Comparison of different methods for measuring the passive film thickness on metals

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ABSTRACT

In situ electrochemical impedance spectroscopy (EIS) and ex situ X-ray photoelectron spectroscopy (XPS) measurements on electrogenerated zirconium oxide films on zirconium (Zr/ZrO$_2$) were used to quantify the oxide film thickness and resistivity profiles through the oxide. The EIS analysis presented here takes advantage of the high-frequency domain at which the constant-phase element (CPE) behavior of the oxide film reverts to a capacitive response and the Cole-Cole representations of the complex capacitance to extract the high-frequency capacitance of the oxide film without reference to the nature of the time-constant distribution within the oxide film. The film thickness of the ZrO$_2$ samples measured from the high-frequency capacitance of EIS were in good agreement with the thickness obtained from XPS. Moreover, the EIS analysis presented is based on the use of the integral solution of the power law model, which allows to obtain in one single EIS experiment, both the film thickness and the resistivity profile in the ZrO$_2$ film. This work suggests a convenient graphical method to extract film properties and serves to validate a key assumption of the power-law model for interpretation of CPE parameters in terms of physical properties.

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1. Introduction

The film thickness of passive layers represents a critical parameter in many relevant applications in electrochemistry such as photovoltaic or corrosion [1]. For this reason, several techniques have been employed to accurately measure the film oxide thickness on different metals. Those techniques are mainly based on either optical (ellipsometry) [2–4], electronic (X-ray photoelectron spectroscopy (XPS)) [5,6] or electric (electrochemical impedance spectroscopy (EIS)) [7,8] properties. Among them, EIS is a widely used technique, which allows investigation of different processes at the electrode/electrolyte interface [9]. Moreover, the use of an electrical equivalent circuit may represent a convenient approach for the analysis of electrochemical impedance data. However, it may result in difficulties for physical interpretation as soon as a time-constant distribution appears [10,11], which is usually represented in the equivalent circuit by a constant phase element (CPE). For instance, in the simplest case of a blocking film

on the electrode surface, the electrochemical impedance Z can be expressed as described in Eq. (1).

$$Z(\omega) = R_e + \frac{1}{(j\omega)^\alpha Q} \tag{1}$$

where R_e is the Ohmic resistance of the electrolyte, and Q and α are the CPE parameters (independent of the frequency ω). Eq. (1) can also be generalized to any electrochemical process, but for any final expression of the impedance, the CPE only corresponds to a pure capacitance when $\alpha = 1$. For this reason, we try to point out in this work the different limitations in the use of a CPE in the equivalent circuit for measuring the passive film thickness. Moreover, we provide a novel approach to exploit the EIS data, which allows to obtain both the film thickness and the resistivity values in the electrode/film and the film/electrolyte interfaces. So far, different formulas have been devised to extract an effective capacitance from the CPE parameters [12,13], since a CPE cannot be directly substituted by a capacitance. Nevertheless, such a transformation must be based on assumptions regarding the physical origin of the time-constant distribution. For instance, the Hsu and Mansfeld formula [13] has been used to investigate the electronic properties

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of passive films on Ni and Ti electrodes [14], or the inhomogeneous distribution of charge in the catalyst layer of a polymer electrolyte fuel cell [15]; whereas, the Brug formula [12] has been used to study the surface roughness of Au porous electrodes [16], to investigate differential capacitance on Ag [17] and Cu [18] single crystal electrodes, but also for the properties of passive films formed on Cr and C22 alloy electrodes [19]. The feasibility of some of those formula have been already discussed in Ref. [11], where it was highlighted that a key point for data analysis is to identify the origin of the time-constant distribution. In their seminal work, Jorcin et al. have used local electrochemical impedance spectroscopy (LEIS) to discriminate between radial and normal surface distributions [20], knowing that the latter corresponds to a distribution of physical properties inside of a thin layer such an oxide film. This approach has then been used to devise a power-law model that accounts for the influence of resistivity distribution along the normal direction to the electrode surface [21]. The power-law model has been already successfully applied in several systems such as aluminum oxides, oxide films on stainless steel, and human skin [22,23]. However, the use of a power-law model in a passive film on a pure metal with bounded resistivity values for the electrode/oxide film interface and oxide film/solution interface (namely ρ_0 and ρ_δ, respectively) introduces a large number of parameters that are difficult to determine experimentally. In particular, the application of this model brings up the product $\rho_\delta^{(1-\alpha)} \times \delta$, in which δ is the thin film thickness. Thus, it is not straight forward from this product to know the resistivity values or the film thickness independently. For this reason, we used here the integral expression for the power law model, which takes into account the high-frequency domain and allows to overcome that problem obtaining the film thickness from the high-frequency capacitance value. Finally, in order to validate the thickness value obtained by EIS in the high-frequency domain, another spectroscopic technique, XPS, was used independently to estimate ex situ the passive film thickness of the Zr/ZrO_2 samples. Furthermore, a specific attention has been devoted to the interpretation of the CPE behavior observed experimentally in terms of effective capacitance using an appropriate representation of the EIS data.

2. Experimental

2.1. Materials

The samples consisted of a pure Zr grade 702 rod (provided by CEZUS; chemical composition and heat treatment are given in Table 1) that were machined to a cylindrical electrode 0.4 cm in radius. The lateral wall was insulated with Teflon, exposing a disk electrode of 0.5 cm² surface area. The surface of the sample was polished in four successive steps using P2000 and P4000 SiC abrasive papers, and then diamond paste (3 μm) and alumina paste (0.03 μm). The Zr was then rinsed and degreased in an ethanol bath and in an ultrasonic ethanol bath for 15 min. The native oxide layer (ZrO_2) thickness was about 4 nm (vide infra), as is usually observed in the literature. The ZrO_2 film was electrochemically formed in nitric acid solution (4 M at 40 °C). The ZrO_2 film was grown by applying a constant potential to the sample (1.15 or 1.5 V/NHE), and varying the treatment duration in order to vary its

thickness (between 20 min and 2 hours). These experimental conditions were selected to obtained film thicknesses lower than 10 nm.

2.2. Methods

All the experiments were performed in a 250 mL cell in a usual 3-electrode configuration. The working and the counter electrodes were a zirconium disk-electrode and a platinum basket, respectively. The reference was a mercury sulfate electrode (Hg-Hg$_2$SO$_4$—MSE, $E = 0.658$ V/NHE) separated from the electrolyte with a salt bridge. All the potentials in the paper are given vs. NHE. The electrochemical device used for all the experiments was a VSP workstation (Biologic). The electrolytic solution was a 4 mol/L HNO$_3$ solution prepared by diluting R.P. NORMAPUR PROLABO 52.5% solutions with demineralized water.

2.3. Characterization

EIS was performed during the deposition procedure and at the end of the oxide growth procedure. Due to the fact that the phase shift shows a clear CPE behaviour in high frequency range, those experimental results were analyzed using the power law model [21,22], which allows the interpretation of EIS spectra and specially the oxide film characterization to be performed on a physical basis. XPS analyses were also performed on the Zr/ZrO_2 samples providing information about chemical composition and oxidation state of the element forming the outer layer (∼10 nm analysis depth). XPS analyses were carried out with a Thermofisher Escalab 250 XI spectrometer using a monochromatic X-ray Al Kα source. The instrument was calibrated in energy with the silver Fermi-level (0 eV) and the $3d_{5/2}$ core level of metallic silver (368.3 eV). The C-$1s$ signal was used to correct a possible charge effect: the C—C/C—H contribution of C-$1s$ spectra was fixed at 285.0 eV. The analysis zone consisted in a 900 μm in diameter spot. The data processing was performed using the commercially available Avantage software, which allowed the estimation of the oxide layer thickness.

3. Results and discussion

3.1. Film formation and XPS characterization

The surface oxide thickness (δ) was estimated from the analysis of the XPS spectrum using the Zr 3d (Zr-3d5/2 = 183.2 eV and Zr-3d3/2 = 185.6 eV) to metal (Zr-3d5/2 = 179.2 eV and Zr-3d3/2 = 181.6 eV) peak ratio (I_{ox}/I_{met}) according to the relationship described in Eq. (2).

$$\delta = \lambda_{ox} cos(\theta) ln \left(\frac{N_{met} \lambda_{met}}{N_{ox}} \frac{I_{ox}}{\lambda_{ox}} \frac{I_{ox}}{I_{met}} + 1 \right) \qquad (2)$$

where $\frac{N_{met}}{N_{ox}}$ is the ratio of the volume densities of Zr atoms in metal to oxide, θ is the angle between the normal of the sample surface and the analyzer (set at 0° in this work), and λ_{met} and λ_{ox} are the inelastic mean free paths (corresponding to the average distance of an electron between two inelastic collisions) in the metal and in the oxide, respectively. In Eq. (2), the major uncertainty lies in the determination of the mean free path values, which can be

Table 1
Chemical composition and heat treatment of Zr grade 702 (Heat treatment: 15 min at 1060 °C with cooling under argon atmosphere).

Zr + Hf (wt%)	Hf (wt%)	Fe + Cr (wt%)	O (wt%)	C (ppm)	Cu (ppm)	H (ppm)	N (ppm)	Ni (ppm)
≥99.2	≤1.0	≤0.1	≤0.135	≤58	≤10	≤25	≤29	≤18