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Kinetics and mechanism of palladium electrodeposition on graphite electrode by impedance and noise measurements

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ABSTRACT

The kinetics of palladium electrocrystallization from 0.01 M $Pd(NH_3)_4Cl_2$, NH_4Cl, and NH_4OH bath (pH = 10) is studied by means of cyclic voltammetry (CV), impedance spectroscopy (EIS) and electrochemical noise (EN). Crossovers in cyclic voltammograms demonstrate that the deposition of palladium proceed via a nucleation/growth. A model for palladium deposition with multi-step mechanism is proposed to account for electrode kinetics. Electrodeposition mechanism takes place trough interfacial reactions with reaction intermediates. Parameters of impedance model in this system can be calculated from the fitting of experimental data to the Faradaic impedance function derived theoretically. With the aid of an equivalent circuit it is possible to determine the charge transfer resistance and the resistance and the capacity of lattice formation. The electrochemical noise is shown to originate from the random birth of edges and therefore birth rate of monolayers was obtained.

1. Introduction

Palladium has excellent physical and chemical properties such as corrosion and wear resistance, thermal stability, and high catalytic activity for various chemical reactions, so that it is mainly used for industrial applications like catalysis and electrical devices [1,2]. Palladium thin films deposited on gold and platinum substrates demonstrate extremely high catalytic activities in the electrooxidation reaction of small organic molecules such as formaldehyde and formic acid [3–5]. The electrodeposition of palladium has been studied on various electrodes such as polymer matrix, and porous stainless steel electrode [6–9]. The electrochemical layer-by-layer growth of the palladium was reported on copper and a gold single crystal electrode [10–12].

Electrochemical impedance spectroscopy (EIS) is an example of frequency response analysis which has proved to be useful in both applied and fundamental electrochemical studies [13–15] as well as in other disciplines [16]. The power of the technique is its ability to distinguish among the interfacial processes with different time constants [17]. EIS is a common and useful technique for studying metals electrocrystallization [18–22]. One of its advantages is the possibility of studying the relaxation of electrode surface from adsorbed species and growth of layers. The impedance spectra of the deposition processes of metals usually show one or several relaxations (capacitive or inductive) [23]. The surface diffusion of Adatoms can be a determining step in the overall mechanism of electrocrystallization (Adatoms model) [24–27].

Two dimensional nucleation and growth and the interactions between growth centers have been extensively studied [28–31]. The impedance characteristic of the response of the deposition successive layers to potential steps of small amplitude have also been studied [32,33]. The multilayer formation has been treated as a cascade process, in which the $(n + 1)$th layer is born out of the nth layer so that the current can be evaluated by a recurrence relationship. Such an approach to multilayer formation implies both the birth by nucleation and the death as a consequences of overlap of each monolayer (model based on random birth and deterministic growth of monolayers). It is known that the formation and development of growth centers during electrodeposition can give rise to a variation of the active area of the electrode and the subsequent changes of the process overpotential. It has been shown that the relaxation of the active area can generate either an inductive or a capacitive loop characterized by distributed time constants [34]. From a different approach based on the assumption of successive monolayers randomly generated and obeying a given aging law, an analytical expression for the electrode impedance has been derived [34].

The impedance model construction is frequently the final aim of an experimental impedance study [35]. As the aim of impedance modeling is knowledge enhancement, the applied models should possess physical significance, i.e., they should correspond to the structure and the properties of processes taking place in the system under study [36,37]. The parameters identification can be made by using these impedance models that gives important information about the influence of the physical parameters [38–41].

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Electrochemical noise measurements have traditionally been analyzed in the frequency domain using power spectral density plots by means of fast Fourier transform (FFT). Xiao and Mansfeld [42,43] have extended the analysis in the frequency domain by introducing spectral noise plots in which the ratio of the FFT of potential and current noise is plotted as a function of frequency in the Bode plot format. Therefore, it has some analogy with the modulus of the electrode impedance. During metal electrodeposition, the electrochemical dynamical parameters, such as current and potential will fluctuate spontaneously, which has been designated as electrocrystallization noise [44–46]. It was shown by Budevski et al. [47,48] that a well-defined electrocrystallization system under constant cathodic overpotential or current, exhibit fluctuations which should contain more information on 2D nucleation and crystal growth process than commonly expected.

The aim of this work is the analysis of impedance and noise characteristics of the palladium electrocrystallization process from 0.01 M $Pd(NH_3)_4Cl_2$, NH_4Cl, and NH_4OH on a graphite substrate. The analysis of the theoretical impedance function provides important information on the process parameters. This information allows the EIS spectrum simulation and, therefore, predicts the system behavior with regard to the variation of the experimental conditions.

2. Experimental

Materials used in this work were analytical grade of Merck origin. The experiments were carried out at 25 °C and pH = 10 in a conventional three-electrode cell. The working electrode was a graphite rod mounted in Teflon with an apparent exposed area of 0.0314 cm^2. Its potential was monitored against an Ag/AgCl with saturated KCl electrolyte reference electrode. A large graphite rod was used as the counter electrode.

Prior to each experiment, the surface pretreatment of working electrode was performed by hand polishing of the electrode surface with successive grades of emery papers down to 3000 grit up to a mirror finish. The polished electrode was then degreased with acetone and washed with running, doubly distilled water.

The methods of cyclic voltammetry, impedance spectroscopy was powered by EG&G model 273A potentiostat/galvanostat and Solartron model 1255 frequency response analyzer runs by a PC through M270 and M398 software. Electrochemical noise measurements were performed by a potentiostat/galvanostat Solarton model 1266. The system is run through corrware commercial software's. The frequency range of 100 kHz to 15 mHz and the modulation amplitude of 5 mV were employed for impedance measurements. Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of home written least square software based on the Marquardt method for the optimization of functions and Macdonald weighting for the real and imaginary parts of the impedance [49,50].

3. Result and discussion

Cyclic voltammogram obtained in the potential range of 0 to −1.1 V vs. Ag/AgCl with a scan rate of 10 $mV\,s^{-1}$ is presented in Fig. 1a. During the scan in the cathodic direction, significant crystallization overpotential can be noticed before palladium electrodeposition occurs; the cathodic current density increases at potential more negative than −0.71 V. The reduction peak is observed at −0.87 V and, at more negative potential, current density increases again due to the hydrogen evolution. The reverse scan shows initially a decrease in current density, and two crossovers are observed, one at more negative than crystallization potential and the other at zero current, characteristic of metal deposition onto substrates of different nature. From Fig. 1, equilibrium potential of the system can be obtained −0.6 V vs. Ag/AgCl. On reversing the scan direction, metal already deposited on the electrode surface continues to grow as a result of the deposition reaction remaining thermodynamically and kinetically favorable. In the following reverse scan, at more positive potential, an anodic peak appears which is associated with the stripping of Pd formed during the scan in negative direction. The relative location of the

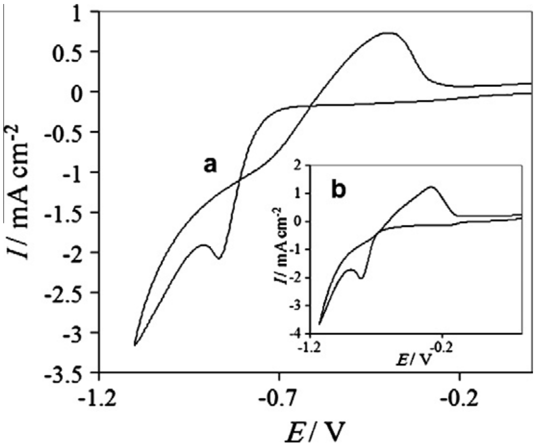

Fig. 1. (a) First cycle of voltammogram of the palladium electrodeposition from 0.01 M $Pd(NH_3)_4Cl_2$, NH_4Cl, and NH_4OH bath. The scan began at 0.2 V vs. Ag/AgCl with a scan rate of 10 $mV\,s^{-1}$. (b) Fifth cycle of voltammogram of the palladium electrodeposition with a scan rate of 10 $mV\,s^{-1}$.

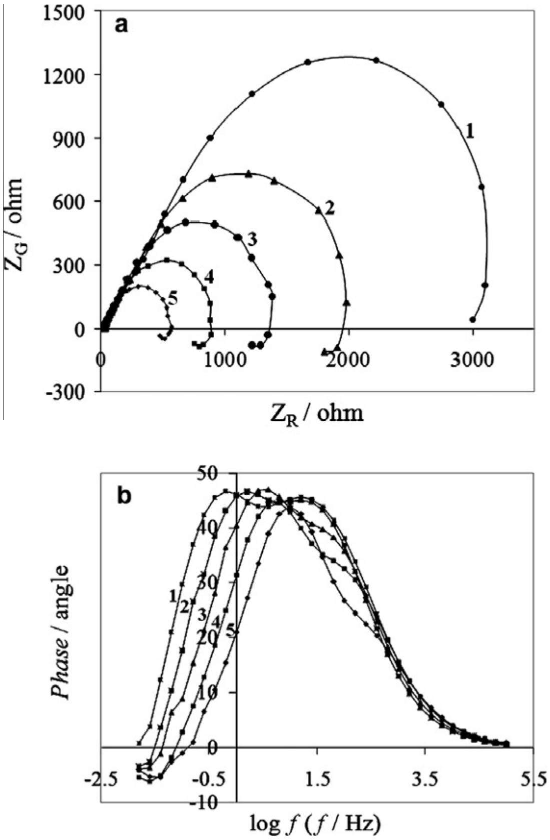

Fig. 2. Experimental (a) Nyquist diagrams and (b) phase shift plots measured for deposition of palladium on graphite at different cathodic potential: (1) −0.75, (2) −0.77, (3) −0.79, (4) −0.81 and (5) −0.83 V vs. Ag/AgCl (*f* is frequency).