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Rhodium deposits on pyrolytic graphite substrate: Physico-chemical properties and electrocatalytic activity towards nitrate reduction in neutral medium

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Abstract

The electrodeposition of metallic rhodium on pyrolytic graphite from 10 mM Na_3RhCl_6 + 0.5 M NaCl aqueous solution was studied by potentiostatic method with the use of a double-pulse technique involving nucleation and growth pulses. Physico-chemical properties of Rh deposits were investigated by electrochemical methods and scanning electron microscopy. The activity of Rh-modified graphite electrodes towards nitrate reduction in neutral medium was demonstrated, the activation energy of nitrate reduction and NO_3^- Langmuir adsorption constant on Rh deposits were determined.

The use of double-pulse technique resulted in enhanced surface coverage in comparison with usual potentiostatic deposition and in decreasing the mean particle size down to 30 nm, while the specific catalyst surface area attains 32 $m^2\ g^{-1}$. The increase in the nucleation pulse duration from 20 to 100 ms enhances the mass catalytic activity towards NO_3^- reduction, which reaches 175 A g^{-1} for the best samples. Irrespectively of electrodeposition parameters, only NH_3 and NO_2^- were detected as nitrate reduction products. The rate of NO_3^- destruction was equal to 5.4 mol $g_{Rh}^{-1}\ h^{-1}$ which is much higher than that of most of Pd/Cu-based nitrate hydrogenation systems and Ag/TiO_2 photocatalysts.

Keywords: Rhodium; Electrodeposition; Double-pulse technique; Nitrate reduction; Electrocatalysis

1. Introduction

Platinum-group metals play an important role in the catalytic conversion of atmospheric pollutants and other electrocatalysis applications [1,2]. Belonging to this group, rhodium (Rh) is very stable to oxidation and possesses a density almost twice lower than platinum one. The catalytic activity of Rh films in many reactions of environmental importance is very well known [3–5], particularly for nitrate reduction in wastewater [6–8]. In our modern society, waste sources of nitrates have been considerably increased because of the impact of present agricultural trends. Actually, nitrate content often exceeds the maximum recommended limits worldwide and their removal becomes important for public health. Several techniques can be applied for the nitrate removal, such as chemical reduction and biological methods [9,10]. However, these techniques encounter numerous problems due to the demand for industrial scale application and proper conditions maintenance. For example, biological denitrification is slow, difficult to control, and it produces an organic residue. Moreover, bacteria are sensitive to heavy-metal ions and to changes in the composition of the influent stream [11]. On the other hand, the electrocatalytic denitrification, involving various catalysts [12–16], proves to be efficient to solve environmental problems, because of the use of ecologically clean reagent, i.e. the electron.

A comparative study of the reactivity of eight transition metals towards the nitrate reduction in acidic media has been recently reported [17–19]. Rhodium was proved to be the most active followed by ruthenium and iridium. Concerning the reaction mechanism, the reduction of nitrate to nitrite was concluded to be the rate-determining step [17]:

$$NO_3^- + 2H^+ + 2e^- = NO_2^- + H_2O$$

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For Rh, no gaseous products of nitrate reduction were found, only NH_2OH and NH_3 are formed [17]. A detailed investigation of reaction pathways and products of nitrate reduction has been performed using differential electrochemical mass spectroscopy (DEMS) and IR spectroscopy [19]. For Rh, Pt or Pt–Rh alloy electrodeposited on Au substrates, the reduction reaction starts with partial N–O breaking and N–N coupling, generating N_2O below 0.4 V versus standard hydrogen electrode (SHE). The evolution of gaseous reaction products reaches a maximum at 0.3 V. Further reduction between 0.2 and 0.0 V leads to the production of NH_4^+ ions. At lower potential, a mixture of various products (N_2H_2, NH_2OH, N_2, etc.) was observed [19].

Different commercial ‘‘rhodium on carbon’’ catalysts were also tested [6,7]. It was confirmed that among platinum metals, rhodium (5% on carbon) is the most effective in removing NO_3^- from groundwater [6]. The application of a potential of -0.4 V versus SHE for 6 h decreased NO_3^- concentration by 68% and during the reduction process, the presence of NO_2^- was not detected. A commercially available carbon cloth with a 30% Rh coated surface was tested and it was shown that, at an applied potential -1.5 V versus saturated calomel electrode (SCE), the NO_3^- concentration in highly diluted solutions decreased almost twice after an electrolysis of 40–60 min [7]. The proposed electrocatalytic reduction process can be used for water with pH between 7 and 8.5, which is in the pH range of most surface and groundwater in the western United States [7]. Recently, a patent has described the electrocatalytic removal of NO_3^- using a Rh coated cathode at which the nitrate ions were converted to nitrogen [8]. More recently, the simultaneous reduction of nitrates and oxidation of formed ammonia in aqueous solutions have been carried out in a zero gap solid polymer electrolyte reactor with Pd–Rh titanium mini-mesh cathode [20].

Due to the high cost of Rh, it is of weighty importance to obtain thin rhodium films and the electrodeposition remains one of the most efficient methods for this purpose. Compared with other methods, the electrodeposition parameters can be much more easily controlled to produce the required deposit properties. Rh electrodeposition has been studied on various substrates, both monocrystalline [21,22] and polycrystalline [23–26]. Regarding Rh sources, different Rh salts have been used [27–30]. Recently, we have reported our results concerning the potentiostatic Rh electrodeposition on pyrolytic graphite involving the cheapest Rh salt, sodium hexachlororhodate(III) Na_3RhCl_6 [31]. In particular, early stages of Rh deposition were investigated; the principal nucleation and growth mechanisms were determined and discussed.

When the electrodeposition conditions provide the massive nucleation and reduced grain growth, it is possible to obtain an enhanced surface coverage with reduced particle size and homogeneous distribution, which is especially important for catalysts. To obtain such Rh deposits, the double-pulse technique firstly introduced by Schedulko and Todorova [32], was used in our investigation. It consists in the application of short potential pulse ($t < 200$ ms) providing massive nuclei formation and followed by their growth at much more positive potential. Previously, this technique was successfully applied for the electrodeposition of a wide variety of metals (Ag [33–35] and Au [33]), and at least one metal oxide (MoO_2) [36].

In this investigation, Rh electrodeposition on pyrolytic graphite involving the double-pulse technique was investigated in details, with the aid of different electrochemical approaches and scanning electron microscopy (SEM). The usual potentiostatic deposition at the same growth pulse potential was performed for comparison. The physico-chemical properties of Rh deposits were determined and their correlation with the activity towards NO_3^- reduction in neutral medium was evaluated. The electrolysis of nitrate-containing solutions was performed in order to determine the efficiency and selectivity of such Rh/graphite electrodes. To our knowledge, this is the first quantitative study of NO_3^- reduction on Rh-modified graphite electrodes in neutral medium.

2. Experimental

2.1. Preparation and characterization of Rh deposits

Before use, pyrolytic graphite electrodes (Electrolytica SG-202, geometrical surface area 2–4 cm^2) were polished with alumina powder (0.05 μm, Buehler), repeatedly washed with ultrapure H_2O (18 MΩ, obtained from a Sybron/Barnstead Nanopure II system), 1 M HNO_3 and CH_3OH subsequently (30 min, with ultrasound), and dried in vacuum at 100 °C for 5 h.

The Rh deposition was investigated at room temperature in a three-electrode, one-compartment electrochemical cell consisting of pyrolytic graphite (working electrode), Pt mesh (counter electrode) and Ag/AgCl (3 M KCl) as a reference electrode. All potentials in the text will be referred to this electrode. The electrochemical equipment was composed of a potentiostat/galvanostat Solartron model 1287 interfaced with a PC and the Corrware 2 and CorrView 2 software (Scribner Associates). All charge and current densities are quoted in terms of apparent geometrical area of the substrate graphite electrode, unless otherwise stated.

The Rh electrodeposition on pyrolytic graphite was carried out from 10 mM $Na_3RhCl_6 \cdot 12H_2O$ (Alfa Aesar) in 0.5 M NaCl aqueous solution under quiescent conditions. All the aqueous solutions used in the present study were prepared using ultrapure H_2O and purged with N_2 for 20 min. Before each potentiostatic experiment the initial potential of 0.6 V was maintained during 20 s. In the case of the double-pulse deposition, a short potential nucleation pulse of -800 mV was applied during either 20 or 100 ms. Then the potentiostatic electrodeposition of rhodium was performed within a wide growth potential range (from -172 to -592 mV). The duration of this growth pulse varied from 60 to 960 s. After the deposition, the electrodes were removed from the precursor solution and carefully washed with ultrapure water.

The morphology of Rh crystallites was examined using a Hitachi S-4300 SE/N microscope equipped with an energy dispersive X-ray (EDX) analysis detector. SEM micrographs were taken both in SEM and in a backscattered electrons (BSE) mode. Then ‘‘general’’ EDX analysis of the sample