Effects of Cu substitution for Sn on the electrochemical performance of La0.7Mg0.3Al0.3Mn0.4Sn0.5−xCuxNi3.8 (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 La₀.7Mg₀.3Al₀.3Mn₀.4Sn₀.5−ₓCuₓNi₃.8 (x = 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 mAh/g (x = 0) to 305.2 mAh/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
La₀.7Mg₀.3Al₀.3Mn₀.4Sn₀.5, effects, xCuₓNi₃.8, alloys, mh, ni, cu, substitution, sn, electrochemical, performance, batteries, 8, x

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Abstract: The effects of substitution of Cu for Sn on the electrochemical discharge capacity performance of La\textsubscript{0.7}Mg\textsubscript{0.3}Al\textsubscript{0.3}Mn\textsubscript{0.4}Sn\textsubscript{0.5–x}Cu\textsubscript{x}Ni\textsubscript{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 La0.7Mg0.3Al0.3Mn0.4X0.5Ni3.8 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 La0.7Mg0.3Al0.3Mn0.4Co0.5–xSnxNi3.8 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 La0.7Mg0.3Ni3.2Co0.35–xCux (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 La0.7Mg0.3Ni3.2Co0.20Cu0.15 (x = 0.15) alloy having the highest electrochemical discharge capacity (318.2 mA·h/g) [10].

Previous work by this author has shown La0.7Mg0.3Al0.3Mn0.4Co0.5Ni3.8 to be a high hydrogen storage capacity alloy [8,9]. In this study, the electrochemical performance properties of AB5-type La0.7Mg0.3Al0.3Mn0.4Sn0.5–xCuxNi3.8 hydrogen storage alloys were systematically investigated and are reported here.

2. Experimental Section

The nominal compositions of the studied alloys were designed as La0.7Mg0.3Al0.3Mn0.4Sn0.5–xCuxNi3.8 (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 cm² in area and 0.1 mm in thickness). The discharge capacity of each electrode was measured in a flooded cell configuration using Ni(OH)₂/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:

\[
HRD = \frac{C_d}{C_d + C_{50}} \times 100\%
\]

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 \(I = 50\) 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 La₀.₇Mg₀.₃Al₀.₃Mn₀.₄Sn₀.₅−ₓCuₓNi₃.₈ (\(x = 0.0–0.5\)) 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 La₀.₇Mg₀.₃Al₀.₃Mn₀.₄Sn₀.₅−ₓCuₓNi₃.₈ (\(x = 0.0–0.5\)) alloys.](image)

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 La₀.₇Mg₀.₃Ni₃.₂Co₀.₃₅−ₓCuₓ 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](image.png)

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

![Figure 3](image.png)

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

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 La0.7Mg0.3Al0.3Mn0.4Sn0.5−xCu xNi3.8 (x = 0.0–0.5) hydrogen storage alloy electrodes subjected to increasing discharge current density. The HRD at 1400 mA/g (HRD1400) 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 LaNiSn phase causes a drastic reduction on the LaNi5 main phase [9]. In this case, the substitution of Cu by Sn may improve the formation of the LaNi5 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 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) alloys.

Table 1. Electrochemical properties of La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}M_{0.5}Ni_{3.8} (M = Sn, Cu or Co) alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C_{max} (mA·h/g)</th>
<th>C_{100}/C_{max} (%)</th>
<th>HRD_{1400} (%) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Sn_{0.5}Ni_{3.8}</td>
<td>239.8</td>
<td>78.0</td>
<td>25.7</td>
</tr>
<tr>
<td>La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Cu_{0.5}Ni_{3.8}</td>
<td>305.2</td>
<td>81.8</td>
<td>80.6</td>
</tr>
<tr>
<td>La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8} [9]</td>
<td>337.1</td>
<td>70.2</td>
<td>68.4</td>
</tr>
<tr>
<td>MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} [17]</td>
<td>283.0</td>
<td>92.2</td>
<td></td>
</tr>
</tbody>
</table>

* 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 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 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.

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