



Development of metal hydride material efficient surface in conditions of galvanostatic charge/discharge cycling



Henryk Bala^{a,*}, Martyna Dymek^a, Henryk Drulis^b

^a Department of Chemistry, Czestochowa University of Technology, Czestochowa, Poland

^b Institute of Low Temperatures and Structure Research PAS, Wroclaw, Poland

HIGHLIGHTS

- Sn-doped hydride electrode cycling increases its efficient surface area.
- Evans approach to electrode potential changes allows surface development evaluation.
- The hydride material porosity increases both during its charging and discharging.

ARTICLE INFO

Article history:

Received 21 March 2014

Received in revised form

27 August 2014

Accepted 15 September 2014

Available online 1 October 2014

Keywords:

Metal hydride electrode

Charge/discharge

Surface development

ABSTRACT

A detailed analysis of potential changes on galvanostatic charge/discharge curves for $\text{LaNi}_{4.5}\text{Co}_{0.5}\text{Sn}_{0.1}$ powder-composite electrode has been carried out with regard to material surface development as a result of hydrogenation. It has been shown that the efficient surface of the electrode increases mainly during its cathodic charging. The surface development caused by hydrogen desorption is evident for the first cycle only. Electrode cycling is prone to continuous surface development which is especially distinct for some first cycles.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The Ni/MH type hydride batteries are considered to be the most promising battery systems for future electric- and hybrid vehicles [1,2]; they are relatively cheap in maintenance, environmentally compatible and do not consume the electrolyte during cycling. The Ni/MH batteries display also many other important advantages, such as high energy density, acceptable high rate capacity, good overcharge- and overdischarge capability and, in spite of presence of 17 at.% of highly active rare earth (RE) elements – generally good corrosion resistance [1–5].

Among the various types of hydrogen storage alloys, the RE_TM_5 alloys ($T = d$ -block element(s), sometimes partly substituted by p -block ones) with hexagonal CaCu_5 -type crystal lattice were the first generation to be used as negative electrode materials [1–3]. The RE_TM_5 type alloys are able to absorb large quantities of hydrogen (up to ca 1.5 mass %) and therefore are the most frequently used as the

negative electrode material for Ni/MH batteries. The important parameter here is a compositional ratio T/RE in as much as it controls properties such as plateau pressure and cycle life. The H absorption process by RE_TM_5 materials may occur both from gaseous phase (H_2 -gas) or by cathodic charging from aqueous solutions.

Hydrogen saturated metal hydride electrode (MH) working in strong alkaline solution (e.g. $\text{M} = \text{LaNi}_5$ -type material cathodically charged in 6 M KOH), in first approximation, can be treated as a simple hydrogen electrode on which the equilibrium process is described by the $\text{H}_{2(g)} + 2\text{OH}^- - 2e \rightleftharpoons 2\text{H}_2\text{O}$ half reaction. The equilibrium potential for $\text{H}_2\text{O}/\text{H}_2$ system ($E_{\text{H}_2\text{O}/\text{H}_2}^{\text{eq}}$) at partial pressure of H_2 equal to 1 bar, at a temperature of 25 °C and at $\text{pH} = 15.12$ (6 M KOH) is -0.894 V (i.e. -0.925 V vs HgO/Hg).

In real experimental conditions, during first steps of cathodic charging, some traces of O_2 , then certain oxide phases of the electrode material undergo reduction (e.g. NiO reduces to Ni etc.) and, in turn, the LaNi_5 -based compound absorbs atomic hydrogen [6–8]. In practice, in case of pure LaNi_5 compound, cathodic charging in atmospheric conditions (external pressure ≈ 1 bar, room temperature) allows to obtain hydrogen concentration corresponding to hydride formula of $\text{LaNi}_5\text{H}_{3.8}$ after 10 charge/

* Corresponding author.

E-mail address: hbala@wip.pcz.pl (H. Bala).

discharge cycles [8–10]. After saturation of the electrode material with atomic hydrogen, further cathodic exposure is prone to water reduction on MH-material particles and evolution of H₂ bubbles. It is worth noting that in case of big granulation of M particles and slow atomic hydrogen transport across the material, the process of H₂ evolution may begin earlier.

It should be noted that lanthanum undergoes slow oxidation both during discharge- and charge cycles. The La₂O₃ oxide cannot be reduced during charge process (i.e. at potentials -1.5 – -1.0 V vs HgO/Hg) because the equilibrium potential of La₂O₃/La system at pH = 15.12 is nearly -3.0 V vs HgO/Hg). The lanthanum oxide, unlike NiO and oxides of many transition metals, is not amphoteric and cannot dissolve in strong alkaline solution. Although NiO, Ni(OH)₂ and HNiO₂ are thermodynamically stable in 6 M KOH at $E > -0.8$ V, part of authors assume that nickel does not oxidize during electrode discharge process [1,6]. Results obtained in some of our latest papers [7–10] indicate that certain amounts of nickel, as well as elements partly substituting nickel (Co, Bi, Zn etc.) oxidize during discharge process, however, they are reduced back during charging. Above mentioned alloying additions reduce H₂ equilibrium pressure which provides high capacities at atmospheric conditions. On the other hand, substitutions of amphoteric elements (Zn, Al, Bi, Sn etc.) improve kinetics of charge/discharge processes, most probably owing to hinder material passivation in strong alkaline environment.

During the RET₅ electrode cathodic treatment in galvanostatic conditions ($I_c = \text{const}$), the electrode potential should continuously decrease with the passage of time until all the oxidized agents undergo reduction. The above statement is valid, however, when the efficient material surface does not change with time.

In the reality, the crystal lattice of periodically hydrogen charged/discharged material is subjected to periodical expansion (during charging) and contraction (during discharging) which releases internal stresses, causes appearance of local cracks, fissures etc. As a consequence, the electrochemical cycling gives rise to material progressive degradation, its further pulverization, and, generally – efficient surface development (i.e. active material surface increase being in contact with electrolyte). Especially distinct efficient surface development occurs in the first charge cycle, mainly owing to composite electrode soaking with electrolyte solution [11]. It has been shown in our earlier papers that cathodic potential continuously increases in the first cycle only [7–10,12].

The phenomenon of drastic increase of material efficient surface as a result of its cathodic treatment is common not only for porous, powder composite electrodes. It has been also observed for massive, polycrystalline electrodes during cathodic polarization – for example, for high-carbon steels etched in mineral acids [13–15].

In present study we evaluate the efficient surface development of the powder composite LaNi_{4.5}Co_{0.5} alloy doped with 1.7 at.% of Sn as the material is hydrogenated (cathodic charging) and dehydrogenated (anodic discharging) and the effect of electrode cycling on this phenomenon.

2. Experimental: material and method

The hydride material with LaNi_{4.5}Co_{0.5}Sn_{0.1} stoichiometry has been obtained by arc-melting of commercial chemical grade purity precursor LaNi_{4.5}Co_{0.5} with corresponding addition of Sn (1.7 at.%), under high purity Ar-atmosphere. The ingots were re-melted 5–6 times for homogeneity. Since Sn component content (the x stoichiometry index) was not bigger than 0.4, the over-stoichiometry of LaNi_{5+x} should be expected according to the equilibrium diagram of the La–Ni system [16]. The XRD examinations were carried out with the use of PANanalytical XPert PRO diffractometer. The analysis of XRD patterns (Rietveld method, XPert HighScore Plus software

fitting program) revealed the predominantly CaCu₅-type structure of the over-stoichiometry La(Ni,Co,Sn)_{5+x} alloy, with slightly increased unit cell volume ($\Delta V/V \approx 0.3\%$) compared to the precursor (see Fig. 1). The test material was mechanically crushed, then ball-milled (Fritsch, Pulverizette, 20 mL, Ar-atmosphere) to powder and sieved to separate 20–50 μm fraction. The composite pellets (\varnothing 5 mm, $h \approx 0.3$ mm) containing 0.0300 ± 0.0001 g of the active material have been prepared by mixing of the powder with 5 mass % of C-graphite and 10 mass % of polyvinylidene fluoride (PVDF) binder and pressing under a pressure of 50 bar. The appearance of the tested powdered material after milling and sieving as well as particle cross section before- and after hydrogenation are presented in Fig. 2.

The pellets have been used as working electrodes in 50 mL teflon cell equipped with Au-auxiliary- and HgO/Hg reference electrodes. The argon saturated 6 M KOH solution with a temperature of 22 ± 0.2 °C has been applied as test solution. The charge/discharge galvanostatic measurements have been carried out using CHI Instruments electrochemical station (Austin, Texas). The cathodic charging with the current density of -186 mA g⁻¹ (-0.5C) lasted 9000 s for each cycle in all experiments. The discharging process ($+0.5\text{C}$) was continued 4000–6500 s, depending on the cycle number, and was being broken off every time when the electrode potential achieved value of -0.50 V vs HgO/Hg. Three repetitions of 10 charge/discharge cycles were carried out. The reproducibility of the results has been better than 3%. More details relating the cell construction and galvanostatic $-i/+i$ measurements can be found in our previously published papers [7–10].

3. Results and discussion

3.1. Electrode potential changes during galvanostatic charge/discharge experiments

In Fig. 3 the results of charge/discharge experiments for the tested electrode are presented. One can notice that the charge/discharge plots for $N = 1$ cycle differ strongly from these for succeeding cycles. This is because after each discharge cycle part of material undergoes oxidation [7,8,10] and the oxide phases are reduced at the first seconds of the successive charge cycles. Only the first charge cycle occurs on non-oxidized material. It is also

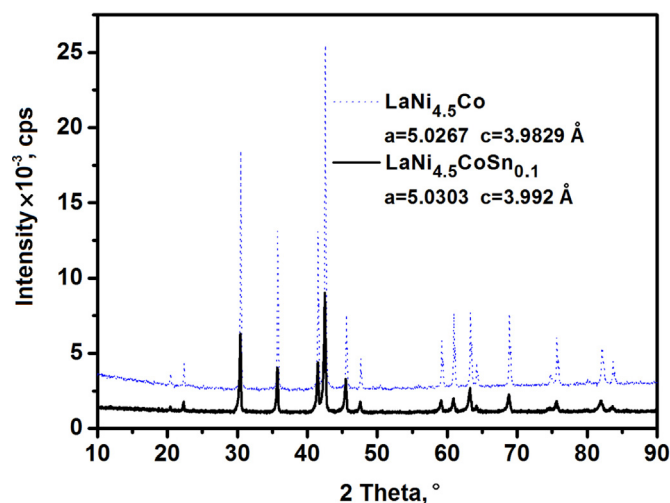


Fig. 1. XRD patterns for LaNi_{4.5}Co_{0.5} precursor and for Sn-doped alloy. The unit cell parameters determined by XPert HighScore Plus software fitting program.

Download English Version:

<https://daneshyari.com/en/article/1521976>

Download Persian Version:

<https://daneshyari.com/article/1521976>

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