Effect of Gd and Co content on electrochemical and electronic properties of $La_{1.5}Mg_{0.5}Ni_7$ alloys: A combined experimental and first-principles study

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Abstract

In this work we investigate the effect of Gd and Co substitutions on the electrochemical and electronic properties of $La_{1.5}Mg_{0.5}Ni_7$ alloy. Two series of $La_{1.5-x}Gd_xMg_{0.5}Ni_7$ (x = 0.0, 0.25, 1.0) and $La_{1.5}Mg_{0.5}Ni_{7-y}Co_y$ (y = 0.0, 0.5, 1.5) alloys are produced using mechanical alloying technique. The X-ray diffraction indicates multi-phase character of the samples with majority of hexagonal Ce_2Ni_7-type and rhombohedral Gd_2Co_7-type structures of $(La,Mg)_2Ni_7$ phase. Partial substitutions of La by Gd or Ni by Co in $La_{1.5}Mg_{0.5}Ni_7$ phase result in increase of cycle stability of the metal hydride (MH_x) electrodes. All considered alloys reach the maximum discharge capacity after three charging-discharging cycles. Two optimal compositions, in respect of electrochemical properties, are subsequently investigated by the X-ray photoelectron spectroscopy (XPS). The experimental analysis of the valence band is further extended by the density functional theory (DFT) calculations. We also discuss the effects of alloying and site preference of dopants on the position of the van Hove-type singularity as observed in the electronic densities of states (DOS) in proximity of the Fermi level.

Keywords: Metal hydrides, Mechanical alloying, XPS, DFT, La-Mg-Ni alloys

1. Introduction

The next generation of electrode materials for nickel-metal hydride (Ni-MH_x) batteries are the $(La,Mg)_2Ni_7$-type hydrogen storage alloys [1–4]. It has been found that the limited cycle stability of the AB_2-type and AB_5-type materials could be compensated in the A_2B_7-type alloys [4]. It has been shown that substitution of La with other rare-earth element [4–9] and Ni with alternative 3*d* element [10–12] also modifies the electrochemical performance of the A_2B_7 materials. However, a cycling stability and high-rate discharge capacity, especially for high discharging rates and material and processing costs, still need improvements to satisfy increasing demands of the market [13, 14].

The most common phases of the multi-phase La-Mg-Ni-based alloys are $(La,Mg)Ni_3$, $(La,Mg)_2Ni_7$ and $(La,Mg)_5Ni_{19}$ [15, 16]. They are all composed of $[A_2B_4]$ and $[AB_5]$ subunits stacked alternatively along the c axis and forming superlattice structures [17]. Studies on the electrochemical performance of the A_2B_7-type single-phase $La_{1.5}Mg_{0.5}Ni_7$ alloy have revealed that both the $(La,Mg)_5Ni_{19}$ and the $LaNi_5$ phases have catalytic effects on the fast discharge of the alloy [7]. A partial replacement of La by the rare earth (RE) atoms and Ni by Co or Al can affect the crystal structure of the A_2B_7 alloys. Nd and Co doped alloys can be applied as negative electrodes in Ni-MH_x batteries, which are characterized by improved cyclic durability [8, 18]. By adjusting the RE concentration in the $(RE\text{-}Mg)_2Ni_7$ alloys it is possible to enhance the electrochemical hydrogen storage properties of the alloy electrodes. For $La_{0.8}Gd_xMg_{0.2}Ni_{3.15}Co_{0.25}Al_{0.1}$ alloys (x from 0.0 to 0.4) it has been shown that Gd substitution significantly affects the phase composition of the alloys [16]. Additionally, the partial substitution of Ni by Co atoms in the A_2B_7 alloy have also resulted in improving the electrochemical discharge capacity [19]. An addition of Co atoms to AB_5 alloys reduces its volume expansion caused by hydriding, which in turn reduces the pulverization and corrosion of the alloys [20, 21]. Lately, it has been shown that the Pr, Nd and Co-free A_2B_7-type, $La_{13.9}Sm_{24.7}Mg_{1.5}Ni_{58}Al_{1.7}Zr_{0.14}Ag_{0.07}$ alloy exhibits excellent hydrogen-storage and electrochemical performance. The high rate discharge abilities were 97%, 86% and 78% at discharge current densities of 330, 970 and 1600 mAh/g, respectively [22]. The improvement of hydrogenation properties of the $(La,Mg)_2Ni_7$ system may be

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