

In situ spectroscopic ellipsometry during electrochemical treatment of zinc in alkaline carbonate electrolyte

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ABSTRACT

In situ spectroscopic ellipsometry (SE, 297–820 nm, 4.4–1.5 eV) during electrochemical oxidation/reduction of zinc in alkaline carbonate electrolyte was performed using a specially designed optical–electrochemical cell. The growth and shrinkage of the interfacial layer on Zn was analysed on the basis of Lekner's first order perturbation theory. For non-absorbing thin films on metal surfaces, an algorithm has been derived to extract the thickness of a surface film directly from ellipsometric data without the need of optical modelling. During cyclic voltammetry (CV), a rapid decrease/increase in the layer thickness in the reduction/oxidation peak has been found. In the potential regime where the surface is oxide-covered, the layer thickness increases/decreases linearly with potential in anodic/cathodic scans. The density of the interfacial region in this regime is constant. During chronoamperometric experiments, a fast correlating jump in thickness was found after potential jumps. An ageing of the films is observed in the absorption spectrum (from the ellipsometric parameter Ψ), which shows changes until ≈ 30 min after potential jumps. Analysis of the current transients points to continuous dissolution of Zn.

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1. Introduction

Zn is one of the most important metals in applications. Due to its oxidation propensity, Zn is a very efficient sacrificial anode in cathodic protection, and used as metallic coating [1]. For most applications, as well as in the deposition process of metallic coatings, electrochemical reactions on the Zn surface are of great importance. In recent years, ZnO as a semiconducting material with wide band gap of 3.4 eV has generated interest due its electronic properties [1–4]. ZnO is commonly found in the corrosion products of Zn and its alloys [1,3]. The semiconducting properties of ZnO have been found to play an important role in the corrosion behaviour of Zn [1,5–7]. Electrochemical works have shown that oxide films with different properties form in different electrolytes, some passivating the zinc surface better than others [1,8].

A number of works focussed on the electrochemistry of zinc over a range of pH values. The passivation of zinc, typically in alkaline media, has been investigated, and different kinds of passivating films have been proposed [1,8–12]. Many passive films are amorphous or nanocrystalline [13,14], with broad distribution functions of distances and

coordination numbers instead of sharp, well-defined values of crystals [3,15,16].

The complexity of the chemical – in addition to electrochemical – reactions on the Zn surface, in particular at alkaline pH, implies the need for additional surface characterisation, preferably in situ, as many of the potentially formed species are prone to structural changes during the drying process needed for modern surface analytics in UHV [1,3,16].

Ellipsometry in general is a sensitive optical method for the measurement of the optical constants and thicknesses of thin films [10,17–19]. In situ ellipsometry can be performed during the modification process of a sample, which can be, e.g. the growth of a thin film, etching or cleaning of a sample [10,20–23]. The technique enables the determination of fundamental process parameters, such as growth or etch rates and variation with time of optical properties, the latter related to structural changes. Surface reactions on many metals and metallic materials, such as iron, copper, steel, aluminium, zinc and silver have been studied by this technique [2,9,21,24,25]. The thickness results obtained by ellipsometry, frequently as a result of fitting to an optical model, have been used to evaluate the growth mechanism and kinetics of oxide films on different metals [2,9,24,25]. One result important for Zn is that after reduction for more than 10 min at a potential $E = -1.4$ V vs. saturated calomel electrode, a Zn surface without the presence of any oxide can be produced [9].

Ellipsometric measurements can either be performed at a single wavelength, or in a spectroscopic ellipsometry (SE) experiment at multiple wavelengths. In the latter case, the recording of spectral changes

Abbreviations: CA, chronoamperometry; CV, cyclic voltammetry; OCP, open circuit potential; PCSA, Polariser-Compensator-Sample-Analyser; SE, spectroscopic ellipsometry; SHE, standard hydrogen electrode.

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provides information on the interfacial electronic structure. SE can also be coupled to electrochemical experiments to study electrochemical reactions. The electrochemical activation and oxide growth on glassy carbon electrode was in situ measured by SE combined with other techniques [26]. The electrochemical oxidation of nickel and precipitation of hydroxide films were observed by in situ SE [27]. Recently, in situ SE has been used to monitor the transient growth and thinning of the passive film on Fe in borate buffer [20]. Moreover, the growth of oxide on a Zn substrate in different atmospheres has been investigated with in situ SE [28].

In this work, SE was used for in situ investigations of electrochemical processes on the Zn/electrolyte interface. Two different electrochemical experiments were performed to study the transformations on the surface, (a) cyclic voltammetry (CV) with dynamic potential scans and (b) chronoamperometry (CA) at certain static potentials, both in carbonate solution. Carbonate electrolyte was used as the complete exclusion of carbonate is difficult under ambient conditions, but affects the reactivity. An analysis based on the perturbation parameter of Lekner [29] is introduced and used to analyse the SE data.

2. Materials and methods

2.1. Materials and sample preparation

Zn foil (99.95%, Goodfellow, Germany) with a thickness of 2 mm was cut into pieces of 20 mm × 30 mm. The sample was then mechanically ground with SiC paper up to 2500 grit, and subsequently further polished with final polishing suspension (100 nm SiO₂, pH = 9) to minimise surface roughness. After that, these samples were sonicated in ethanol for 10 min and dried in a nitrogen stream. To reduce possible contamination and further oxidation, the sample after this treatment was directly put in the cell for electrochemical measurement. As the surface is already oxide-covered and was exposed to carbonate, surface reactions on the time-scale of the transfer are expected to have only a limited effect on the layer. The oxide is protecting the Zn, and after transfer is immersed in a solution similar to the previous one, so that the oxide/electrolyte interface is expected to be in a similar state as before the transfer. Therefore, no special transfer chamber to avoid contact with the outside air was constructed.

2.2. Design of optical-electrochemical cell

Details of the design of the sample cell were described in a different context elsewhere [28]. In addition to the previously described application of measurements in different gas atmospheres, the cell can also be filled and rinsed with different solutions. Four optical windows enable measurements at two incident angles, 50° and 70°. The cell contains a conventional three-electrode electrochemical setup. A platinum mesh as counter electrode and an Ag/AgCl/3 M KCl electrode as reference electrode (DriRef-2SH microreference electrode, $E = +0.208$ mV vs. standard hydrogen electrode (SHE), World Precision Instruments Inc., USA) were used for electrochemical treatment. The connection of a metallic sample was realised by putting it in direct contact with the copper base part, which was connected to the working electrode connection of the potentiostat. In this work, all measurements were done at an incidence angle of 70°.

2.3. Electrochemistry

Electrochemical treatment of Zn was performed in 1.0 M Na₂CO₃ aqueous solution with a Gamry potentiostat (PHE200, Gamry Instruments Inc., USA) at room temperature (22 ± 2 °C). Most data presented here were obtained in the cell described above. In this cell, the electrode surface area is well-defined, which is why the results of these measurements are presented as current densities I .

For reference, additional CV measurements were conducted in a standard electrochemical cell in a conventional three-electrode setup, where the current is flowing between the working electrode (i.e. the surface under study) and a counter electrode, whilst the reference electrode is used to precisely measure the electrode potential difference to the working electrode [30]. In this cell, the surface area A was difficult to determine because the electrode was Zn sheet with two sides and also the faces and corners exposed to the electrolyte. Therefore, for this cell (only in Fig. 1) current i instead of I is given.

2.4. Ellipsometry

In situ SE measurements were performed using a UV–vis spectroscopic ellipsometer (SE 800, Sentech Instruments GmbH, Germany) working in the wavelength range 297 nm–820 nm (4.4–1.5 eV). In each measurement, data for 856 wavelengths were recorded on the instrument's CCD line detector. The light source was a Xenon lamp. For in situ measurements, the sample was mounted inside the optical–electrochemical cell described above.

In PCSA geometry [17], the polariser was fixed at an angle of +45°. Intensity measurements at 20 different analyser positions were used with and without a fixed retarder using the protocols implement in the instrument's control software. For each wavelength λ in the range between 297 and 820 nm, the ellipsometric angles Ψ and Δ were extracted [31]. Ellipsometric spectra were acquired during CVs with a scan rate of 2 mV s⁻¹ between +0.3 V and -1.7 V where acquisition of one spectrum took 43 ± 1 s, as well as during CA (-1.3, +0.2 and +1.2 V) measurements, where acquisition of one spectrum took 34 ± 1 s.

The angles Ψ and Δ were transformed into the ellipsometric ratio $\rho = \frac{r_p}{r_s} = \tan(\Psi) \exp(j\Delta)$ with $j = \sqrt{-1}$ [17]. This ratio of the amplitude reflection coefficients r_p and r_s for p - and s -polarised light, respectively, was analysed using a perturbation approach [29]. For individual layers and layer systems with a total thickness small compared to the wavelength, ρ is expanded to first order around a step profile in the dielectric function with ρ_0 , yielding [29]

$$\rho = \rho_0 - \frac{2jq_1K^2(q_1 + q_2)}{(q_1 - q_2)\epsilon_1^2\epsilon_2(q_1/\epsilon_1 + q_2/\epsilon_2)^2}J_1, \quad (1)$$

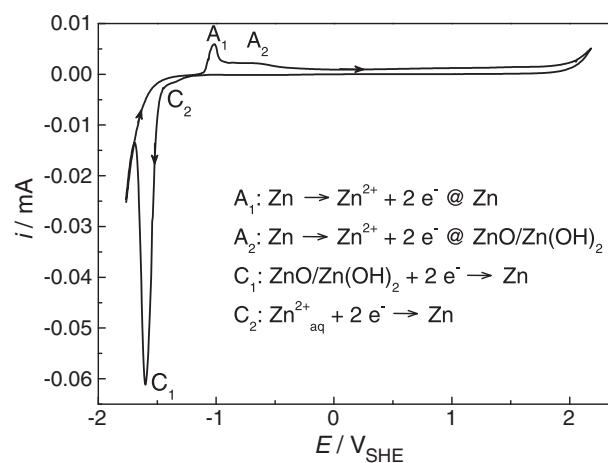


Fig. 1. CV of polycrystalline Zn in 1.0 M Na₂CO₃ in electrochemical cell. Scan rate: 50 mV/s. Peak assignments according to [11].

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