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Electrochemical properties and characteristics of the fluorinated $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Ni_{1.3}La_{0.05}$ electrode

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Abstract

Improvement of the initial activation characteristics and electrochemical reaction activity of the Laves-phase alloy surface are of basic importance for the application of hydriding alloy to Ni/MH batteries which exhibit larger discharge capacity than those of AB_5. The fluorination effects of the electrode made by $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Ni_{1.3}La_{0.05}$ Laves phase alloy on the electrochemical properties and characteristics, especially on the initial charge–discharge capability and electrochemical reaction activity were investigated in terms of the electrochemical impedance and surface microstructures. The fluorination procedure employed to the La-incorporated Laves phase is significantly effective for improving initial activation characteristics. The Specific surface area of the fluorinated particles were increased by about 20 times larger than those of the untreated one from 0.27 to 5.31 m^2/g which were contributed to the formation of La-fluoride, and also by the implantation of nickel over the particle surface. Fluorination treatment employed in this study for the La-incorporated Laves phase alloy was found effective for increasing the specific surface area and the surface charge acceptance during the initial charge process.

Keywords: Laves phase alloy; Surface structure; Fluorination; Impedance

1. Introduction

Laves phase alloy hydrides have been considered attractive because of their theoretically higher *H*-capacity. However, it has been well known that they are shown to have the disadvantages of poor initial activation, C/D cycle life, and also poor high rate capabilities. This is one of the most serious reasons which restrict their application to Ni/MH batteries, especially the application of sealing activation in Ni/MH batteries. In order to improve the initial activation, extensive studies have been carried out with respect to the composition of alloy [1,2], an anodic oxidation treatment [3], a hot charging technique [4] and a surface modification [5,6]. Yan et al. [1] improved the activation property of $Zr_{0.5}Ti_{0.5}V_{0.75}Ni_{1.5}$ electrode by La-substituting on account of the precipitate of La–Ni phase. Jung et al. [4] found that the hot-charging process gave a favorable effect on the initial activation of Zr–Ti–Cr–Mn–V–Ni electrode due to the formation of new clean surfaces with fine cracks. Fluorination technique developed in this laboratory demonstrated effective for improving initial activation of Laves phase alloy in both the gas–solid reaction and electrochemical reaction [5,6].

In this work, surface structure and electrochemical properties of the $Zr_{0.9}Ti_{0.1}V_{0.2}$ $Mn_{0.6}Ni_{1.3}La_{0.05}$ alloy after a specific fluorination treatment have been investigated. The effects of La-incorporation and fluorination treatment on the initial electrochemical activation and discharge capacity as a function of discharge current density are reported here with the experimental surveys on specific surface area, electrochemical impedance spectra (EIS) and scan electron microscopy (SEM).

2. Experimental details

The $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Ni_{1.3}La_{0.05}$ alloy was prepared by arc-melting under an argon atmosphere. The ingot was then annealed at 1100°C for 18 h under an argon atmosphere. Then the alloy was pulverized to average size smaller than 25 m by repeated hydriding and dehydriding reactions. The alloy powder was treated by F5+F4 as described in detail in Refs. [7–9]. The surface microstructure was observed by SEM (EPMA 8705, Shimazu). The specific surface area was determined by BET method.

For the electrochemical evaluation, the button-type hydride electrode was made by mixing the alloy powder with Ni powder and PTFE powder in a weight ratio of

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0.25/0.75/0.05, and then compressed into a pellet with a diameter of 13 mm and a thickness of 1.5 mm under a mechanical load of 4 ton cm^{-2}. These electrodes were placed at the half cell by using a sintered nickel electrode as counter-electrode and a Hg/HgO (6N KOH) electrode as reference electrode. The electrochemical properties of the electrode were measured by charging at a current density of 200 mA/g for 3 h and then discharging at a current density of 150 mA/g to a cut-off potential of −0.6V with respect to the Hg/HgO (6N KOH) electrode after resting for 1 h at 20°C. The electrochemical impedance spectra were measured from 10 kHz to 10 mHz at 5 mV of the amplitude of perturbation by using an IM6 impedance measurement unit (ZAHNER).

3. Results and discussion

3.1. Surface state

It can be seen from Fig. 1 that the surface of the untreated $Zr_{0.9}Ti_{0.1}V_{0.2}Mn_{0.6}Ni_{1.3}La_{0.05}$ alloy was smooth, however, the F-treated surface was covered uniformly by the fine La-fluoride layer with network structure (Fig. 1(b)) as has been observed in the fluorinated $LaNi_{4.7}Al_{0.3}$ alloy [10]. The network structure formed by the La-fluoride was covered by the fine nickel particles, which reduced from F-solution. The network structure size of the La-fluoride and the fine nickel particle was less than 0.3 m and 0.1 m, respectively (as indicated in Fig. 1(c,d)). ICPS analysis of nickel amount before and after fluorination in F-solution demonstrated that nickel was completely transferred from F-solution to particle surface during fluorination process. The specific surface area of the fluorinated particles was increased by about 20 times larger than these of the untreated particles (from 0.27 to 5.31 m^2/g) which were caused by formation of the fine network structure of the La-fluoride with the fine nickel particles.

Generally, it is hard to obtain nickel-rich layer having the fine network structure on hydrogen absorbing alloy particle surface by an ordinary modification method. Nickel cluster is thought to be a good catalyst for hydrogen dissociation in the gas–solid reaction and electrochemical reaction because of its high specific surface area and low activation energy [11]. However, Nickel cluster on surface of hydrogen storage alloy has not been observed directly from experimental observation including SEM and TEM published until now. Although the nickel particle with the fine network structure was not considered to be nickel cluster, but the specific surface structure formed still resulted in the great improvement of electrochemical properties of the electrode as shown below.

3.2. Electrochemical initial activation

The initial charge–discharge curves of the untreated and F-treated electrodes were shown in Fig. 2. It was found that the absolute charge potential value of the untreated electrode increased before 15 min, and then decreased gradually. This meant that the charge process was an activation process. Alloy pulverization and generation of new surface, which occurred during charging process, contributed to the increase of surface charge acceptance for the untreated electrode. On the contrary, the absolute charge potential value of the F-treated alloy electrode increased during charging process which is attributed to the nickel-rich layer with the fine network structure and significantly increased specific surface area. In addition, it was obvious that a polarization potential of the untreated alloy electrode was too high for charging and discharging process under the same charge current density.

An improvement of the initial charge properties and an increase of the surface charge acceptance of Laves phase alloy electrode were important in view of a sealing activation in Ni/MH batteries, especially for decreasing an internal pressure of Ni/MH batteries. It was found from Fig. 3 that the F-treated electrode demonstrated a faster initial activation characteristics and reached to the maximum discharge capacity of 347 mAh/g only after 3 C/D cycles where the initial discharge capacity reached to about 97% of its maximum discharge capacity. On the other hand, the untreated electrode needed at least 15 cycles to reach the maximum capacity of 338 mAh/g. However, the C/D cycle life for both untreated and F-treated electrodes were found almost identical in their capacity decay tendencies. Therefore, the fluorination technique employed in this study was effective for improving the initial activation characteristics.

3.3. Electrochemical impedance measurements

The electrochemical impedance spectra were measured under an open circuit for both the F-treated and untreated electrodes after 1st charge and full activation (at 30th charge) at 20°C and were illustrated in Fig. 4. The surface electrochemical reaction resistance was obtained from the larger semicircle in the low frequency region [12]. It was evident that surface electrochemical reaction resistance of the F-treated electrode significantly decreased compared to the untreated alloy electrode after 1st charge due to the formation of both the La-fluoride and the nickel-rich layer with fine network structure and increased specific surface area of the fluorinated particles. After full activation, the electrochemical reaction resistance of the untreated electrode decreased, which was caused by the generation of cracks and new surfaces. However, it was interesting to point out that the electrochemical reaction resistance of the F-treated electrode increased slightly compared to first charge. The surface reaction activity of the F-treated electrode was significantly improved only after first charge, which led to the excellent initial activation. Therefore, the fluorination technique was effective for decreasing surface electrochemical reaction resistance due to the

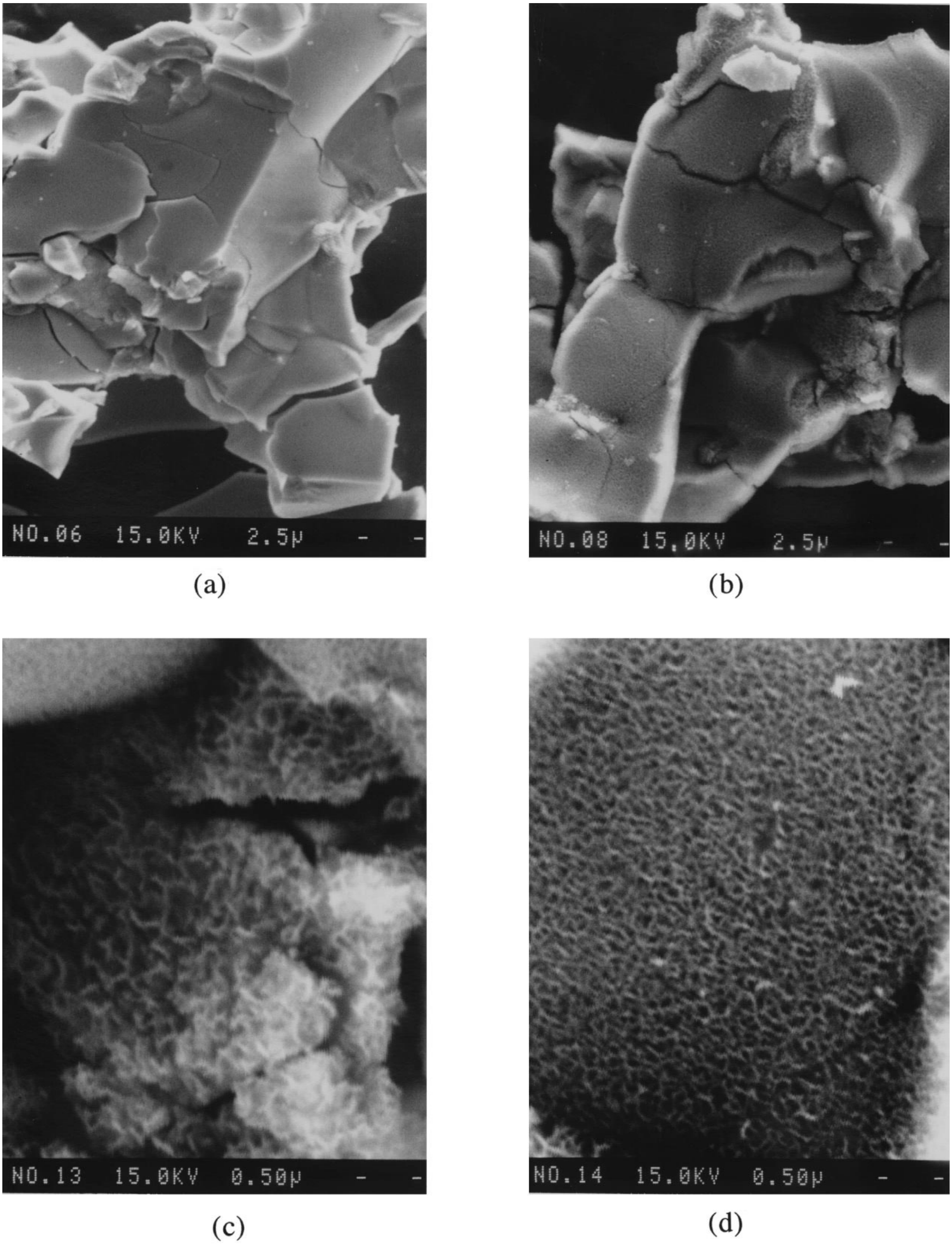

Fig. 1. The surface morphology of the F-treated and untreated alloys: (a) Untreated alloy, magnification ×4000; (b) F-treatment, magnification ×4000; (c) F-treatment, magnification ×20,000 (network structure of the La-fluoride); (d) F-treatment, magnification ×20,000 (network structure of the nickel-rich layer).

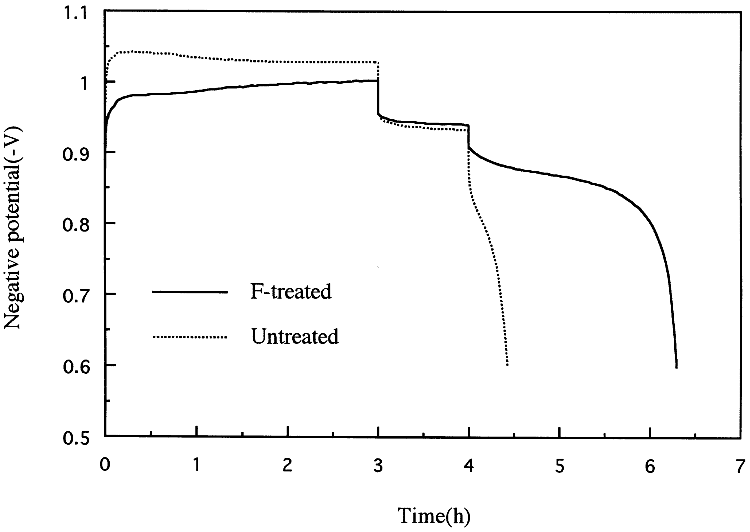

Fig. 2. The initial charge–discharge curves of the F-treated and untreated alloy electrodes.

formation of the fine network structures of both the La-fluoride and the nickel-rich layer.

3.4. High rate discharge characteristics

A high rate discharge capability is the most important electrochemical performance in the application of metal hydride electrodes. The discharge current dependency of the discharge capacity of both the F-treated and untreated electrodes were shown in Fig. 5. It was confirmed that the discharge capacity for both the F-treated and untreated electrodes was similar below the discharge current density of 200 mAh/g, however, the high rate discharge capability was significantly improved for the F-treated electrode at higher current density due to the differences in the particle surface state. Consequently, the improvement of the high rate discharge capability of the F-treated electrode was mainly attributed to the lower surface reaction resistance and increased specific surface area of the fluorinated particles.

4. Conclusions

It was found that the fluorination technique which employed for La-incorporated Laves phase alloy is significantly effective for increasing specific surface area of the fluorinated particles which were caused by the formation of the fine network structures of both the La-fluoride and the nickel-rich layer. The special surface structure formed resulted in the significant improvement of electrochemical properties. After the fluorination, (1) the initial

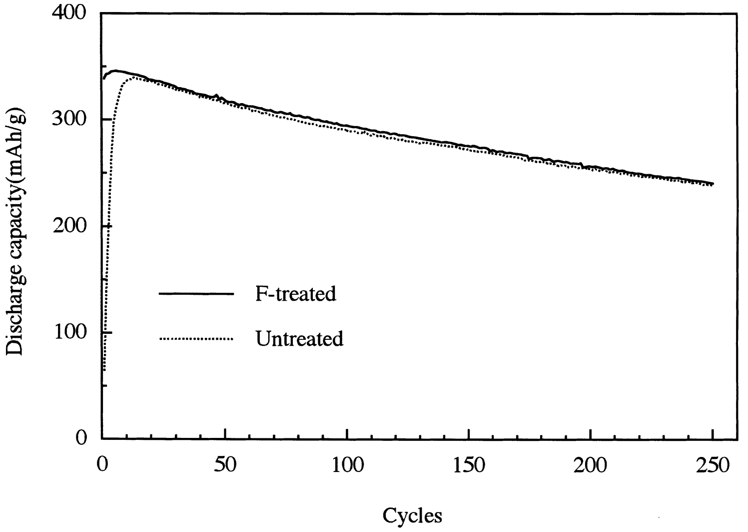

Fig. 3. The initial activation and cycle life of the F-treated and untreated alloy electrodes.

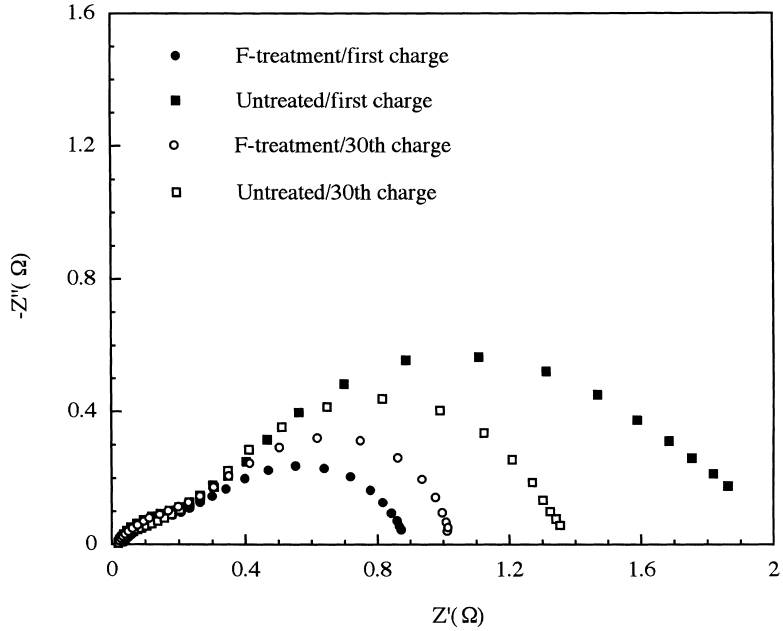

Fig. 4. The impedance spectra of the F-treated and untreated alloy electrodes after 1st and 30th charge.

discharge capacity reached to about 97% of its maximum discharge capacity; (2) the surface reaction activity was significantly improved only after first charge; and (3) high rate discharge capability was greatly increased.

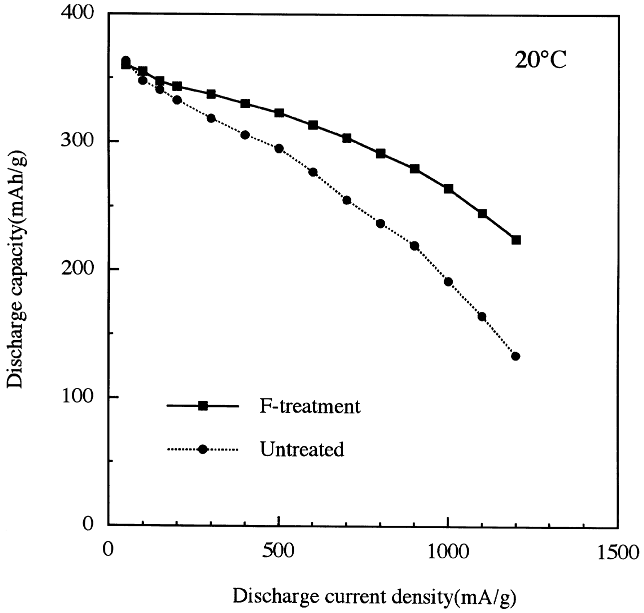

Fig. 5. The discharge current dependency of discharge capacity of the F-treated and untreated alloy electrodes after full activation.

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