

The study of hydrogen electrosorption in layered nickel foam/palladium/carbon nanofibers composite electrodes

J.M. Skowroński^{a,*}, A. Czerwiński^b, T. Rozmanowski^a, Z. Rogulski^c, P. Krawczyk^a

^a *Poznań University of Technology, Institute of Chemistry and Technical Electrochemistry, ul. Piotrowo 3, 60-965 Poznań, Poland*

^b *Warsaw University, Department of Chemistry, ul. Pasteura 1, 02-093 Warsaw, Poland*

^c *Industrial Chemistry Research Institute, ul. Rydygiera 8, 01-793 Warsaw, Poland*

Received 4 August 2006; received in revised form 4 December 2006; accepted 7 December 2006

Available online 15 December 2006

Abstract

In the present work, the process of hydrogen electrosorption occurring in alkaline KOH solution on the nickel foam/palladium/carbon nanofibers (Ni/Pd/CNF) composite electrodes is examined. The layered Ni/Pd/CNF electrodes were prepared by a two-step method consisting of chemical deposition of a thin layer of palladium on the nickel foam support to form Ni/Pd electrode followed by coating the palladium layer with carbon nanofibers layer by means of the CVD method. The scanning electron microscope was used for studying the morphology of both the palladium and carbon layer. The process of hydrogen sorption/desorption into/from Ni/Pd as well as Ni/Pd/CNF electrode was examined using the cyclic voltammetry method. The amount of hydrogen stored in both types of composite electrodes was shown to increase on lowering the potential of hydrogen sorption. The mechanism of the anodic desorption of hydrogen changes depending on whether or not CNF layer is present on the Pd surface. The anodic peak corresponding to the removal of hydrogen from palladium is lower for Ni/Pd/CNF electrode as compared to that measured for Ni/Pd one due to a partial screening of the Pd surface area by CNF layer. The important feature of Ni/Pd/CNF electrode is anodic peak appearing on voltammetric curves at potential *ca.* 0.4 V more positive than the peak corresponding to hydrogen desorption from palladium. The obtained results showed that upon storing the hydrogen saturated Ni/Pd/CNF electrode at open circuit potential, diffusion of hydrogen from carbon to palladium phase occurs due to interaction between carbon fibers and Pd sites on the nickel foam support.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Nickel foam; Palladium; Carbon fibers; Ni–Pd–carbon fibers composite; Hydrogen electrosorption

1. Introduction

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) represent an intriguing classes of carbon materials, which offer a wide range of potential application. Owing to structural and chemical properties the CNTs and CNFs are regarded as promising electrode materials for chemical power sources such as lithium-ion cells [1,2], supercapacitors [3–5] and reversible hydrogen reservoirs [6–13]. During the last decade the ability of the mentioned carbon materials for storing hydrogen has attracted a great interest due to the possibility of modification of their physicochemical properties allowing the increase of hydrogen sorption. Although the maximum amount of hydrogen stored in carbon materials is still a matter of discussion, there is without

any doubt that the effectiveness of the electrochemical hydrogen sorption depends on a lot of factors, among which the crystalline and porous structure, chemical composition of carbon surface and the presence of metallic inclusions of catalysts, remaining in the carbon matrix after the process of the CNT and CNF production, are believed to play the most significant role. Chemical and physical activation of CNTs and CNFs leading to the development of their micro- and mesoporosity and surface area and to the enrichment of the carbon surface with specific functional groups give rise to the increase in the hydrogen storage capacity [5,14–19]. In opposite to the purification of the carbon products, focused on the preparation of possibly pure materials, the other attempts to increase the hydrogen storage capacity are based on the filling carbon matrix with some catalysts allowing the synthesis of CNTs and CNFs and simultaneously exhibiting catalytic activity in the reaction of hydrogen electrosorption and oxidation [10,20–22]. Metals exhibiting a low overpotential in the hydrogen adsorption/absorption reaction, such as Pt,

* Corresponding author.

E-mail address: Jan.Skowronski@put.poznan.pl (J.M. Skowroński).

Pd, Ni and interstitial metal alloys are concerned as the most promising.

From the viewpoint of the specific volume of hydrogen capacity, palladium is on the top of this list. Unfortunately, due to a high density, an easy loss of hydrogen after the process of electrosorption and high price, the use of this metal as electrode material for chemical power sources has little chance for practical application.

The aim of this paper was to examine the influence of carbon nanofibers deposited onto palladium layer coating a nickel foam support on the kinetics of the electrochemical hydrogen sorption/desorption reaction and to concern the reasons for beneficial decrease of self-discharge of hydrogen from Ni/Pd/CNF electrode effected by the presence of CNF film.

2. Experimental

Ni/Pd modified electrodes were prepared by the open-circuit spontaneous deposition of Pd on Ni foam (produced by Nitech, thickness 1.6 mm, density 500 g cm^{-2} and porosity higher than 95%). After cleaning in acetone Ni foam piece ($5 \text{ mm} \times 10 \text{ mm}$ dimension) were immersed in solution of 0.11 M PdCl_2 in 1 M HCl for 30 min. The amount of Pd deposit was calculated from direct UV–vis measurements (Multispec 1500 Shimadzu) of Pd and Ni ions concentrations in the electroplating solution before and after deposition of palladium on the Ni foam as well as electrode weighting before and after Pd electrolysis. The amount of absorbed hydrogen introduced into the Pd layer was calculated from the hydrogen oxidation charge determined from cyclic voltammograms.

To obtain Ni/Pd/CNF electrodes, Ni/Pd electrodes were coated with a carbon nanofiber layer. The synthesis of carbon nanofibers was carried out by the CVD (chemical vapor deposition) method in a tube furnace coupled to the flowmeter system ensuring the control of the amounts of gases passing through the inner quartz reactor. Before starting the gas and temperature system a Ni foam/Pd sample ($5 \text{ mm} \times 20 \text{ mm}$) was inserted to the reactor. The deposition of carbon nanofibers onto Ni foam/palladium (Ni/Pd) support was carried out 650°C in the acetylene/nitrogen mixture with the flow rates of C_2H_2 and N_2 set up 30 and 100 sccm, respectively. After 0.5 h of reaction, the reactor was cooled down under nitrogen, and the nickel foam/palladium/carbon nanofibers (Ni/Pd/CNT) sample was taken out. For observing the morphological changes of Ni support resulting from the deposition of Pd and CNF layers, the scanning electron microscopy (SEM) analysis was carried out using a Tescan-Vega 5153 with the acceleration voltage of 15 kV.

The process of hydrogen sorption/desorption into/from the working Ni/Pd and Ni/Pd/CNF electrodes (geometrical area 1 cm^2) was measured at ambient temperature by cyclic voltammetry (CV) method using a potentiostat-galvanostat PGSTAT30 AutoLab (EcoChemie B.V.). The CV measurements were carried out in a three-electrode cell in deaerated 6 M KOH solution. A Hg/HgO/6 M KOH was used as the reference electrode. All potentials throughout the paper are referred to this electrode. Platinum gauze was used as a counter electrode. Unless oth-

erwise stated, the CV measurements were carried out in the potential range of -1.1 to $+0.3 \text{ V}$. Starting from the rest potential of electrode with a scan rate 10 mV s^{-1} , the potential was changed in the negative direction (cathodic polarization) to reach -1.1 V and after the reversal of polarization the potential was increased until the limit potential $+0.3 \text{ V}$ was attained. At this moment the polarization was again reversed. In separate experiments the CV measurements were started in the positive direction after the working electrode was potentiostatically saturated with hydrogen at a chosen potential. The process of hydrogen saturation was carried out in three modes: (i) after reaching the rest potential of electrode at the end of the third cycle, the potential of electrode was further lowered down to -1.1 V , automatically stopped for 15 min for the saturation of electrode with hydrogen and then the fourth cycle (see Figs. 3 and 5) was continued in the positive direction; (ii) the CV measurements were started at the rest potential of electrode and the potential was changed in the negative direction to reach gradually more negative potential of reversion at which electrode was saturated with hydrogen. The lower limit potential was set at -1.1 , 1.15 , 1.20 and 1.25 V for four consecutive cycles (see Figs. 6 and 7); (iii) the first cycle was started at the rest potential of electrode and the potential was changed in the negative direction to reach a limit potential of reversion of -1.1 V . At this potential the electrode was saturated with hydrogen for 15 min and then polarized in the positive direction (a) without any interruption at open-circuit (0 min), (b) after 30 min of the rest at open-circuit, and (c) after 60 min of the rest at open-circuit (see Figs. 8 and 9). Before the electrode was saturated with hydrogen at a constant potential (measurements (ii) and (iii)), three cycles were performed in a given potential range to ensure a steady-state behavior of electrode. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 1a shows SEM micrographs for nickel foam. As seen from this figure, the nickel skeleton has an open pore structure and is built of holed cells linked to each other. The arch ribs of these cells with sharp edges are non porous. Only grain boundaries are visible at a high magnification (Fig. 1b). Upon coating the nickel support with palladium, porous deposit is formed onto the nickel surface (Fig. 1c). Porous grains of Pd layer are mostly $0.1\text{--}1 \mu\text{m}$ in diameter. The tightness of Pd layer coating a Ni support was checked by recording CV curves in the potential range of -1.2 to 0.55 V (not shown here). As reported recently for nickel foam electrode [13,23], the limit value of 0.55 V in 6 M KOH solution is high enough to record the anodic peak associated with the $\text{Ni}(\text{OH})_2 \rightarrow \text{NiOOH}$ transformation. The lack of the peak at about 0.4 V on CV curves for Ni/Pd electrode proves the Pd layer to be impermeable to electrolyte to reach a Ni sublayer. The palladium catalytic particles appeared to be nucleation seeds for the growth of carbon nanofibers (Fig. 1d and e). The carbon fibers deposit synthesized onto the palladium layer coating nickel foam (Fig. 1e) is very porous and consists of many curled nanofibers. The fiber diameters are ranging from 50 to 200 nm. Because the carbon fiber tangling

Download English Version:

<https://daneshyari.com/en/article/195899>

Download Persian Version:

<https://daneshyari.com/article/195899>

[Daneshyari.com](https://daneshyari.com)