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Comparative study of hydrogen electrosorption from alkali metals electrolytes and hydrogen sorption from gas phase in AB_5 alloy

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ABSTRACT

AB_5-type metal alloy (LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$) was investigated in alkali metal hydroxide electrolytes (LiOH, NaOH, KOH, RbOH, CsOH) at various temperatures (0–30 °C) with no binding materials used. Limited volume electrode approach (LVE) was used in all electrochemical measurements. PCT Sievert's method was used to determine maximum hydrogen capacity of the alloy to be 4.7 at.H/f.u. (289 mAh/g). The highest electrochemical hydrogen capacity, nearly reaching the maximum value, was obtained in 6 M KOH solution at 30 °C (275.1 mAh/g) and in mixed 6 M LiOH/KOH solution at 30 °C (276.1 mAh/g). Temperature influence on electrochemical capacity of the alloy was investigated. In the temperature range of 0–30 °C the capacity is high and stable in 6 M KOH solution and mixed 6 M LiOH/KOH and 6 M NaOH/KOH solutions. It is possible to improve the capacity of the alloy by designign mixed alkali metal hydroxide solutions.

1. Introduction

Nickel-metal hydride batteries (Ni-MH) are very popular electrochemical power sources used to power portable devices or Hybrid Electric Vehicles [1–3]. Although the Ni-MH batteries are much less toxic than nickel-cadmium batteries and much cheaper and safer than lithium-ion batteries, their usage is limited because of not suitable current densities attainable. Ni-MH are also still inappropriate for using at low temperatures. One of the ways leading to improve properties of these power sources is modification of hydrogen storage materials used as anode [4]. In this paper, we continue investigation of a hydrogen storage AB_5-type metal alloy LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ [5] and we present the characterisation of the material in respect to determine optimum composition of the electrolyte.

Among the main goals of this study we show: (i) determination of maximum hydrogen capacity of the alloy using PCT Sievert's method, (ii) determination of electrochemical capacity of the alloy in 1 M and 6 M alkali metal hydroxide electrolytes, (iii) design of an optimum alkali metal hydroxide electrolyte giving the highest possible electrochemical capacity of the alloy, (iv) investigation of temperature influence of the capacity of the alloy in 1 M and 6 M solutions.

2. Experimental

2.1. Working electrode material

LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ – AB_5 type alloy for hydrogen storage has been used in our experiments. This material is widely used by producers as negative electrode in Ni-MH rechargeable batteries [5]. We have shown basic characterisation of LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ alloy in our previous paper [5]. The alloy crystallizes in hexagonal unit cell (P6/mmm) with unit cell parameters a = b = 5.0079(5) Å, c = 4.0521(4) Å, V = 88.007(16) $Å^3$ [5]. $CaCu_5$ structure was adopted according to native LaNi5 [6,7]. The grains of powder alloy precede average spherical coefficient of 1.146. The specific mass surface and volume surface of the alloy are equal 606 cm^2/g and 1539 cm^2/cm^3, respectively [5].

2.2. Preparation of Limited Volume Electrode (LVE)

Limited Volume Electrode approach is our proposition to work with powder electrode materials [8]. LVE method considers electrode preparation by high-pressure compression of AB_5 powder on gold matrix without any binders [5,9]. Avoiding binding materials (i.e. PTFE, PVA, graphite, metal powders) is

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important because they could influence the observed electrochemical behavior of the alloy investigated [1,10,11,12,13].

Limited Volume Electrodes were prepared (AB_5-LVE) by compression of LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ alloy into a golden metal mesh (Good Fellow, nominal aperture 0.25 mm, 99.99% Au) under pressure up to 20 MPa [8]. Thickness of the electrode was designed to reflect radius of the alloy particles, which were determined to be c.a. 50 μm. Golden matrix was chosen due to its electrochemical neutrality in wide potential window, chemical inertinite to hydrogen electrosorption processes, very good electric conductivity and malleable and plastic properties allowing formation of a stable electrode pallet. The working LVE electrode was then placed into PTFE holder specially designed by us for this purpose [5,9]. The electrode was immobilized between two pieces of polyethylene separator, type used in commercial Ni-MH batteries.

Such construction of the working electrode allows to obtain the electrode made of pure AB_5 alloy without any additives or contaminating materials. The electrochemical response of the electrode reflects properties of the neat LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ alloy.

2.3. Measurement conditions and electrochemical techniques

All the measurements were performed in a three-electrode system using a PTFE vessel using AB_5-LVE as working electrode Hg|HgO (6 M KOH, HYDROMET, Poland) as reference electrode and gold sheet (Mint of Poland) as counter electrode. In this paper, all the measured potentials are referred to electrode Hg|HgO.

Prior to the experiments, the AB_5-LVE working electrodes were activated during 50 cycles at 2 mV/s in the potential range between −1.1 V and −0.4 V vs. reference electrode Hg|HgO. Chronoamperometric (CA) and voltammetric (CV) measurements were performed with electrochemical AUTOLAB 30 analyser (The Netherlands, Eco Chemie B.V.). Lauda thermostat (Proline 855) with KRYO51 bath was used for temperature stabilisation.

2.4. Hydrogen sorption from the gas phase

PCT (pressure composition isotherms) were measured by the Sievert's method using HTP1 Hiden Isochema. H_2 gas and He gas were used, both with 99.9999% purity. PCT measurements were performed under hydrogen pressure up to 90 atm in the temperature range 35–150 °C. AB_5 alloy was activated under vacuum at 200 °C.

2.5. Other techniques

EDS and SEM measurements were performed to determine the composition of the studied alloy. FE-SEM Merlin form Zeiss EDS was used for data collection.

3. Results and discussion

3.1. Sorption of gaseous hydrogen

To have a clear reference point in determination of the capacity of the alloy form electrosorption experiments, we have performed PCT measurements to determine equilibrium pressure of hydrogen uptake and maximum hydrogen capacity of LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ alloy. The Sivert's results are shown in Fig. 1.

We noticed that investigated alloy can be charged with hydrogen under pressure of 0.7 atm at room temperature. For comparison, an equilibrium pressure of hydrogen sorption in $LaNi_5$ alloy is as high as 1.7 atm [14]. Thus, hydrogenation of LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ alloy is much easier in comparison to the neat $LaNi_5$ alloy.

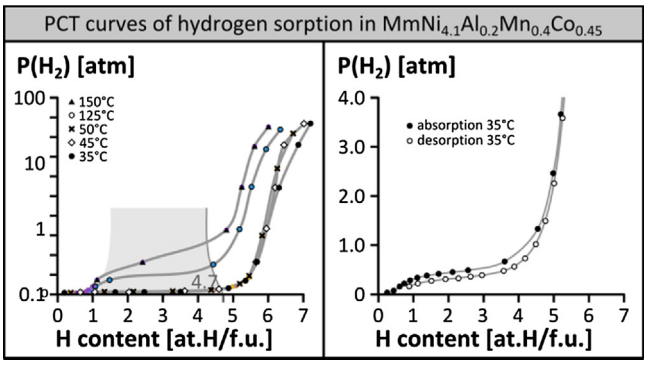

Fig. 1. Hydrogen sorption PCT curves of LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ alloy: absorption curves in the temperatures range of 35–150 °C (left), absorption and desorption curves at 35 °C (right).

We determined maximum hydrogen capacity of the investigated alloy to be 4.7 hydrogen atom per formula unit, which is smaller than capacity of $LaNi_5$ alloy (5.5 at.H/f.u.). Observed hysteresis (0.1–0.2 atm) is much smaller than hysteresis characteristic for $LaNi_5$ alloy observed to be 0.5 atm. It is worth mentioning that capacity of 4.7 at.H/f.u. corresponds to electrochemical capacity of 289 mAh/g.

We have determined thermodynamic parameters of gaseous hydrogen sorption in the AB_5 alloy using van't Hoff equation (Fig. 2). Due to low hysteresis observed (0.1–0.2 atm) for calculations we used absorption curves only. Enthalpy effect (−33.5 kJ/mol H_2) and entropy effect (−161.3 kJ/K mol H_2) of hydrogen sorption in the investigated material show they are comparable to other similar AB_5 type alloys (Table 1). At room temperature under 1 atm formation of hydrogenated phase is unflavoured (ΔG° = 14.56 kJ/mol). We determined equilibrium temperature to be 207.7 K (−65.3 °C).

We investigated mechanical resistance of the AB_5 alloy to the process of hydrogen uptake and release. SEM images show magnified pictures of the alloys surface after hydrogenation from gaseous phase and form solution (Fig. 3). In both cases hydrogenation of the alloy causes cracks due to high strain of the lattice, which resulted from differences between the volumes of the unit cells of the pure alloy and hydrogenated alloy. This phenomenon is well known and describe in the literature [14], however, one can see that damages caused by sorption of gaseous hydrogen are significantly larger than results of hydrogen electrosorption form aqueous solutions. This difference might origin from different mechanism of hydrogen uptake when solid/gas

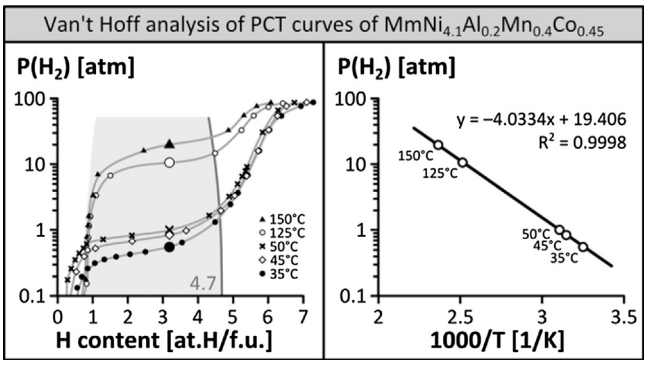

Fig. 2. Determination of thermodynamics of hydrogen sorption in LaMm–$Ni_{4.1}Al_{0.3}Mn_{0.4}Co_{0.45}$ alloy using Van't Hoff equation: PCT absorption curves (left) and Van't Hoff curve (right).