Direct Synthesis of La-Ni Based Hydrogen Storage Alloys from the Oxide Form

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Abstract
In this study A2B7 type La2Ni7, La2(Ni0.80Co0.20)7 and (La0.75Mg0.25)2(Ni0.8Co0.2)7 alloys were synthesized directly from sintered mixture of La2O3 + NiO + CoO+ MgO in the molten electrolyte by the electro-deoxidation method and the electrochemical hydrogen storage characteristics of the synthesized alloys were observed. Sintering (at 1200°C for 3h) converted the hygroscopic La2O3 into the non-hygroscopic oxides. The X-ray diffraction peaks indicated LaNi5 and La2Ni7 phases were the main phases present in the synthesized alloys. It was observed that synthesized alloys had promising discharge capacities changed between 207 mAhg⁻¹ (La2Ni7) and 356 mAhg⁻¹ ((La0.75Mg0.25)2(Ni0.8Co0.2)7) depending on the alloy content. The results obtained in this study showed that the electro-deoxidation technique is very promising in the synthesizing of the high performance hydrogen storage alloy.

1. Introduction
La-Mg-Ni-based hydrogen storage alloys have been extensively investigated as one of the negative electrode materials for nickel/metal hydride batteries due to their high storage capacity, long cycle life and environmental friendliness [1,2]. La–Mg–Ni-based hydrogen storage alloys are typically prepared by melting (induction, arc, magnetic levitation), powder metallurgy and sintering [3-9]. Generally, after these processes products need annealing for several time [11,12,15,17]. Annealing is helpful to get the homogeneous alloy with single phase structure [10]. (La,Mg)2Ni7 type alloys and their hydrogen storage properties studied extensively [3, 6,8,10,11].

Fray-Farthing-Chen discovered a new process in 1997. FFC Cambridge process is a novel method for obtained of metals and alloys directly from their oxides in a molten salt [12,13]. Many hydrogen storage alloys like CeNi5, TbNi5, CeCo5, LaNi5, La2Ni5, Tb85Zr0.15Ni, ZrMn2 [14-22] etc, have been effectively synthesized by electro-deoxidation technique.

In this work A2B7 type La-Mg-Ni-Co hydrogen storage alloys were synthesized in the molten CaCl2 electrolyte by the electro-deoxidation method. The hydrogen storage characteristics of the synthesized alloys were determined.

2. Material and Method
Commercially available La2O3, NiO, MgO and CoO powders were obtained from Alfa Aesar. Required amounts of the oxide powders were mixed homogeneously in anhydrous ethanol includes 3% (by weight) polyethylene glycol (PEG) with a planetary ball mill. The powder was then dried overnight at room temperature. Dried powder was cold pressed into pellets of 10 mm in diameter, under a pressure of 1.5 tonne cm⁻². The oxide mixture pellet of La2O3+NiO+CoO+MgO was then sintered at 1200°C for 3 h.

100 gr CaCl2 was mixed with 1 gr CaO and placed into graphite crucible. Before electro-deoxidation process CaCl2-CaO powder mixture was dried under Ar gas. Drying was carried out by slow heating to the target temperature (for non Mg including alloy 850°C and for Mg including alloy 750 °C) for the electro-deoxidation experiments.

In order to fully remove the water and the possible redox-active impurities, pre-electrolysis were carried out at 2.5 V and target temperature for 4 h. During the pre-electrolysis graphite crucible was used as anode and another graphite rod was used as cathode. The electro-deoxidation was conducted at 3.2 V for various times at target temperatures. The potential control was carried out by the programmable direct current source.

After the electro-deoxidation experiments the pellet electrodes were removed from the molten melt. The solidified salt on the pellet was washed out by tap water. After slight surface grinding the pellets were kept in 1 M HCl for few minutes. Finally the deoxidized pellet samples were dried at 100°C for 24 h under vacuum.

The deoxidized pellet samples were ground into fine powder (alloy powder). Working electrodes were prepared by mixing 0.1 g alloy powder with 0.3 g nickel
powder and then cold pressing into pellets of 10 mm in diameter, under a pressure of 147 MPa. The working electrode was wrapped by Ni mesh and a Ni lead wire was attached to Ni mesh by spot-welding to prepare a hydrogen storage alloy electrode (negative electrode). Hg/HgO reference electrode was used in 6 M KOH solution. Tests were performed with GAMRY Model Reference 3000 potentiostat/galvanostat unit. The charge current density was 100 mAg⁻¹ and the charging was carried out down to the severe gassing potential. The charging was followed by a 10 min rest before the discharging. The discharge current density was 25 mAg⁻¹ and the discharge cut-off potential was -0.5 V Hg/HgO.

The phase structure of the synthesized alloy powders was examined by the X-ray diffractometer (Bruker axs D8) using Cu Kα radiation. The powder morphologies were observed by ZEISS SUPRATM 50 VP Scanning Electron Microscope (SEM).

2. Experimental Procedure
2.1. The Molten Salt Electrolysis

The XRD patterns of the sintered La₃Ni₇, La₄(Ni₅₀Co₅₀)₇ and (La₀.₇₅Mg₀.₂₅)₂(Ni₀.₈Co₀.₂)₇ alloys are provided in Fig. 1. Partial substitution of Ni by Co and La by Mg change the sintered structure. NiO is present in all samples. In addition to these oxide La₃NiO₄, LaNiO₃, Mg₀.₄Ni₀.₆O are present in La₃Ni₇, La₄(Ni₅₀Co₅₀)₇ and (La₀.₇₅Mg₀.₂₅)₂(Ni₀.₈Co₀.₂)₇ alloys, respectively. Instead of hygroscopic La₂O₃, the formation of nonhygroscopic oxides during sintering makes synthesizing of A₂B₇ type alloys possible by electro-deoxidation technique in molten CaCl₂ salt.

LaNi₅ phase can be seen in all compositions in this work. After 20h electrolysis of La₃Ni₇ and La₄(Ni₅₀Co₅₀)₇ alloys LaNi₅ and La₃Ni₇ form as the electro-deoxidation product. After 20h electrolysis of (La₀.₇₅Mg₀.₂₅)₂(Ni₀.₈Co₀.₂)₇ alloy, LaNi₅ and La₁.₅Mg₀.₅Ni₇ form as the electro-deoxidation product. Obviously during the electrolysis the sintered structures are completely deoxidized. The X-ray diffraction analyses revealed that electro-deoxidized material has multi-phase structure.

The scanning electron micrographs of the as-sintered and 20h deoxidized (La₀.₇₅Mg₀.₂₅)₂(Ni₀.₈Co₀.₂)₇ alloy morphologies are provided in Fig. 3a and 3b, respectively.

Figure 1. XRD patterns of the sintered samples prepared to obtain La₃Ni₇, La₄(Ni₅₀Co₅₀)₇ and (La₀.₇₅Mg₀.₂₅)₂(Ni₀.₈Co₀.₂)₇ alloys.

Figure 2. XRD patterns of the 20h electro-deoxidized samples prepared to obtain La₃Ni₇, La₄(Ni₅₀Co₅₀)₇ and (La₀.₇₅Mg₀.₂₅)₂(Ni₀.₈Co₀.₂)₇ alloys.

Figure 3. XRD patterns of a) as sintered and b) 20 h electro-deoxidized (La₀.₇₅Mg₀.₂₅)₂(Ni₀.₈Co₀.₂)₇ alloy morphologies are provided in Fig. 3a and 3b, respectively.
Like in Fig. 3a, all the sintered samples have typical fine oxide powder appearances. At the end of 20h electro-deoxidation process, however, the typical large crystalline metallic powder morphology develops (Fig. 3b) for all the alloys. The porous structure of the alloy is also observable clearly in Fig. 3b.

2.2. The Hydrogen Storage Characteristics of the Synthesized Alloys

Fig. 4 shows charge/discharge curves of 20h electro-deoxidized La-Mg-Ni-Co alloy electrodes for various charge/discharge cycles. The maximum discharge capacities of La2Ni7, La2(Ni0.80Co0.20)7, and (La0.75Mg0.25)2(Ni0.8Co0.2)7 alloys are 207 mAhg−1, 332 mAhg−1 and 356 mAhg−1, respectively. As expected, Co and Mg improves the discharge capacities of the alloys. Magnesium, as the additive element, increases the maximum discharge capacity, but decreases the capacity retention rate.

4. Conclusion

La-Mg-Ni-Co alloys were synthesized directly from sintered oxide mixture by the molten salt electro-deoxidation method and the electrochemical hydrogen storage characteristics of the synthesized alloys were observed. The following conclusions may be deduced:

- Sintering converted the hygroscopic La2O3 into the non-hygroscopic La2NiO4, LaNiO3 and Mg0.4Ni0.6O.
- The maximum discharge capacity of (La0.75Mg0.25)2(Ni0.8Co0.2)7 alloy was higher than those of La2Ni7, La2(Ni0.80Co0.20)7 alloys.
- As expected, Co and Mg improved the discharge capacities of the alloys.
- Electro-deoxidation is an effective method of synthesizing La-Ni based alloys for hydrogen storage materials.

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References