



A new AB₄-type single-phase superlattice compound for electrochemical hydrogen storage

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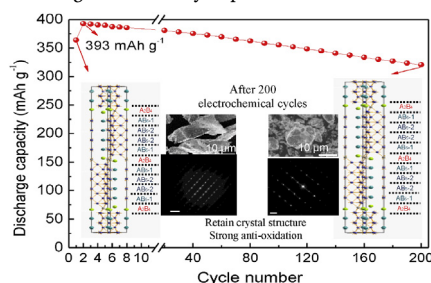


HIGHLIGHTS

- A new AB₄-type single-phase MH superlattice compound is obtained.
- The AB₄-type compound exhibits a high capacity and superior rate discharge ability.
- It possesses great crystal structure stability and strong anti-oxidation ability.
- The discrete lattice expansion between α and β phases leads to a lattice strain.
- The capacity decay is mainly due to particle pulverization from the lattice strain.

GRAPHICAL ABSTRACT

For the first time, a novel AB₄ single-phase superlattice MH compound affording high capacity, rate-capability and long-term stability is presented.



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ABSTRACT

Metal-hydride based hydrogen storage materials have recently been designed for rechargeable batteries where protons serve as charge carriers. However, the metal-hydride materials generally suffer from poor cycling stability during electrochemical hydrogen storage process. Herein, we report, for the first time, a new AB₄-type single-phase La_{0.78}Mg_{0.22}Ni_{3.67}Al_{0.10} metal-hydride superlattice compound with excellent electrochemical hydrogen storage properties. This metal-hydride compound is able to deliver a high discharge capacity of 393 mAh g⁻¹, according to its hydrogen gas absorptivity (1.50 wt%), and exhibit a superior rate capability of 180 mAh g⁻¹ even at 1.8 A g⁻¹. In addition, the compound retains its crystalline structure when subjects to electrochemical cycling and shows strong anti-oxidation ability in alkaline electrolyte, indicative of excellent cyclability. Our results demonstrate that the AB₄-type superlattice structure metal-hydride can be a promising electrode material for hydrogen storage, and provide a new avenue for the applications of metal-hydride batteries.

1. Introduction

Hydrogen, an environmentally attractive fuel, is a genuine substitute to current carbon dependence for energy production [1–4].

Hydrogen can be produced from many sources such as photocatalysis [5], biomass conversion [6], and water splitting by electrolysis [7]. To date, the implementation of hydrogen lies on the engineering of hydrogen storage in a safe, efficient, and reversible system to a large

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extent [8,9]. Metal hydrides (MHs) have been serving as one of the most important hydrogen storage materials, and recently designed for hydrogen sensors, switchable mirrors, rechargeable batteries, and other energy-storage and conversion-related applications [10]. Meanwhile, rechargeable nickel/metal hydride (Ni/MH) batteries incorporated with hydrogen in the form of MHs during battery charging have been in widespread use. Notwithstanding the over-decade challenges of the higher power density for Lithium-ion batteries (LIBs) [11,12], Ni/MH batteries are still crucial for hybrid electrical vehicles (HEV) and large-scale energy storage systems (ESS) manifested by the advantages such as its resistance to overcharge and overdischarge, high rate discharge ability, easily recycled and outstanding safety characteristics [13–15]. As a popular negative electrode material of Ni/MH batteries, misch metal based AB_5 -type MH compounds deliver enhanced electrochemical properties, but the major issue concerns its low discharge capacity, which is not compatible with the demand of increased capacity density.

La–Mg–Ni-based hydrogen storage compounds are a new class of negative electrode materials of Ni/MH batteries that fulfil the needs of high power applications and thereby attracting considerable interest [16]. These kinds of compounds have superlattice structures where $[AB_5]$ and $[A_2B_4]$ subunits stack alternatively along c axis in ratios of 1:1, 2:1 or 3:1 forming AB_3 , A_2B_7 or A_5B_{19} phases, respectively [17,18]. However, the low capacity retention of the compounds in alkaline electrolytes has been hindering them from widespread applications, attributed to factors of the intense pulverization and oxidation/corrosion of active components [19–21]. Recently, studies found that the instability of the superlattice structures can also lead to the capacity decay, as the superlattice structures can be distorted or destroyed to amorphous states by the repeated hydrogen absorption/desorption, resulting in reduced discharge capacity [22–24]. Further studies found that the structural stability of the superlattice structure is closely related to the two $[A_2B_4]$ and $[AB_5]$ subunits. Liu et al. reported that an increased ratio of $[AB_5]/[A_2B_4]$ can increase the property match with the subunits, producing lower lattice strain, and thus reducing pulverization and amorphization [25]. These studies raise the question as to whether $[AB_5]$ and $[A_2B_4]$ subunits can stack by a higher ratio, where the enhanced structural stability is expected in the formed structure.

Indeed, $[AB_5]$ and $[A_2B_4]$ subunits can stack along the c axis in a higher ratio of 4:1 to form an AB_4 -type superlattice structure in the $La_{0.8}Mg_{0.2}Ni_{3.2}Co_{0.3}(MnAl)_{0.2}$ compound, and this is interpreted by the selective occupation of Mg and Al atoms [26]. Such a superlattice structure had been predicted earlier by Khan et al. in the RE–Co system [27]. Zhang et al. subsequently obtained a AB_4 phase with a content of 75 wt% in the $La_{0.85}Mg_{0.15}Ni_{3.8}$ compound by a spark plasma sintering method, and found that the anisotropic effect of the unit cell of the AB_4 phase was greatly decreased compared to that of A_5B_{19} and A_2B_7 phases after hydrogen absorption [28]. Unfortunately, in particular, the structural changes of the intrinsic stacking subunits of the $[AB_5]$ and $[A_2B_4]$ and its structural stability upon hydrogen absorption/desorption are still unknown. To understand the issue, it is crucial to prepare a compound with a pure AB_4 phase structure and identify its electrochemical hydrogen storage properties, but no AB_4 single phase has been obtained due to rather similar formation temperature and composition of the superlattice phases. Herein, we for the first time prepared a single-phase AB_4 type $La_{0.78}Mg_{0.22}Ni_{3.67}Al_{0.10}$ hydrogen storage compound by an induction melting method. The structural characteristics of the AB_4 phase involved in the hydrogen absorption/desorption and its electrochemical hydrogen storage properties are studied, as well as the mechanism of the discharge capacity degradation.

2. Experimental

2.1. Sample preparation

The $La_{0.78}Mg_{0.22}Ni_{3.67}Al_{0.10}$ compound was prepared by induction

melting the constituent metals, including La, Mg, Ni and Al, with a purity of 99.5% under argon (Ar) atmosphere. The blocky original compound was placed in a vacuum furnace and then annealed at 1223 K for 14 h under an argon atmosphere (0.02 MPa), which first heated from room temperature to 873 K with 5°C min^{-1} and then heated to 1223 K with 1°C min^{-1} , and finally quenched at room temperature. The elemental compositions of the original and annealed compounds were confirmed by a Varian Liberty 100 inductively coupled plasma (ICP) analyzer, and the obtained compositions are listed in Table S1.

2.2. Materials characterization

The original and annealed compounds were crushed mechanically into particles (< 400 mesh) for X-ray diffraction (XRD) measurements using a Rigaku D/Max-2500/PC X-ray diffractometer (Cu $K\alpha$ radiation) at 50 kV. The structural change of the compounds upon hydrogen absorption/desorption and cycling were characterized by ex situ X-ray diffraction method. The XRD data were collected over a range of 2θ from 10° to 80° with a step of 1° min^{-1} increment and analyzed by the Rietveld method using RIETICA software. Crystal structure was depicted by Material studio 6.0 and simulated to X-ray pattern by the Reflex module inside. Morphology of the compound was characterized by S-4800 scanning electron microscopy (SEM) and the phase composition was studied by Energy Dispersive X-Ray Spectroscopy (EDX). Transmission electron microscope (TEM) analysis was performed on JEM-2010 operating at 20.0 kV. X-ray photoelectron spectrometry (XPS) analysis was performed on an ESCALABMKLL X-ray photoelectron spectrometer with monochromatic Al $K\alpha$ radiation.

2.3. Hydrogen absorption and desorption measurements

Pressure-composition-temperature (PCT) characteristic for the sample was measured using Sieverts' method at 303, 323 and 353 K. Prior to taking PCT measurements, the sample was firstly held at 298 K under 3 MPa hydrogen atmosphere until the sample was fully hydrogenated. After activation, the sample was dehydrogenated against a backpressure of 0.0000 MPa for 2 h. The hydrogen absorption/desorption property of the compound was measured at 298 K under 2 MPa hydrogen atmosphere. For structural change studies of the compounds upon hydrogen absorption/desorption process, the powder sample was taken out in a glove box and measured immediately.

2.4. Electrochemical measurements

Each sample was firstly ground mechanically into powders between 200 and 400 meshes, and the powders (0.15 g) was mixed with nickel powders (0.75 g) to cold press into a pellet as a negative electrode. Then the negative electrode was assembled in a half-cell with a $Ni(OH)_2$ sintered electrode as the positive electrode and 6 M KOH solution as the electrolyte. The half-cell was charged at a current density of 60 mA g^{-1} (0.2C) for 8 h (the over-charged ratio approximately 20%) and then discharged at the same current density for activation at 298 K. For cycling, we changed the current density into 360 mA g^{-1} and charged for 1.6 h, and then discharged the cell at 60 mA g^{-1} with a cut-off potential of 1.0 V at 298 K. For high rate dischargeability (HRD) measurement, the discharging current density was tuned to 300 (1C), 600 (2C), 900 (3C), 1200 (4C), 1500 (5C) and 1800 (6C) mA g^{-1} , respectively at 298 K. The low-temperature and high-temperature properties of the cell were tested in a cooling and heating system in a three electrode cell, which Hg/HgO was used as the reference electrode, respectively, where the cell was charged at 0.2C at 298 K, and discharged to 1.0 V after 2 h conservation at 233, 243, 253, 318 and 333 K, respectively. The linear polarization curves and the potential static step discharge curves were performed on CHI660C potentiostat at 298 K in a three electrode cell, which were measured at a scanning rate of 5 mV min^{-1} from -5 to

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