

USE OF MOLTEN SALT METHOD IN THE SYNTHESIS OF METAL HYDRIDE ELECTRODE MATERIALS

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Abstract: La-Ni based alloys are being used in the commercial secondary nickel metal hydride batteries. Economical synthesis of these alloys may cause large scale utilization of them especially in the electrical vehicles. The electro-deoxidation, which is accepted as the revolutionary technique in the extractive metallurgy, is very promising in the metal hydride alloy synthesis since it provides direct synthesis of the alloys from their oxide raw materials. In this study $\text{La}(\text{Ni}_{0.8}\text{Co}_{0.2})_5$ (AB₅ type) and $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ (A₂B₇ type) alloys were synthesized in the molten CaCl_2 electrolyte at 850°C and the charge/discharge characteristics of the synthesized alloys were observed. Sintering caused the hygroscopic La_2O_3 to disappear and the non-hygroscopic LaNiO_3 to form. LaOCl was observed to form chemically upon contact of the sintered pellet with the melt. The X-ray diffraction peaks indicated that the sinter products reduced to LaNi_5 and La_2Ni_7 phases within 2 h and 6 h electro-deoxidation process, respectively. The sluggish reduction kinetics of LaOCl phase was observed to retard the appearance of La_2Ni_7 phase. The discharge capacities of $\text{La}(\text{Ni}_{0.8}\text{Co}_{0.2})_5$ and $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloys were determined as 325 mA h g⁻¹ and 332 mA h g⁻¹, respectively. The results obtained in this study showed that the electro-deoxidation technique is very promising in the synthesizing of the high performance hydrogen storage alloys.

Keywords: La-Ni Alloys, Electro-deoxidation, Hydrogen Storage

Introduction

A novel technique called electro-deoxidation, which is also known as Fray-Farthing-Chen (FFC) Cambridge process (Chen, 2000, Mohandas, 2004), is reported as very promising for the economical synthesis of the alloys directly from their oxide mixtures (Zhu, 2007, Tan, 2010, Anik, 2014). Lanthanum-Nickel based alloys are generally synthesized by the melting and casting under the protective atmosphere (Srivastava, 1999, Hayakawa, 2005, An, 2013). Of course the individual elements (La and Ni) must be already extracted and refined for the melting and casting processes. The cast products need annealing for several hours to get the structural homogeneity (Huang, 2002). Obviously this production pathway for the La-Ni based hydrogen storage alloys is not very encouraging especially for the large scale applications like battery systems of the electrical vehicles. The electro-deoxidation method looks more cost-effective since it provides direct synthesis of the alloy with final stoichiometry from the raw materials (oxides). In this work AB₅ and A₂B₇ type intermetallic alloys were synthesized by the molten salt electro-deoxidation method and the electrochemical hydrogen storage was applied to the final alloy structures.

Materials and Methods

Commercially available La_2O_3 , NiO 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 pellets were then sintered at 1200°C for 3 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 during the electro-deoxidation process.

100 gr CaCl_2 was mixed with 1 gr CaO and placed into graphite crucible. Before electro-deoxidation process CaCl_2 -CaO powder mixture was dried under Ar gas. Drying was carried out by slow heating (about 1°C min⁻¹) to

150°C and holding at 150°C for 15 h and then slow heating to 300°C and holding at 300°C for 15 h and then finally slow heating to the target temperature of 850°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°C for 4 h. During the pre-electrolysis graphite crucible was used as anode and another graphite rod 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 as a cathode. The electro-deoxidation was conducted at 3.2 V for various times at 850°C. 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 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°C for 24 h under vacuum.

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. 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 discharge current density was 25 mA g⁻¹ and the discharge cut-off potential was -0.5 V_{Hg/HgO}.

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

Results and Discussion

The alloy development stages of La(Ni_{0.8}Co_{0.2})₅ alloy during electro-deoxidation are shown in XRD patterns in Figure 1. Sintering of La₂O₃ + NiO + CoO mixture at 1200°C for 3 h yields formation LaNiO₃ phase in the expense of La₂O₃ as in the following reaction:

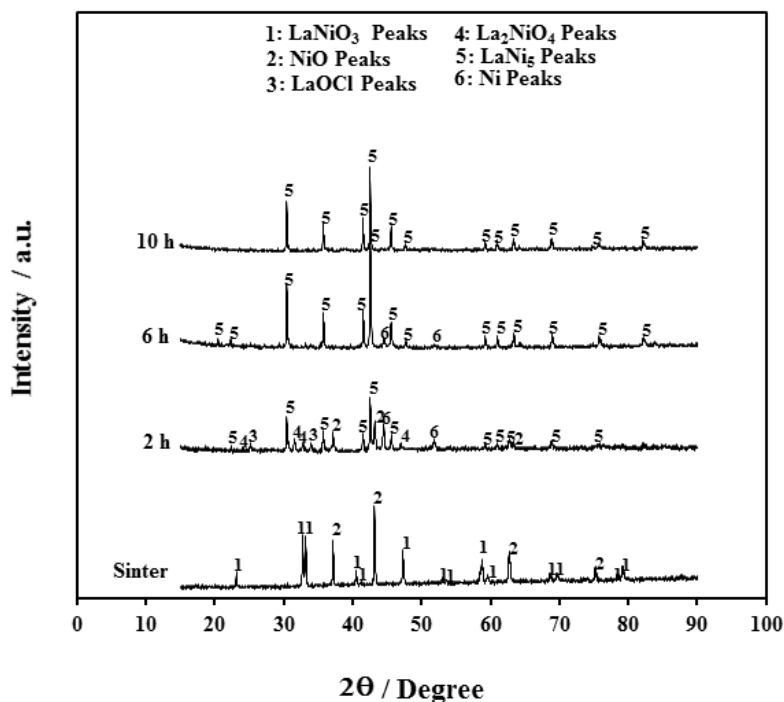


Figure 1. XRD patterns show the alloy development stages at various electro-deoxidation times for La(Ni_{0.8}Co_{0.2})₅ alloy.

After 2 h electro-deoxidation the sinter product LaNiO_3 phase disappears and La_2NiO_4 phase forms probably as a result of the following reduction reaction:



The remaining reactions can be expected as in the followings:



After 6 h electro-deoxidation La_2NiO_4 phase disappears due to the completion of Reactions 3 and 5, and the following reactions couple to the above reactions:



10 h electro-deoxidation looks to enough to get stable alloy structure with 100% LaNi_5 phase. There is no any Co phase in Figure 1 since Co makes Co-La and Co-La-O phases with the exactly same stoichiometry of Ni-La and Ni-La-O phases. Therefore peak positions of Co phases are exactly same with those of Ni phases and it impossible to differentiate them in the XRD patterns.

Alloy development stages of $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloy are depicted with the XRD patterns in Figure 2. Reactions 1-7 look also valid for the $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloy development. In the final stage there is following extra reaction:

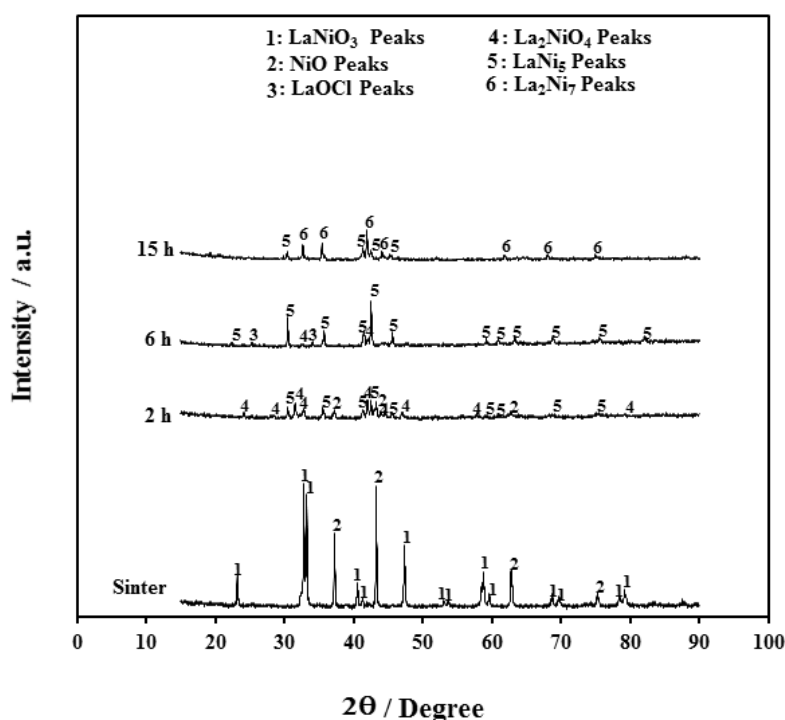


Figure 2. XRD patterns show the alloy development stages at various electro-deoxidation times for $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloy.

The presence of Reaction 8 retards the gaining of the stable structure for $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloy and it takes 15 h to complete electro-deoxidation process. There is also retained LaNi_5 phase in the alloy structure probably due to the inefficiency of Reaction 8 since it requires elemental diffusion of La and Ni. Segregation of these elements to the

pellet surface may destroy the homogeneity of the pellet and Reaction 8 cannot take place completely.

Scanning electron micrographs of the as-sintered oxide powders and fully deoxidized powders of both $\text{La}(\text{Ni}_{0.8}\text{Co}_{0.2})_5$ and $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloys are provided in Figure 3. As-sintered powders have typical fine oxide powder appearance. At the end of the electro-deoxidation process, however, the large crystalline metallic powder morphology develops. The porous structure of the developed alloys are also apparent in Figure 3.

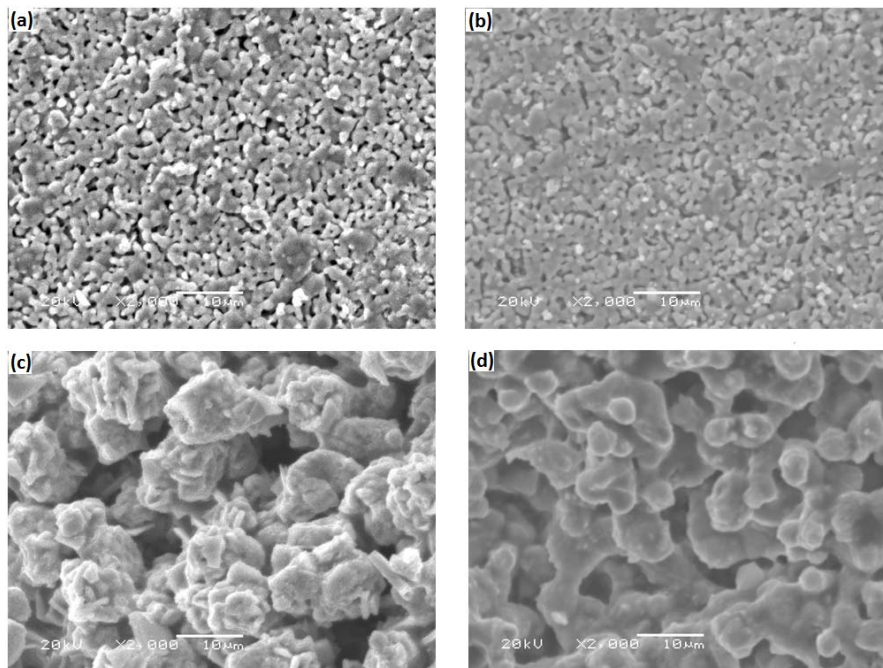


Figure 3. Powder morphology of sintered (a) $\text{La}(\text{Ni}_{0.8}\text{Co}_{0.2})_5$ and (b) $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloys, and the fully deoxidized powder morphology of (c) $\text{La}(\text{Ni}_{0.8}\text{Co}_{0.2})_5$ and (d) $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloys.

After synthesizing alloys with a final structure the discharge capacities as a function charge/discharge cycles are obtained as in Figure 4. The synthesized alloys need few cycles for activation to reach their maximum discharge capacities. The maximum discharge capacities of $\text{La}(\text{Ni}_{0.8}\text{Co}_{0.2})_5$ and $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloys are 325 mA h g^{-1} and 332 mA h g^{-1} , respectively.

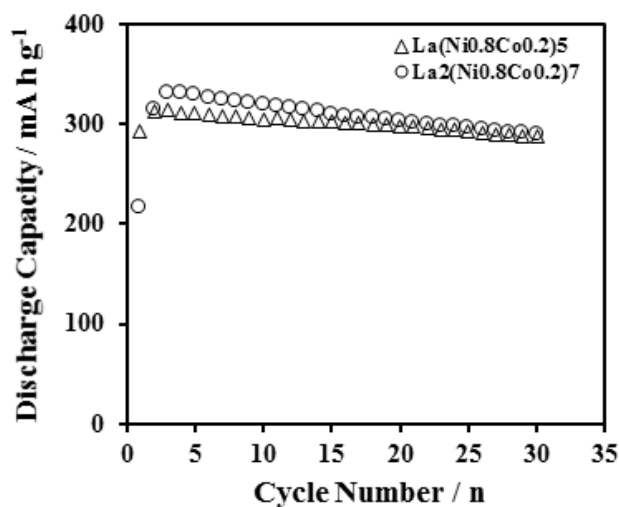


Figure 4. Discharge capacities of $\text{La}(\text{Ni}_{0.8}\text{Co}_{0.2})_5$ and $\text{La}_2(\text{Ni}_{0.8}\text{Co}_{0.2})_7$ alloys as a function of charge/discharge cycles.

This work clearly shows that electro-deoxidation may become very effective and probably more economical method in the synthesis of the energy storage materials.

Conclusion

La(Ni_{0.8}Co_{0.2})₅ (AB₅ type) and La₂(Ni_{0.8}Co_{0.2})₇ (A₂B₇ type) alloys were synthesized in the molten CaCl₂ salt at 850°C. Sintering caused the hygroscopic La₂O₃ to disappear and the non-hygroscopic LaNiO₃ to form. LaOCl was observed to form chemically upon contact of the sintered pellet with the melt. The X-ray diffraction peaks indicated that the sinter products reduced to LaNi₅ and La₂Ni₇ phases within 2 h and 6 h electro-deoxidation process, respectively. The sluggish reduction kinetics of LaOCl phase was observed to retard the appearance of La₂Ni₇ phase. The discharge capacities of La(Ni_{0.8}Co_{0.2})₅ and La₂(Ni_{0.8}Co_{0.2})₇ alloys were determined as 325 mA h g⁻¹ and 332 mA h g⁻¹, respectively. The results indicated that the electro-deoxidation technique is very promising in the synthesizing of the high performance hydrogen storage alloys

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