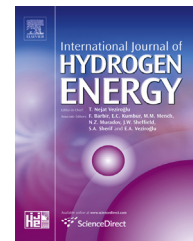


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Molybdenum effect on the kinetic behavior of a metal hydride electrode

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ABSTRACT

In the present investigation, the effect of the Mo in the $\text{LaNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{(0.4-x)}\text{Al}_{0.3}\text{Mo}_x$ AB5-type hydrogen storage alloys was studied. The alloys structural and microstructural characterizations were performed by means of X-ray diffraction phase analysis and scanning electron microscopy.

The electrochemical properties were studied through the measurements of discharge capacity, activation process, rate capability and electrochemical impedance spectroscopy of the electrodes.

The replacement of manganese by molybdenum, in the intermediate concentration tested (2% w/w) has a positive effect. This alloy presents the greatest discharge capacity, the closest potential to system equilibrium potential and therefore the lowest overpotentials. This alloy also has the best behavior for high-rate dischargeability and in concordance, the lowest charge transfer resistance. This improvement is thought to be due to an increase in the active area.

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1. Introduction

Metal hydride alloys are mostly used as materials for negative electrodes in alkaline rechargeable cells and hydrogen storage.

Nickel-metal hydride batteries are currently applied in many fields such as portable electronic devices and electric vehicles hybrid electric vehicles. These batteries depict larger gravimetric and volumetric energy densities than nickel–cadmium

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batteries. Besides, they are friendlier towards the environment. The performance of a nickel-metal hydride battery strongly depends on the characteristics on the anode [1–8].

The investigations carried out with intermetallic AB₅ alloys; seek to partially replace the constituent elements of the LaNi₅ compound by other chemical elements to enhance its electrochemical properties. The developed alloys, such as LaNi_{4.8}Co_{0.5}Sn_{0.25}, La_{0.89}Nd_{0.2}Ni_{4.75}Co_{0.5}Sn_{0.25} and La_{0.8}Ce_{0.2}Ni_{4.8}Sn_{0.25}, which inner compositions retain lanthanum and nickel elements, are those that exhibit better behaviors. The latter presents a lower equilibrium pressure and minimum hysteresis in the curves of charge/discharge, as well as depicts a wide range of hydrogen absorption [2–9].

Recently, much more interest has grown in the study of metal hydrides based on Laves phases of zirconium, i.e. AB₂ type intermetallic compounds due to their greater storage capacity, and hence greater electrical charge capacity of the battery. However, its power density was not comparable to those of AB₅ type, which motivate investigation developments in order to optimize its composition [10–12].

Metal alloy plays a fundamental role in electrode processes of hydrogen absorption, defining the hydrogen reaction rate with the metal as well as the incorporation into its structure.

Different processes occur during activation [3,13–16] such as: i) reduction of surface oxides that interfere with the absorption of hydrogen, ii) reduction of the particle size due to the fractures caused by the increase in volume, iii) change in the chemical composition and/or metal surface structure [12].

Recently, AB₅ [17–21] metal hydride (MH) alloys have been intensively investigated to improve the performance of based Ni/MH batteries. Molybdenum was found to be beneficial to the low-temperature applications [22–25]. Besides, it was found that the addition of molybdenum improved the –40 °C charge efficiency through the enhancement of surface charge-transfer reaction [24]. The improvement in low-temperature performance in the molybdenum-containing AB₅ alloy was also confirmed by Iwakura et al. They connected the performance improvement of this alloy to its better bulk hydrogen diffusion and surface charge-transfer reaction [26]. Jaksic demonstrated a reduction in the hydrogen overpotential inside the alloy that had its surface being modified by galvanic codeposition of molybdenum and cobalt [27]. Furthermore, it was reported an increased hydrogen storage capacity with the substitution of nickel or cobalt by molybdenum [28,29]. Small amounts of molybdenum-substitution were found to increase the room temperature high-rate dischargeability (HRD) and surface charge-transfer current [30,31].

Although many general characteristics of molybdenum-modified AB₅ alloys have been reported, a more systematic study on the influence of molybdenum to the structural and electrochemical properties is needed and will be presented in this paper.

The present study examines the electrochemical properties of the LaNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3} electrode material and their correlations with structural-microstructural characteristics. The effect of manganese substitution by molybdenum in this material is also evaluated, at room temperature, with regard to electrochemical and structural-microstructural properties.

2. Experimental

2.1. Synthesis of alloys and fabrication of negative electrodes

The alloys are prepared by arc melting adequate proportions of the composition elements (purity better than 99.9%) inside a copper-cooled hearth under high purity argon (99.998%). The alloys were remelted for the purpose of homogenization. After then, it was mechanically pulverized for the electrode formation. For the electrochemical characterization, electrodes were prepared by compacting a mixture of 50 mg of sample powders with equal amounts of teflonized carbon (Vulcan XC-72), inside a cylindrical die to a pressure of 200 MPa at room temperature, resulting the total electrode surface of 2 cm². A nickel wire was used as current collector. Details of electrode preparation are depicted in a previous work [9].

Three alloys were synthesized replacing manganese by molybdenum: AB₅M0 (Mo 0% w/w), AB₅M1 (Mo 2% w/w) and AB₅M2 (Mo 5% w/w).

2.2. Structural and microstructural characterization of MH electrodes

The prepared electrodes were subjected to X-ray diffraction characterization. X-ray powder diffraction data were collected for all the samples using a Rigaku ULTIMA IV, 285 mm radius, powder diffractometer operating in Bragg Brentano geometry. CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) monochromatized with a diffracted beam bent germanium crystal was used to collect data over the 10–110° 2 θ range in steps of 0.02° using a scintillation detector. Fixed slits of 1/3° were used for data collection to prevent beam spillage outside the 2 cm long sample (along the beam-path) at low angles. Peak positions were extracted from the data using the software POWDERX [32] and peak indexing and unit cell determination was performed with the software DICVOL04 [33] in order to determine the unit cell and space group symmetry of the crystalline samples.

Further analysis consisted in the full pattern profile fitting, using the Rietveld method [34] by means of the EXPGUI-GSAS suite [35,36] that allowed to extract relevant structural parameters and corresponding weight fraction in the case of multiphase systems.

Before electrochemical testing of the electrodes, the surface alloy microstructures were examined by means of a scanning electron microscope (SEM, JEOL JSM 5900) that employed a 25 kV secondary electron imaging mode.

2.3. Electrochemical characterization

We worked with AB₅-type alloys with nominal compositions AB₅M0, AB₅M1 and AB₅M2. The hydride forming electrodes were made as it just has detailed [9]. The mixture was pressed onto a nickel mesh at room temperature. The geometrical area of the electrodes was 2 cm² and the thickness was around 1 mm.

Electrochemical measurements were made in a three-compartment cell with the corresponding working electrode (metal hydride electrode), counter electrode (nickel mesh) and

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