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Molten salt synthesis of $\text{La}(\text{Ni}_{1-x}\text{Co}_x)_5$ ($x = 0, 0.1, 0.2, 0.3$) type hydrogen storage alloys

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ABSTRACT

$\text{La}(\text{Ni}_{1-x}\text{Co}_x)_5$ ($x = 0, 0.1, 0.2, 0.3$) alloys were synthesized directly from sintered mixture of $\text{La}_2\text{O}_3 + \text{NiO} + \text{CoO}$ in the molten CaCl_2 electrolyte by the electro-deoxidation method at 850°C and the electrochemical hydrogen storage characteristics of the synthesized alloys were observed. Sintering (at 1200°C for 2 h) converted the hygroscopic La_2O_3 (by the reaction with NiO) into the non-hygroscopic La_2NiO_4 , LaNiO_3 , $\text{La}_3\text{Ni}_2\text{O}_{6.5}$, $\text{La}_3\text{Ni}_2\text{O}_{6.84}$ and $\text{La}_4\text{Ni}_3\text{O}_9$ depending on the Co content of the oxide mixture. The X-ray diffraction peaks indicated that La_2NiO_4 was the main La–Ni–O phase to initiate the LaNi_5 phase formation. The increase in the Co content of the sample was observed to delay the La_2NiO_4 formation and thus the reactions initiated by La_2NiO_4 reduction. LaOCl formed chemically was the last oxygen including phase remained in the alloy before obtaining the final alloy structure. The porous alloy structure was beneficial for higher hydrogen storage capacity and it was observed that $\text{La}(\text{Ni}_{1-x}\text{Co}_x)_5$ ($x = 0, 0.1, 0.2, 0.3$) alloys had promising discharge capacities changed between 223 mA h g^{-1} (LaNi_5) and 325 mA h g^{-1} ($\text{La}(\text{Ni}_{0.7}\text{Co}_{0.3})_5$). This work clearly indicated that the electro-deoxidation was a very effective method in the synthesis of the hydrogen storage materials.

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Introduction

Fray, Farthing and Chen developed a revolutionary extractive metallurgy process (FFC Cambridge process) enables the direct production of pure metals from their oxides in the molten salt [1,2]. Although the initial focus was only on Ti, many elements in the periodical table can be produced by FFC Cambridge process [3]. More exciting binary or ternary alloys can be synthesized directly from their respective oxide mixture [4–6].

FFC Cambridge process, which is also known as electro-deoxidation, has appeared as a very promising method in

the synthesis of the hydrogen storage alloys recently, the motivation being the economical synthesis of them especially for the large scale applications like the battery systems of electrical vehicles [7–11]. Lanthanum-nickel based alloys, which is one of the well-known commercial hydrogen storage alloy groups, are generally synthesized by the melting and casting under the protective atmosphere [12–16]. The cast products need annealing for several hours to get the structural homogeneity [17]. Obviously as compared to the melting and casting, the electro-deoxidation provides more cost-effective pathway since it makes possible the direct synthesis of the alloys with the final stoichiometry from the raw materials (oxides) [18].

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Recently, we have reported the alloy development mechanism for A_2B_7 type La–Ni–Co alloys during the electro-deoxidation process [10,11]. In this work, we conducted the same studies for AB_5 type La–Ni–Co alloys and we presented the alloy development stages from their oxide mixtures. The electrochemical hydrogen storage characteristics of the synthesized alloys were also provided.

Experimental

Commercially available La_2O_3 , NiO and CoO powders (with at least 99.9% purity) 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 (Fritsch, Pulverisette P-7). 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 $1.5 \text{ tonne cm}^{-2}$. The oxide mixture pellet of $La_2O_3 + NiO + CoO$ was then sintered at $1200 \text{ }^\circ\text{C}$ for 2 h.

The electrochemical experiments were performed in a quartz cell which was located inside a homemade programmable electrical furnace. The upper end of the quartz cell was closed tightly with a quartz cover which has holes for the electrode leads, thermocouple, gas inlet and outlet. The quartz cell was continuously purged with Ar gas ($200\text{--}250 \text{ ml min}^{-1}$) during the electro-deoxidation process.

100 gr $CaCl_2$ was mixed with 1 gr CaO (to enhance the current efficiency [19]) and placed into graphite crucible. Before electro-deoxidation process $CaCl_2\text{--}CaO$ powder mixture was dried under Ar gas. Drying was carried out by slow heating (about $1 \text{ }^\circ\text{C min}^{-1}$) to $150 \text{ }^\circ\text{C}$ and holding at $150 \text{ }^\circ\text{C}$ for 15 h and then slow heating to $300 \text{ }^\circ\text{C}$ and holding at $300 \text{ }^\circ\text{C}$ for 15 h and then finally slow heating to the target temperature of $850 \text{ }^\circ\text{C}$ 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 $850 \text{ }^\circ\text{C}$ for 4 h. During the pre-electrolysis graphite crucible (length = 15 cm and inner diameter = 6.5 cm) was used as anode and another graphite rod (diameter = 0.8 cm) was used as cathode. For the electro-deoxidation experiments the graphite rod was removed from the cell and the prepared oxide pellet electrode was inserted into the quartz cell with the help of Kanthal wire which was mounted into the pre-opened hole on the center of the pellet. Kanthal wire served also as the cathode current collector. The electro-deoxidation was conducted at 3.2 V for various times at $850 \text{ }^\circ\text{C}$. The potential control was carried out by the programmable direct current source (GWINSTEK PPH-1503).

After the electro-deoxidation experiments the pellet electrodes were removed from the molten melt and they were located in the upper part of the quartz cell which was cooled down by keeping the Ar gas purging. 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 $100 \text{ }^\circ\text{C}$ 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 10 tonne cm^{-2} . 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 mA g^{-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 mA g^{-1} and the discharge cut-off potential was $-0.5 V_{\text{Hg/HgO}}$.

The phase structure of the synthesized alloy powders (well mixed to get homogeneity) was examined by the X-ray diffractometer (Bruker axS D8) using Cu $K\alpha$ radiation. The powder morphologies were observed by ZEISS SUPRATM 50 VP Scanning Electron Microscope (SEM).

Results and discussion

The sintered structures

The oxide mixtures prepared to get $La(Ni_{1-x}Co_x)_5$ ($x = 0, 0.1, 0.2, 0.3$) alloys are sintered at $1200 \text{ }^\circ\text{C}$ for 2 h [10,11] and the obtained XRD patterns from the sintered samples are provided in Fig. 1. All the samples include excess NiO. The stoichiometry of the La-including oxide phases, however, looks to change depending on the Co content in Fig. 1. The non-Co-including sample ($x = 0$; $LaNi_5$) has La_2NiO_4 and $La_3Ni_2O_{6.84}$ phases that were formed probably as a result of the following reactions during sintering:

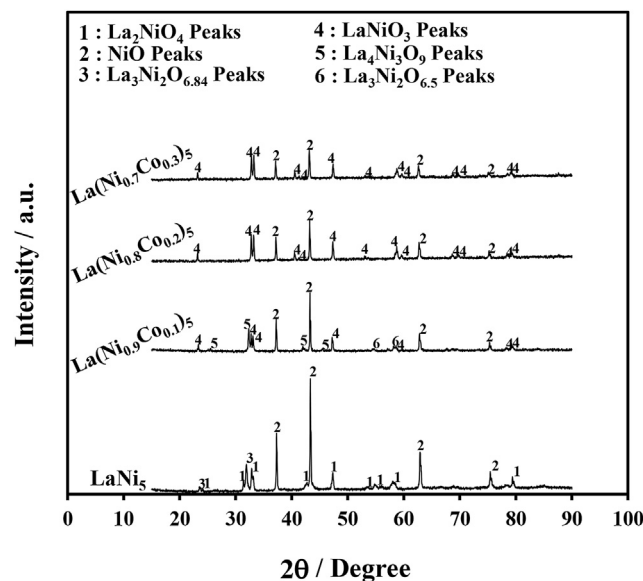


Fig. 1 – XRD patterns of the sintered (at $1200 \text{ }^\circ\text{C}$ for 2 h) samples prepared to obtain $La(Ni_{1-x}Co_x)_5$ ($x = 0, 0.1, 0.2, 0.3$) alloys.

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