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Effects of Cu Substitution for Sn on the Electrochemical Performance of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0–0.5$) Alloys for Ni-MH Batteries

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Abstract: The effects of substitution of Cu for Sn on the electrochemical discharge capacity performance of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0, 0.1, 0.2, 0.3$, and 0.5) negative electrode alloys were investigated. Results indicate that increasing Cu content enhanced electrochemical behavior by increasing the maximum discharge capacity from 239.8 mA h/g ($x = 0$) to 305.2 mA h/g ($x = 0.5$), the discharge capacity retention at the 100th cycle from 78.0% ($x = 0$) to 81.8% ($x = 0.5$), and the high rate dischargeability (HRD) from 25.7% ($x = 0$) to 80.6% ($x = 0.5$).

Keywords: hydrogen storage alloys; nickel metal hydride (Ni-MH) batteries; rare earth alloys; discharge capacity

1. Introduction

Hydrogen storage alloys are being studied because of their potential as effective clean energy storage materials. Specifically, AB₅-type alloys are currently used as active materials in nickel metal hydride (Ni-MH) batteries. Ni-MH batteries have higher energy densities than lead-acid and Ni-Cd batteries, but are relatively more expensive to manufacture given recent increases in material costs, particularly for Ni and Co. It has thus become necessary to develop lower cost alloys by partially or totally replacing Ni or Co with cheaper metals such as Mo, Fe, and Cu. Although such alloys are less expensive, their electrochemical performance is not yet satisfactory. It has therefore become necessary to improve the chemical properties and reduce the cost of the low Co AB₅-type alloys [1–5].

These AB₅-type alloys have been optimized for long cycle life, structural integrity, corrosion resistance, and low cost. Typically, Mm(Ni,Co,Mn,Al)₅ where Mm represents mischmetal (La: 26%, Ce: 52%, Nd: 16%, Pr: 6% (in atom%)) alloy or closely related compositions are used for batteries. However, a big problem with using mischmetal instead of lanthanum is that the discharge capacity is dramatically decreased because of a high concentration of cerium [6].

Because La is costly, its replacement with the relatively cheaper mischmetal can be attractive and, in other cases, La can be replaced by Mg to improve the electrochemical performance. As reported by Cuscueta *et al.* [7], who studied the effect of La by Mg in the electrochemical properties of La-Ni base alloy, found that this substitution does not increase the discharge capacity; however, it enhances the electrochemical behavior of cycling stability and rate capability. The use of Nb as a replacement for Co has been reported for the La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}X_{0.5}Ni_{3.8} alloys (X = Co, Nb). However, the microstructure of the Nb-doped alloys contained an NbNi₃ phase, which is associated with a decrease in the discharge capacity of a battery from 324 mA h/g (Co alloy) to 221 mA h/g (Nb alloy) [8]. Recently, the effects of substituting Sn for Co in AB₅-type La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8} hydrogen storage alloys have been reported. It was found that a new phase, LaNiSn, was formed as the Sn content increased [9]. Other work involved the replacement of Cu for Co in La_{0.7}Mg_{0.3}Ni_{3.2}Co_{0.35-x}Cu_x (x = 0, 0.05, 0.15, and 0.2) alloys. The authors reported that the electrochemical discharge capacity first increased and then decreased with increasing Cu content, with the La_{0.7}Mg_{0.3}Ni_{3.2}Co_{0.20}Cu_{0.15} (x = 0.15) alloy having the highest electrochemical discharge capacity (318.2 mA h/g) [10].

Previous work by this author has shown La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8} to be a high hydrogen storage capacity alloy [8,9]. In this study, the electrochemical performance properties of AB₅-type La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5-x}Cu_xNi_{3.8} hydrogen storage alloys were systematically investigated and are reported here.

2. Experimental Section

The nominal compositions of the studied alloys were designed as La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5-x}Cu_xNi_{3.8} (x = 0.0, 0.1, 0.2, 0.3, and 0.5). The purity of all elements was at least 99.9%. The alloys were prepared by induction melting in a water-cooled copper crucible under an argon atmosphere. The ingots were then melted twice for homogeneity.

For all electrochemical measurements, the alloys were firstly mechanically pulverized and sieved through 200 mesh (<75 μm). All test electrodes were prepared by mixing alloy powder and nickel powder

(<3 μm) with a weight ratio of 1:4. The mixture was cold pressed in nickel gauze (40 mesh) under a pressure of 15 MPa (about 1 cm^2 in area and 0.1 mm in thickness). The discharge capacity of each electrode was measured in a flooded cell configuration using $\text{Ni}(\text{OH})_2/\text{NiOOH}$ as the counter electrode and 6 M KOH solution as the electrolyte. The system was charged at 100 mA/g for 5 h followed by a 10 min rest and then discharged at 50 mA/g to the cut-off potential of 0.8 V.

High rate dischargeability (HRD) represents the kinetic property of hydrogen storage alloy electrodes and was calculated using the following formula:

$$\text{HRD} = \frac{C_d}{C_d + C_{50}} \times 100\% \quad (1)$$

where C_d is discharge capacity with a cut-off potential of 0.8 V at the discharge current density I_d ; and C_{50} is the residual discharge capacity with a cut-off potential of 0.8 V at the discharge current density $I = 50 \text{ mA/g}$ after the electrode has been fully discharged at I_d . HRD values were calculated when each electrochemical cell became active.

3. Results and Discussion

3.1. Discharge Capacity

Figure 1 shows the activation profiles of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0\text{--}0.5$) electrodes. It can be seen that all electrodes are easily activated to their maximum discharge capacities within five cycles.

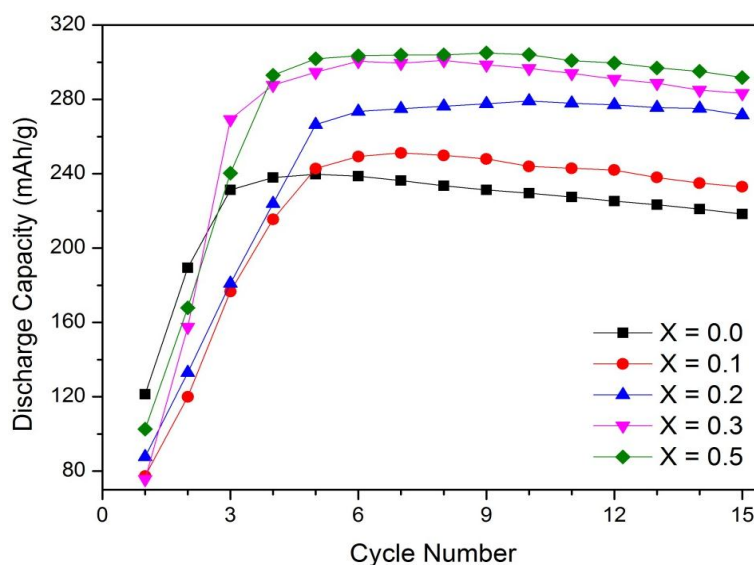


Figure 1. Activation profiles of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0\text{--}0.5$) alloys.

The maximum discharge capacities (C_{max}) of the electrode alloys are summarized in Figure 2, which shows that electrochemical capacity increases markedly from 239.8 mA h/g ($x = 0.0$) to 305.2 mA h/g ($x = 0.5$) with increasing Cu content. Similar results were reported by Huang *et al.* [10,11] who studied $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.2}\text{Co}_{0.35-x}\text{Cu}_x$ alloys. The maximum discharge capacity increases from 287 mA h/g ($x = 0.0$) to 318 mA h/g ($x = 0.15$) and then decreases to 299 mA h/g with complete substitution. As indicated by Mungole *et al.* [12], the variation of discharge capacity could be explained by the microstructure of

the alloys. The gradual decrease may be explained by the formation of a LaNiSn phase, which tends to disappear as complete substitution of Cu by Sn is reached [9].

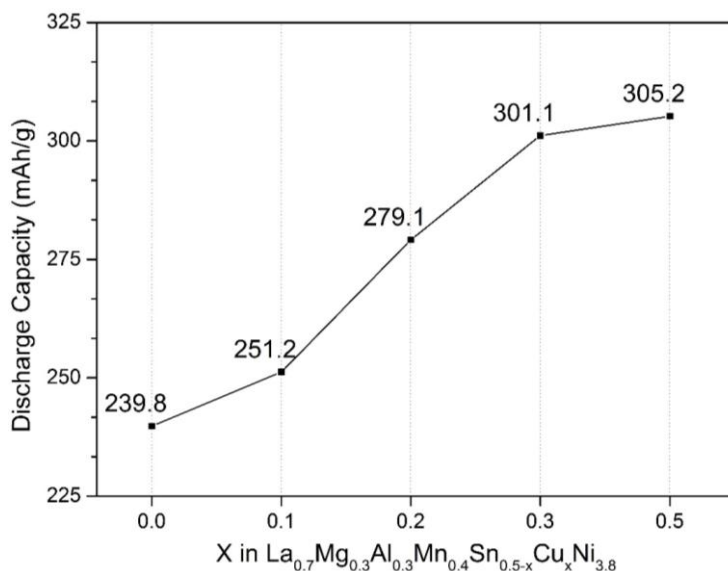


Figure 2. The maximum discharge capacity of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0\text{--}0.5$) alloys.

3.2. Capacity Retention

The cycle stability is an extremely important factor that directly affects the service life of a hydrogen storage alloy. Figure 3 shows the cycle life curves of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0\text{--}0.5$) negative electrodes.

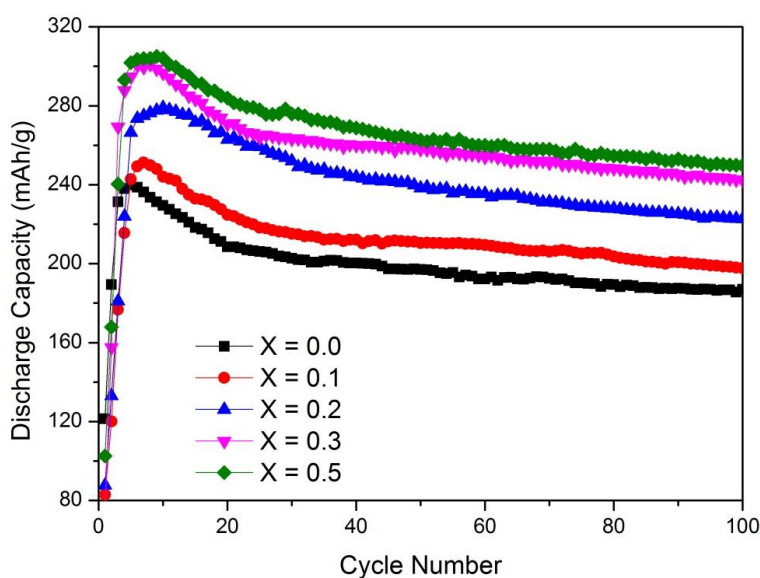


Figure 3. Cyclic stability of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0\text{--}0.5$) alloys.

The discharge capacity retention (C_{100}/C_{max}) of the electrodes after 100 charge-discharge cycles is also illustrated in Figure 4, where C_{100} is the discharge capacity of the 100th cycle. It can be observed that the discharge capacity retention of the electrodes increases from 78.0% ($x = 0.0$) to 81.8% ($x = 0.5$)

after 100 charge-discharge cycles. The pulverization of the alloy particles during the electrochemical cycles could be the main source of efficacy loss in the alloy electrodes [13].

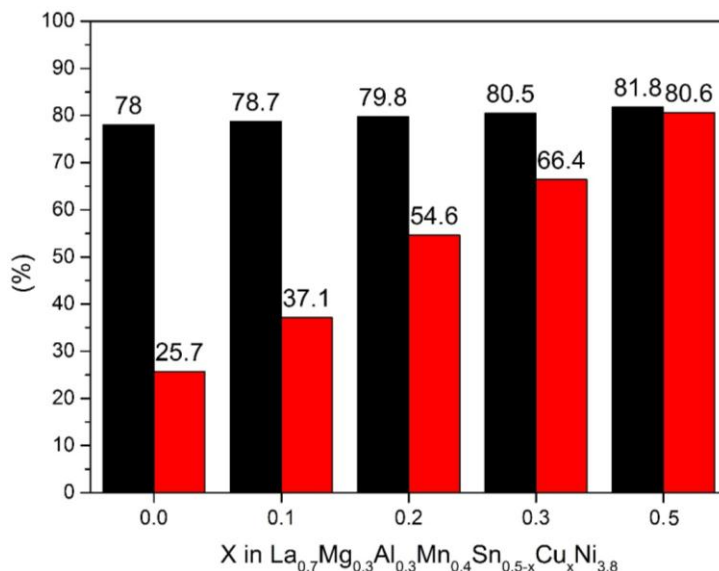


Figure 4. C_{100}/C_{max} (black bars) and HRD_{1400} (red bars) of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5-x}Cu_xNi_{3.8}$ ($x = 0.0-0.5$) negative electrode alloys. HRD : high rate dischargeability.

These results show that increase of Cu content effectively improves the cyclic stability of the electrode alloys. As reported by Liu *et al.* [14], the alloy particle pulverization is caused by lattice mismatch stresses during charge/discharge cycles. This may be one of the explanations for cyclic stability enhancement of the Cu alloys. However, structural and phase distribution analyses must still performed.

3.3. High Rate Dischargeability

In hydride electrode battery applications, minimizing discharge capacity loss at high discharge current density is important [15]. Figure 5 shows HRD trends for $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5-x}Cu_xNi_{3.8}$ ($x = 0.0-0.5$) hydrogen storage alloy electrodes subjected to increasing discharge current density. The HRD at 1400 mA/g (HRD_{1400}) is also illustrated in Figure 4. It is apparent from Figures 4 and 5 that HRD increases when Cu content is increased in the alloys for all discharge currents. Results show that the HRD increased drastically from 25.7% ($x = 0.0$) to 80.6% ($x = 0.5$) at high discharge current density ($I_d = 1400$ mA/g). It is well known that the HRD of metal hydride electrodes is dominated by the charge transfer reaction at the electrode/electrolyte interface and the mass transport properties characterized by the hydrogen diffusion rate within the electrode where hydrogen diffuses into alloy particles [16]. As previously reported, the increase of the $LaNi_5$ phase causes a drastic reduction on the $LaNi_5$ main phase [9]. In this case, the substitution of Cu by Sn may improve the formation of the $LaNi_5$ phase causing the increase of hydrogen diffusion into the main phase in the Cu content alloys.

Table 1 shows a comparison of the properties of two alloys investigated in this study: an alloy reported in previous work and a composition reported as commercial metal hydride electrode with similar composition reported in this article. It is evident that Co substitution resulted in improved discharge capacity (337.1 mA h/g) over Sn and Cu substitution. The Sn-substituted alloy exhibited the lowest HRD (25.7%). Cu substitution yielded good overall electrochemical performance of the negative electrode alloys,

showing only a small discharge capacity loss of 9.5% with an 11.6% enhancement of discharge capacity retention at the 100th cycle, and a 12.2% increase in *HRD* at a discharge current density of 1400 mA/g.

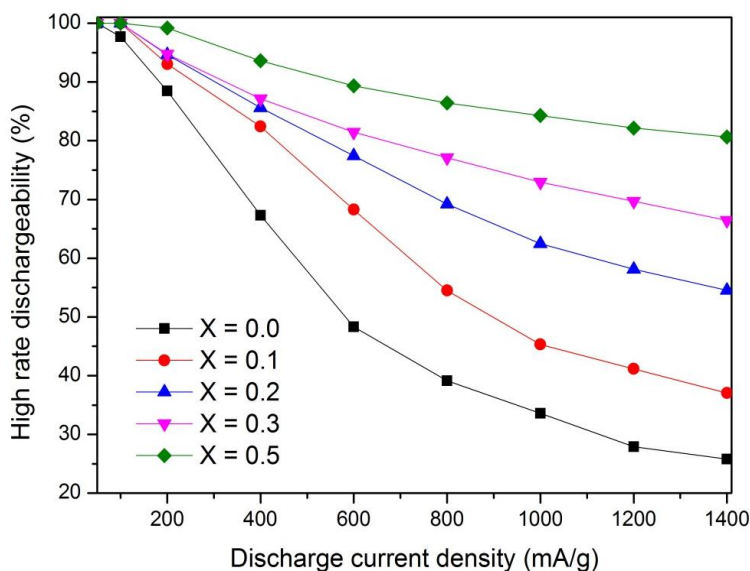


Figure 5. *HRD* of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0\text{--}0.5$) alloys.

Table 1. Electrochemical properties of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{M}_{0.5}\text{Ni}_{3.8}$ ($M = \text{Sn, Cu or Co}$) alloys.

Alloy	C_{max} (mA h/g)	C_{100}/C_{max} (%)	$HRD_{1400}(\%)^a$
$\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5}\text{Ni}_{3.8}$	239.8	78.0	25.7
$\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Cu}_{0.5}\text{Ni}_{3.8}$	305.2	81.8	80.6
$\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Co}_{0.5}\text{Ni}_{3.8}$ [9]	337.1	70.2	68.4
$\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ [17]	283.0	92.2	

^a The *HRD* at a current density of 1400 mA/g.

4. Conclusions

The work presented here investigated the effects of substituting Cu for Sn in $\text{La}_{0.7}\text{Mg}_{0.3}\text{Al}_{0.3}\text{Mn}_{0.4}\text{Sn}_{0.5-x}\text{Cu}_x\text{Ni}_{3.8}$ ($x = 0.0\text{--}0.5$) hydrogen storage alloys on electrochemical performance. Results indicate that increasing the content of Cu from $x = 0$ to $x = 0.5$ improved the maximum discharge capacity from 239.8 mA h/g to 305.2 mA h/g, the capacity retention at the 100th cycle from 78.0% to 81.8% (1400 mA/g discharge current density), and the *HRD* of the alloy electrodes from 25.7% to 80.6%.

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Author Contributions

Julio Cesar Serafim Casini wrote the manuscript and performed the experiments. Zaiping Guo and Hua Kun Liu performed batteries experiments and analyzed the batteries data. Rubens Nunes de Faria and Hidetoshi Takiishi conceived the project and edited the manuscript. All authors contributed equally to the writing and organization of the paper.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Sakai, T.; Yoshinaga, H.; Miyamura, H.; Kuriyama, N.; Ishikawa, H. Rechargeable hydrogen batteries using rare-earth-based hydrogen storage alloys. *J. Alloy. Compd.* **1992**, *180*, 37–54.
2. Tang, W.; Gai, Y.; Zheng, H. Deterioration of copper-containing mischmetal-nickel-based hydrogen absorption electrode materials. *J. Alloy. Compd.* **1995**, *224*, 292–298.
3. Yang, S.; Han, S.; Song, J.; Li, Y. Influences of molybdenum substitution for cobalt on the phase structure and electrochemical kinetic properties of AB₅-type hydrogen storage alloys. *J. Rare Earths* **2011**, *29*, 692–697.
4. Liu, B.; Hu, M.; Li, A.; Zhang, B.; Zhu, X. Microstructure and electrochemical characteristics of La_{0.7}Ce_{0.3}Ni_{3.75}Mn_{0.35}Al_{0.15}Cu_{0.75-x}(V_{0.81}Fe_{0.19})_x hydrogen storage alloys. *J. Rare Earths* **2012**, *30*, 769–774.
5. Ren, J.; Zhanga, T.; Feng, M.; Wang, G.; Zhao, X.; Wang, X. Microstructures and electrochemical properties of cobalt-free LaNi_{4.0}Al_{0.2}Fe_{0.4}Cu_{0.4-x}Sn_x ($x = 0-0.4$) electrode alloys prepared by casting. *J. Rare Earths* **2006**, *24*, 574–578.
6. Zhang, Y.H.; Dong, X.P.; Wang, G.Q.; Guo, S.H.; Wang, X.L. Effect of substituting Mm with La on the electrochemical performances of Co-free La_xMm_{1-x}(NiMnSiAlFe)_{4.9} ($x = 0-1$) electrode alloys prepared by casting and rapid quenching. *J. Power Sources* **2005**, *140*, 381–387.
7. Cuscueta, D.J.; Melnichuka, M.; Perettia, H.A.; Salva, H.R.; Ghilarduccia, A.A. Magnesium influence in the electrochemical properties of La-Ni base alloy for Ni-MH batteries. *Int. J. Hydrog. Energy* **2008**, *33*, 3566–3570.
8. Ferreira, E.A.; Serra, J.M.; Casini, J.C.S.; Takiishi, H.; Faria, R.N. Microstructure and electrochemical properties of a LaMgAlMnCoNi based alloy for Ni/MH batteries. *Mater. Sci. Forum* **2012**, *727–728*, 80–84.
9. Casini, J.C.S.; Ferreira, E.A.; Guo, Z.; Liu, H.K.; Faria, R.N.; Takiishi, H. Effect of Sn substitution for Co on microstructure and electrochemical performance of AB₅ type La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5-x}Sn_xNi_{3.8} ($x = 0-0.5$) alloys. *Trans. Nonferrous Met. Soc. China* **2015**, *25*, 520–526.
10. Huang, T.; Wu, Z.; Han, J.; Sun, G.; Yu, J.; Cao, X.; Xu, N.; Zhang, Y. Study on the structure and hydrogen storage characteristics of as-cast La_{0.7}Mg_{0.3}Ni_{3.2}Co_{0.35-x}Cu_x alloys. *Int. J. Hydrog. Energy* **2010**, *35*, 8592–8596.

11. Huang, T.; Yuan, X.; Yu, J.; Wu, Z.; Han, J.; Sun, G. Effects of annealing treatment and partial substitution of Cu for Co on phase composition and hydrogen storage performance of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.2}\text{Co}_{0.35}$ alloy. *Int. J. Hydrog. Energy* **2012**, *37*, 1074–1079.
12. Mungole, M.N.; Balasubramaniam, R.; Rai, K.N. Correlation between microstructure and hydrogen storage capacity in MmNi_5 alloys with Al, Mn and Sn substitutions. *Int. J. Hydrog. Energy* **1999**, *24*, 467–471.
13. Chartouni, D.; Meli, F.; Züttel, A.; Gross, K.; Schlapbach, L. The influence of cobalt on the electrochemical cycling stability of LaNi_5 -based hydride forming alloys. *J. Alloy. Compd.* **1996**, *241*, 160–166.
14. Liu, B.; Hu, M.; Ji, J.; Fan, Y.; Wang, Y.; Zhang, Z.; Li, A. Phase structure and electrochemical properties of $\text{La}_{0.7}\text{Ce}_{0.3}\text{Ni}_{3.75}\text{Mn}_{0.35}\text{Al}_{0.15}\text{Cu}_{0.75-x}(\text{Fe}_{0.43}\text{B}_{0.57})_x$ hydrogen storage alloys. *J. Alloy. Compd.* **2012**, *516*, 53–57.
15. Zhang, X.B.; Zi, D.; Yin, W.Y.; Chai, Y.J.; Zhao, M.S. Crystallographic and electrochemical characteristics of $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{5.0-x}(\text{Al}_{0.5}\text{Mo}_{0.5})_x$ hydrogen-storage alloys. *ChemPhysChem* **2005**, *6*, 520–525.
16. Pan, H.; Ma, J.; Wang, C.; Chen, S.; Wang, X.; Chen, C.; Wang, Q. Studies on the electrochemical properties of $\text{MmNi}_{4.3-x}\text{Co}_x\text{Al}_{0.7}$ hydride alloy electrodes. *J. Alloy. Compd.* **1999**, *293–295*, 648–652.
17. Chandra, D.; Chien, W.M.; Talekar, A. Metal hydrides for NiMH battery applications. *Mater. Matters* **2011**, *6*, 48–53.

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