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In operando neutron diffraction study of $LaNdMgNi_9H_{13}$ as a metal hydride battery anode

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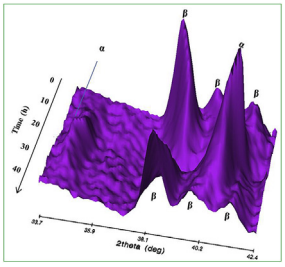
HIGHLIGHTS

- $LaNdMgN_9$-D_2 system studied *in operando* by neutron diffraction.
- Nd substitution enhances the high rate discharge performance.
- H/*M* ratio is higher for the metal-D_2 gas system as for the electrochemical charging.
- Both *alpha* metal and *beta* deuteride phases have extended solid solution ranges.
- D atoms fill 7 types of interstitial sites.

GRAPHICAL ABSTRACT



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ABSTRACT

La_2MgNi_9-related alloys are superior metal hydride battery anodes as compared to the commercial AB_5 alloys. Nd-substituted $La_{2-y}Nd_yMgNi_9$ intermetallics are of particular interest because of increased diffusion rate of hydrogen and thus improved performance at high discharge currents. The present work presents *in operando* characterization of the $LaNdMgNi_9$ intermetallic as anode for the nickel metal hydride (Ni-*M*H) battery. We have studied the structural evolution of $LaNdMgNi_9$ during its charge and discharge using *in situ* neutron powder diffraction. The work included experiments using deuterium gas and electrochemical charge-discharge measurements. The alloy exhibited a high electrochemical discharge capacity (373 mAh/g) which is 20% higher than the AB_5 type alloys. A saturated β-deuteride synthesized by solid-gas reaction at $P_{D2} = 1.6$ MPa contained 12.9 deuterium atoms per formula unit (D/f.u.) which resulted in a volume expansion of 26.1%. During the electrochemical charging, the volume expansion (23.4%) and D-contents were found to be slightly reduced. The reversible electrochemical cycling is performed through the formation of a two-phase mixture of the α-solid solution and β-hydride phases. Nd substitution contributes to the high-rate dischargeability, while maintaining a good cyclic stability. Electrochemical Impedance Spectroscopy (EIS) was used to characterize the anode electrode on cycling. A mathematical model for the impedance response of a porous electrode was utilized. The EIS showed a decreased hydrogen transport rate during the long-term cycling, which indicated a corresponding slowing down of the electrochemical processes at the surface of the metal hydride anode.

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1. Introduction

Rechargeable batteries should provide high energy density, safety, environmental compatibility, low cost, long calendar life, small size and light weight, with properties tailored towards the demand required from applications. Aiming at satisfying these requirements, nickel-metal hydride (Ni-*M*H) batteries, belonging to the green batteries, have been developed and commercialized [1,2]. In the Ni-*M*H batteries, hydrogen storage alloys (their hydrides) are used as active materials immersed into an aqueous alkaline electrolyte (KOH). $LaNi_5$ was the first anode material used in the *M*H battery. However, its rapid capacity decay on cycling limited its commercial application [3]. This drawback was addressed by modifying $LaNi_5$ via a substitution of Ni by Co and Al and of La by a mischmetal [4]. Thus, a rapid market growth of the Ni-*M*H batteries took place and they became the dominant advanced battery technology for hybrid electric vehicles (HEVs) fulfilling the requirements set by automotive companies [5].

A variety of hydrogen storage alloys have been studied, including the rare earth based AB_5-type alloys, Ti and Zr based AB_2 alloys, *AB*, Mg-based and the Rare Earth (*RE*)-Mg-Ni based alloys as active anode materials [6,7]. The latter alloys include a series of ternary rare earth magnesium based hydrogen storage alloys with a stoichiometric composition RE_2MgNi_9 (where, RE = La) reported back in 2000 [8]. Development of the Mg-containing alloys allowed increasing electrochemical discharge capacity, from 320 mAh/g (AB_5) to 400 mAh/g, for the Mg-containing alloys.

Recently, systematic theoretical and experimental studies of the La–Mg–Ni-based hydrogen storage alloys with super-stacking structures have been performed [9], as they are regarded as high performance negative electrode materials of the Ni-*M*H batteries. Liao et al. [10] reported electrochemical discharge capacity of the La_2MgNi_9 electrode is 397 mAh/g. Modelling of the electrochemical discharge process of the metal hydride electrode [9], allowed an optimization of the metal hydride electrodes, based on estimation of the diffusion coefficient of hydrogen and equilibrium content of H in the solid solution domain in the metal hydrides.

Ternary La-Mg-Ni intermetallics include three different stoichiometric ratios between *A*-elements (A = Mg and Rare Earths *RE*) and *B*-elements (B = Ni), AB_3, A_2B_7 and A_5B_{19}, which all show a good performance as battery anodes in the high energy/high power Ni-*M*H batteries [11,12]. These compounds belong to the hybrid AB_x layered structures, where individual Laves type AB_2 layer, $La_{1-y}Mg_yNi_2$, and Haucke type AB_5 layers, $LaNi_5$, stack along the hexagonal/trigonal axis in different ratios ($3\ AB_3 = AB_5 + 2\ AB_2$; $2\ A_2B_7 = 2\ AB_5 + 2\ AB_2$; $A_5B_{19} = 3\ AB_5 + 2\ AB_2$).

A detailed review on the structural, thermodynamic and electrochemical properties of the metallic hydrides belonging to the pseudo-binary family *RE*–Mg–Ni has been published recently [13]. Improving the hydrogen storage properties of La–Mg–Ni-based alloys by such methods as elemental substitution in the alloy composition [12,14–16], rapid quenching [17], composite alloying (by Mn, Al) and surface modification [18] have been employed by several groups. Among these methods elemental substitution was found to be the most efficient way to improve the cycling stability of La–Mg–Ni-based alloys.

Hydrogen absorption–desorption behaviours, electrochemical performance and cycling stability of La_2MgNi_9 alloy can be significantly improved by annealing [19]. *In situ* neutron diffraction has been utilized to study the mechanism and kinetics of the temperature-induced phase-structural transformations in La_2MgNi_9 [20]. Interactions of La–Mg–Ni alloys with hydrogen were also studied by *in situ* synchrotron X-ray and neutron powder diffraction [21]. $LaNi_5$ and $LaMgNi_4$ layers were found to be occupied by D atoms to form $LaNi_5D_{5.2}$ and $LaMgNi_4D_{7.9}$ compositions showing that the hydrogen to metal atomic ratio (H/M) varies between 0.87 ($LaNi_5$ layer) and 1.32 H/M ($LaMgNi_4$ layer). Four D-sites are located within the $LaMgNi_4$ slab, two within the $LaNi_5$ slabs and two sites are placed at a boundary between the slabs.

Partial substitution of La by Nd is considered as an effective way to improve the electrochemical properties of La–Mg–Ni-based alloys [22]. Studies revealed that Nd has a positive influence on several features: (a) it improves the resistance to oxidation; (b) it increases the exchange current at the surface of the anode electrode; (c) it increases the rate of the bulk diffusion of hydrogen atoms in the $(La,Ce,Pr,Nd)_2MgNi_9$ alloy. As a consequence, these three features contribute together to enhance the cycle life and high rate dischargeability of the anodes. Most of the studies put an emphasis on investigating the effects of the different ratio between La substitutions by Nd on the electrochemical properties of La–Mg–Ni-based alloys [23–27].

In general, chemical compositions of the studied alloys and their crystal structures can be separated into (a) AB_3 alloys with $PuNi_3$ type of structure; (b) A_2B_7 with Ce_2Ni_7 and Gd_2Co_7 types of structure. The general regularities of their interaction with hydrogen and properties of the metal hydrides have many common features. Recently, our group [28] found that with a partial substitution of Nd for La, the formed $La_{1.5}Nd_{0.5}MgNi_9$ alloy showed improvement in the cycling stability and high rate dischargeability. Changes in hydrogen diffusion rate in the $La_{1.5}Nd_{0.5}MgNi_9$ anode appeared to be related to the changes in hydrogen content [29]. The diffusion coefficient reached a maximum at 85% of discharge.

The overall focus of our work is on the AB_3 type alloys based on La, Mg and Ni. La substitution for Nd and Pr is as a part of the strategy to achieve the best high rate performance of the battery anodes at optimized content of the constituents. Here, neutron scattering on deuterated samples provides important information on the mechanism and kinetics of phase-structural transformations as related to their performance of hydrogen storage materials and battery anodes.

Earlier we have performed *in situ* NPD experiments on the lanthanum-based systems, $La_{3-x}Mg_xNi_9$-D_2. The alloys with a variable Mg content were studied by monitoring solid-D_2 gas interactions and during electrochemical charge-discharge of the metal hydride anode electrodes [21,30,31]. Study of $La_2MgNi_9D_{13}$ revealed a novel type of the metal-hydrogen ordering built by a stacking of the MgH_6 and NiH_4 polyhedra [32], while $LaNi_5$-assisted hydrogenation of $MgNi_2$ has been observed in the structure of $LaMg_2Ni_9$ at pressures up to 100 MPa D_2 [33].

In contrast, much less is known on the structural and hydrogen sorption properties of the compounds containing other light rare-earth metals, mainly Pr and Nd. However, these alloys could be very important as electrode materials because of a much increased mobility of hydrogen in the Nd based hydrides [34]. A partial substitution of La by Pr/Nd is expected to improve their cyclic stability and high-rate dischargeability [22,34]. Thus, replacement of La by other *RE* together with optimization of Mg content [31] provides complementary possibilities to improve the alloys. Nd-doped La_2MgNi_9 showed a better performance at high current densities [13,28].

Table 1 summaries the available data on structure and on the thermodynamics and electrochemistry of the metal hydrides formed by three intermetallic with RE_2MgNi_9 composition, which were characterized in our earlier studies [28], including La_2MgNi_9, $La_{1.5}Nd_{0.5}MgNi_9$ and Nd_2MgNi_9.

Earlier, phase-structural transformations in an Mg-and Nd-modified $LaNi_3$ intermetallic have been studied by NPD experiments [28,29,35]. Although the work on $La_{1.5}Nd_{0.5}MgNi_9$ showed that Nd substitution for La can significantly improve the electrochemical properties of the alloys, it is essential to make a more