



Electrochemical Impedance Spectroscopy study of the preparation of electrocatalysts through galvanic displacement reactions



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ABSTRACT

To explore the potential of Electrochemical Impedance Spectroscopy (EIS) in monitoring a galvanic displacement reaction, the deposition of Rh by displacement of Ni has been investigated, using both Ni disc electrodes of small size and Ni foam electrodes. The Ni dissolution/Rh deposition rate has been evaluated from EIS data and compared with values obtained by an independent method. The variation of the electrode double layer capacity with the reaction duration, caused mainly by the growth of Rh deposits, has been compared with the time dependence of the Rh surface area assessed by cyclic voltammetry (through the measurement of the H desorption charge). The quality of the agreement between different methods and possible reasons for discrepancies are discussed. It is shown that EIS may be a useful tool in the study of galvanic displacement processes.

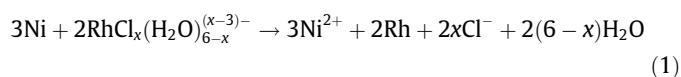
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1. Introduction

The galvanic displacement of a less noble metal by a precious metal with more pronounced electrocatalytic activity has been used by several groups in the preparation of cathodes and anodes with a wide range of compositions and shapes. The earliest reports are probably those of Grove [1] and Cameron et al. [2], who obtained Pt and PtRu alloy deposits onto Ni by simple immersion of the Ni substrate in acid solutions of the noble metal chlorides. Many other reports were published more recently. A non-exhaustive list includes the modification of solid metals [3], (nano)particles [4,5], adsorbed metal layers [6,7], smooth [8–12] and highly porous metal electrodeposits [13–16], and commercial metal foams [17–22]. In all these cases, the galvanic displacement procedure allows to improve the catalytic properties of the electrodes using only minor amounts of noble metal, thus enhancing their mass activity.

Galvanic displacement is a corrosion process occurring at open circuit. Therefore, not requiring an externally applied potential, it is especially suitable to treat objects with complex shapes for which electrodeposition might lead to heterogeneous deposits, due to uneven current distribution. On the other hand, the rate of an electrodeposition process may be followed by measuring the current (provided the efficiency is known), whereas the rate of galvanic

displacement cannot be directly assessed in real time with simple techniques. EQCM may provide very significant information [23], but its use is restricted to electrodes that consist of thin metal films deposited on a quartz resonator. Since galvanic displacement is a corrosion process, when the noble metal deposition is the only cathodic process which compensates for the non-noble metal dissolution, i.e. when parasitic reactions like oxygen reduction or hydrogen evolution are negligible, the measurement of the corrosion rate is equivalent to the measurement of the noble metal deposition rate. It is well known that Electrochemical Impedance Spectroscopy (EIS) is a powerful tool for estimating corrosion rates. However, to the best of our knowledge, an assessment of its potential and limitations in the study of galvanic displacement reactions has not been attempted. Therefore, we have undertaken an impedance study on the galvanic displacement of Ni by Rh, a reaction which we have used to prepare both electrocatalysts [22] and catalysts for partial oxidation of CH₄–H₂ mixtures [24]. Taking into account the different aqua/chloro-complexes of Rh, the Ni/Rh galvanic displacement reaction can be written:



In the present work, we report deposition rates determined from EIS data and compare them with deposition rates measured with an independent method. We have previously observed that both the dissolution of the non-noble metal and the deposition

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of the noble metal may lead to the roughening of the electrode surface, with a consequent increase in its real surface area [14–16,20–22]. In this work, we have used EIS data also to determine the dependence on the reaction duration of such surface area, through the measurement of the double layer capacity, and we have compared the values thus obtained with those independently measured by cyclic voltammetry.

2. Experimental

2.1. Chemicals and materials

$\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ (Alfa Aesar), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar), NaCl (Sigma–Aldrich, ACS reagent), and HCl (Sigma–Aldrich) were used as received. Ni wire (99.5% purity, 0.5 mm diameter) and Rh wire (99.9% purity, 0.5 mm diameter) were purchased from Alfa Aesar and Goodfellow, respectively. Ni foam was a grade 50 INCOFOAM™ sheet 1.7 mm thick, with apparent density 0.22 g cm^{-3} , corresponding to a void volume fraction of 0.975.

2.2. Equipment and electrochemical cells

Chronopotentiometric, voltammetric and EIS experiments were carried out with an Autolab PGSTAT 302 N, using a two-compartment cell; the working electrode was placed in the centre of the main cylindrical compartment, and a Pt wire counter electrode was fastened to the cell inner wall. The reference electrode was placed in a side compartment connected with the main one through a Luggin capillary. An SCE was used in acid chloride solutions; an Hg/HgO/1 M KOH electrode in basic solutions. Throughout this paper, all potential values are referred to SCE. Ion chromatography was performed with a Metrohm 850 Professional IC liquid chromatographer equipped with a Metrohm 887 UV–Visible detector and a METROSEP A SUPP 15–50 anionic column.

2.3. Electrodes

Three kinds of working electrodes were used in different experiments: (i) Ni and Rh disk electrodes (0.5 mm diameter) both sealed in glass sheaths, were used in galvanic displacement and EIS experiments. Before use, they were polished with $0.05 \mu\text{m}$ alumina, sonicated and rinsed in high purity water. (ii) Larger, stationary Ni electrodes (99.5% purity, 5 mm diameter), polished as above, were used in tests aimed at measuring the Rh loading (L_{Rh}). The same electrodes, rotating at $3000 \text{ rev min}^{-1}$, were used for recording polarization curves used for Tafel analysis. (iii) Some EIS experiments were performed using Ni foam as working electrodes. These electrodes were parallelepipeds with variable volume (between 0.0425 and 0.17 cm^3). Before use, they were successively washed with acetone and dichloromethane, dried in an air stream, etched in 2 M HCl at $60 \text{ }^\circ\text{C}$ for 15 min, and rinsed with high purity water, to ensure reproducible behavior [22].

2.4. Solutions and procedures

The solutions used in galvanic displacement experiments, briefly called “GD solutions” throughout this paper, contained $1 \times 10^{-3} \text{ M Na}_3\text{RhCl}_6$, $1 \times 10^{-3} \text{ M NiCl}_2$, 1 M NaCl, and the HCl necessary to adjust pH at 2.0. Polarization curves used for Tafel analysis were recorded in the GD solution. The working electrode was kept at open circuit for an appropriate equilibration time (5–8 min) and then the potential was scanned linearly at a low rate (0.1 mV s^{-1}). Since the aqua/chloro complexes of Rhodium exchange ligands with a slow kinetics [25,26], the Na_3RhCl_6 solutions were aged during several days prior to use, to ensure repro-

ducibility of results. In aged solutions $\text{RhCl}_5(\text{H}_2\text{O})_2^{2-}$ was the main Rh(III) complex, with minor amounts of $\text{RhCl}_2(\text{H}_2\text{O})_4^+$. All solutions were deaerated and thermostated at $25 \text{ }^\circ\text{C}$.

Cyclic voltammeteries aimed at measuring the Rh surface area, according to a previously described method [22], were recorded in 1 M KOH solution, with a 50 mV s^{-1} scan rate between a -1.02 V cathodic limit and a -0.12 V anodic limit (vs. SCE).

EIS measurements during galvanic displacement were performed after allowing the open circuit potential (E_{OC}) to stabilize for different time durations (t_{GD}), then externally imposing this potential value and superposing a 10 mV rms modulation, low enough to ensure linear response. Generally, the modulation frequency was varied between 10 mHz and 100 kHz, recording 8 points per decade. EIS curve fitting was performed with the Metrohm NOVA software, using weighing coefficients proportional to the impedance modulus.

The mass of Rh deposited onto Ni samples was evaluated by measuring the decrease in the concentration of Rh(III) complexes caused by galvanic displacement experiments, using ion chromatography [27]. For these experiments, stationary Ni discs with a 5 mm diameter and solution volumes of 10 mL were used.

3. Results and discussion

3.1. E_{OC} -time dependence – chronopotentiometric curves

In order to record impedance spectra representative of the galvanic displacement conditions the open circuit potential of the system must be stable. To ascertain under which conditions and after how long the Ni/Rh galvanic displacement reaction reached a steady state, Ni disc electrodes (0.5 mm diameter) were immersed in the GD solutions and their potentials were recorded vs. immersion time (t_{GD}). Fig. 1 shows three curves obtained with a solution containing $1 \times 10^{-3} \text{ M Na}_3\text{RhCl}_6$, $1 \times 10^{-3} \text{ M NiCl}_2$, 1 M NaCl and HCl to give pH 2.0. The volume of the solution was ca. 50 mL, large enough to maintain an essentially constant Rh(III) concentration throughout the experiment; the solution contained NiCl_2 , so as to minimize the time dependence of the concentration of Ni(II) ions.

The three chronopotentiometric curves, recorded in three experiments that differed for their durations, were very close to each other, despite some differences in the initial E_{OC} values. The substantial overlap of the three curves proved good reproducibility. E_{OC} became more negative as the reaction progressed, and stabilized in all cases at very similar values ($-0.230 \pm 0.005 \text{ V}$), after ca. 2 h. Therefore, most EIS measurements were made for $t_{\text{GD}} \geq 2 \text{ h}$ (see below).

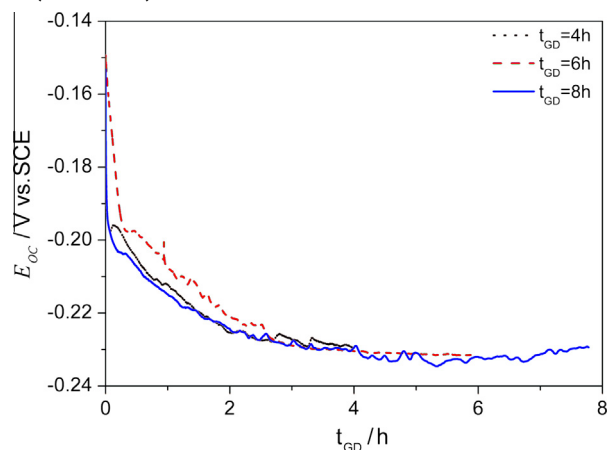


Fig. 1. Chronopotentiometric curves recorded at open circuit with Ni disc electrodes (0.5 mm diameter) in a solution containing $1 \times 10^{-3} \text{ M Na}_3\text{RhCl}_6$, $1 \times 10^{-3} \text{ M NiCl}_2$, 1 M NaCl (pH 2.0).

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