

The “rolling up” effect of platinum layer obtained on nickel surface by interaction with solution of H_2PtCl_6 and its electrocatalytic properties in hydrogen evolution reaction during water electrolysis in alkaline medium

M. V. Kaneva, V. P. Tolstoy*

Institute of Chemistry, Saint Petersburg State University,
26 University Prosp, St. Peterhof, Saint Petersburg, 198504, Russia
skt94@bk.ru, *v.tolstoy@spbu.ru

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We have shown for the first time that a platinum layer has been obtained on the surface of nickel foil as a result of Galvanic Replacement Reaction (GRR) when interacting with an aqueous solution of H_2PtCl_6 , during drying in air, partially rolling up into incompletely formed microscrolls with a unique 3D morphology. Analysis of the wall of these microscrolls by FESEM, TEM, HR-TEM, and SAED methods showed that they are porous and formed by platinum nanocrystals with sizes of 5 – 10 nm, and their packing density over the wall thickness differs. Nickel foil samples with the layer of platinum microscrolls deposited on their surface exhibit high electrocatalytic activity in hydrogen evolution reaction (HER) during water electrolysis in the alkaline medium. In particular, the overpotential value is 32 mV and the Tafel slope is 32.5 mV/dec for an electrode with the platinum layer with a thickness of 120 – 140 nm.

Keywords: Platinum, nanocrystals, microscrolls, galvanic replacement reaction, hydrogen evolution reaction, nickel electrode.

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1. Introduction

As is known, the processes of “rolling up” planar structures into more complex geometric shapes are the basis of various methodological techniques for obtaining new nanoscale materials. For example, novel metamaterials were obtained using this approach [1] and new types of 3D devices with small form factors [2–4]. There are also known works devoted to the synthesis and research of nanoscrolls of hydrosilicates of metals [5–8], as well as microtube of a number of oxides [9, 10], fluorides [11] and sulfides of metals [12]. As shown by the authors of these works, the reason for this rolling up is mechanical forces that arise inside planar structures due to density or composition gradients.

The aim of this work was to synthesize platinum nanocrystals under the conditions of galvanic replacement reaction (GRR) on the surface of a polycrystalline nickel foil with the participation of an H_2PtCl_6 solution and to determine the conditions for carrying out this reaction under which the planar geometry of the resulting nanocrystal layer is distorted and 3D microstructures are formed on the surface. The study of such a reaction is of undoubted practical interest, since platinum nanocrystals are, for example, active electrocatalysts of various electrochemical processes. One would expect such 3D microstructures to have unique electrocatalytic properties, for example, in HER during water electrolysis. Previously, GRR with the participation of these reagents was studied, in particular, in articles [13, 14] on the examples of nickel nanoparticles and nickel foam.

2. Experimental

Dihydrogen hexachloroplatinate (IV) hydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, JSC “Aurat”) and Ni foil with a size of $0.5 \times 7.0 \times 20.0$ mm were used as precursor and a substrate, respectively, to synthesize the platinum layer by GRR. Ni plates were degreased with acetone by ultrasonic treatment for 30 min and treated according to [15] in hydrochloric acid (HCl, 3 M). Then the substrates were washed in deionized water. Thereafter, Ni plates were immersed into a solution of H_2PtCl_6 ($C = 0.005$ M) for 20 min. The GRR was carried out at room temperature and atmospheric pressure. As a result, the platinum nanolayer is formed on the surface and during drying in air rolls up into microscrolls.

FESEM and TEM methods were used to characterize the samples. FESEM micrographs were obtained using a Zeiss Merlin electron microscope. TEM and HR-TEM micrographs were obtained using a Zeiss Libra 200 microscope. Electrochemical experiments were conducted at room temperature using a standard three-electrode cell connected to an ElinsP-45X-FRA-24M potentiostat. Carbon rod and an Ag/AgCl (aq. KCl sat.) electrode were used as the counter electrode and the reference electrode, respectively. The sample of Ni foil with the platinum layer obtained by GRR was used as the working electrode. The electrolyte was Ar-saturated 1 M KOH solution ($\text{pH} \approx 14.0$). The polarization curves were recorded at a scan rate of 5 mV/s. The electrochemical measurements were performed

with iR compensation. The overpotential from the Ag/ AgCl electrode scale was converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation. The equation $|\eta| = b \log(|j|) + a$, was used to calculate the Tafel slope (b – Tafel slope, η – overpotential, j – current density and a – intercept).

3. Results and discussions

As a result of GRR, when nickel interacts with a 0.005 M H_2PtCl_6 solution, a light gray platinum layer is formed on its surface. FESEM studies of this layer have shown it is formed by nanocrystals. A sample of chemically polished nickel obtained with a treatment time of 20 minutes or more has a morphology different from planar due to partial “rolling up” with the formation of incompletely formed microscrolls (Fig. 1). The wall thickness of such a microscroll is 120 – 140 nm (Fig. 1b) and its cross-section shows that it consists of nanoparticles with a size of 5 – 10 nm and is porous. Moreover, the packing density of such nanoparticles changes over the layer thickness and the pores are partially oriented across the wall. In the micrographs 1c and 1d, showing a top view of the substrate surface, it can be seen that these nanoparticles also form microglobules with a size of 20 – 80 nm and their shape on the outer and inner surface of the layer with respect to the substrate is different. So, on the outer surface, these globules have a certain asymmetry, and some of them contain acute-angled vertices oriented perpendicular to the plane of the layer. The study of fragments of this layer by the TEM and HR-TEM methods also showed that the sizes of nanoparticles are 5 – 10 nm (Fig. 2a,b) and, as follows from the micrographs shown in Fig. 2b and Fig. 2c, these nanoparticles are platinum nanocrystals.

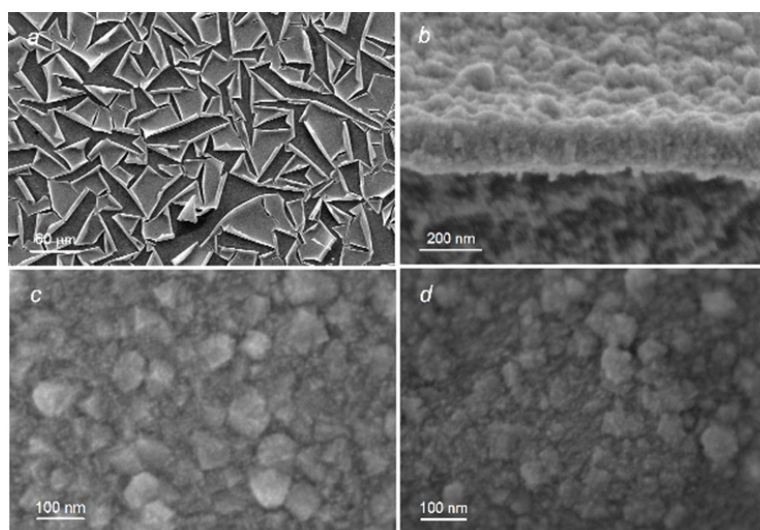


FIG. 1. FESEM images of the platinum layer on the nickel surface obtained by treating it for 20 minutes with a 0.005 M H_2PtCl_6 solution. (a) – general top view, (b) – side view of the platinum layer, (c) – top view of the layer area inside the scroll, (d) – top view of the layer area outside the scroll

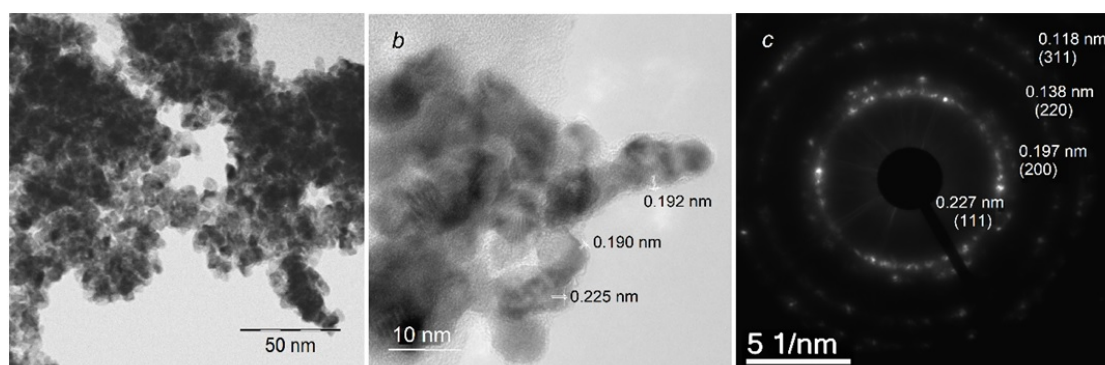


FIG. 2. (a) – TEM image of platinum nanocrystals, (b) – HR-TEM image of platinum nanoparticles, (c) – SAED pattern of platinum nanoparticles

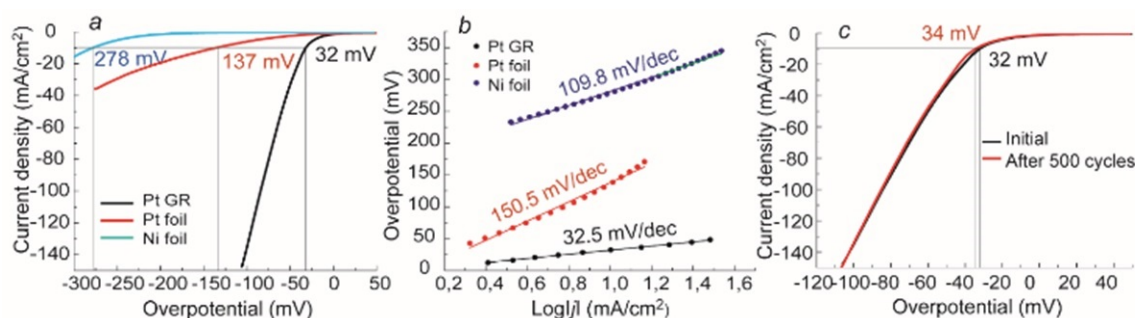


FIG. 3. HER polarization curves (a) and Tafel plots (b) of the platinum layer on the nickel surface obtained by treating it for 20 minutes, Pt foil and Ni foil in 1 M KOH solution. (c) – HER polarization curves of the platinum layer on the nickel surface before and after 500 potential cycling

TABLE 1. Comparison of overpotential and Tafel slope values for platinum-based electrocatalysts in HER during water electrolysis in 1 M KOH solution

| Electrocatalyst | Synthesis method | Substrate | Overpotential (mV at 10 mA/cm ²) | Tafel slope (mV/dec) | Reference |
|--|---|----------------|--|----------------------|-----------|
| Pt | GRR | Ni foil | 32 | 32.5 | This work |
| Pt/NiO@Ni/NF | Electrodeposition, electrochemical reduction | Ni foam | 34 | 40 | [16] |
| Pt _{SA} -Ni ₃ S ₂ | Electrochemical process | Ni foam | ≈50 | 43.29 | [17] |
| Pt _{SA} -Ni ₃ S ₂ @Ag NWs | | flexible cloth | 33 | 34.7 | |
| Pt/NiRu-OH | Hydrothermal method, electrochemical atom trapping method | Ni foam | 38 | 39.0 | [18] |
| Pt-Fe-Na | Corrosion engineering approach | Ni foam | 31 | 35.98 | [19] |
| Pt NSs/CNTs | Electrochemical reduction | GC electrode | 36 | 44.0 | [20] |
| PtSA/NC-DG | Pyrolysis, electroless deposition | GC electrode | 41 | 40.0 | [21] |

Explaining the observed effects, it should be noted, first of all, that upon contact of the nickel surface with the H₂PtCl₆ solution, GRR occurs at the interface with the formation of platinum nanocrystals and Ni²⁺ cations. Over time, the number of such nanocrystals increases, and they eventually form the porous layer on the nickel surface, which also consists of agglomerates of such nanocrystals. Through the pores of this layer PtCl₆⁻ anions enter the interface and nickel cations are removed. In this case, the degree of porosity near the interface and on the outer side with respect to the substrate are different. This fact and the noted asymmetry of the microglobules' shapes lead to the appearance of mechanical forces that contribute to cracking and partial twisting of this layer during its drying.

The study of the electrocatalytic properties of such a layer showed (Fig. 3) that the values of the overpotential and the Tafel slope are 32 mV and 32.5 mV/dec, respectively, in HER. Comparison of these values with the results of other authors shown in Table 1 indicates that the noted values are currently among the best. In our opinion, the observed effect of reducing the overpotential values is due to the unique morphology of the electrode surface. In particular, the surface has many points at the tops of the microscrolls present, on which HER occurs, as well as the presence of an internal space in the microscrolls, in which bubbles are formed at a lower concentration of dissolved hydrogen.

It is important that the overpotential value increases by only 2 mV upon repeated 500-fold potential cycling (Fig. 3c) and this indicates a high stability of the electrocatalyst properties over a relatively long time. This result shows that these incompletely formed platinum microscrolls are relatively tightly bound to the nickel surface and are

not removed from it when immersed in an aqueous solution of KOH and during the operation of the electrolyzer electrode.

4. Conclusion

Under the proposed GRR conditions between nickel and an aqueous solution of H_2PtCl_6 , the porous platinum layer forms on its surface, which cracks during drying and partially rolls up into incompletely formed microscrolls with a unique 3D morphology. Electrodes created on their basis exhibit high electrocatalytic activity in HER during electrolysis of an aqueous alkaline medium. In particular, the overpotential value is 32 mV and the Tafel slope is 32.5 mV/dec for an electrode with the platinum layer with a thickness of 120 – 140 nm.

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