Crystallographic and Electrochemical Hydrogen Storage Performances of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ ($x$ = 0-0.20) Alloys

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Herein, a hyper-stoichiometry Fe$_{0.43}$B$_{0.57}$ addition was used to improve the electrochemical hydrogen storage characteristics of Co-free high-Mn alloy. Microstructures and electrochemical performances of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ ($x$ = 0-0.20) alloys are investigated. X-ray diffraction and backscattered electron results indicate that the pristine alloy is LaNi$_5$ phase, while the alloys containing Fe$_{0.43}$B$_{0.57}$ consist of LaNi$_5$ matrix phase and La$_3$Ni$_{13}$B$_2$ secondary phase. The relative abundance of La$_3$Ni$_{13}$B$_2$ phase increases, and the $a$, $c$ and $V$ of LaNi$_5$ phase decrease with increasing $x$ value. Maximum discharge capacity of the alloy electrodes monotonically decreases from 329.1 mAh/g ($x$ = 0) to 314.7 mAh/g ($x$ = 0.20). High-rate dischargeability of the alloy electrodes first increases with increasing $x$ from 0 to 0.10, and then decreases until $x$ increases to 0.20. Cycling capacity retention rate at the 100th cycle increases from 51.1% ($x$ = 0) to 72.2% ($x$ = 0.20) with increasing $x$ value, which is ascribed to the improvement in pulverization resistance. It is demonstrated that the addition of Fe$_{0.43}$B$_{0.57}$ is an effective approach to improve the comprehensive electrochemical performances of Co-free high-Mn alloy electrodes.

Keywords: Electrochemical hydrogen storage performances; X-ray diffraction; Microstructures; Electrochemical properties; Nickel/metal hydride battery

1. INTRODUCTION

Nickel/metal hydride (Ni/MH) secondary batteries have been adopted in various portable electronic devices, and are serving in almost all commercial Ni/MH batteries AB$_5$-type alloys as
negative electrode materials due to their good overall electrode properties [1]. High cost of cobalt (Co) in AB₅ alloy motives the researchers to develop low Co or Co-free AB₅-type hydrogen storage alloys [2]. Many attempts have been made by substituting Co with foreign metals, such as, Mn, Fe, Cu, Si, etc [3-5], and thereafter the Co-free high-Mn alloys were developed and commercially produced due to high performance/cost ratio [6]. However, the electrochemical performances, especially high-rate dischargeability and cycling stability, of Co-free high-Mn alloys are not yet satisfying.

Non-stoichiometry is considered as a special doping and multicomponent alloying technique for intermetallic compounds, and can effectively improve the electrochemical hydrogen storage properties of AB₅-type alloys [7]. Deviating AB₅-type compound composition from a stoichiometry to hyper-stoichiometry contributed to high-rate dischargeability and cycling stability of hydrogen storage alloy [8, 9]. Therefore, adding hyper-stoichiometry element is always used to modify microstructure and hydrogen storage performances of AB₅ alloy [10-12].

Ye et al. [13] reported that the addition of boron modified the activation performance and significantly improved the high-rate capacity of Mm₃.₃₅Co₀.₇₅Mn₀.₄Al₀.₃B₅ alloy though the electrochemical capacity is lower than that of commercial Mm₃.₃₅Co₀.₇₅Mn₀.₄Al₀.₃ alloy. Zhang et al. [14] studied low Co AB₅-type MmNi₃.₈Co₀.₄Mn₀.₆Al₀.₃B₅ alloys and pointed out that the addition of B made the cycling stability improved, activation performance modified, high rate discharge capability and discharge voltage increased. Obviously, the addition of B element and increasing stoichiometric ratio is effective to enhance activation performance, high-rate dischargeability and cycling stability. However, the pure B is very expensive and unpractical to be used in the Co-less or Co-free alloy. Fortunately, the price of commercial Fe₀.₄₃B₀.₅₇ alloy is less than 5% price of pure B, and the melting point of Fe₀.₄₃B₀.₅₇ alloy is much lower than that of pure B. More importantly, Fe introduction in AB₅ alloy can remarkably improve cycling stability due to the improvement in the anti-pulverization of alloy electrode [15,16]. Therefore, it can be expected that the overall electrochemical characteristics could be improved by adding Fe₀.₄₃B₀.₅₇ in Co-free high-Mn AB₅-type alloys.

Here, on the basis of the merits of Fe₀.₄₃B₀.₅₇ and the belief that the Fe and B additions may result in some noticeable modification of electrochemical hydrogen storage performances, microstructures and electrochemical hydrogen storage characteristics of La₀.₇₅Ce₀.₂₅Ni₃.₈₀Mn₀.₉₀Cu₀.₃₀(Fe₀.₄₃B₀.₅₇)ₓ (x = 0-0.20) alloys have been investigated.

2. EXPERIMENTAL PROCEDURES

La₀.₇₅Ce₀.₂₅Ni₃.₈₀Mn₀.₉₀Cu₀.₃₀(Fe₀.₄₃B₀.₅₇)ₓ (x = 0-0.20) alloys were synthesized by induction melting of the metal elements (La, Ce, Ni, Mn, Cu: 99.9% in purity and commercial Fe-B alloy contained 57.0 at.% B and the other were Fe and trace impurities.) in argon atmosphere, and then were annealed. The ingots were annealed by at 1223 K for 10 h in argon atmosphere with the pressure of 0.08 MPa.

X-ray diffraction (XRD) measurement was carried out on X’pert PROMPD X-ray diffractometer with Cu Kα radiation in the range from 20° to 80° with 0.02 °/min, and the results were analyzed by means of Rietveld refinement (using the software MAUD).
The alloy powders of measuring electrodes were obtained by grinding the inner part of alloy ingots in Ar atmosphere. All measuring electrodes for test were prepared by cold pressing a mixture of 0.15 g alloy powders of 200-400 mesh and 0.75 g nickel carbonyl powders into a pellet of 10 mm in diameter under 15 MPa. Electrochemical measurements were performed at 298 K in a standard tri-electrode system, consisting of a working electrode (metal hydride), a counter electrode (Ni(OH)$_2$/NiOOH), and a reference electrode (Hg/HgO) with 6 mol/L KOH solution as electrolyte. Each electrode was charged for 7 h at 60 mA/g and discharged to -0.6 V versus Hg/HgO at 60 mA/g at 298 K. After every charging/discharging, the rest time was 10 min. In evaluating the high-rate dischargeability, discharge capacity of the alloy electrodes at different discharge current density was measured. The high-rate dischargeability (HRD, %) was defined as HRD=$C_d/C_{max} \times 100\%$, where $C_d$ was the discharge capacity at the discharge current density $I_d$ ($I_d = 60, 300, 600, 900$ and $1200$ mA/g, respectively), and $C_{max}$ was the maximum discharge capacity at the discharge current density of 60 mA/g. The electrochemical impedance spectrums (EIS) were performed on a PARSTAT 2273 Advanced Potentiostat/Galvanostat station by scanning in the frequency range of 100 kHz to 10 mHz at 50% depth of discharge (DOD) at 298 K. The potential step measurements were tested on the same instrument at 100% charge state. A +500 mV potential was applied and the discharge time was 3600 s.

3. RESULTS AND DISCUSSION

3.1 Crystal structure

![XRD patterns](image)

Figure 1. XRD patterns of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloys (a) XRD patterns for $x = 0$-0.20 (b) Rietveld analysis pattern for $x = 0.15$
Table 1. The characteristics of phases in La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloys

<table>
<thead>
<tr>
<th>Samples $x$</th>
<th>Phases</th>
<th>Lattice parameter (Å)</th>
<th>Cell Volume (Å$^3$)</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>LaNi$_5$</td>
<td>$a = 5.072$ $c = 4.091$</td>
<td>91.14</td>
<td>100</td>
</tr>
<tr>
<td>$x = 0.05$</td>
<td>LaNi$_5$</td>
<td>$a = 5.072$ $c = 4.085$</td>
<td>90.99</td>
<td>96.43</td>
</tr>
<tr>
<td></td>
<td>La$<em>3$Ni$</em>{13}$B$_2$</td>
<td>$a = 5.1055$ $c = 11.0407$</td>
<td>3.57</td>
<td></td>
</tr>
<tr>
<td>$x = 0.10$</td>
<td>LaNi$_5$</td>
<td>$a = 5.069$ $c = 4.078$</td>
<td>90.75</td>
<td>91.38</td>
</tr>
<tr>
<td></td>
<td>La$<em>3$Ni$</em>{13}$B$_2$</td>
<td>$a = 5.1067$ $c = 11.0481$</td>
<td>8.62</td>
<td></td>
</tr>
<tr>
<td>$x = 0.15$</td>
<td>LaNi$_5$</td>
<td>$a = 5.059$ $c = 4.080$</td>
<td>90.44</td>
<td>90.25</td>
</tr>
<tr>
<td></td>
<td>La$<em>3$Ni$</em>{13}$B$_2$</td>
<td>$a = 5.1075$ $c = 11.0576$</td>
<td>9.75</td>
<td></td>
</tr>
<tr>
<td>$x = 0.20$</td>
<td>LaNi$_5$</td>
<td>$a = 5.059$ $c = 4.075$</td>
<td>90.36</td>
<td>89.88</td>
</tr>
<tr>
<td></td>
<td>La$<em>3$Ni$</em>{13}$B$_2$</td>
<td>$a = 5.1089$ $c = 11.0597$</td>
<td>10.12</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1a presents XRD patterns of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloys. Fig. 1b shows the XRD pattern and Rietveld analysis pattern of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_{0.15}$ alloy. As can be seen from Fig. 1a, La$_{0.75}$Ce$_{0.25}$Ni$_{3.75}$Mn$_{0.90}$Cu$_{0.35}$ alloy is LaNi$_5$ phase with CaCu$_5$ type hexagonal structure. The alloys containing Fe$_{0.43}$B$_{0.57}$ are composed of LaNi$_5$ matrix phase and La$_3$Ni$_{13}$B$_2$ secondary phase. Lattice parameters, cell volume and phase relative abundance of the alloys are listed in Table 1. The relative abundance of La$_3$Ni$_{13}$B$_2$ phase increases, and the lattice parameter $a$, $c$ and cell volume $V$ of LaNi$_5$ phase decrease with increasing $x$ value from 0 to 0.20.

3.2 Activation capability and maximum discharge capability

The number of cycles ($N_a$) needed to reach the maximum capacity and maximum discharge capacity ($C_{max}$) of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes are given in Table 2. It is noted that the $N_a$ of the alloy electrodes increases from 2 ($x = 0$) to 4 ($x = 0.20$) with increasing $x$ value, which indicates that the addition of Fe$_{0.43}$B$_{0.57}$ lowers down the activation process. The initial activation in the first few cycles is usually attributed to the particle size reduction and surface reconstruction [17]. It is confirmed that increasing stoichiometry contributes to the anti-pulverization of the alloy due to good compound homogeneity and low internal stain [18]. The stoichiometric ratio increases with increasing $x$ value, and then improves the anti-pulverization, which is detrimental to the activation. Moreover, Zhang et al. [19] pointed out that the phase interface or grain boundary was buffer areas for the release of distortion and stress of crystal lattice in the charging/discharging process, and then restricted the pulverization. According to the XRD results, the La$_3$Ni$_{13}$B$_2$ second phase increases with increasing $x$ values, which causes the increment of phase interface and then enhances ant-pulverization. This is also unfavorable to activation process. In addition, Wu et al. [20] reported the oxidation film formed on the alloy surface increased the additive internal energy, which led to the poorer activation performance. Due to the low surface energy of Fe, the increase in Fe content makes the surface oxide layer become thick and causes the increase in internal energy, and then degrades activation property. The $C_{max}$ of the alloy electrodes decreases monotonically from 329.1 mAh/g ($x = 0$) to 314.7 mAh/g ($x = 0.20$) with increasing $x$ value, which should be ascribed to
following factors. Firstly, the hydrogen storage capacity of La$_3$Ni$_{13}$B$_2$ phase is 157 mAh/g [20], which is much lower discharge capacity than LaNi$_5$ matrix phase. The La$_3$Ni$_{13}$B$_2$ phase gradually increases with increasing $x$ value, which is unfavorable for the discharge capacity. Secondly, Brateng et al. [22] pointed out that the larger the cell volume is, the discharge capacity is the higher. The maximum discharge capacity is closely correlated with the unit cell volume of compound [23]. The $V$ of the LaNi$_5$ phase decreases with increasing $x$ value, which is detrimental to the discharge capacity. Thirdly, the increase in Fe content leads to the surface oxide film thicker, which degrades the charge-transfer reaction on the alloy surface, as well as decreases the number of activity sites on the alloy surface and then makes the diffusion of hydrogen from the inner to the surface more difficultly.

Table 2. Electrochemical properties of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$$(Fe_{0.43}B_{0.57})_x$ alloy electrodes

<table>
<thead>
<tr>
<th>$x$</th>
<th>$C_{\text{max}}$ (mAh/g)</th>
<th>$N_a$</th>
<th>HRD$_{1200}$</th>
<th>$S_{100}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>329.1</td>
<td>2</td>
<td>67.5</td>
<td>51.1</td>
</tr>
<tr>
<td>0.05</td>
<td>324.2</td>
<td>3</td>
<td>70.4</td>
<td>55.1</td>
</tr>
<tr>
<td>0.10</td>
<td>321.6</td>
<td>3</td>
<td>76.8</td>
<td>62.0</td>
</tr>
<tr>
<td>0.15</td>
<td>317.8</td>
<td>3</td>
<td>74.5</td>
<td>65.5</td>
</tr>
<tr>
<td>0.20</td>
<td>314.7</td>
<td>4</td>
<td>63.5</td>
<td>72.2</td>
</tr>
</tbody>
</table>

$^a$ The high-rate dischargeability at the discharge current density of 1200 mA/g.
$^b$ The number of cycles needed to activate the electrode.

3.4 High-rate dischargeability and electrochemical kinetics

Fig. 2 shows the relationship between the high-rate dischargeability (HRD) and the discharge current density of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$$(Fe_{0.43}B_{0.57})_x$ alloy electrodes. The HRD of the alloy electrodes first increases with increasing $x$ from 0 to 0.10, and then decreases when $x$ increases to 0.20. The HRD at the discharge current density of 1200 mA/g (HRD$_{1200}$) is listed in Table 2. It can be seen that HRD$_{1200}$ first increases from 67.5% ($x = 0$) to 76.8% ($x = 0.10$), and then decreases to 63.5% ($x = 0.20$).

It is well known that the HRD of the metal-hydride electrodes is dominated by the charge-transfer reaction at the electrode/electrolyte interface and the hydrogen diffusion rate within the bulky alloy electrode, which are reflected in the value of surface exchange current density ($I_0$), being a measure of the catalytic activity of an alloy, as well as in the hydrogen diffusion coefficient ($D$), which characterizes the mass transport properties of an alloy electrode [25].

The EIS of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$$(Fe_{0.43}B_{0.57})_x$ alloy electrodes at 50% DOD are shown in Fig. 3. On the basis of the equivalent circuit [26], the charge-transfer resistance values ($R_{ct}$) are obtained and listed in Table 3. The $R_{ct}$ values of the alloy electrodes first decreases from 91.2 m$\Omega$ g ($x = 0$) to 65.1 m$\Omega$ g ($x = 0.10$), and then increases to 106.7 m$\Omega$ g ($x = 0.20$) with increasing $x$ value.
Furthermore, the $I_0$ can also describe the charge-transfer process. The $I_0$ value can be calculated according to the following formula [27].

$$I_0 = \frac{RT}{F R_{ct}}$$  \hspace{1cm} (1)

**Figure 2.** HRD of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$Fe$_{0.43}$B$_{0.57}$$_x$ alloy electrodes

where $R$, $T$, $F$, $R_{ct}$ are the gas constant, absolute temperature, Faraday constant and the polarization resistance, respectively. The $I_0$ values are calculated by Eq. (2) and listed in Table 3. It is clear that the $I_0$ first increases from 281.6 mA/g ($x = 0$) to 394.5 mA/g ($x = 0.10$), and then decreases to 240.7 mA/g ($x = 0.20$). It is reported that the formation of the La$_3$Ni$_{1.3}$B$_2$ secondary phase in AB$_5$ alloys improves the catalytic activity of the alloys [28]. As mentioned above, the secondary phase La$_3$Ni$_{1.3}$B$_2$ increases with increasing $x$ value, which is of benefit to improve the electrocatalytic activity of the surface of alloy electrode and the charge-transfer reaction. Moreover, the addition of B contributes to the electrochemical activity [29], which is favorable to the charge-transfer reaction of the alloy electrodes. Unfortunately, the increase in Fe content on the alloy surface with increasing $x$ value degrades the charge-transfer reaction because of the increase of oxide film on the alloy surface. Therefore, it is reasonable to assume that, when $x \leq 0.10$, the favorable effect is chiefly responsible for the increase of the exchange current density for alloy electrodes. However, when $x > 0.10$, the decrease of the exchange current density for alloy electrodes is mainly ascribed to the disadvantageous factors. Consequently, the threshold content of Fe$_{0.43}$B$_{0.57}$ is 0.10 in present system.

Figure 3. EIS of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes

Fig. 4 shows the semi-logarithmic plots of the anodic current vs. the time response of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes. It can be seen that the current-time responses can be divided into two time domains [30], in the first time region, the oxidation current of hydrogen rapidly declines due to the rapid consumption of hydrogen on the surface. However, in the followed second time region, the current declines more slowly and drops linearly with time. Zheng et al. [30] reported that in a large anodic potential-step test, after a long discharge time, the diffusion current varies with time according to the following equation:

$$\text{lg} i = \text{lg}(\frac{6FD}{da^2}(C_0 - C_s)) - \frac{\pi^2 D}{2.303 a^2} t$$

(2)

where $i$ is anodic current density (A/g), $D$ the hydrogen diffusion coefficient (cm$^2$/s), $d$ the density of the alloy (g/cm$^3$), $a$ the radius of the alloy particle, $C_0$ the initial hydrogen concentration in the bulk of the alloy (mol/cm$^3$), $C_s$ the surface hydrogen concentration of the alloy (mol/cm$^3$) and $t$ is the discharge time (s). Assuming that the alloy has a similar particle distribution with an average particle radius of 13 µm according to previous study [31], $D$ was calculated and summarized in Table 3. The $D$ of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes first increases from 6.53 $\times$ 10$^{-11}$ (x = 0) to 8.60 $\times$ 10$^{-11}$ cm$^2$/s (x = 0.10), and then decreases to 5.58 $\times$ 10$^{-10}$ cm$^2$/s (x = 0.20). As mentioned above, the formation of the secondary phase increases the fraction of phase boundaries, which provides extra tunnels for the diffusion of hydrogen atoms. The increase of La$_3$Ni$_1$B$_2$ secondary phase causes the increase in the phase boundary, which can decrease the lattice distortion and strain energy formed in the process of hydrogen absorption. Moreover, it is well known that the A-side lanthanide atoms form the stable metal hydrides, while the B-side transitional atoms form the unstable metal hydrides.
The lower hydride stability facilitates the release of bonded hydrogen, which is favorable to the hydrogen diffusion of the alloys [32]. The addition of Fe$_{0.43}$B$_{0.57}$ results in the decrement of A-side atoms and the increment of B-side transitional atoms, which lowers the stability of the alloy hydride and then accelerates hydrogen diffusion. Conversely, Khalid et al. [33] have reported that the oxidation of Fe on the alloy surface limited the hydrogen transfer from the surface to the bulk. As mentioned above, the increase of Fe content causes the increase of surface oxide film, which will degrade the hydrogen diffusion. Therefore, it is certain that the diffusion coefficient has a maximum value with increasing $x$ value.

Iwakura et al. [34] have reported that linear dependence of the high-rate dischargeability on exchange current density and activation energy of hydrogen diffusion indicated that the charge transfer and hydrogen diffusion are responsible for discharge efficiency. Fig. 5 shows the HRD$_{1200}$ as a function of exchange current density and hydrogen diffusion coefficient for La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes. It is evident that the HRD$_{1200}$ increases with the increase of $I_0$ and $D$, and shows a linear relationship with $I_0$ and $D$, respectively. This implies that both charge-transfer reaction at the electrode/electrolyte interface and the hydrogen diffusion of alloy electrodes should be responsible for the HRD at a discharge current density of 1200 mA/g.

**Figure 4.** Semilogarithmic curves of anodic current vs. time of response of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes

**Table 3.** Electrochemical kinetic characteristics of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes

<table>
<thead>
<tr>
<th>$x$</th>
<th>$R_p$ (mΩ g)</th>
<th>$I_0$ (mA/g)</th>
<th>$D$ ($\times 10^{-11}$ cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>91.2</td>
<td>281.6</td>
<td>6.53</td>
</tr>
<tr>
<td>0.05</td>
<td>82.5</td>
<td>311.3</td>
<td>7.34</td>
</tr>
<tr>
<td>0.10</td>
<td>65.1</td>
<td>394.5</td>
<td>8.60</td>
</tr>
<tr>
<td>0.15</td>
<td>74.9</td>
<td>342.8</td>
<td>7.52</td>
</tr>
<tr>
<td>0.20</td>
<td>106.7</td>
<td>240.7</td>
<td>5.58</td>
</tr>
</tbody>
</table>
Figure 5. HRD at 1200 mA/g as a function of exchange current density for La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes

3.3 Cycling stability

Cycling stability is an extremely important factor for the service life of hydrogen storage alloys. The cycling capacity retention rate is expressed as $S_n(\%) = C_n/C_{\text{max}} \times 100$ (where $C_n$ is the discharge capacity at the $n^{\text{th}}$ cycle). The cycling capacity retention rate of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes as a function of cycle number is shown in Fig. 6. Obviously Fe$_{0.43}$B$_{0.57}$ addition conduces to the cycling stability of alloy electrodes. The $S_{100}$ of the alloy electrodes are listed in Table 2. It can be seen that $S_{100}$ increases from 51.1% ($x = 0$) to 72.2% ($x = 0.20$). The fundamental reasons for the capacity decay of alloy electrode are attributed to the pulverization and corrosion of the alloy in the charging-discharging cycle [35, 36]. As mentioned above, the phase interface or grain boundary was buffer areas for the release of distortion and stress of crystal lattice in the charging/discharging process, and then restricted the pulverization [19]. The increment of La$_3$Ni$_{13}$B$_2$ second phase causes the increment of phase interface and then enhance ant-pulverization and the cycling stability. Moreover, it is well accepted that alloy having a smaller volume expansion on hydriding would lead to a lower degree of pulverization and thus exposes less surface area to the corrosive electrolyte, and hence corrodes less and has a better cycling stability [37]. Fe addition can strongly reduce the lattice expansion, and the decrease of lattice expansion suppresses the pulverization [38]. Increasing Fe content with increasing $x$ value will restrain lattice expansion in the charging process and then enhance the pulverization resistance, which is favorable to the cycling stability. Unfortunately, it is well-known that Fe easily oxidized due to the lower surface energy and forms coarse oxide film. The increase in Fe content not only causes the deterioration of corrosion resistance and then increases the loss of the alloy, but also degrades the electrochemical kinetics on the
alloy surface, which is detrimental to the discharge capacity. Thus, it is reasonable to believe that the improvement in pulverization resistance of alloy electrode is one of critical reasons for the increment of cycling stability in present work.

![Figure 6](image_url)  
**Figure 6.** Cycling stability of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloy electrodes

### 4. CONCLUSIONS

On the basis of microstructures and electrochemical characteristics of La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ hydrogen storage alloys, the following conclusions can be drawn:

- Bimodal microstructures of LaNi$_5$ matrix and La$_3$Ni$_{13}$B$_2$ secondary phase are observed in La$_{0.75}$Ce$_{0.25}$Ni$_{3.80}$Mn$_{0.90}$Cu$_{0.30}$(Fe$_{0.43}$B$_{0.57}$)$_x$ alloys. Moreover, the relative abundance of La$_3$Ni$_{13}$B$_2$ increases with the increment of $x$ value.
- Activation property and maximum discharge capacity of the alloy electrodes degrades with increasing Fe$_{0.43}$B$_{0.57}$ content.
- HRD$_{1200}$ first increases from 67.5% ($x = 0$) to 76.8% ($x = 0.10$), and then decreases to 63.5% ($x = 0.20$), which is determined by the exchange current density and hydrogen diffusion coefficient.
- Adding Fe$_{0.43}$B$_{0.57}$ effectively conduces to the cycling stability of alloy electrodes, which is mostly affected by the improvement in the anti-pulverization.

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References


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