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In situ and operando observation of surface oxides during oxygen evolution reaction on copper

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ABSTRACT

Formation and dissolution of oxide on copper under transpassive conditions, i.e. during OER and transpassive dissolution, in alkaline electrolyte was investigated by a combination of electrochemical techniques and in situ and operando Raman and photoluminescence (PL) spectroscopy, as well as spectropscopic ellipsometry. Experiments were conducted under potentiodynamic and potentiostatic polarisation in 0.1M NaOH. In chronoamperometry experiments with steps between potentials, oxide thickness continued increasing beyond the onset of OER. The thickness dropped significantly from >10 nm to <5 nm $\approx$400 mV above the OER onset. The presence of CuO, Cu_2O and Cu_4O_3 was observed by Raman spectroscopy after the onset of OER. Correlating with the thickness drop, strong PL was observed at 1.55 eV, indicating the formation of singly charged oxygen vacancies V_O^+, following the classical PL spectrum interpretation from the literature. PL observation speaks against vacancy pair coalescence as mechanism of dissolution. After electrochemical experiments, the films were n-type semiconductors, not p-type conductors as expected for copper oxides. Results indicate that transpassive dissolution may be triggered by the instability of the oxide with respect to defect formation.

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1. Introduction

Many metals form a passivating oxide layer at potentials above their reversible dissolution potential [1–3]. In many cases, the oxide layers loose their protective properties above a certain potential, when transpassive dissolution occurs, accompanied by the oxygen evolution reaction (OER) if the potential is sufficiently high [1–3]. OER is in general linked to transpassive metal dissolution, which is in turn related to the stability of the surface oxide [4–7]. It is generally accepted that an oxide layer is present on the electrode surface during OER [8–14]. Hence, understanding the properties of the oxide film on the electrode during OER is critical to foster water splitting. In particular, it is relevant to investigate what drives the transition from the passive to the transpassive state, and how the state of the oxide is after this transition.

Three theoretical concepts are dominating the literature discussion to explain the transition from the passive to the transpassive state of an electrode: (i) the bipolar passive film model, (ii) the

surface charge approach, and (iii) the point defect model [15–19]. The bipolar passive film model treats the passive film as an ionic flow rectifier which limits ion adsorption and ingress, and prevents localized corrosion [15]. The surface charge approach assumes that the passive film consists of an n-type semiconductor|insulator|p-type semiconductor (n-i-p) structure [17]. According to this model, oxygen vacancies (donors) are formed during the film growth near the metal, while metal vacancies (acceptors) are generated during dissolution at the layer|electrolyte interface. In this model, the accumulation of positive and negative defects brings non-stationary film growth with complex processes including defect formation, uncontrolled film growth and dissolution. In the point defect model, the concentration of both positive and negative defects increases during passivity break down [19]. Moreover, it is proposed that condensation of the mobile cation vacancies at the film / electrolyte interface causes the destruction of the barrier layer. All aforementioned models were deduced from electrochemical methods and mathematical modelling [2]. During OER on certain metals, e.g. Co, Ni and Mn, the presence of metal cations in a high valance state was proposed [14,20–22]. These species were proposed to be active species for OER catalysis [14,21,22]. For a further understanding of the effect of OER on transpassive dissolution,

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it is crucial to assess the changes in the oxide film that are occurring during and after the onset of OER. Spectroelectrochemical techniques can be used to probe the interface in situ and operando during the electrochemical treatment.

In situ Raman spectroscopy has been used repeatedly to observe nature, stability of oxides during OER, and indirectly, also metal oxidation state [14,23–28]. Electrochemistry combined with Raman spectroscopy on Ni-Fe electrocatalysts identified the formation of different oxides and suggested that disordered NiOOH species are the catalytically active species for OER [23]. The presence of Fe in Ni catalysts was also found to increase the redox potential of the reaction of Ni(OH)$_2$ to NiOOH [24]. In situ UV-vis spectroscopy studies of an NiFeB catalyst suggested a darkening of the active catalyst during OER. Moreover, for this catalyst the presence of negatively charged NiOO$^-$ sites has been reported [25]. Formation of γ-NiOOH before the OER has been shown [25,26]. It was shown via in situ X-ray absorption spectroscopy that mixed Ni-Fe electrocatalysts include Ni^{III} species during OER [27]. For Co, in situ Raman studies showed that during OER, first Co$_3$O$_4$ formed, which then underwent a transformation to CoO(OH) [28]. Overall, in situ Raman spectroscopy studies suggest that metal cations in a high valance state and hydroxide species are the active species for OER for some specific systems. It remains to be discussed how general these observations are, e.g. on metals which are not usually occurring in high oxidation states. Further, it is necessary to understand the electronic structure of the oxides during running OER.

This work focusses on the structural and electronic properties of copper oxides during the electrochemical water oxidation. Cu was chosen as a model because it is a unique metal with its electron configuration 3d^{10} 4s^1 [29], and because it is one of the few metals whose oxides are predominantely p-type semiconductors [2]. Copper oxides have attracted considerable interest due to their low band gap ranging between 2.1 and 1.4 eV and also as being intrinsic p-type semiconductors [30]. The character of the oxide on a metal in the passive and transpassive state is critical for electron transfer reactions on its surface [2].

The aim of this study is to understand the relation between surface electronic state, defects, and nature of oxide under conditions of transpassive dissolution and OER in alkaline solution. The stability and oxide growth was investigated via in situ and operando spectroscopic ellipsometry. The structural properties were studied by in situ Raman spectroscopy, while electronic structure of the oxide layer was deduced both from in situ spectroscopic ellipsometry (SE) and photoluminescence (PL) spectroscopy. To connect the results from here to more versatile electron-spectroscopic characterisation methods typically employed in vacuum, optical post mortem ex situ investigations were complemented by X-ray photoelectron spectroscopy (XPS) analysing both photoelectron and Auger peaks. As comparison of ex situ and in situ Raman spectra has already shown significant differences for the copper system [31], the use of ex situ methods has been limited here.

2. Materials and methods

2.1. Sample preparation

Evaporated copper on silicon wafers was used as a working electrode for in situ spectroscopic ellipsometry experiments. Si(100) wafers (Siegert Wafer, Aachen, Germany) were cleaned with neutral detergent (Extran; VWR), rinsed with deionised water and 2-propanol, and finally dried. Firstly, a 10 nm chromium adhesion layer was deposited on the silicon surface by evaporation. Subsequently, copper was deposited by electron beam evaporation. Chromium and copper pellets with purity 99.999% (Wieland Edelmetalle, Pforzheim, Germany) were used. All evaporation was

carried out in a Leybold Univex 450 chamber. During evaporation, the pressure was around $6 \cdot 10^{-7}$ mbar. Copper was evaporated at an evaporation rate of 10 nm min^{-1}. Typically, a layer with thickness of 200 nm was obtained.

Polycrystalline Cu foil of 4 mm thickness with a purity of 99.5% (Goodfellow) was used as alternative working electrode for in situ Raman spectroscopy experiments.[1] The samples were mechanically ground with SiC paper up to 4000 grit and subsequently polished with polishing suspensions (3 μm, 1 μm and 100 nm SiO$_2$, pH = 9) to obtain a smooth surface. Afterwards, the sample was sonicated in ethanol for 5 min and dried in a nitrogen stream.

2.2. In situ spectroscopic ellipsometry (SE)

In situ spectroscopic ellipsometry experiments were performed using an SE 800 spectroscopic ellipsometer (Sentech Instruments, Krailling/Berlin, Germany) working in the wavelength range of 280-810 nm (1.5-4.4 eV). The measurements were carried out during both dynamic potential scan (cyclic voltammetry; CV) and potentiostatic polarisation (chronoamperometry; CA). The electrode potential was controlled by a Compactstat potentiostat (Ivium Technologies, Eindhoven, The Netherlands). The details of the in situ cell were described elsewhere [32,33].

A freshly prepared Cu sample was directly mounted in the optical-electrochemical cell, which was equipped with liquid flow connections. Cu tape was used to provide the electric contact to the surface of the sample. A Pt mesh counter electrode and an Ag|AgCl|3M KCl microreference electrode (DriRef-2SH, World Precision Instruments, Sarasota, FL, USA) were used to conduct the electrochemical part of the experiment. The electrode potential of the microreference electrode has been determined as +0.208 mV vs. standard hydrogen electrode by a calibrated Ag|AgCl|3M KCl electrode (Metrohm, Filderstadt, Germany). All electrode potentials reported in this work are referenced against Ag|AgCl|3M KCl. 0.1M NaOH was used as electrolyte. The electrolyte was externally purged with argon, and flowed through the cell with a rate of 2 mL min^{-1} using a peristaltic pump (Ismatec IDEX Health and Science, Glattbrugg, Switzerland). During the measurement, the pump rate was reduced to 10.6 μL min^{-1}. In this work, duration of a single ellipsometric measurement was 23.5 s.

Ellipsometric measurements during CV were conducted during scanning the electrode potential at a rate of 2 mV s^{-1} in the potential range of -1.3 V to 0.8 V. An initial potential of 0 V was applied to start the experiments with an initial cathodic scan to -1.3 V. After this reduction of the surface, the sample was oxidised and held at potentials up to 0.8 V. The CA experiments were performed starting from -1.0 V to clean the surface. Subsequently, the surface was oxidised in steps of 0.1 V up to 1.0 V. Each potential was applied for 100 s, except the initial reduction at -1.0 V, which was applied for 5 min.

Data analysis was conducted as described in detail previously [31,32]. In brief, an extension of Lekner's first order perturbation approach [34] without using any optical data modelling was used. The first order perturbation parameter J_1 for a substrate-layer-ambient system was defined in terms of dielectric functions, which is related to the complex refractive index $n + I k$, where $I = \sqrt{-1}$. Experimentally, J_1 was extracted from differences in measurements of ellipsometric parameters Ψ and Δ of the oxide free, reduced surface at low electrode potentials, and measurements of surfaces with different degrees of oxidation. Furthermore, the data analysis

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[1] In some experiments, Cu foil was used rather than evaporated Cu on Si to prevent ambiguities in the spectrum interpretation due to the presence of the extremely strong fundamental Si phonon at 520 cm^{-1}. This peak might appear if significant amounts of copper had been dissolved.