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Improvement of electrochemical cyclic durability of Zr-based AB_2 alloy electrodes

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Abstract

Zr-based AB_2 Laves phase alloys are promising materials for the negative electrode in Ni–MH batteries. In this work, we attempted to improve their cyclic durability in the electrolyte by using hyper-stoichiometric and Cr-substituted alloys. It was found that the hyper-stoichiometric alloys exhibited improved cycle life as a result of increased mechanical stability during the cycling. The Cr-incorporated alloys showed a low level of vanadium dissolution and small change in surface area after the cycling, but their overall electrochemical performances were discouraging. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zr-based Laves phase alloy; Electrochemical cyclic durability; Hyper-stoichiometry

1. Introduction

Zr-based AB_2 Laves phase alloys are one family of alloys with high hydrogen storage capacity and have the potential of being used as the negative electrode material in Ni–metal hydride batteries. Unfortunately, their overall electrochemical performance is not good enough to meet industrial requirements. In recent years, we have devoted considerable research efforts to improving their activation properties and high-rate charging–discharging capability and found that a wet ball milling fluorination treatment can successfully make these properties satisfactory [1]. However, we also found that the cyclic durability of our alloy electrodes was not sufficient. Our research showed that the oxidation and dissolution of component elements V and Mn as well as a further particle size reduction during cycling resulted in the capacity degradation of the alloy electrodes [2].

As a long cyclic durability is essential for a hydrogen storage alloy to be used in Ni–MH batteries, it is necessary to improve the long-term cyclic durability of our F-treated alloys without severely impairing other properties. Notten and co-workers [3,4] have reported that non-stoichiometric Cu-containing AB_5-type alloys ($AB_{x>5}$) had better cycling stability than the stoichiometric ones while keeping high electrocatalytic activity. In this work, we prepared hyper-stoichiometric Zr-based AB_2 alloys $Zr_{0.9}Ti_{0.1}(Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1})_{1+x}$ ($x=0.0$, 0.05, 0.1) and examined their electrochemical properties, especially their cycle life. On the other hand, it is well known that Cr substitution is effective in improving the electrochemical cycle life of AB_2 alloys [5,6]. Therefore, we also examined effects of Cr substitution on the cycle life of our alloy in this work. The cyclic lives of these alloys were compared and correlated with their surface characteristics and pulverization behavior to further clarify the reasons of capacity degradation of Zr-based Laves phase alloys.

2. Experimental

In this study, alloys were prepared by arc-melting the pure constituent metals in an argon atmosphere and annealing at 1100°C for 18 h to ensure a homogeneous and single phase product. Alloy ingots were then pulverized by five hydriding and dehydriding cycles in H_2 gas to a size <25 μm. The alloy powder was then treated by a Ni^{2+}-containing fluoride solution at 70°C for 30 min (denoted as F5 treatment), washed and finally dried in a vacuum oven at 20°C.

Two kinds of pellet-type alloy electrodes were prepared: electrodes with Ni powder as a conductive additive (type A electrodes) and electrodes without conductive additives (type B electrodes). Type A electrodes were made by mixing 0.25 g alloy powder with 0.75 g Ni powder (Inco Ni 255) as well as 0.05 g PTFE, enveloping the mixture with a nickel net (100 mesh) and then pressing at 4

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ton/cm^2. Type B electrodes were prepared with 1 g alloy powder and 0.05 g PTFE.

Electrochemical cycling tests were carried out at 20°C in a three-electrode system, consisting of a negative electrode, a counter electrode and a Hg/HgO reference electrode. The electrolyte was 6 M KOH. Type A electrodes were cycled by charging at 68 mA/g (0.2 C) for 6 h and discharging at 68 mA/g to −0.6 V vs. Hg/HgO. Type B electrodes were first activated by charging and discharging at 68 mA/g (0.2 C) for five cycles and then cycled by charging and discharging at 340 mA/g (1 C) for 500 cycles and finally five cycles at 0.2 C. The cut-off potential was −0.6 V vs. Hg/HgO.

After the cycling, the type B electrodes were immersed in and then washed by deionized water several times, dried in vacuum before they were subjected to SEM (scanning electron microscopy) analysis and surface area measurement by the BET method. The KOH electrolyte and solid remains in the cells were separated and subject to inductively coupled plasma spectroscopy (ICPS) analysis.

3. Results and discussion

3.1. Hyper-stoichiometric alloys $Zr_{0.9}Ti_{0.1}(Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1})_{1+x}$ (x=0, 0.05, 0.1)

To examine the effect of alloy stoichiometry on the cycle life of AB_2 Laves phase alloy electrodes, alloys with the composition of $Zr_{0.9}Ti_{0.1}(Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1})_{1+x}$ ($x=$ 0, 0.05, 0.1) were prepared. The stoichiometry of the alloys was increased by increasing all the B side elements in order to avoid effects of one single element. The XRD analysis revealed that they all had a C15 single phase structure after the annealing treatment. As shown in Table 1, the lattice parameter decreases on increasing the stoichiometry. The *PC* isotherms obtained by gas–solid reaction are shown in Fig. 1. The plateau pressure increases and the hydrogen storage capacity decreases when the stoichiometry of the alloys increases, as a result of the cell volume contraction after some A side atom positions were occupied by B side atoms.

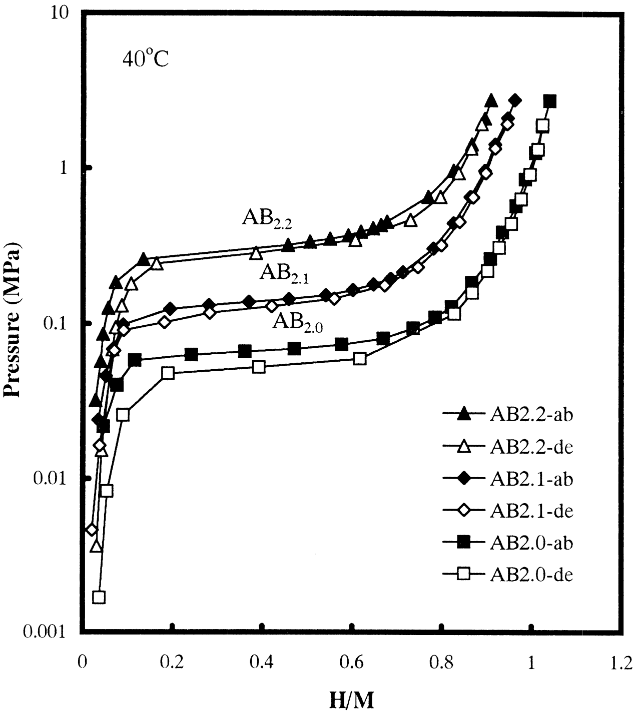


Fig. 1. *PC* isotherms of the hyper-stoichiometric alloys at 40°C.

The electrochemical cycle life of the alloys was tested in two kinds of electrodes: type A and type B electrodes. Type A electrodes containing Ni powder as a conductive material were made to measure intrinsic electrochemical properties of alloys. Type B electrodes were prepared to test electrode performances of alloys and to make the instrumental analyses more convenient.

Fig. 2 shows that all the type A alloy electrodes demonstrated a fast activation process after the F5 fluorination surface treatment. Although the maximum discharge capacity decreases with increasing the alloy stoichiometry, the discharge capacity of the $AB_{2.1}$ alloy electrode was still high enough. Fig. 2 also clearly shows that the alloy electrodes with hyper-stoichiometric compositions had better cyclic durability than the stoichiometric one. The durability difference exists mainly between the $AB_{2.1}$ alloy and the $AB_{2.0}$ base alloy. As indicated in Table 1, the

Table 1
Crystallographic, thermodynamic and electrochemical properties of the alloys

Alloys	Lattice parameter (Å)	P_{eq} at 40°C (MPa)	C_{max} (mAh/g)	C_{500} (mAh/g)	Capacity loss (%) $(1-C_{500}/C_{max})$
$Zr_{0.9}Ti_{0.1}(Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1})_{1+x}$					
$AB_{2.0}$ ($x=0.0$)	7.049	0.056	395	169	57
$AB_{2.1}$ ($x=0.05$)	7.035	0.136	383	244	36
$AB_{2.2}$ ($x=0.1$)	7.024	0.317	328	206	37
$Zr_{0.9}Ti_{0.1}Mn_{0.6-y}Cr_yV_{0.2}Co_{0.1}Ni_{1.1}$					
$y=0.1$	7.050	0.050	383	155	60
$y=0.2$	7.049	0.048	357	227	36

C_{max} is the maximum capacity of the alloy in the type A electrode at 0.2 C. C_{500} is the discharge capacity at 500th cycle of 0.2 C.

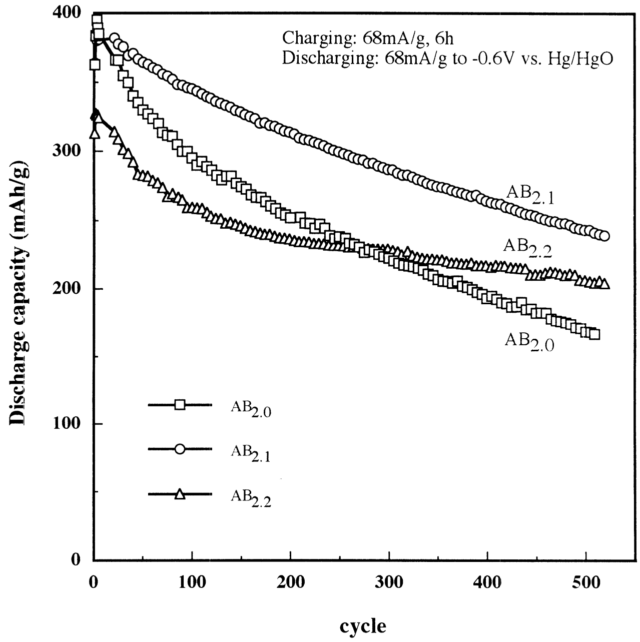


Fig. 2. Cycle life curves of the hyper-stoichiometric alloy electrodes (type A electrodes).

$AB_{2.1}$ alloy electrode shows a 36% capacity loss after 500 cycles at 0.2 C rate, compared to the 57% capacity loss of the $AB_{2.0}$ base alloy.

In the type B electrodes, the alloys fulfilled the activation within five 0.2 C cycles. When discharged at a higher 1 C rate, the electrodes immediately reached the maximum capacity as shown in Fig. 3. Although the hyper-stoichiometric alloy electrodes showed somewhat lower discharge capacities, they evidently exhibited better cyclic durability during the 1 C cycling.

As described in our previous paper [2], the capacity degradation of the stoichiometric AB_2 alloy $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ can be ascribed to two main causes. One is the oxidation and dissolution of its constituent elements V and Mn. Vanadium forms a soluble corrosion product in the KOH electrolyte while the corrosion product of manganese precipitates from the electrolyte. They can be detected by ICPS analysis of the KOH electrolyte and the solid deposits in the cells. The other reason is the continuous pulverization of alloy particles during the cycling. It speeds up the corrosion of electrodes by enlarging the contact area of alloy surface with the electrolyte. The pulverization behaviors of alloys can be observed by SEM observation. The change of specific surface area during the cycling also reflects the cyclic stability of alloys.

In this study, the cells of the type B electrodes after 500 cycles at 1 C were disassembled to undergo following examination: the KOH electrolyte and solid remains in the cell were subject to ICPS analysis, the alloys in the electrodes were subjected to SEM observation and BET measurement. The ICPS analysis results are shown in Table 2, from which it can be seen that the hyper-stoichiometric alloy electrodes demonstrated restrained vanadium dissolution. The BET measurement results shown in Table 3 also reveal that the specific surface areas before and after the cycling for the hyper-stoichiometric alloys were smaller than those for the stoichiometric alloy. All these results indicate that the cyclic durability of the hyper-stoichiometric alloy electrodes was improved compared with the stoichiometric alloy.

Notten and co-workers [3,4] ascribed the good cyclic durability of the non-stoichiometric AB_5 alloys to their improved mechanical stability. We make a similar observation for our hyper-stoichiometric AB_2 alloys. The SEM photographs in Fig. 4 show that the average alloy particle

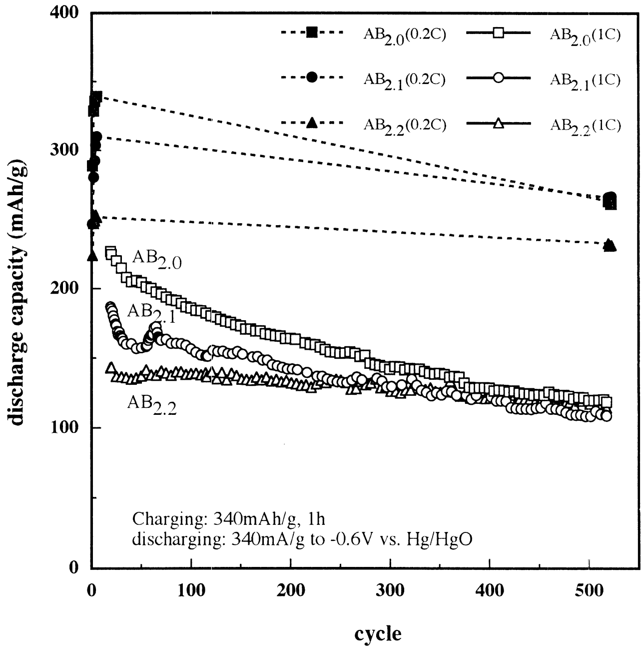


Fig. 3. Discharge capacity vs. cycle for the hyper-stoichiometric alloy electrodes (type B electrodes).

Table 2
ICPS analysis results of the electrolyte and deposits in the cells of type B electrodes after 500 cycles at 1 C rate

Alloys	In the electrolyte (wt.%)[a]		Deposit outside the electrode (wt.%)[a]
	Zr	V	Mn
$Zr_{0.9}Ti_{0.1}(Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1})_{1+x}$			
$AB_{2.0}$ ($x=0.0$)	0.58	21.26	3.57
$AB_{2.1}$ ($x=0.05$)	0.87	12.54	4.94
$AB_{2.2}$ ($x=0.1$)	1.22	10.97	3.65
$Zr_{0.9}Ti_{0.1}Mn_{0.6-y}Cr_yV_{0.2}Co_{0.1}Ni_{1.1}$			
$y=0.1$	0.67	5.74	4.46
$y=0.2$	0.75	4.78	5.70

[a] Wt.%, element weight in the electrolyte or deposit/element weight in the original electrode.

Table 3
Specific surface areas of the alloys in the type B electrodes before and after 500 cycles at 1 C

Alloy	S.S.A (m^2/g)	
	Before cycling	After cycling
$Zr_{0.9}Ti_{0.1}(Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1})_{1+x}$		
$AB_{2.0}$ ($x=0.0$)	2.06	31.51
$AB_{2.1}$ ($x=0.05$)	1.53	22.11
$AB_{2.2}$ ($x=0.1$)	0.76	7.28
$Zr_{0.9}Ti_{0.1}Mn_{0.6-y}Cr_yV_{0.2}Co_{0.1}Ni_{1.1}$		
$y=0.1$	1.14	1.95
$y=0.2$	0.69	3.35

size in the $AB_{2.2}$ alloy electrode after the cycling is larger than that in the stoichiometric alloy electrode. We believe that in the case of AB_2 alloys, the hyper-stoichiometric alloys also have better mechanical stability than the stoichiometric one. On the other hand, we suppose that the improvement of corrosion resistance of unit surface area for the hyper-stoichiometric alloys was less possible because the relative amounts of corrodible elements Mn and V were increased in these alloys. Therefore we ascribe the improvement of the electrochemical cyclic durability of the hyper-stoichiometric alloys to their improved mechanical stability during the cycling, that is, a small surface area in contact with the electrolyte.

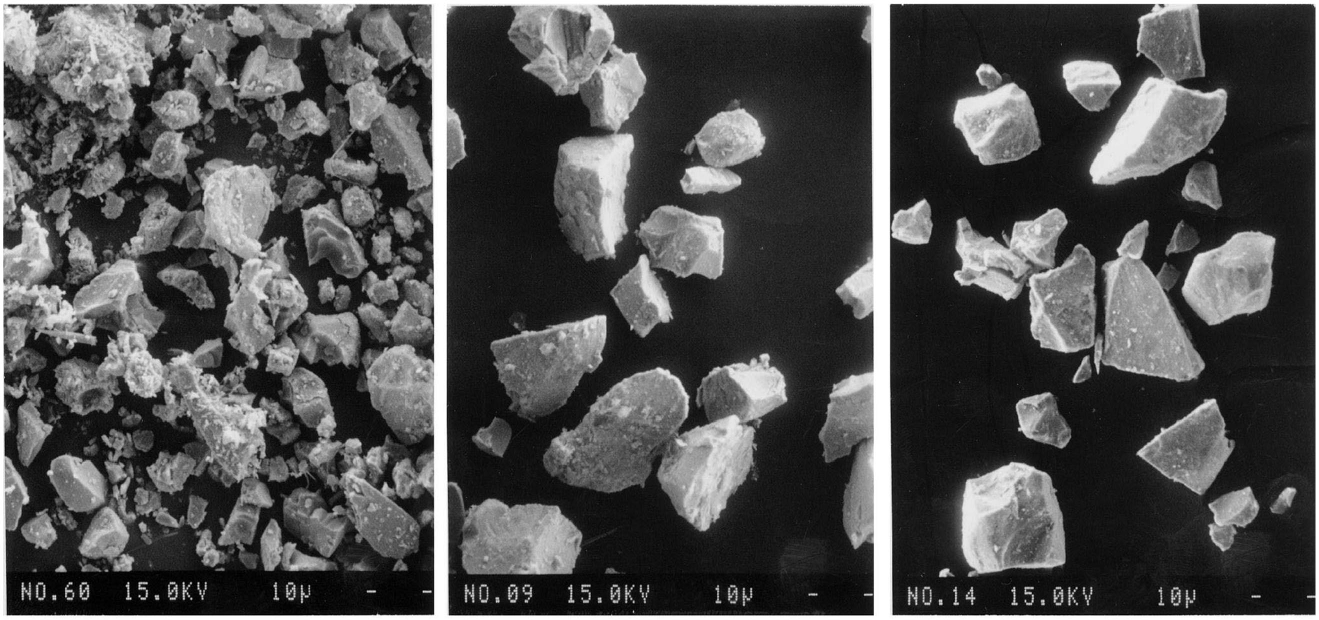
As a large surface area is favorable for high-rate capability, the decrease of surface area would result in a poor high-rate capability. However, in the case of the hyper-stoichiometric alloys, the increase of B side elements, some of which are responsible for the electrochemical catalytic activity of the surface, compensated somewhat for the effect of the surface area decrease; otherwise, the decrease of high-rate capability would be larger.

3.2. Cr-substituted alloys $Zr_{0.9}Ti_{0.1}Mn_{0.6-y}Cr_yV_{0.2}Co_{0.1}Ni_{1.1}$ ($y=0$, 0.1, 0.2)

In this study, the effect of Cr substitution on the electrochemical cycle life was examined by partially replacing Mn in the base alloy $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$. The XRD analysis showed that there was no change of the C15 structure in these alloys except that a small amount of C14 phase appeared when Cr was increased to 0.2 atomic ratio. As shown in Fig. 5, the *PCT* plateau pressure and hydrogen storage capacity does not change much after the Cr substitution. This is consistent with the small change of lattice parameters as indicated in Table 1.

As illustrated in Fig. 6, it is disappointing to observe that the cycle life was not improved until the Cr amount was increased to 0.2. Moreover, the cycle life improvement of the $Zr_{0.9}Ti_{0.1}Mn_{0.4}V_{0.2}Cr_{0.2}Co_{0.1}Ni_{1.1}$ alloy electrode mainly resulted from the prolongation of its activation process as the capacity decay speed in the later part of the cycle life curve was not much reduced.

Fig. 7 shows the cycle life curves of the type B electrodes. During the 1C cycling, the Cr-added alloy electrodes demonstrated lower discharge capacities and a longer activation process. Even though the 1 C capacities did not show decrease in these Cr-added alloy electrodes,



(a) $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ (b) $Zr_{0.9}Ti_{0.1}(Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1})_{1.1}$ (c) $Zr_{0.9}Ti_{0.1}Mn_{0.4}Cr_{0.2}V_{0.2}Co_{0.1}Ni_{1.1}$

Fig. 4. SEM photographs of the alloy particles in the type B electrodes after 500 cycles at 1 C rate. (a) Base alloy $AB_{2.0}$, (b) hyper-stoichiometric alloy $AB_{2.2}$, (c) Cr-substituted alloy ($y=0.2$).

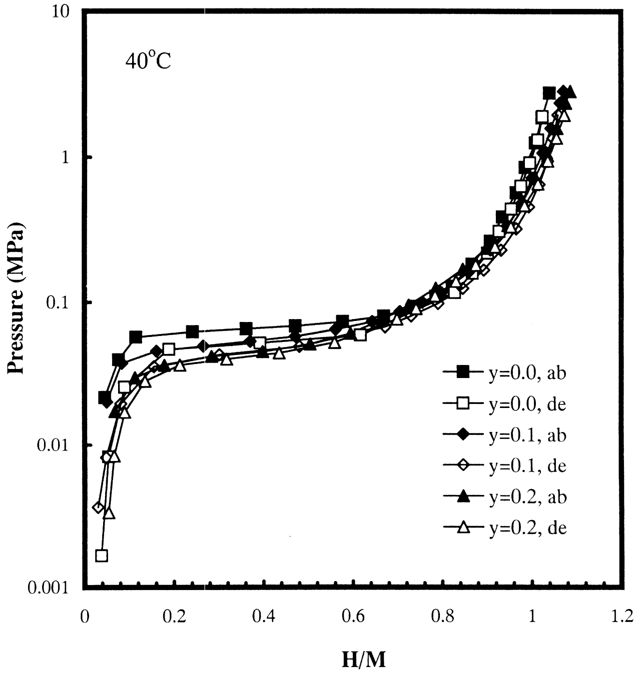


Fig. 5. *PC* isotherms of the $Zr_{0.9}Ti_{0.1}Mn_{0.6-y}Cr_yV_{0.2}Co_{0.1}Ni_{1.1}$ ($y=0.0$, 0.1, 0.2) alloys at 40°C.

the 0.2 C discharge capacities measured after 500 cycles of 1 C showed a considerable decrease. This suggests that the capacity decay was also proceeding in these Cr-incorporated alloy electrodes despite the fact that their high rate discharge capacity was still improving.

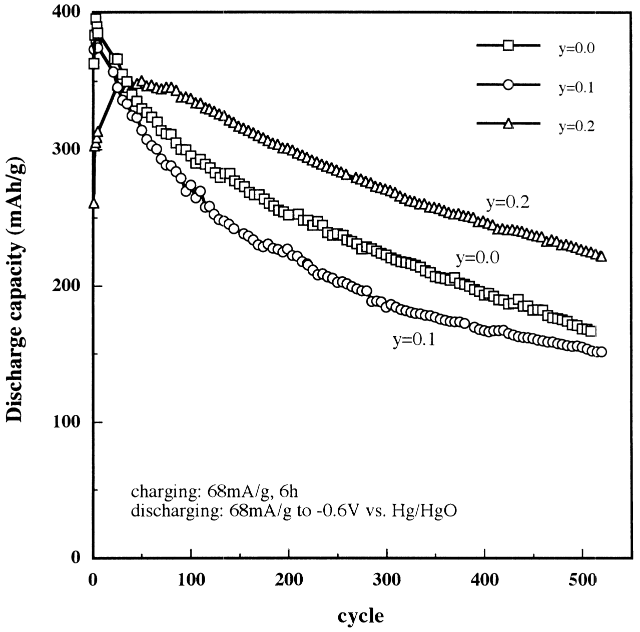


Fig. 6. Cycle life curves of the $Zr_{0.9}Ti_{0.1}Mn_{0.6-y}Cr_yV_{0.2}Co_{0.1}Ni_{1.1}$ ($y=$ 0.0, 0.1, 0.2) alloy electrodes (type A electrodes).

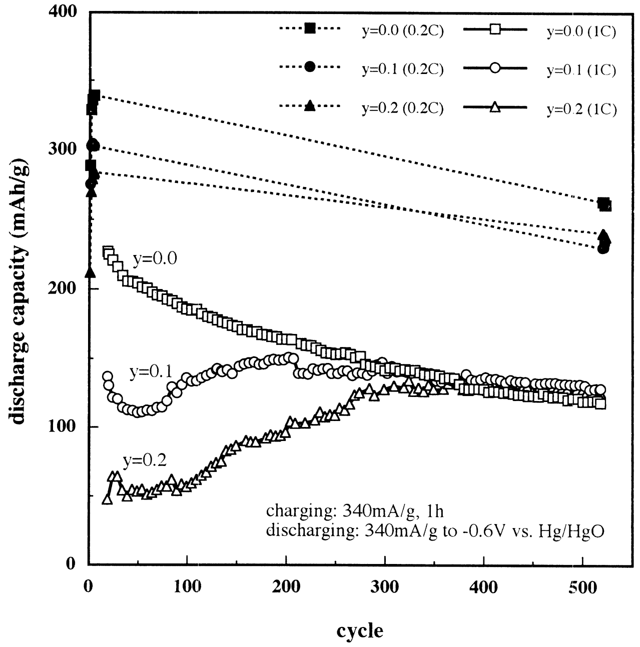


Fig. 7. Discharge capacity vs. cycle for the $Zr_{0.9}Ti_{0.1}Mn_{0.6-y}Cr_yV_{0.2}Co_{0.1}Ni_{1.1}$ ($y=0.0$, 0.1, 0.2) alloy electrodes (type B electrodes).

The ICPS analysis (Table 2) show that the V dissolution was depressed to a large extent in the Cr-added alloy electrodes, though they still show considerable Mn dissolution. More remarkably, there was only a slight increase of the specific surface area in these Cr-added electrodes after 500 cycles, implying not only a stable particle size but also a small change of the surface during the cycling. The stability in particle size can also be observed in the SEM photos (Fig. 4). These suggest that the Cr-added alloys were not only resistant to particle pulverization, but also to surface corrosion, especially the V dissolution. However, further investigation is needed to explain why the alloys with less than 0.2 Cr atomic ratio still show similar capacity loss to the base alloy at low discharge rates.

As the cyclic durability and kinetic properties of hydrogen storage alloy electrodes depend on the same factors, such as the alloy surface area, it is difficult to improve one without affecting the others. For example, the activation property and rate capability were severely impaired after the Cr substitution. Considering the overall electrochemical performance, the $AB_{2.1}$ alloy is more favorable than the other alloys.

4. Conclusions

Two series of AB_2 Laves phase alloys were prepared in an attempt to improve the cyclic durability of alloy electrodes. The hyper-stoichiometric alloys exhibited improved cycle life while keeping good kinetic properties. The cycle durability of alloy electrodes was also enhanced by Cr-incorporation but on a penalty of lowering down the activation property and rate capability.

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