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Short communication

Electronic properties of passive films from the multi-frequency Mott–Schottky and power-law coupled approach

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ABSTRACT

The electronic properties of the passive film formed on pure chromium in an acidic sulfate medium at 30 °C was studied by using the multi-frequency Mott–Schottky approach and the point defect model. Conversely to common Mott–Schottky experiments, the relevance of the multi-frequency Mott–Schottky analysis relies on the determination of the space charge capacitance from a large frequency range impedance diagram. To analyze the Constant-Phase-Element behavior commonly observed for the impedance diagrams which characterize the passive film, the power-law model was used and allowed to determine the space charge capacitance. The consistency of the results showed that it was relevant to combine the power-law model to the predictive point defect model. The aim of this study is to extract the semi-conductive parameters of a passive film from impedance measurements using a sensitive analytical method.

1. Introduction

Passive films are thin compact oxide/hydroxide layers that act to limit detrimental electrochemical reactions at the metal/environment interface. Among different processes, the transfer of electrons and the migration of ionic species through them are the main features governing the efficiency of their barrier properties [1,2]. In the point defect model (PDM) which accurately describes the electrochemical processes at metal/passive film and passive film/electrolyte interfaces, point defects are the ionic species of major interest [2,3]. Indeed, their distribution and their migration through the passive film are closely related to passive film growth, steady state and breakdown kinetics. Point defects, cation or anion vacancies within the oxide lattice, are also considered as charge carriers as in non-equilibrated stoichiometric oxide. Consequently, they provide the passive film with semi-conductive properties. According to the PDM, the electronic properties are related to the electrochemical processes and have to be thoroughly studied.

Based on the band structure approach at the semi-conductor/electrolyte interface, the electronic properties of passive films are generally investigated by differential capacitance measurements according to the Mott–Schottky (MS) theory [4]. In conventional MS experiments, space charge capacitance is usually estimated from single-frequency impedance measurements performed at different imposed potentials on the passive range. Nevertheless, a so-obtained capacitance measurement is closely dependent on the choice of the selected frequency which may alter the electronic properties estimation, even at high frequency [5,6]. Since the space charge capacitance is extracted from the fitting of a wide electrochemical impedance spectrum, a multi-frequency MS experiment does not have this disadvantage [6,7]. Generally, the metal/electrolyte interface shows a Constant-Phase-Element (CPE) behavior, which can be explained by surface heterogeneities or the non-uniform distribution of physical properties, for example, leading to a frequency dispersion of time constants. The accuracy of the electronic properties determination depends closely on how the capacitance is extracted from CPE parameters [7]. Recently, the power-law model (PLM), proposed by Hirschorn et al., gives physical meaning to the CPE behavior observed for passive films, attributed to the normal distribution of resistivity through passive film, and offers an approach on how to extract the capacitance [8–10].

Nowadays, very few studies combine multi-frequency MS experiments and the PLM to study the semiconductive properties of passive films. Even fewer studies compare the results obtained with the PDM to confront them. The aim of this communication is to prove the relevance and the physical meaning of a coupled approach between multi-frequency MS experiments and the PLM to describe the semiconducting characteristics of pure chromium passive films formed at different potentials in a pH 2 sulfate solution at 30 °C. The results were discussed with regard to the PDM.

2. Theoretical approach

The semi-conductive nature of a passive film is commonly determined by using the MS theory, which enables us to determine

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the carrier density N_q from the representation of the space charge capacitance (C_{sc}) as a function of the applied potential:

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{e\varepsilon\varepsilon_0 N_q}\right)\left(-E + E_{fb} - \frac{k_B T}{e}\right) \tag{1}$$

where e is the electron charge, ε the relative dielectric constant of the oxide, ε_0 the vacuum permittivity, k_B the Boltzmann constant, T the absolute temperature and E_{fb} the flat band potential. Eq. (1) refers to the MS relationship for a p-type semiconductor as usually determined for chromium oxide film [11,12]. In the present study, C_{sc} is extracted using a PLM for each impedance diagram.

The PLM explains the CPE behavior by 3D distribution of the resistivity, supposing that the dielectric constant of the film is constant through the passive film thickness. According to this approach, the impedance of a material showing a CPE impedance response is:

$$Z(\omega) = g\frac{\delta\rho_\delta^{1-\alpha}}{\left(\rho_0^{-1} + j\omega\varepsilon\varepsilon_0\right)^\alpha} \tag{2}$$

The space charge capacitance of a passive film could be expressed as:

$$C_{sc,\mathrm{PL}} = Q(\rho_\delta\varepsilon\varepsilon_0)^{1-\alpha}g \tag{3}$$

where

$$Q = \frac{(\varepsilon\varepsilon_0)^\alpha}{g\delta\rho_\delta^{1-\alpha}} \tag{4}$$

and

$$g = 1 + 2.88\left(\frac{1}{1-\alpha}\right)^{-2.375} \tag{5}$$

with α and Q the CPE parameters, δ the passive film thickness, Ω the pulsation and ρ_0 and ρ_δ the resistivity at the pure chromium/passive film and passive film/electrolyte interfaces, respectively.

3. Experimental

The electrochemical measurements were performed using a double wall three-electrode cell. It contained a platinum counter electrode, a mercury/mercurous sulfate reference electrode (MSE) and a pure chromium (<99.7%, from Goodfellow® Company) 0.5 cm^2 sample cross-section area as a WE. Prior to any experiments, the WE was ground with SiC paper down to 1200. The electrolyte was a naturally aerated sulfuric aqueous solution (pH 2), containing 10 g.L^{-1} of sodium sulfate.

All electrochemical measurements were performed at 30 °C, using a GAMRY Reference 600™ potentiostat. In order to reduce the native oxide film formed in contact with air, a cathodic polarization at −1.7 V/MSE for 10 min was firstly applied to the WE (i). Then, under different potentiostatic conditions (from −0.8 V/MSE to +0.4 V/MSE), the current density was measured for 1 h (ii). After each step (ii), to obtain the multi-frequency MS plot, successive impedance measurements were performed from −0.4 V/MSE to +0.4 V/MSE (iii). The impedance diagrams were obtained over a frequency range of 1 kHz to 1 Hz with 10 points per decade using a 10 mV peak-to-peak sinusoidal voltage, and were fitted by using the PLM with MATLAB software.

4. Results and discussion

The current density measured after 1 h of polarization (ii) in the applied potential range from −0.8 V/MSE to +0.4 V/MSE, varied from 5.5 10^{-8} to 4.5 10^{-7} A cm^{-2}. This result is in agreement with the fact that a chromium passive film is a cation conducting formation film. The average value obtained on the passive plateau was 2.7 10^{-7} A cm^{-2}. It is assumed that the steady-state was reached for each passive film growing condition.

For each condition, impedance measurements were performed in the applied potential range corresponding to the validity domain of MS theory. Fig. 1a–c shows some impedance diagrams obtained for the passive film grown at +0.30 V/MSE for 1 h, at −0.30 V/MSE (Fig. 1a), 0 V/MSE (Fig. 1b) and +0.30 V/MSE (Fig. 1c). Independently of the applied potential, the impedance diagrams are characterized by a single time constant attributed to the passive film. The impedance modulus at 1 Hz decreases when the applied potential becomes more anodic. This result is in agreement with the transpassive dissolution of the passive film at high anodic potentials. The CPE parameters (α and Q) were graphically determined for each impedance diagram [13]. Then, the impedance diagrams were analyzed by using the PLM by taking ε fixed to 12 [14]. The experimental and fitted results are very close (Fig. 1 a–c). The passive film thicknesses (δ) obtained from the fitting were the same order of magnitude that determined from previous XPS analysis [15]. For the film grown at +0.30 V/MSE, the resistivity decreases from 10^{12} Ω.cm (ρ_0) to 10^5 Ω.cm (ρ_δ) through the chromium oxide. The resistivity ρ_δ decreases from 1.04 10^5 Ω.cm to 10^5 Ω.cm in the range of applied potential [−0.30 V/MSE; +0.30 V/MSE]. This evolution of the resistivity may explain the decreasing of the impedance modulus at 1 Hz when the potential becomes more anodic. It should be emphasized that the value of ρ_δ is strongly dependent on the α parameter [16]. To our knowledge, very few data are given for these physical parameters but they are coherent with the limit resistivity obtained for others systems [7,9,17].

For the passive film grown at +0.30 V/MSE for 1 h, the evolution of space charge capacitance, obtained from Eq. (3), as a function of the potential is plotted on Fig. 1d. The MS representation highlights two negative slopes, typical of p-type semiconductor behavior with inhomogeneous charge carrier distribution [12]. The curve reaches a maximum corresponding to the inversion potential below which the main electronic carrier changes from the electron hole to the electrons. The p-type semi-conductive nature indicates that cation vacancies are predominant point defects within the oxide [2]. The flat band potential (E_{fb}) is equal to 0.2 V/MSE and corresponds to chromium oxide in acidic solution. This result is representative of the applied potential range of pure chromium passive film formation (from −0.8 V/MSE to +0.4 V/MSE).

From the MS relationship carried out for each passive film conditioning, the evolution of the main charge carrier density as a function of the film forming potential is plotted on Fig. 2. The curve shows an exponential decrease of N_q when the potential increases. This trend is consistent with the PDM. The exponential decay of N_q with applied potential is related to the considered concentration profiles and the linear dependence of the passive film thickness [2,3]. At the steady-state, the passive film thickness (L_{ss}) is to be expressed as a function of the film formation potential V as followed:

$$L_{ss=\frac{1-a}{E_0}V+B} \tag{6}$$

Where $\frac{1-a}{E_0}$ is the anodizing constant with E_0 the electric field strength and a the polarizability (generally $0.2 < a < 0.8$ [3]), and B depends on the physicochemical conditions and the electrochemical reaction kinetics [18]. Fig. 3 shows the linear evolution of the film thickness obtained from the PLM (δ_{PL}) as a function of the film forming potential. Supposing that the steady-state is reached in the [0; 0.3 V/MSE] range of potential and taking the polarizability equals to 0.521 [3,19], the anodizing constant is found to be equal to about 7 Å/V and the electric field strength E_0 is 7.0 10^6 V.cm^{-1}. It could be emphasized that these values obtained from the space charge capacitance extracted from the PLM are in agreement with previous studies [3,20,21].