



Studies on metal hydride electrodes containing no binder additives

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ARTICLE INFO

Article history:

Received 15 September 2009

Accepted 12 December 2009

Available online 21 December 2009

Keywords:

Ni-MH battery

Hydrogen sorption

Diffusion coefficient

Limited Volume Electrode

AB₅ alloy

ABSTRACT

Electrochemical properties of hydrogen storage alloys (AB₅ type: LaMm-Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}) were studied in 6 M KOH aq using Limited Volume Electrode (LVE) method. Working electrodes were prepared by pressing alloy powder (without binding and conducting additives) into a metal net wire serving as a support and as a current collector. Cyclic voltammetry curves reveal well defined hydrogen sorption and desorption peaks which are separated from other faradic processes, such as surface oxidation. Voltammograms of LVE resemble the curves obtained by various authors for single particle metal alloy electrodes. Hydrogen diffusion coefficient calculated at room temperature for LV electrodes and for 100% state of charge reaches a constant value of ca. 3.3×10^{-9} and 2.1×10^{-10} cm² s⁻¹, for chronoamperometric and chronopotentiometric measurements, respectively. A comparison of the electrodes with average alloy particle sizes of ca. 50 and 4 μm allows us to conclude that at room temperature hydrogen storage capability of AB₅ alloy studied is independent on the alloy particle size. On the other hand, reduction of the particle size increases alloy capacity at temperatures below -10 °C and reduces time of electrochemical activation of the electrode.

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1. Introduction

The nickel-metal hydride (Ni-MH) and Lithium Ion/Polymer batteries represent one of the most important segments of modern battery market. Although excellent for powering of many of portable devices or Hybrid Electro Vehicles (HEV) [1–3], the attainable current densities of these batteries are not sufficient for the use in devices in low temperature or requiring very high power densities, like e.g. power-tools. This limitation prohibits effective replacement of containing toxic elements Ni–Cd batteries in nearly all segments of the battery market.

It is well established that the weight of the materials used for battery construction reduces the theoretical energy density, even by a factor of two. As a consequence, the actual energy that is available from a battery under practical, close to optimum, discharge conditions constitutes only about 30% of the theoretical energy of the active materials [1]. Thus, new electroactive materials are under development and the construction of batteries is modified in order to improve their energy efficiency. Such a development, however, requires considerations of various factors that have significant influence on the electrode performance. In the

case of nickel-metal hydride battery these factors include: the electrode configuration, the active material porosity and the thickness, the alloy composition, the alloy particle size and structure and the electrolyte composition [4–13].

A huge variety of metal hydride materials has been examined for application in NiMH batteries. Some of them cannot be applied in industrial scale due to high hydrogen equilibrium pressure at room temperature or instability when in contact with the electrolyte [14–17]. Investigation of a new hydrogen storage material, such as thin films of magnesium based alloys, requires optimization of the procedure of the electrode preparation. Typically, the metal hydride electrodes for electrochemical tests are prepared by mixing and pressing of a hydrogen storage alloy powder together with a binding material, e.g., PTFE, PVA, graphite, or metal powders [1,5,7–9]. The binding material absorbs the forces generated due to volume expansion during charging of alloy particles and, thereby, helps preserving the mechanical integrity of the electrode. The metallic and carbon additives also improve the overall electronic conductivity of the electrode. The presence of the additives, however, has a significant influence on the electrode resistance and stability of hydrogen inside the alloy. When a new material for a metal alloy hydride electrode is tested, the intrinsic electrochemical properties of hydrogen absorbing alloy are the first to be determined. This task requires preparation of a new type of electrode containing only the alloy studied and free of binding

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materials. The electrodes especially useful for studying bulk electrode processes, such as hydrogen sorption, are Limited Volume Electrodes, LVE, already applied in our previous studies of hydrogen absorption in metals and alloys [18–20]. The Limited Volume Electrode (LVE) is an electrode containing a thin layer of a hydrogen storage material attached, e.g. by electrochemical deposition, to a matrix which is neutral in respect to hydrogen absorption processes and acts as a current collector [18–20]. Cyclic voltammetry is the method excellently showing advantages of application of LVE. Voltammograms of bulk hydrogen absorbing materials, such as Pd wires or foils, are dominated by high currents due to hydrogen absorption and its subsequent oxidative removal [18]. The oxidation of a large amount of hydrogen dissolved in the bulk of the metal occurs slowly due to diffusional limitations. This resulted in overlapping of currents of hydrogen desorption and surface oxidation. Under such conditions the surface oxides reduction peak is poorly defined and separation of surface oxidation currents from the currents of oxidative hydrogen desorption is practically impossible [18]. On the contrary, potentiodynamic desorption of hydrogen absorbed in a Pd-LVE is faster and takes place in a narrow potential range being completed well before the onset potential of the surface oxidation. Thus, the use of LVEs results in cyclic voltammetry curves with well separated signals of hydrogen absorption/desorption and surface oxidation/oxides reduction currents and being of comparable magnitude [18]. Moreover, formation of a very thin layer of MH alloy particles in a LV electrode allows omission of binding materials which are essential in construction of thicker MH alloy electrodes. Thus, Limited Volume Electrodes allow studying intrinsic electrochemical properties of the alloy particles without any influence of typical MH electrodes additives.

The aims of our works were: (i) preparation of thin electrodes (Limited Volume type) with various amounts of a metal hydride active material and without binder additives, (ii) determination of the stability of such prepared electrodes, (iii) evaluation of the electrochemical performance of the new metal-hydride electrodes and modified metal-hydride alloys.

2. Experimental

2.1. Limited Volume Electrode (LVE) preparation

Limited Volume type working electrodes were prepared by pressing a small amount (up to 22 mg) of an AB₅-type alloy (LaMm-Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}) in an Au metal mesh (99.9%, Goodfellow) under pressure of up to 20 MPa. Two kinds of alloy materials with the above composition were investigated: the standard one with a mean particle size of ca. 50 μm (VARTA, Germany), and the modified one, developed in the HydroNanoPol project, with the particle size reduced to 2–6 μm. Au metal mesh served as a support for the alloy and as a current collector. The gold was selected as a matrix material due to: (i) high electrochemical and chemical stability; (ii) electrochemical neutrality with a wide potential window without faradic processes; (iii) neutrality in respect to hydrogen absorption processes; (iv) good electronic conductivity and (v) softness and compressibility allowing pressing of the alloy particles into the gold net without damaging the structure of the formers.

2.2. Electrochemical setup and techniques

All the electrochemical tests were performed in a three-electrode system in a Teflon cell. MH alloy pressed into a gold mesh was used as a working electrode, Hg|HgO|6 M KOH (HYDROMET, Poland) and a gold sheet (Mint of Poland) served as a reference and counter electrodes, respectively. All the potentials in the text are referred to Hg|HgO. LV-MH electrodes were placed in gold clamps

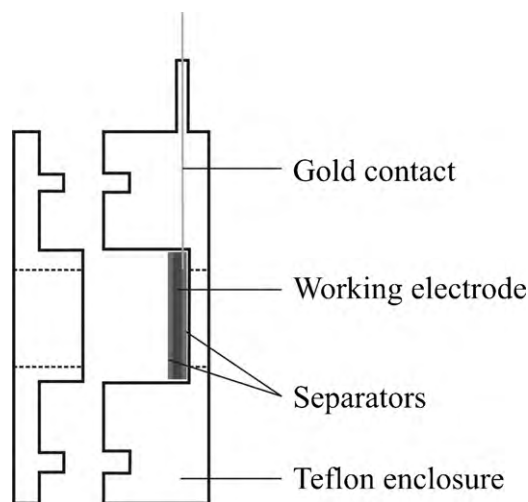


Fig. 1. Cross-section of Teflon holder containing limited volume type electrode.

acting as current collectors. The experiments with various depth of immersion of gold clamps proved that their contributions to the electrochemical signals measured was negligible. In some of the experiments, the LV-MH electrodes were placed in a Teflon holder with a design similar to the one used by Zheng et al. [4] and presented in Fig. 1.

The electrode was inserted between two pieces of a separator used in standard Ni-MH cell and a gold wire located between the electrode and one of separators acted as an electric contact. We found that such a design significantly reduces loss of the capacity of the MH-alloy electrode. The counter electrode was placed in a separated compartment and connected with the main cell compartment through a porous frit. The electrolyte solution of 6 M KOH was prepared with analytically grade reagents (POCH, Poland). Water used for preparation of solutions was subjected to two step purification procedure: double distillation as a first step and purification with Millipore system as a final step. The working solution was constantly deoxygenated with a small stream of pure argon (Multax, Poland) flowing through (before the measurements) and over the solution (during the measurements).

MH alloy electrodes were activated by 50 potential cycles in potential range between -1.1 and -0.4 V vs. Hg/HgO at 2 mV s^{-1} and subsequent three cycles of constant-current charging at 60 mA g^{-1} and discharging at 45 mA g^{-1} . The voltammetric, chronoamperometric and chronopotentiometric measurements were performed with an AUTOLAB 30 (Eco Chemie B.V., Netherlands) electrochemical analyzer. A scanning electron microscope LEO 435VP coupled with an EDS analyzer (Röntec EDR286) was used to analyze the structure and composition of the electrodes.

Low temperature measurements were carried out in Teflon cell described above and immersed in a KRYO51 bath in a Lauda (Pro-line 855) thermostat. The electrodes were fully charged at room temperature, and, after completing the charging process, temperature of the cell was lowered to the desired value in the range from -10 to -30 °C. This way, we were able to determine the influence of temperature on the process of the electrode discharge only.

3. Results

3.1. Physical characterisation of MH-alloy LV electrodes

Fig. 2 presents a SEM image of a freshly prepared working electrode. The image is combined with an EDS linear scan for Au shown on the bottom of the figure. We observe that the active alloy mass fills hollows of Au net with some uncovered parts of the net exposed

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