INFLUENCE OF Fe DOPING ON ELECTROCHEMICAL PROPERTIES OF Ml(Ni, Co, Mn, Ti)$_5$ HYDROGEN STORAGE ALLOY①

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ABSTRACT During the producing of mischmetal and melting of hydrogen storage electrode alloy, the mischmetal and alloy are susceptible to be contaminated by iron. Considering this factor, the effects of doped Fe on electrochemical properties of Ml(Ni, Co, Mn, Ti)$_5$ alloy were systematically studied. Results show that doping trace Fe ($\leqslant$0.64%) can improve the discharge capacity of the alloy, however, as the content of doped Fe increases from 0.64% to 6.07%, the discharge capacity is degraded gradually. The activation behaviour and cycling stability of the alloy have been enhanced to some degree as the content of doped Fe increases, while the high-rate-dischargeability of the alloy has been deteriorated to some degree.

Key words Fe doping hydrogen storage electrode alloy electrochemical property

1 INTRODUCTION

Owing to their excellent properties and cost ratio, mischmetal-based AB_5-type hydrogen storage electrode alloys are widely used as negative electrode materials of Ni/MH batteries. The alloys in industrial production have an A-side composition of commercial mischmetal, and a B-side composition of Ni and partial substitution elements (e.g. Mn, Co, Al, Ti, etc.)[1-6]. However, content of Fe impurities (0.1% ~ 8.0%) in commercial mischmetal is different with different ores and extracting methods [5,7,8]. On the other hand, in the melting process of alloy, owing to the interaction among high temperature melting flux and melting crucible or water-cooled steel mold, the alloy will be contaminated by tiny amount of Fe, Si or other elements. The doped elements will have substantial influence on the electrochemical properties of alloys, but the kinds of doped elements and such influence have not been reported yet, so it is difficult to correctly judge and control impurities in mischmetal or hydrogen storage electrode alloys during industrial production. On above reasons, the influence of doped Fe on electrochemical properties of Ml (Ni, Co, Mn, Ti)$_5$ (Ml is La-rich mischmetal)[1] alloy have been investigated in this paper.

2 EXPERIMENTAL

The composition of doped alloys were designed as Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.30, 0.40, 0.50), i. e. intentionally doping various contents of Fe to the original Ml(Ni, Co, Mn, Ti)$_5$ alloy, in order to study the effects of doped Fe on electrochemical properties of the alloy. The doped alloy samples were prepared by an arc furnace under an argon atmosphere in a water-cooled copper crucible. The purity of raw materials are: mischmetal (Ml) 98.10% (Including: 68.00% La, 7.40% Ce, 15.68% Pr, 8.24% Nd, 0.36% Fe, 0.02% Si, 0.10% Mg), Ni 99.95%, Co 99.5%, Mn

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99.7%, Ti 99.5%, Fe 99.9%. The alloys were ground into powders of 74~33 μm, and mixed with Cu powders in a ratio of 1∶2, then pressed to round-disc electrodes (about 100 mg hydrogen storage alloy powders per electrode) with a diameter of 10 mm. The electrodes were tested at 25 ℃ in open-cells with an electrolyte of KOH (6 mol/L), a positive electrode of $Ni(OH)_2/NiOOH$ and a reference electrode of Hg/HgO/KOH (6 mol/L). The discharge capacity, activation behaviour, high-rate-dischargeability and cycling stability of the alloy were tested respectively under following conditions:

(1) In activation behaviour and discharge capacity test, charging at 30 mA/g for 15 h and discharging at 60 mA/g;

(2) In high-rate-dischargeability test, charging at 30 mA/g for 15 h and discharging at 300 mA/g;

(3) In cycling stability test, charging at 300 mA/g for 1.2 h and discharging at 300 mA/g for cycling, testing discharge capacity after every 100 cycles. The end of the discharge was set to −0.6 V (vs Hg/HgO).

3 RESULTS AND DISCUSSION

3.1 Effects of doped Fe on discharge capacity and activation behaviour of Ml(Ni, Co, Mn, Ti)$_5$ alloy

The relationship between the content of doped Fe and the discharge capacity of Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ alloys are shown in Table 1. It can be seen from Table 1 that doping with trace of Fe (≤0.64%) can improve the discharge capacity of the alloy, and the maximum capacity of 320 mAh/g is reached. However, when the content of doped Fe increases excessively, the discharge capacity decreases gradually, for example, the maximum capacity of the alloy with 6.07% Fe doping is only 257 mAh/g.

The activation behaviour of Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ alloys are shown in Fig. 1. As shown in Fig. 1, with the content of doped Fe increasing, the activation behaviour of the alloy becomes better, and the activation number decreases. For example, when the content of doped Fe ≤0.64%, the activation number is 5; and when the content of doped Fe ≥3.73%, the activation number is only 2.

3.2 Effect of doped Fe on high-rate-dischargeability of Ml(Ni, Co, Mn, Ti)$_5$ alloy

The high-rate-dischargeability of alloy

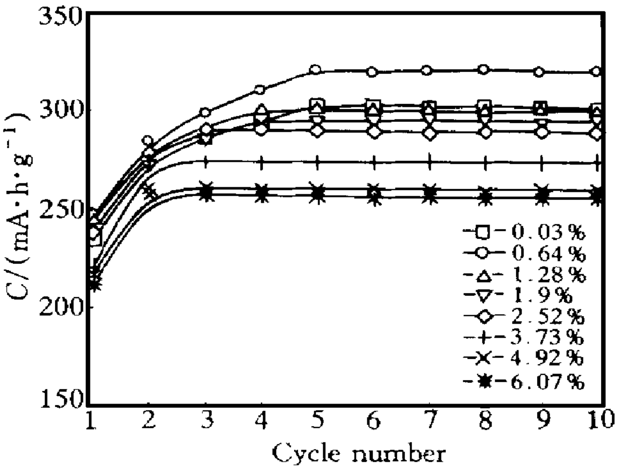

Fig. 1 Activation behaviour of Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ alloys with various contents of doped Fe

Table 1 Electrochemical properties of Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ alloys (25 ℃)

x	Fe content/%	$C_{max}^{①}$/(mAh·g^{-1})	$C_h^{②}$/(mAh·g^{-1})	(C_h/C_{max})/%	$C_{200}^{③}$/(mAh·g^{-1})	(C_{200}/C_{max})/%
0	0.03	302	237	78.5	249	82.5
0.05	0.64	320	244	76.3	266	83.1
0.10	1.28	300	218	72.7	258	86.1
0.15	1.90	295	219	74.2	245	83.1
0.20	2.52	290	215	74.1	244	83.9
0.30	3.73	274	201	73.4	242	88.3
0.40	4.92	260	179	68.8	234	90.0
0.50	6.07	257	183	71.2	232	90.2

① C_{max} —The maximum discharge capacity being measured by charging at 30 mA/g for 15 h and discharging at 60 mA/g to −0.6 V (vs Hg/HgO); ② C_h —High-rate-discharge capacity being measured by charging at 30 mA/g for 15 h and discharging at 300 mA/g to −0.6 V (vs Hg/HgO); ③ C_{200} —Discharge capacity at 200th cycle cancanbe described by the ratio of high-rate-discharge capacity (C_h) to the maximum capacity (C_{max}), the higher the ratio, the better the high-rate-dischargeability. The results of high-rate-discharge capacities (C_h) and high-rate-dischargeabilities (C_h/C_{max}) of Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ alloys in Table 1 show that doped Fe has deteriorated the high-rate-dischargeability of the alloy to some degree. When the content of doped Fe is 0.64%, its high-rate-dischargeability (76.3%) has decreased by 2.2% compared with original alloy (78.5%); and when the content of doped Fe is 4.92%, its high-rate-dischargeability is only 68.8% which has decreased by 9.7% compared with original alloy.

3.3 Effect of doped Fe on cycling stability of Ml(Ni, Co, Mn, Ti)$_5$ alloy

The cycling stability of alloy can be described by the ratio of its discharge capacity at 200th cycle (C_{200}) to the maximum capacity (C_{max}). The higher the ratio, the better the cycling stability.

Fig. 2 indicates the cycle life curves of Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ alloys. As shown in Fig. 2 and Table 1, doped Fe can improve the cycling stability of the alloy to some degree. For example, the discharge capacity of original alloy at 200th cycle is 249 mAh/g, and its cycling stability is only 82.5%; when the content of doped Fe is 6.07%, the discharge capacity at 200th cycle is 232 mAh/g, although its maximum capacity is only 257 mAh/g, its cycling stability is as high as 90.2%.

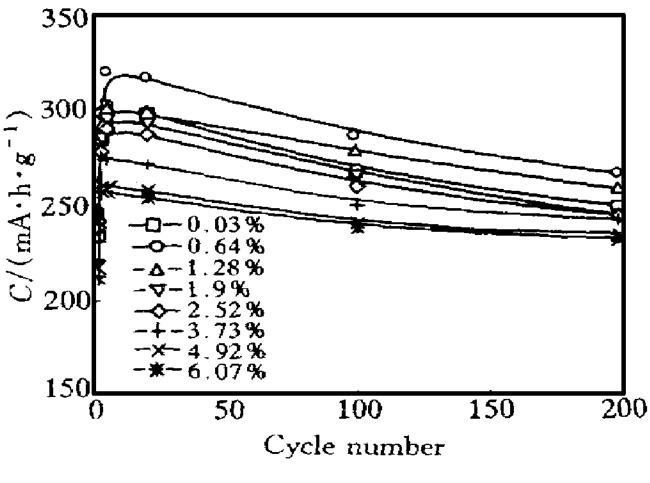

Fig. 2 Cycle life curves of Ml(Ni, Co, Mn, Ti)$_5$Fe$_x$ alloys with various contents of doped Fe

4 CONCLUSIONS

(1) Doping trace of Fe (≤0.64%) can improve the discharge capacity of Ml(Ni, Co, Mn, Ti)$_5$ alloy, but doping with excessive Fe will deteriorate it.

(2) Increasing the content of doped Fe can improve the activation behaviour of the alloy.

(3) Doped Fe will deteriorate the high-rate-dischargeability of the alloy to some degree.

(4) Doped Fe can enhance the cycling stability of the alloy to some degree.

Therefore, doping trace of Fe (≤0.64%) will degrade slightly the high-rate-dischargeability of the alloy, but its activation behaviour, discharge capacity and cycling stability have been enhanced to some degree, so the alloy can be used practically. However, doping with excessive Fe will apparently deteriorate the discharge capacity and high-rate-dischargeability, though its cycling stability has been increased to some degree, its practical application is hindered.

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