Journal of Electroanalytical Chemistry 774 (2016) 95–101

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

An electrochemical study of the nickel hydroxide-gold modified electrode employing the surface resistance technique

R. Tucceri

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CONICET, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, (1900) La Plata, Argentina

ARTICLE INFO

Article history:
Received 2 December 2015
Received in revised form 25 February 2016
Accepted 6 May 2016
Available online 7 May 2016

Keywords:
Nickel hydroxide-gold modified electrode
Surface resistance
Nickel hydroxide surface coverage
Nickel adatoms
Field and size effects in thin film electrodes

ABSTRACT

Simultaneous cyclic voltammetry (CV) and surface resistance (SR) measurements were employed to study the electrochemical behaviour of the nickel hydroxide-gold modified electrode. To this end, firstly, gold film electrodes of different thicknesses were synthesized, and their CV and SR responses within the potential regions corresponding to hydroxide ion adsorption (OH_{ads}) and gold oxide (AuO) formation in alkaline medium were analysed. Then, these gold film electrodes were modified with different nickel hydroxide surface coverages, and their CV and SR responses were compared with those of bare gold films within the same potential regions and electrolyte solution. While cyclic voltammetric responses of the bare gold film electrode and the nickel hydroxide-gold film modified electrode are practically the same within the whole potential range $-0.5\ V < E < 0.35\ V$ (SCE), SR responses are the same only within the potential range $-0.3\ V < E < 0.35\ V$. Strong differences between the SR responses of the bare gold electrode and the nickel hydroxide-gold modified electrode within the potential range comprised between −0.5 V and −0.3 V are observed. SR data were interpreted in terms of the field effect and size effect theories formulated to study adsorption processes at thin metallic films. With regard to the bare gold film electrode, the field effect theory allows one to conclude that within the potential region corresponding to hydroxide ion adsorption, 77% of the electron density charge of gold is involved in the hydroxide ion–gold interaction. Besides, a linear relation between the surface resistance change (ΔR) and the degree of oxidation (θ_{ox}) at fixed gold film thickness (ϕ_m) is obtained within the potential region corresponding to gold oxide formation. In agreement with the size effect theory, the $\Delta R/\theta_{ox}$ slope exhibits a linear dependence on ϕ_m^{-2}. The same SR responses for the nickel hydroxide-gold modified electrode and the bare gold electrode within the potential range $-0.3\ V < E < 0.35\ V$ indicate that the nickel hydroxide layer does not directly interact with the gold film surface. However, after the reduction of OH_{ads} and AuO layers, at potential values more negative than −0.3 V (SCE), an increase of the surface resistance is observed for the nickel hydroxide-gold modified electrode, which was attributed to nickel adatoms that directly interact with the gold film surface. On the basis of the electron conduction scattering model employed to describe the interaction of a metal film surface with a foreign atom layer, one can conclude that nickel film growth involves an initial stage in which nickel islands and then, compact structures are formed.

1. Introduction

Surface resistance (SR) changes of thin metal films have been widely used as a tool to study surface coverage in gas phase [1] as well as in electrochemistry [2]. The resistance of a thin metal film is affected by the presence of lattice defects, foreign entities on its surface and the thickness, which hinder the movement of the electrons in the sample. The SR technique has contributed to the knowledge of the microscopic structure of the metal/solution interface, particularly about the role played by the conduction electrons of the metal in different electrochemical processes [2]. The technique has also been recently extended to study the redox process of an electroactive material, such as poly(*o*-aminophenol), deposited on a gold film electrode [3,4]. In order to extend the use of the SR technique to study different electrochemical systems, in this work we have focused on analysing the effect of nickel hydroxide layers on the electron transport properties of a gold film electrode. Nickel hydroxide is an important electroactive material that, supported on different electrode materials, has been used for many applications of interest [5–8]. In this work, a thin gold film electrode was modified with different nickel hydroxide surface loadings, and the electrode behaviour within potential values corresponding to hydroxide ion adsorption and gold oxide formation was simultaneously studied employing cyclic voltammetry (CV) and SR. While CV allows one to monitor the electroactivity of the nickel hydroxide layer deposited on the gold electrode in terms of ion and electron exchange with the

---

E-mail address: rtucce@inifta.unlp.edu.ar.

http://dx.doi.org/10.1016/j.jelechem.2016.05.006
1572-6657/

solution, complementary SR measurements allows one to study the nickel hydroxide/gold interface in terms of the electron motion change of the gold base substrate due to the presence of the nickel hydroxide layer. To our knowledge, this is the first example of a study on the gold/nickel hydroxide interface employing the SR technique. However, as SR studies of gold film electrodes in alkaline medium are also scarce, we firstly study the SR response of the sole substrate (gold film) in alkaline medium and then, that of the nickel hydroxide-gold modified electrode. Predictions of the field effect and size effect theories formulated for metallic film thicknesses in the order of the mean free path of the conduction electrons [2] are employed to explain the observed SR response. In this work our interest is only to study the effect of nickel species on the conduction properties of the gold film electrode, and then, these species are here considered as "foreign entities" on the gold film surface that impede the electron movement (scatterers) along the film, increasing the resistance of the substrate. Further work is in progress to elucidate the chemical and physical transformations that alter the conducting properties of a gold film after deposition of nickel hydroxide. As the SR technique can be considered as a non-traditional approach in electrochemistry, a brief interpretation of the resistance changes exhibited by a thin metal film in terms of both the surface charge induced by electric fields and the diffuse scattering of conduction electrons from the inside of the metal film to the metal film surface is given to the readers in Section 3.

2. Experimental

2.1. Synthesis of gold films and nickel hydroxide-gold film modified electrodes

Firstly, five gold film electrodes of different thicknesses (ϕ_m = 30 nm; 24 nm; 18 nm; 14 nm and 10 nm) were synthesized to study the SR response of the bare gold electrode in the presence of an alkaline solution. Gold films were prepared by vacuum evaporation, as was previously described [2,9–11]. The relationship between the length, *l*, and the width, *w*, ($G = l/w$) of these gold film electrodes was 25. The electrode area was 0.69 cm^2. It is well-known that thin metal films obtained by evaporation (low rate of evaporation) exhibit specular surfaces with a relatively low number of defects as compared with a massive metal surface (see Section 3). Each gold film electrode was conditioned electrochemically by cycling the potential between −0.5 V and 0.6 V for 150 cycles at a scan rate of 10 mV s^{-1} in a deoxygenated 0.2 M Na(OH) solution. Then, five series of eight nickel hydroxide coated gold film electrodes each were prepared (see columns 3 to 7 in Table 1) to study the CV and SR responses of the nickel hydroxide-gold modified electrode. The thickness of the eight gold films of each series is indicated in the heading of columns 3 to 7 in Table 1. The nickel hydroxide surface coverage of each one of the eight films of each series is listed in column 2 of Table 1. It should be indicated that the use of an evaporated gold film as base electrode to deposit nickel hydroxide films leads to reproducible CV and SR data. The good reproducibility can be attributed to the use of a smooth and renewable gold surface, obtained by evaporation, to deposit the nickel hydroxide film in each experiment. Nickel hydroxide was deposited on the gold film electrodes employing the procedure described elsewhere [12], that is, each one of the eight gold films of each series, after being subjected, for a different time period, to a constant potential of −0.5 V in a deoxygenated 0.5 M $Ni(NO_3)_2$ solution, was transferred to a deoxygenated 0.2 M Na(OH) solution and cycled between −0.5 V and 0.6 V (vs. SCE) at 10 mV s^{-1} until a stable voltammogram was achieved (150 cycles). This procedure allows one to obtain different nickel hydroxide surface coverages ($\Gamma_{Ni(OH)2}$) on each one of the eight films of each series. The surface coverage of the different $Au/Ni(OH)_2$ modified electrodes was estimated from the voltammetric oxidation (or reduction) charge ($Q_{Ni(OH)2}$) evaluated in the supporting electrolyte solution (0.2 M NaOH) by using the equation $\Gamma_{Ni(OH)2} = Q_{Ni(OH)2} / nFA$, where $Q_{Ni(OH)2}$ is the anodic (or cathodic) voltammetric charge corresponding to the oxidation (or reduction) process, assuming that all the nickel redox sites are electroactive on the voltammetric time scale; *F* is the Faraday's constant; *A* is the geometric surface area of the gold electrode; and *n* is the number of electrons transferred in the Ni (II) ⟺ Ni (III) oxidation (reduction) reaction. As can be seen from column 2 of Table 1, the sequence of $\Gamma_{Ni(OH)2}$ values was always the same for each one of the five series. A large-area gold grid was used as counter-electrode in all experiments. All the potentials reported in this work are referred to the SCE.

2.2. Cyclic voltammetry and surface resistance measurements

Firstly, CV and SR measurements within the potential region comprised between −0.5 V and 0.6 V were performed with each one of the five bare gold film electrodes of different thicknesses indicated above, in contact with a deoxygenated 0.2 M Na(OH) solution. Then, CV and SR measurements within the same potential region were carried out with the nickel hydroxide-gold film modified electrodes in contact with the same electrolyte solution. Each one of the nickel hydroxide-gold modified electrode listed in Table 1 was successively employed as working electrode in an individual experiment. All measurements were performed employing electrolyte solutions previously deoxygenated by N_2 bubbling for 5 h. The reduction of the oxygen content in the electrolyte solution is necessary in order to avoid the interference of the O_2 reduction process in the CV and SR responses at potential values more negative than −0.3 V (SCE).

The experimental set-up for simultaneous voltammetric and SR measurements on thin film electrodes has previously been described

Table 1
$\Delta R/R$ change of the gold film electrode coated with different nickel hydroxide surface coverage.

Goldfilm[a]	$\Gamma_{Ni(OH)2}$/nmol cm^{-2} [b]	$10^3 \Delta R/R$[c] ($R = 20\ \Omega$) Thickness $\phi_m = 30$ nm (Serie 1)	$10^3 \Delta R/R$[c] ($R = 25\ \Omega$) Thickness $\phi_m = 24$ nm (Serie 2)	$10^3 \Delta R/R$[c] ($R = 33\ \Omega$) Thickness $\phi_m = 18$ nm (Serie 3)	$10^3 \Delta R/R$[c] ($R = 43\ \Omega$) Thickness $\phi_m = 14$ nm (Serie 4)	$10^3 \Delta R/R$[c] ($R = 60\ \Omega$) Thickness $\phi_m = 10$ nm (Serie 5)
1	0.7	1.58	1.97	2.16	3.14	5.95
2	1.2	2.65	3.33	4.01	5.13	9.12
3	1.8	3.70	4.63	5.87	7.17	13.51
4	3.1	6.55	8.19	10.31	12.61	23.32
5	6.2	7.18	8.98	10.98	13.58	23.12
6	9.4	7.07	8.84	11.04	13.79	23.21
7	16	7.27	9.10	11.11	13.79	23.19
8	25	7.32	9.15	11.07	13.79	23.12

[a] Numbers 1 to 8 represent each gold film.

[b] Different nickel hydroxide surface coverage. The surface coverage was estimated from the voltammetric oxidation (or reduction) charge (*Q*) evaluated in the supporting electrolyte solution (0.2 M NaOH) by using the equation $\Gamma_{Ni(OH)2} = Q/nFA$, where *Q*, is anodic (or cathodic) voltammetric charge of the wave centered at about 0.35 V corresponding to the Ni (III)⟺Ni (II) oxidation (reduction) process.

[c] $\Delta R/R$ value of the gold film electrode at $E = -0.5$ V (SCE) for each nickel hydroxide surface coverage indicated in column 2.