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Structure and electrochemical properties of $\text{LaCo}_{11-x-y}\text{Ni}_x\text{M}_y$ (M=Fe, Mn and Al) compounds

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Structure and electrochemical properties of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds

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Abstract

The crystal structure and electrochemical charge/discharge properties of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0 \leq x \leq 6$) compounds have been studied. It was found that when $x \leq 2$, the samples are composed mainly of the LaCo_{13} -type compound. Heat treatment has a very important effect on the formation of the LaCo_{13} -type compound. The electrochemical experimental results show that the electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0 \leq x \leq 2$) compounds increase with increasing temperature. The substitution of Ni for Co increases the electrochemical capacity of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds when $x \leq 0.8$. When $x \geq 0.8$, the electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds change very little with increasing Ni content. The highest electrochemical capacity of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0.8 \leq x \leq 2$) compounds is about 359 mAh/g at 60 mA/g charge/discharge current density, which is obtained at about 70°C. We believe that the electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds associated with the absorption and desorption of hydrogen atoms are similar to LaNi_5 -type compounds. The disadvantages of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds are their lower electrochemical capacity at room temperature and the poor cycle lifetime due to the dissolution of Co atoms in the KOH electrolyte. The amount of Co dissolved increases with increasing temperature. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: LaCo_{13} -based compounds; Crystal structure; Hydrogen storage material; Metal–hydrogen electrode

1. Introduction

With the development of the electronic and communication industries, the demand for rechargeable batteries has increased rapidly. The Ni-metal hydrogen storage rechargeable battery (Ni-MH battery) was regarded as one of the best rechargeable batteries due to the high capacity, long cycle lifetime and absence of environment pollution.

The hydrogen storage alloy used as cathode in the Ni-MH battery is mainly a LaNi_5 -type rare earth intermetallic compound. In order to improve the property of the battery, many other hydrogen storage materials, such as AB_2 -type Zr-based alloys, AB-type Ti–Zr-based alloys and A_2B -type Mg_2Ni -based alloys, have been studied extensively [1–3].

The LaCo_{13} -based compounds, in which Co is replaced by other elements (such as Fe, Al, Si, Ga, etc.), have been researched extensively in the past. These investigations were mainly focused on their magnetic properties [4–11]. Also, we studied the magnetic properties and magnetic entropy changes of LaCo_{13} -based compounds [12,13]. In

this investigation, the crystal structure of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0 \leq x \leq 6$) compounds and their electrochemical properties as cathodes of the Ni-MH battery were studied.

2. Experimental

Specimens were prepared by arc melting under a very pure argon atmosphere and were then annealed in a vacuum of 10^{-5} Torr at 900°C for 36 or 100 h. The purity of all elements was better than 99.9%. An extra amount of rare earth was added to compensate for the weight losses due to the arc melting process. The ingots were crushed and ground mechanically to produce powder below 250 mesh. X-ray diffraction analysis was used to determine the crystal structure of the specimens.

For the electrochemical capacity and voltage measurements, approximately 1 g of $\text{LaCo}_{13-x}\text{Ni}_x$ powder was mixed with Ni powder, in a weight ratio of 1:1, and a small amount of polyvinyl alcohol solution as a binder, and then cold pressed to a pellet ($d = 15$ mm) used as the negative electrode. The counter-electrode used was the same positive nickel electrode $[\text{Ni}(\text{OH})_2\text{–NiOOH}]$ as that employed in the Ni-MH battery. The capacity of the

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counter-electrode was designed to be sufficiently large so that the capacity was determined by that of the negative electrode. A mercury oxide electrode (Hg/HgO/6 M KOH) was used as the reference electrode. The electrochemical characteristics of the negative electrode were examined using a home-built instrument, which was introduced in Ref. [14]. Using this instrument, the negative electrode was charged for 6.5 h at 60 mA or for 3 h at 150 mA and, after resting for 20 min, it was discharged to 0.5 V vs. the Hg/HgO electrode. It was then charged again.

3. Result and discussion

It was reported in Ref. [15] that the crystal structure of LaCo_{13} compound is the NaZn_{13} -type cubic structure with lattice parameter $a = 11.344 \pm 0.001$ Å. Fig. 1 shows the X-ray diffraction results for $\text{LaCo}_{13-x}\text{Ni}_x$ ($x = 0, 0.8, 2.0$). It can be seen that, except for a small amount of impurity phase, the samples are composed mainly of LaCo_{13} -type compounds. From Fig. 2 it can be derived that the impurity

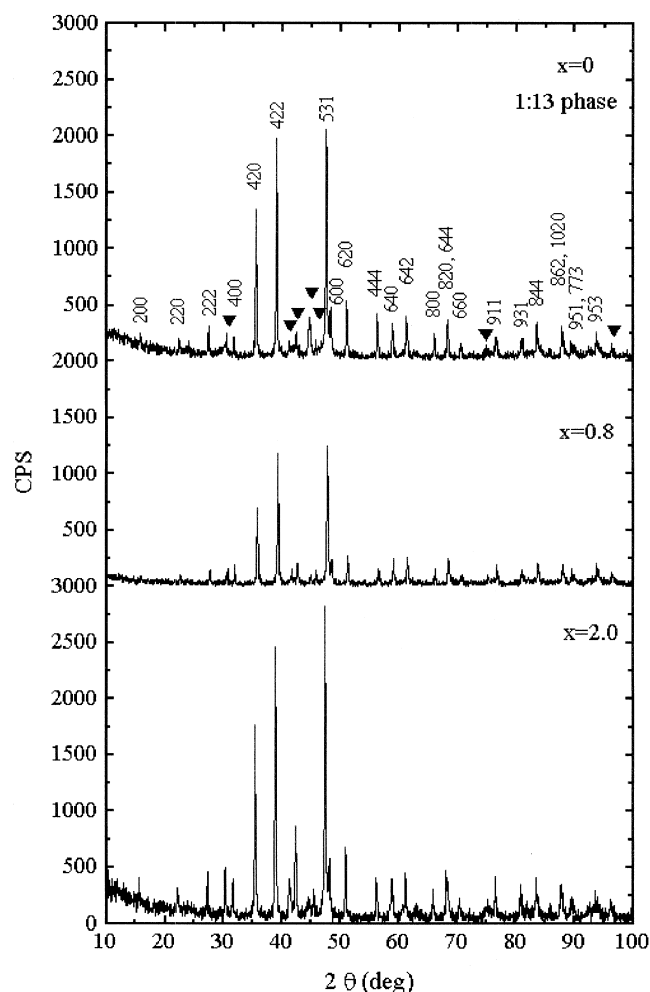


Fig. 1. X-ray diffraction results for $\text{LaCo}_{13-x}\text{Ni}_x$ ($x = 0, 0.8, 2.0$) (Cu target).

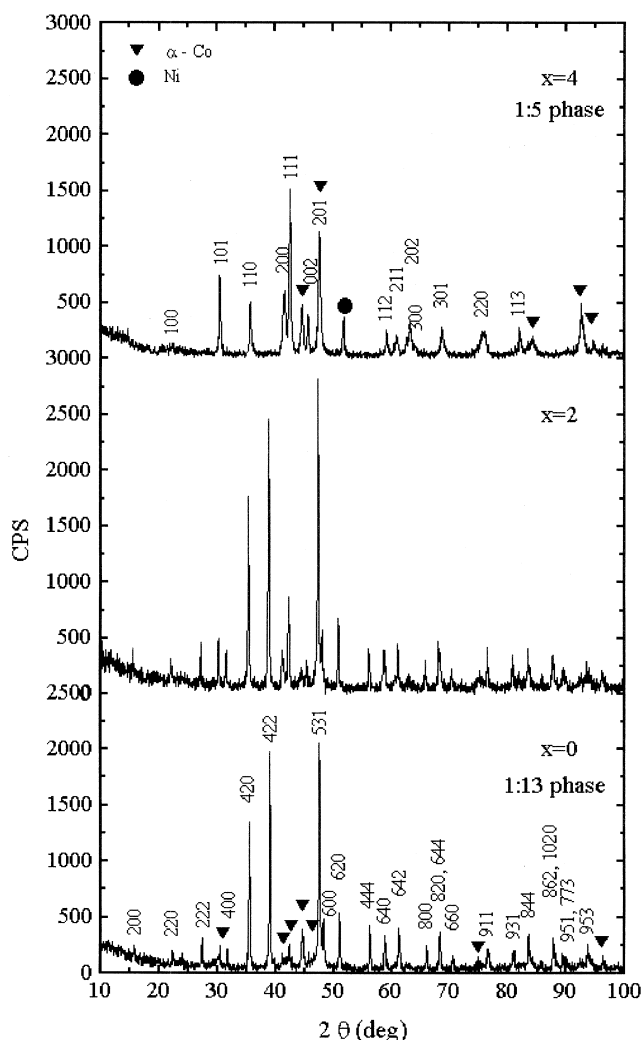


Fig. 2. X-ray diffraction results for $\text{LaCo}_{13-x}\text{Ni}_x$ ($x = 0, 2.0, 4.0$) (Cu target).

phase is the 1:5-type LaNi_5 compound. Also, it can be seen from Fig. 2 that the $x = 4$ sample is composed of the 1:5-type phase and a little Ni and Co, but no 1:13 compound is present. It can be seen from Fig. 3 that the heat-treatment condition is very important for the formation of a single-phase 1:13-type compound. When the samples were heat treated at 900°C , the amount of 1:5 impurity phase decreased with increasing heat-treatment time.

Fig. 4 shows the results of electrochemical capacity measurements of $\text{LaCo}_{13-x}\text{Ni}_x$ ($x = 0, 0.4, 0.8, 1.6, 2.0$) compounds and the LaNi_5 -type $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ compound at 60 mA/g charge/discharge current density in the range from 25 to 80°C . It can be seen that the electrochemical capacities of the $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ compound reaches a highest value of 290 mAh/g at 30°C , and that the electrochemical capacity decreases with increasing temperature. However, the relationships between the electrochemical capacities and tem-

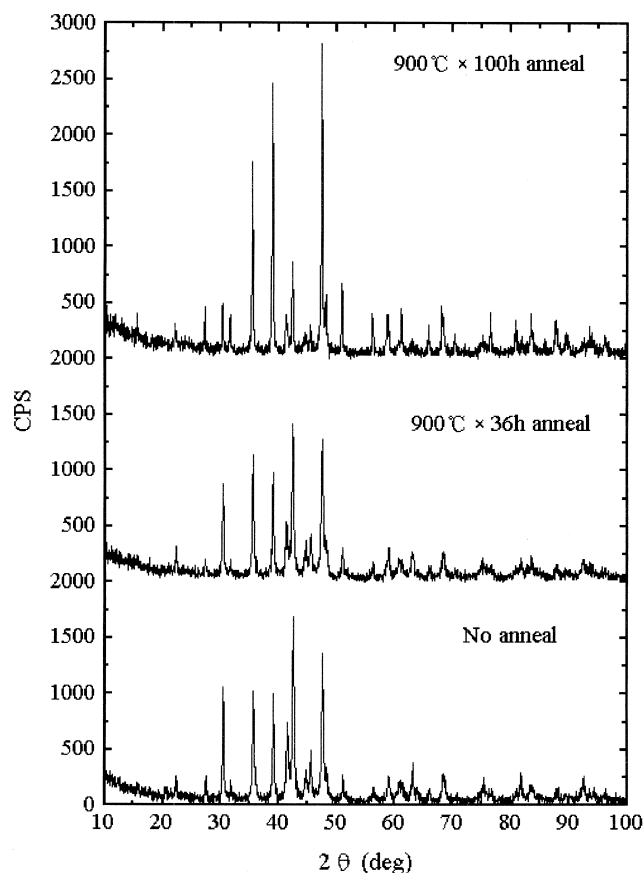


Fig. 3. X-ray diffraction results for $\text{LaCo}_{11.4}\text{Ni}_{1.6}$ (Cu target) under different heat-treatment conditions.

perature of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds are quite different from that of the $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ compound. Their electrochemical capacities increase with increasing temperature. When $x \leq 0.8$, the substitution of Ni for Co markedly increases the electrochemical capacity of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds. The highest electrochemical capacity increases from 152 mAh/g ($x = 0$) to 233 mAh/g ($x = 0.8$) at 25°C and at 60 mA/g charge/discharge current density. It increases from 188 mAh/g ($x = 0$) to 350 mAh/g ($x = 0.8$) at 70°C and at 60 mA/g charge/discharge current density. When $x \geq 0.8$, the electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds change only little with increasing Ni content. The highest electrochemical capacity of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0.8 \leq x \leq 2$) compounds is about 359 mAh/g at 60 mA/g charge/discharge current density, which is obtained at about 70°C. The electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0.8 \leq x \leq 2$) compounds are higher than the highest electrochemical capacity of the $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ compound when the experimental temperature is higher than 40°C.

Where does the electrochemical charge/discharge capacity of the $\text{LaCo}_{13-x}\text{Ni}_x$ system compounds come from? It is known that the electrochemical capacity of LaNi_5 -type compounds originates from the absorption and desorption of hydrogen atoms. The electrochemical reaction is

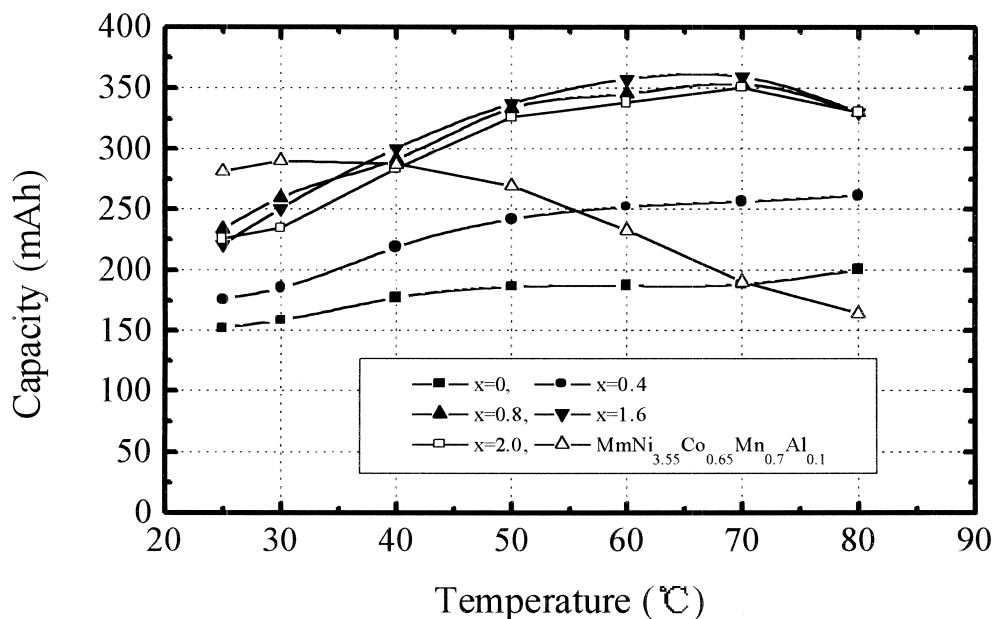
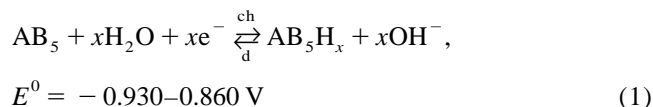


Fig. 4. Electrochemical capacity measurement results for $\text{LaCo}_{13-x}\text{Ni}_x$ ($x = 0, 0.4, 0.8, 1.6, 2.0$) compounds and the LaNi_5 -type $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ compound at 60 mA/g charge/discharge current density from 25 to 80°C.

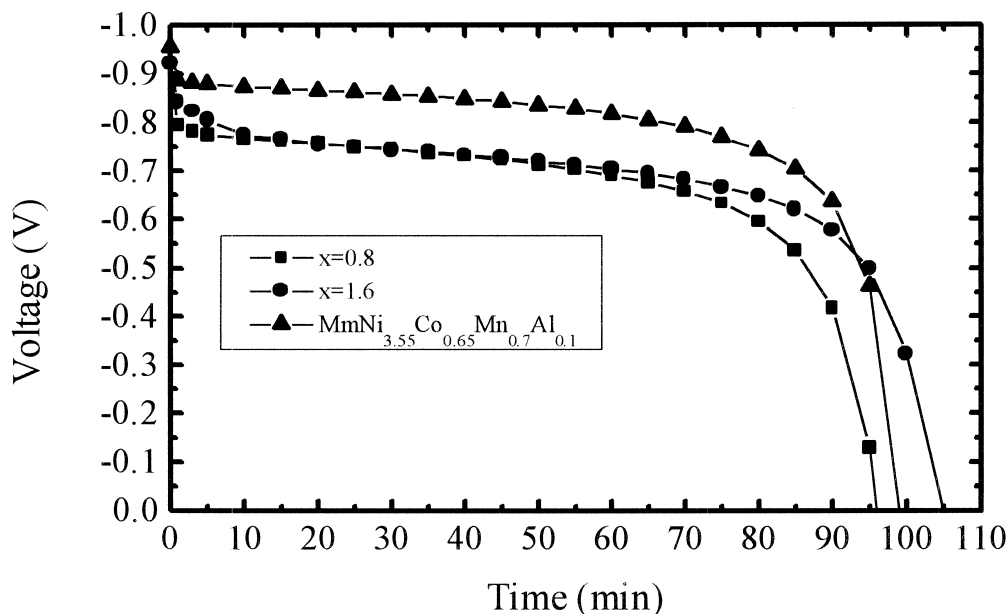
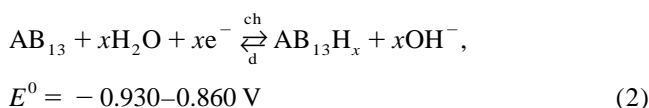


Fig. 5. Electrode potential measurement results for $\text{LaCo}_{13-x}\text{Ni}_x$ ($x = 0.8, 1.6$) at 40°C and $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ at 30°C with respect to a Hg/HgO (6 M KOH) reference electrode at 150 mA/g discharge current density.

Fig. 5 shows the electrode potentials of $\text{LaCo}_{13-x}\text{Ni}_x$ ($x = 0.8, 1.6$) at 40°C and $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ at 30°C with respect to a Hg/HgO (6 M KOH) reference electrode at 150 mA/g discharge current density. It can be seen that the electrode potential of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds is higher but very close to that of the $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ compound. Therefore, it can be assumed that the electrochemical charge/discharge capacity of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds also comes from the absorption and desorption of hydrogen atoms. The electrochemical reaction is



The crystal structure of LaCo_{13} belongs to the cubic NaZn_{13} -type structure. Fig. 6a shows the unit cell structure of LaCo_{13} [16]. It consists of eight LaCo_{13} formula units. Fig. 6b shows a formula unit of LaCo_{13} . The 13 Co atoms lie in the center of a cube, and the La atoms lie at the four corners of the cube. The formula unit of LaCo_{13} is a body-centered cubic structure if the 13 Co atoms are thought as a cluster or a Co atomic radical as given in Fig. 6c. The largest hole in the body-centered cubic structure is the tetrahedral hole. Thus, the absorbed hydrogen atoms will occupy the tetrahedral hole. Fig. 6c shows the tetrahedron and tetrahedral hole of the LaCo_{13} unit. It is found that two La atoms and two Co atomic radicals lie at the four corners of the tetrahedron. Twelve hydrogen atoms can be absorbed per LaCo_{13} formula unit due to the existence of 12 tetrahedral holes as shown in Fig. 6b. The

theoretical electrochemical capacity of the compound can be calculated according to the equation

$$Q = \frac{6.023 \times 10^{23} \times 1.6 \times 10^{-19} \times 10^3}{3600} \frac{N}{M} \text{ (mAh/g)} \quad (3)$$

where N is the number of hydrogen atom which are absorbed by the compound and M is the molecular weight of the compound. The theoretical electrochemical capacity of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0 \leq x \leq 2$) compounds can be calculated according to Eq. (3) as being equal to about 355 mAh/g. The experimental results of Fig. 4 show that, for $\text{LaCo}_{13-x}\text{Ni}_x$ ($0 \leq x \leq 2$) compounds, when $x < 0.8$, the electrochemical capacities are lower than this theoretical value at all the experimental temperatures. When $0.8 \leq x \leq 2$, the electrochemical capacities increase with increasing temperature and approach their theoretical value for a temperature of about 70°C . For the LaNi_5 compound, it is known that every LaNi_5 unit can absorb six hydrogen atoms. The theoretical electrochemical capacity of LaNi_5 can be calculated according to Eq. (3) as 371 mAh/g. Comparing the theoretical value for LaNi_5 with that for LaCo_{13} it can be stated that the theoretical electrochemical capacity of LaCo_{13} is lower than, but very close to, that of LaNi_5 . However, LaNi_5 cannot be used in a practical battery due to the high hydrogen absorption pressure and the too short cycle lifetime. Thus far, the electrochemical capacity of LaNi_5 -based compounds used in practical Ni-MH batteries is about 300 mAh/g. Thus it can be stated that LaCo_{13} -based compounds are potential candidates for negative materials used in rechargeable Ni-MH batteries. The disadvantages of the $\text{LaCo}_{13-x}\text{Ni}_x$ compounds that we

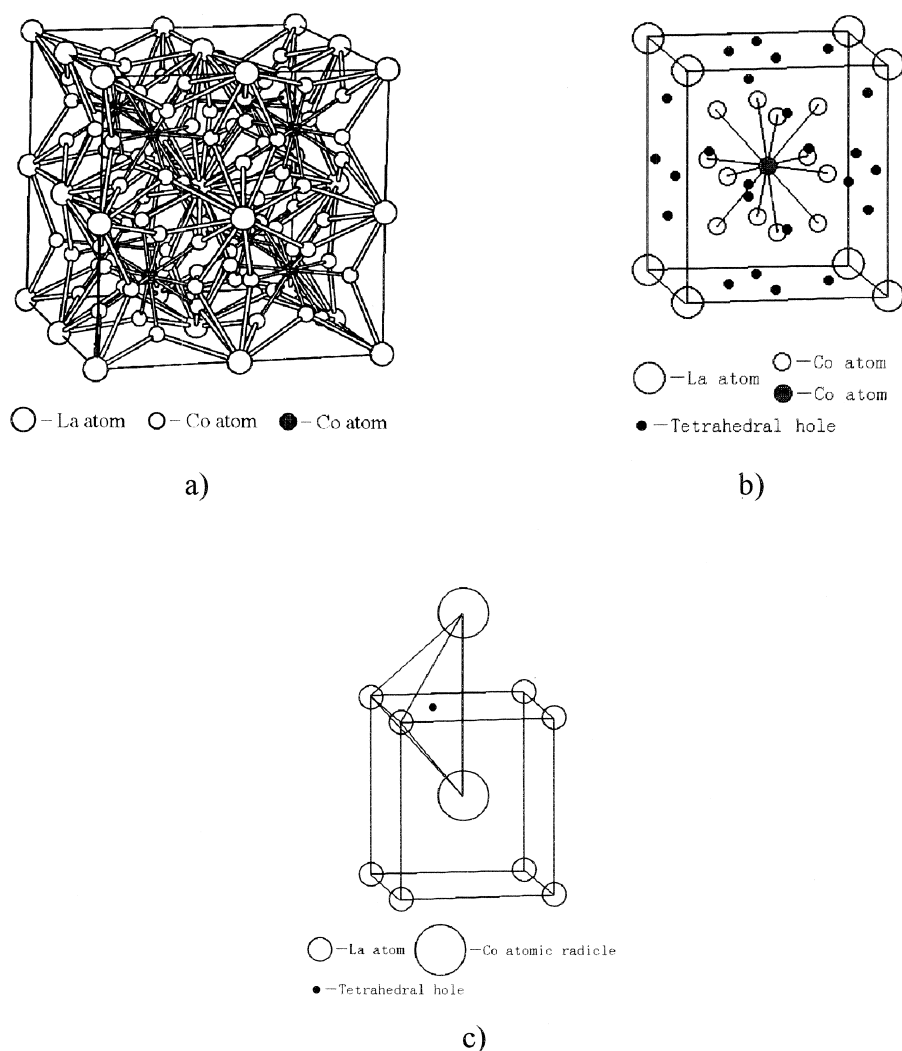
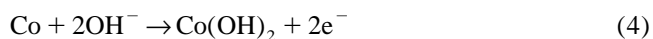


Fig. 6. (a) Unit cell structure of LaCo_{13} . (b) Schematic view of one LaCo_{13} unit. (c) Schematic view of the tetrahedron and tetrahedral hole of the LaCo_{13} unit.

researched here are the higher cost due to the higher Co content and the lower capacity at room temperature. This needs to be improved by further research.

Another important property for battery application is the cycle lifetime. Fig. 7 shows the first 30 electrochemical cycles of $\text{LaCo}_{12.2}\text{Ni}_{0.8}$ at 40 and 60°C, $\text{LaCo}_{11.4}\text{Ni}_{1.6}$ at 40°C and $\text{MmNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ at 30°C measured with 150 mA/g charge/discharge current density. It can be seen that the $\text{LaCo}_{13-x}\text{Ni}_x$ compounds have a better activation behavior. But their cycle lifetimes still need to be improved. Especially at high temperature, the capacity shows a stronger decrease. In our experiment it was found that some Co dissolved in the KOH electrolyte according to the reaction



The amount of Co dissolved increased with increasing temperature. Therefore, it can be assumed that the capacity

decrease of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds comes from the dissolution of Co in the KOH electrolyte.

4. Conclusion

The $\text{LaCo}_{13-x}\text{Ni}_x$ ($0 \leq x \leq 6$) alloys, for $x \leq 2$, except for small amounts of an impurity phase, are composed mainly of LaCo_{13} -type compounds. Heat treatment has a very important effect on the formation of LaCo_{13} -type compounds. The electrochemical experimental results show that the electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0 \leq x \leq 2$) compounds increase with increasing temperature. For $x \leq 0.8$, the substitution of Ni for Co markedly increases the electrochemical capacity of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds. For $x \geq 0.8$, the electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds do not change much with increasing Ni content. The highest electrochemical capacity

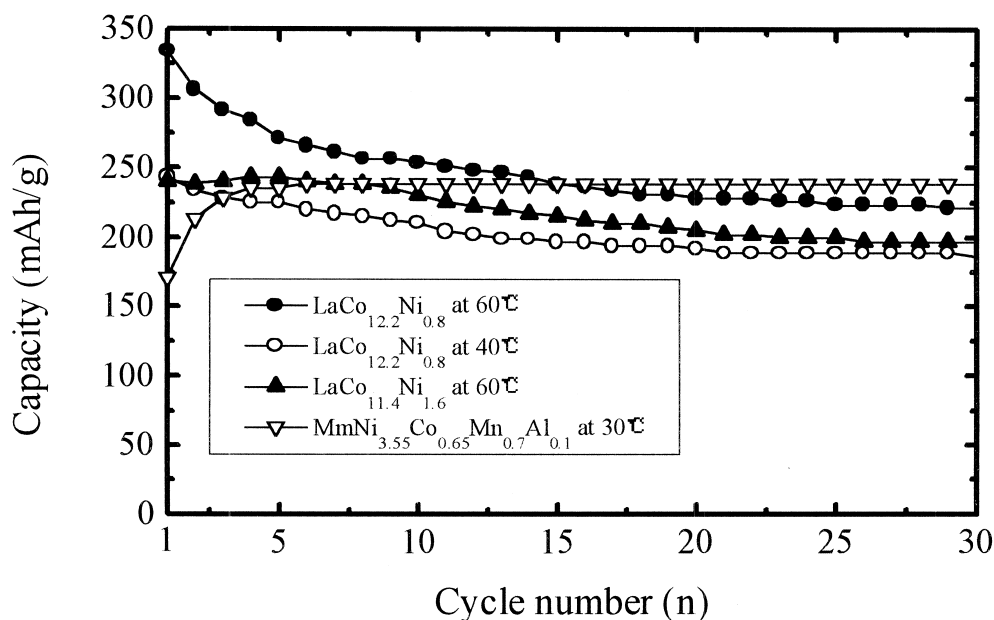


Fig. 7. The first 30 cycles of electrochemical capacity measurements of $\text{LaCo}_{12.2}\text{Ni}_{0.8}$ at 40 and 60°C, $\text{LaCo}_{11.4}\text{Ni}_{1.6}$ at 40°C and $\text{MnNi}_{3.55}\text{Co}_{0.65}\text{Mn}_{0.7}\text{Al}_{0.1}$ at 30°C and 150 mA/g charge/discharge current density.

of $\text{LaCo}_{13-x}\text{Ni}_x$ ($0.8 \leq x \leq 2$) compounds is about 359 mAh/g at 60 mA/g charge/discharge current density, which is obtained at about 70°C. Clearly, the electrochemical capacities of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds originate from the absorption and desorption of hydrogen atoms in the same way as for LaNi_5 -type compounds. The disadvantages of $\text{LaCo}_{13-x}\text{Ni}_x$ compounds are their lower electrochemical capacity at room temperature and the poor cycle lifetime due to the dissolution of Co atoms in the KOH electrolyte. The amount of Co dissolved increases with increasing temperature.

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