hydroxide. The potential influence on C_{sc} under depletion conditions is described by Mott–Schottky equation [16,19] while potential dependent thickness of C_{sc}, the d_{sc}, can be calculated on the basis of Eq. (2) [19]:

$$C_{sc} = \frac{\varepsilon_0 \varepsilon_r A}{d_{sc}} \tag{2}$$

where A is the electrode area and ε_r and ε_0 are dielectric permittivity of the semiconducting layer and vacuum, respectively. When the polarisation of a semiconductor in the depletion region increases, the d_{sc} increases as follows from Poisson and Mott–Schottky equations and, for sufficiently thin oxidised layers, the space charge layer may cover the whole thickness of the oxidised layer, d_{ox} [20]. Under such conditions (Eqs. (3a) and (3b)):

$$C_{sc} = \frac{\varepsilon_0 \varepsilon_r A}{d_{ox}} \tag{3a}$$

or

$$C_{int} = \frac{\varepsilon_0 \varepsilon_r A}{d_{ox}} = C_{ox} \tag{3b}$$

with Eq. (3b) for $C_{int} \approx C_{sc}$. Eq. (3b) is applicable also for dielectric and insulating oxides oxides/hydroxides when $C_{int} \approx C_{ox}$.

Gold oxides are known to possess n-type semiconducting properties [21], as follows from photocurrent measurements and Mott–Schottky plot analysis [12,22–24]. An analysis based on a relation between C_{ox} and d_{ox} described by Eq. (3b) was applied in studies of Au oxidation in 1 M HClO₄ [13]. A linear relation between C_{int}^{-1} and d_{ox} was found and $\varepsilon_r = 16$ was calculated for 1.9 V vs. reversible hydrogen electrode but the value of C_{dlO} has not been determined [13]. Results

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presented in [12] indicate formation of the depletion layer in semiconducting Au oxides in potential range of surface oxidation of gold.

Conversely, contribution from the capacitance of the oxidised layer to C_{int} was disregarded in [2,3]. The effect of decrease of C_{int} upon surface oxidation was attributed exclusively to the influence of the electrode oxidation on C_{dlO} value [2,3]. In such case, C_{dlO} of the oxidised surface should be smaller than C_{dl} of the metallic one, even by 70% [3].

A short review of the works devoted to the double layer capacitance of the oxidised metal|aqueous electrolyte interface shows that the views concerning C_{dlO} values are often contradictory. Assumed or measured values of C_{dlO} are smaller [25], comparable [26] or significantly greater [27] than for metallic surfaces. Thus, the problem of the double layer capacitance of oxidised metal electrodes needs thorough analysis. Many electrocatalytic processes, including oxygen evolution or oxidation of many organic compounds, take place on oxidised Au surface [e.g. 28–31]. The knowledge about properties of the double layer of the oxidised electrodes is important for correct analysis of these processes.

This communication deals with the discussion of how the presence of thin, oxidised layers affects the interfacial capacitance of a polycrystalline Au electrode in an aqueous 0.1 M $HClO_4$ electrolyte. $HClO_4$ was selected due to low significance of anion adsorption [32,33]. Although some adsorption of perchlorates is expected to take place at potentials of "the double layer charging" region [34,35], the experimental evidence indicates that adsorption of the anions on the surface of oxidised gold can be neglected [3,36]. The value of the double layer capacitance of an oxidised, polycrystalline gold electrode in 0.1 M $HClO_4$ is discussed.

2. Experimental details

2.1. Electrodes and electrolyte

A three electrode system with a polycrystalline gold wire (geometrical area of 0.16 cm^2, 99.9%, Mint of Poland), Pt gauze wire and Ag|AgCl| 1 M KCl serving as working, counter and reference electrodes, respectively, was used. 0.1 M $HClO_{4(aq)}$ solutions were prepared with analytical grade reagents and a water from a Millipore system (18.2 MΩ cm). The electrolyte was deoxygenated with N_2 (5N, Air Products), during the experiments the gas stream was directed above the solution level. The experiments were carried out at 293 K (VWR 1146D thermostat). Au and Pt electrodes were degreased with acetone and further cleaned in a concentrated HNO_3. No other pre-treatment methods, such as flame annealing, were applied. The Au electrode was conditioned by a long-time continuous potential cycling in 0.1 M $HClO_4$ (0.44–1.55 V) until a stable voltammetry curve was obtained.

Cyclic voltammetry and electrochemical impedance experiments were carried out with a CHI660D (CHIInstruments) potentiostat and a Metrohm Faraday cage. Fig. 1 presents an example of cyclic voltammetry curves with cathodic sections recorded for various thicknesses of the oxidised layer. The surface oxidation currents are clearly distinguishable above ca. 1.09 V (A1 region), while the currents of Au oxides reduction constitute peak C1. The double layer charging region extends from the surface oxidation onset to the onset of hydrogen evolution reaction ($E^o_{H+/H2} \approx -0.2$ V).

Oxidation of Au electrodes in acidic electrolytes has been widely discussed in the literature [34,37–48]. In the present work the oxidised layers were formed by a constant potential oxidation at $1.55 \leq E_p \leq 1.8$ V for various polarisation times, t_p, up to 600 s. Under such conditions, up to 3 monolayers, ML, of surface Au atoms are oxidised to form compact oxides [38]. Oxidised layers with thicknesses above 3 ML have non-compact sandwich-like structures with layers containing oxides with different compositions, structures or physical properties [49–51]. Such non-homogeneity may complicate analysis of the capacitance data.

The real surface area was determined on the basis of the charge of peak C1, q_{ML}, obtained for a CV scan performed up to anodic current
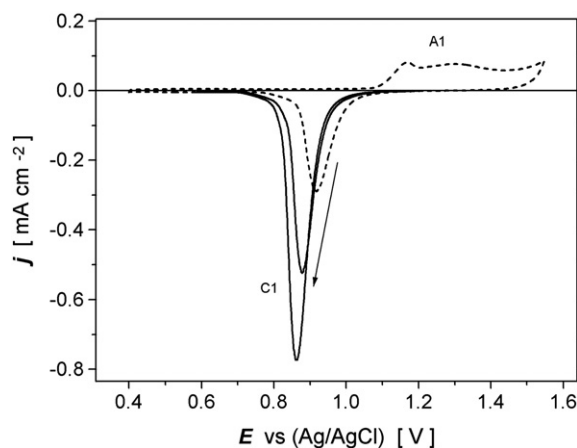

Fig. 1. Cyclic voltammetry curve of a polycrystalline gold electrode recorded in an aqueous 0.1 M $HClO_4$ with 50 mV s^{-1} at 293 K. Dashed line: continuous potential scan in potential range 0.40–1.546 V, solid lines: reduction peaks for 2 and 3 monolayers of the oxide formed by a constant potential polarisation at 1.70 and 1.80 V, respectively. The thickness of the oxide layer obtained during continuous potential scan up to 1.546 V (dashed line) was 1.3 monolayer. Currents due to surface oxidation (A1) and peak of reduction of the oxidised surface (C1) are indicated. The arrow indicates trend in changes in C1 peak when the oxide thickness increases.

minimum at 1.439 V. The value of the real surface area was calculated by dividing q_{ML} by the charge required for complete oxidation of the topmost layer of Au atoms, i.e. 386 μC cm^{-2} [1,52–55]. Estimated roughness factor was ca. 5.1. The thickness of the oxidised layer, d_{ox}, was calculated by dividing the charge of C1 peak by q_{ML} [56]. All respective parameters are expressed in respect to the real surface area.

2.2. Impedance measurements

The impedance experiments were carried out for the oxidised surface for $1.25 \leq E_m \leq 1.6$ V and for various oxide thicknesses. The impedance measurements at potentials of surface oxidation are complicated by limited stability of thin oxidised layer. The oxidised surface may change during long time acquisition of the impedance spectra due to a continuous oxide growth at potentials of the oxide formation [25,57] or due to a partial reduction of the oxides at potentials lower than that of their formation [58]. Proper selection of the method of data acquisition allows overcoming this problem.

The method applied in this work was similar to that described in [59]. For the oxidised surface the impedance was measured with a single frequency value at potentials, E_m, changing with 0.050 or 0.1 V steps between the upper limit of $1.45 \leq E_m \leq 1.6$ V and the lower limit of 1.25 V, i.e. in the region more positive than the apparent onset of reduction of the oxides. 10 frequencies from 10 kHz to 5 Hz with 5 mV amplitude were applied for each of the oxide thicknesses. The order of changes of the applied frequencies was random for each of the thicknesses and the direction of the potential scan for various AC frequencies was changed alternatively from cathodic (from the upper to the lower limit) to the anodic one (from the lower to the upper limit). The purpose of application of such procedure was to reduce the influence of possible evolution of the oxidised layer on collected data. This procedure can be considered as an equivalent of the impedance validity tests based on forward and backward frequency scans for constant potential measurements [25] or forward and backward potential scans for constant frequency experiments [59]. After completing collection of the impedance data, the oxidised layer was reduced and its thickness was determined.

The d_{ox} and E_m values were selected in such a way that the thickness of the oxide examined at a specified value of E_m was not smaller than that formed after at least 10 min. of polarisation at the same value of potential. Therefore, the upper limit of the potential scan ($1.45 \leq E_m \leq 1.6$ V) was a function of the oxide thickness with the less positive values for the