



Investigations of AB₅-type negative electrode for nickel-metal hydride cell with regard to electrochemical and microstructural characteristics

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ABSTRACT

In the present investigation, AB₅-type hydrogen storage alloys with compositions Mm_{0.8}La_{0.2}Ni_{3.7}Al_{0.38}Co_{0.3}Mn_{0.5}Mo_{0.02} and Mm_{0.75}Ti_{0.05}La_{0.2}Ni_{3.7}Al_{0.38}Co_{0.3}Mn_{0.5}Mo_{0.02} are synthesized by radio-frequency induction melting. The electrochemical properties are studied through the measurements of discharge capacity, activation process, rate capability, self-discharge rate and cyclic stability of both the electrodes. Pressure-composition isotherms are plotted by converting the electrode potential into the hydrogen pressure following the Nernst equation. The structural and microstructural characterizations are performed by means of X-ray diffraction phase analysis and scanning electron microscopy of as-fabricated and electrochemically tested electrodes. An attempt is made to correlate the observed electrochemical properties with the structural–microstructural characteristics.

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1. Introduction

The continuous increasing requirement of energy demands the fast development of secondary batteries as power sources. Due to the quality of high specific energy, the capability of performing at high charging–discharging rates, environmental friendliness and interchangeability with a nickel–cadmium battery, the nickel–metal hydride (Ni–MH) battery has been widely investigated and applied in portable telecommunications equipment, electric tools and hybrid electric vehicles [1–3].

In state-of-the-art hydrogen technology, two hydrogen storage systems, namely AB₂ (TiMn₂) and AB₅ (LaNi₅/MmNi₅) are viable negative electrode materials in Ni–MH batteries [4–7]. Most of the early and recent work on the AB₅-type hydrogen storage system for the MH electrode has been based on the composition typified by Mm(Ni–Al–Co–Mn)₅ [8–18]. Nowadays, the MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75} alloy is one of the compounds that are used as commercialized electrode materials (Mm = mischmetal). Cobalt (Co) is an expensive metal and in the aforementioned alloy it accounts for almost 50% of the total cost of the raw material [19]. Hence it is desirable to replace Co by a less expen-

sive element without decreasing the hydrogen storage capacity significantly. Some preliminary studies on a low-Co variant typified by Mm_{0.8}La_{0.2}Ni_{3.7}Al_{0.38}Co_{0.3}Mn_{0.5}Mo_{0.02} have been carried out and a discharge capacity close to 300 mAh g^{−1} has been obtained [20]. The cycle performance and correlation between structural–microstructural characterizations have not, however, been extensively explored for this material.

The present study examines the electrochemical properties of the Mm_{0.8}La_{0.2}Ni_{3.7}Al_{0.38}Co_{0.3}Mn_{0.5}Mo_{0.02} electrode material and their correlations with structural–microstructural characteristics. The effect of titanium substitution in this material is also evaluated with regard to electrochemical and structural–microstructural properties.

2. Experimental details

2.1. Synthesis of material and fabrication of negative electrode

The ingredients of the alloy in a stoichiometric ratio were mixed, pelletized and then melted in a radio-frequency induction furnace under an argon atmosphere. The pellets were remelted three times for the purpose of homogenization. The as-synthesized ingot was mechanically pulverized and the powder of particle size <50 μm was selected for the formation of the electrode. In the present investigation graphite was used as a conductor for the fabrication of negative electrode. A roll-compacted negative electrode was prepared by taking the alloy, graphite powder and Teflon suspension

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in a ratio of 85, 10 and 5 (wt.%). The resulting mixture was rolled against a smooth glass plate. The rolled sheet of the active material with additives was folded around a nickel mesh (dimension: 2 cm × 2 cm) and pressed at $6.4 \times 10^6 \text{ kg m}^{-2}$ for 15 min. The physical thickness of the resulting electrode was about 0.3 mm. The metal hydride (MH) electrodes thus prepared were subjected to formation in electrochemical cells that contained 6 M KOH electrolyte. Sintered nickel hydroxide electrodes were placed on either side of a MH electrode in each cell. The electrochemical capacity of the positive electrode was designed to be sufficiently larger than that of the negative electrode. Both the electrodes were inserted into the pockets made out of the polypropylene separator cloth. The potential of the negative electrode was measured with respect to a Hg|HgO|6 M KOH electrode in an open cell at 298 K. The negative electrode containing 0.5 g of hydrogen storage alloy was charged for 14 h and discharged to -0.6 V , both at 33 mA g^{-1} . The potential of the negative electrode was monitored with an x-y recorder.

2.2. Structural and microstructural characterization of MH electrodes

As-fabricated and electrochemically tested electrodes were subjected to X-ray diffraction characterization, employing a Philips X-ray diffractometer (PW 1710) equipped with a graphite monochromator that operated with copper K_{α} radiation. Before and after electrochemical testing of the electrodes, the surface microstructures were examined by means of a scanning electron microscope (SEM, Philips XL-20 series) that employed a 30 kV secondary electron imaging mode.

3. Results and discussion

3.1. Structural characterization

The X-ray diffraction (XRD) profiles of as-fabricated and electrochemically tested electrodes using $\text{Mm}_{0.8}\text{La}_{0.2}\text{Ni}_{3.7}\text{Al}_{0.38}\text{Co}_{0.3}\text{Mn}_{0.5}\text{Mo}_{0.02}$ or $\text{Mm}_{0.75}\text{Ti}_{0.05}\text{La}_{0.2}\text{Ni}_{3.7}\text{Al}_{0.38}\text{Co}_{0.3}\text{Mn}_{0.5}\text{Mo}_{0.02}$ alloys are shown in Figs. 1 and 2, respectively. All synthesized alloys are found to have a single phase structure and a homogeneous composition. Both the alloys crystallize with a hexagonal CaCu_5 -type structure of symmetry $\text{P6}/\text{mmm}$. The lattice parameters and unit cell volumes of these alloys are given in Table 1.

The substitution of Ti at the place of mischmetal (Mm) in the parent alloy ($\text{Mm}_{0.8}\text{La}_{0.2}\text{Ni}_{3.7}\text{Al}_{0.38}\text{Co}_{0.3}\text{Mn}_{0.5}\text{Mo}_{0.02}$) gives an increase in both the 'a' and 'c' parameters (Table 1) by 0.11 and 0.17%, respectively. During the hydriding/electrochemical charging process, hydrogen atoms enter the alloy lattice and result in lattice expansion [21,22]. Because of this expansion, the unit cell volume also increases. Due to residual hydrogen, a small increase in the unit cell volume occurs in electrochemically tested electrodes. Changes in the lattice parameters of electrochemically tested electrodes of the parent alloy are $\Delta a = 0.69\%$ and $\Delta c = 0.54\%$ with respect to the as-fabricated alloy. Similarly, these changes are calculated as $\Delta a = 0.22\%$ and $\Delta c = 0.59\%$ for the Ti-substituted alloy. A comparison of both the alloys reveals an almost equal change in the lattice parameter 'c' after electrochemical testing. On the other hand, the change in the lattice parameter 'a' is small (0.22%) in Ti-substituted alloy in comparison to the parent alloy (0.69%). Similarly, the change in the unit cell volume for Ti-substituted alloy after electrochemical testing is 1.03%, which is less than that of the parent alloy (viz., 1.93%).

The X-ray diffraction patterns in Figs. 1a and 2a indicate that as-fabricated electrodes of both the alloys contain the peaks of single phase metal hydride (MH), graphite and the binder. The analysis of the XRD pattern shown in Fig. 1b reveals the presence of extra

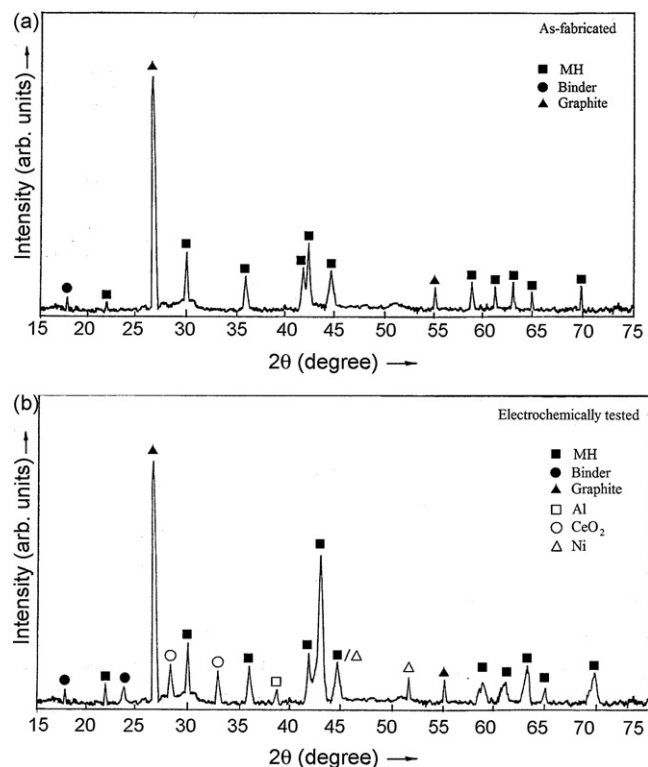


Fig. 1. X-ray diffraction patterns of (a) as-fabricated and (b) electrochemically tested electrodes of $\text{Mm}_{0.8}\text{La}_{0.2}\text{Ni}_{3.7}\text{Al}_{0.38}\text{Co}_{0.3}\text{Mn}_{0.5}\text{Mo}_{0.02}$; notice the presence of XRD peaks corresponding to CeO_2 , Al and Ni.

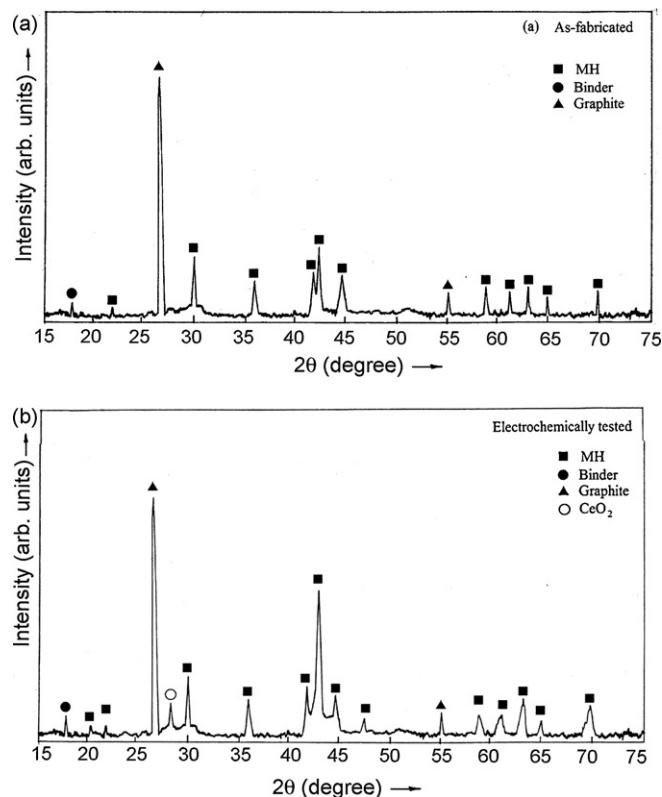


Fig. 2. X-ray diffraction patterns of (a) as-fabricated and (b) electrochemically tested electrodes of $\text{Mm}_{0.75}\text{Ti}_{0.05}\text{La}_{0.2}\text{Ni}_{3.7}\text{Al}_{0.38}\text{Co}_{0.3}\text{Mn}_{0.5}\text{Mo}_{0.02}$; notice that XRD peaks of only CeO_2 are present.

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