

# Zr-Cr-Ni BASED MULTICOMPONENT METAL HYDRIDE ELECTRODES<sup>①</sup>

Yang Xiaoguang, Lei Yongquan, Chen Yanglin, Wang Qidong

*Department of Materials Science and Engineering,  
Zhejiang University, Hangzhou 310027*

**ABSTRACT** The electrochemical discharge capacity, cyclic stability, self-discharge properties of Zr-Cr-Ni based multicomponent hydride electrodes were investigated. Research result for electrodes of  $\text{Zr}(\text{Cr}_x\text{Ni}_{1-x})_2$  Laves phase alloys with Cr content in the range of  $0.30 \leq x \leq 0.50$  was introduced. Substitution effect of Cr or Ni by V or Mn in the form of  $\text{Zr}(\text{Cr}_x\text{M}_y\text{Ni}_{2-x-y})$  ( $\text{M} = \text{V}$  or  $\text{Mn}$ ,  $x + y = 0.7 \sim 1.2$ ) on the electrochemical discharge capacity were also studied. The alloys with  $x + y = 0.7 \sim 1.0/AB_2$  formula has larger hydrogen storage and electrochemical discharge capacities. When Ti is used to substitute Zr partly in  $\text{Ti}_y\text{Zr}_{1-y}\text{M}_2$  ( $y = 0.0 \sim 0.3$ ) alloys, the plateau pressure of the hydride tends to increase with increasing  $y$ , however its electrochemical capacity decreases as well due to lower reversible hydrogen storage density. The electrochemical cycling deterioration increases with increasing Ti content. Electrodes with no Ti or very low Ti content preserve 86% of their discharge capacities after 820 cycles under 65% depth of discharge, exhibit excellent electrochemical stability. It was found that the activation of  $\text{Zr}_{0.9}\text{La}_{0.1}\text{Cr}_{0.36}\text{Mn}_{0.36}\text{V}_{0.18}\text{Ni}_{1.4}$  electrode is improved with  $\text{LaNi}_5$  synthesized by arc-melting, but its cyclic stability is deteriorated severely. The charge retention of hydride electrodes is related to the hydrogen pressure plateau, therefore more Mn substituted for Cr, Ti for Zr and higher superstoichiometric degree and storing temperature will decline its self-discharge property.

**Key words** Zr-based hydride electrodes alloying effect electrochemical discharge capacity cyclic stability self-discharge properties

## 1 INTRODUCTION

Metal hydrides are promising materials for negative electrodes in nickel/metal hydride batteries which are the potential candidate for electric vehicles (EV) power in the following decades<sup>[1]</sup>. However rapid decay of the discharge capacity by repetition of charge and discharge is a remaining problem for the misch-metal-based multicomponent hydrides<sup>[2, 3]</sup>, the disintegration of  $AB_5$  type alloys arising from grain boundaries and high activity of misch-metals are thought to be the main causes of the capacity decay. Therefore more and more attention has been paid to the  $AB_2$  type Zr-based Laves phase alloys with higher hydrogen storage density and excellent anti-oxidation. Up to now, three main types above-mentioned alloys,  $\text{ZrV}_2$ ,  $\text{ZrCr}_2$  and  $\text{ZrMn}_2$ , have been alloyed with electrochemical

catalytic element Ni to form  $\text{Zr-V-Ni}$ <sup>[4, 5]</sup>,  $\text{Zr-Cr-Ni}$ <sup>[6, 7]</sup> and  $\text{Zr-Mn-Ni}$ <sup>[8, 9]</sup>-based hydride electrodes. V alloying appears to enlarge the hydrogen storage capacity obviously, but also deteriorate cyclic stability due to the severe dissolution of V in alkaline solution<sup>[10]</sup>. In the  $\text{Zr}(\text{Mn}_{0.8-x}\text{Cr}_x\text{Ni}_{1.2})$  system alloys, when the amount of Cr increased ( $x = 0.2 \sim 0.8/AB_2$ ), the homogeneity and the crystal lattice constants of the alloy ( $a = 0.7054 \sim 0.7061 \text{ nm}$ ) did not change very much, but both the hysteresis and the flatness of the plateau pressure decreased, which led to lower dischargeability.

Recent study on  $\text{Zr}(\text{Cr}_x\text{Ni}_{1-x})_2$  three-component hydride electrodes showed that the alloys with  $x = 0.3 \sim 0.5$  had favorable electrochemical discharge capacity and excellent electrolytic cycling stability for the compact oxide layer of Zr and Cr, which brought forth the demerit of dif-

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difficulty in activating<sup>[6]</sup>. The activation process was accelerated by pretreatment with dilute HF solution to remove the impenetrable oxide layer of the alloy particles and improve its hydrogen electrolytic charge-discharge ability, as well as cycling in gaseous H<sub>2</sub> to get fine powder with much more defects in the alloy bulk<sup>[6]</sup>. In the present work the effect of alloying with V, Mn, Ti and Fe *etc.* on the electrochemical properties of the Zr-Cr-Ni based alloys were extensively studied.

## 2 EXPERIMENTAL

The ingots of the Zr-Cr-Ni based Laves phase alloys prepared by arc melting technique were pulverized mechanically to a particle size of - 360 mesh for XRD analysis and hydride electrodes test as described previously<sup>[6]</sup>.

The following Zr-M-Ni Laves phase intermetallics were studied (M = Cr, V, Mn) in the composition range specified:

- (1)  $\text{ZrCr}_{0.7-x}\text{Mn}_x\text{Ni}_{1.3}$  ( $0.0 \leq x \leq 0.5$ );
- (2)  $\text{ZrCr}_{0.6}\text{Mn}_x\text{Ni}_{1.4-x}$  ( $0.0 \leq x \leq 0.4$ );
- (3)  $\text{Zr}_{0.9}\text{La}_{0.1}\text{Cr}_{0.36}\text{Mn}_{0.36}\text{V}_{0.18}\text{Ni}_{1.4}$ ;
- (4)  $\text{Ti}_y\text{Zr}_{1-y}(\text{MnNi})_2$  ( $0.0 \leq y \leq 0.30$ ), M = Cr, V, Mn and Fe;
- (5)  $\text{Zr}(\text{Cr}_x\text{M}_y\text{Ni}_{2-x-y})$ , ( $0.15 \leq x \leq 0.60$ ), ( $0.30 \leq y \leq 0.65$ ), M = Mn or V.

The self-discharge properties test was carried out as follows: The activated hydride electrodes were first fully charged and stored in an open standard three-electrode electrolysis cell for a different rest time and at selected temperature, then discharged at normal current density ( $50 \text{ mA} \cdot \text{g}^{-1}$ ) to measure its residual capacity.

## 3 RESULTS AND DISCUSSION

### 3.1 Electrochemical capacity dependence of alloy composition

In our previous work<sup>[6]</sup>, it has been found that the main crystal structure of  $\text{Zr}(\text{Cr}_x\text{Ni}_{1-x})_2$  ( $0.15 \leq x \leq 0.65$ ) changes from C15 to C14 at  $x = 0.45 \sim 0.50$ , and the alloy  $\text{Zr}(\text{Cr}_{0.35}\text{Ni}_{0.65})_2$  has the maximum electrochemical discharge capacity of  $305 \text{ mAh} \cdot \text{g}^{-1}$  at ambient tem-

perature. Accordingly, we attempt to modify the B site metals (Cr, Mn except for Ni) with the number of which is fixed to 0.7 in  $\text{AB}_2$  formula.

The effect of substitution of Mn for Cr on the electrode capacity of alloys  $\text{ZrCr}_{0.7-x}\text{Mn}_x\text{Ni}_{1.3}$  ( $0.0 \leq x \leq 0.5$ ) is shown in Fig. 1. Higher Mn content, especially when  $x \geq 0.3$ , decreases electrochemical capacity greatly. The decrease in capacity is probably due to the lower affinity of hydrogen to Mn and smaller atomic radius of Mn compared to Cr, hence a smaller radius of the tetrahedral interstitial sites in the host lattice and higher hydrogen equilibrium pressure (*e. g.* above 0.1 MPa) or lower hydride stability on the test condition.

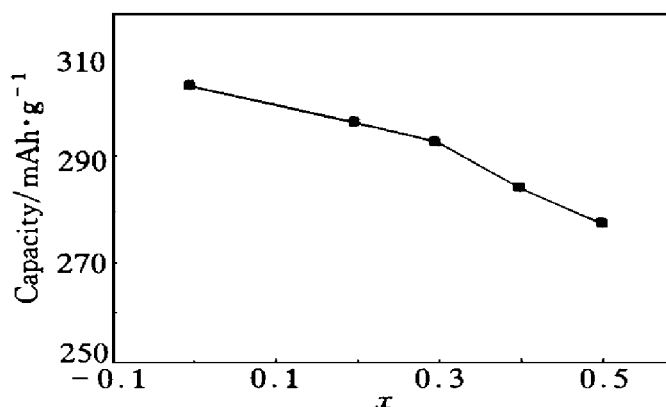
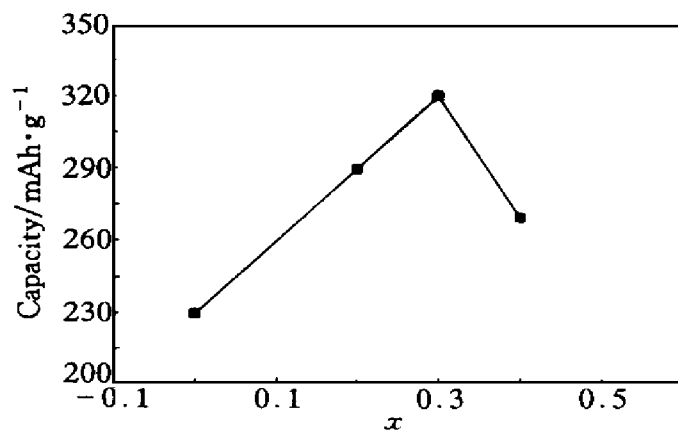


Fig. 1 The effect of substitution of Mn for Cr on capacity of  $\text{ZrCr}_{0.7-x}\text{Mn}_x\text{Ni}_{1.3}$  ( $0.0 \leq x \leq 0.5$ )

Another Mn-containing alloy series  $\text{ZrCr}_{0.6}\text{Mn}_x\text{Ni}_{1.4-x}$  ( $0.0 \leq x \leq 0.4$ ) was prepared and tested. Fig. 2 shows the relationship between the amount of substituted Ni with Mn and the discharge capacity. The alloy  $\text{ZrCr}_{0.6}\text{Mn}_{0.3}\text{Ni}_{1.1}$  reaches the highest capacity of  $320 \text{ mAh} \cdot \text{g}^{-1}$  (303 K) in this series.

Table 1 presents the crystallographic parameters of some representative alloys. Generally the hydrogen storage capacity of alloys increases as its cell volume enlarges. More Mn-containing instead of Cr might reduce lattice parameter *a* obviously with no change of crystalline type, which results in the affinity to H of A site atoms playing a crucial role in discharge capacity. Despite that the alloy  $\text{Zr}_{0.7}\text{Ti}_{0.3}\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}$



**Fig. 2 Relationship between the amount of substituted Ni with Mn and the discharge capacity of  $\text{ZrCr}_{0.6}\text{Mn}_x\text{Ni}_{1.4-x}$  ( $0.0 \leq x \leq 0.4$ )**

$\text{Ni}_{1.3}$  has smaller cell volume than that of  $\text{ZrCr}_{0.4}\text{Mn}_{0.4}\text{Ni}_{1.2}$ , they have the same capacities at ambient temperature. We attribute it to the stronger bond of  $\text{Ti-H}$  and relative lower molecular weight.

**Table 1 The crystallographic parameters of some representative alloys**

Alloy	Main phase	$a/\text{nm}$	$V/\text{nm}^3$
$\text{ZrCr}_{0.2}\text{Mn}_{0.5}\text{Ni}_{1.3}$	C15	0.7038	0.3486
$\text{ZrCr}_{0.4}\text{Mn}_{0.3}\text{Ni}_{1.3}$	C15	0.7050	0.3504
$\text{ZrCr}_{0.25}\text{Mn}_{0.6}\text{V}_{0.05}\text{Ni}_{1.3}$	C15	0.7054	0.3510
$\text{ZrCr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$	C15	0.7063	0.3523
$\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$	C15	0.7043	0.3494
$\text{Zr}_{0.7}\text{Ti}_{0.3}\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$	C15	0.6998	0.3427
$\text{ZrCr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.2}\text{Fe}_{0.1}$	C15	0.7062	0.3522

Table 2 lists the electrochemical capacity of multicomponent Zr-Cr-Ni based hydride electrodes when Cr or Ni is substituted with another transition metals M ( $\text{M} = \text{V}, \text{Ti}, \text{Fe}$  or  $\text{Co}$ ). Larger Fe to Ni substitution drastically reduces the electrochemical discharge capacity from 305  $\text{mAh} \cdot \text{g}^{-1}$  ( $\text{ZrCr}_{0.70}\text{Ni}_{1.3}$ ) to 50  $\text{mAh} \cdot \text{g}^{-1}$  ( $\text{ZrCr}_{0.70}\text{Fe}_{1.0}\text{Ni}_{0.3}$ ). Boulghallat *et al*<sup>[11]</sup> found that replacement Ni by Fe in the same proportion, *i. e.*  $\text{Zr}(\text{M}_{0.4}\text{Cr}_{0.6})_2$  ( $\text{M} = \text{Ni}, \text{Fe}$ ), anomalously raised the  $\text{H}_2$  equilibrium pressure by reference to

what can be predicted from the volume change, and to some extent decreased the gaseous  $\text{H}_2$  capacity (343 ~ 383 K). Sharp decrease in the electrolytic capacity of  $\text{ZrCr}_{0.70}\text{Fe}_{1.0}\text{Ni}_{0.3}$  alloy is related to its electrode kinetics factors for poor Ni concentration on the electrode surface. Small amounts of V alloyed increase the discharge capacity noticeably when the total ratio of Cr, Mn and V in the  $\text{AB}_2$  formula is low (less than 0.7). Also the addition of a small amount of group VIII 3d transition metals increases the electrochemical capacity for the hydride electrodes  $\text{ZrCr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.2}\text{M}_{0.1}$  in the order:  $\text{Fe} < \text{Co} < \text{Ni}$ . We ascribe this to the improvement of electrocatalytic properties, *i. e.* better kinetics.

**Table 2 Discharge capacities of Zr-based multicomponent hydride electrodes**

Alloy	Temperature / K	Discharge capacity / $\text{mAh} \cdot \text{g}^{-1}$
$\text{ZrCr}_{0.7}\text{Ni}_{1.3}$	298	305
$\text{ZrCr}_{0.70}\text{Ni}_{0.3}\text{Fe}_{1.0}$	298	50
$\text{ZrCr}_{0.15}\text{Mn}_{0.50}\text{Ni}_{1.3}$	298	274
$\text{ZrCr}_{0.15}\text{Mn}_{0.65}\text{Ni}_{1.3}$	298	281
$\text{ZrCr}_{0.30}\text{Mn}_{0.40}\text{Ni}_{1.3}$	298	285
$\text{ZrCr}_{0.40}\text{Mn}_{0.30}\text{Ni}_{1.3}$	298	294
$\text{ZrCr}_{0.50}\text{Mn}_{0.20}\text{Ni}_{1.3}$	298	298
$\text{ZrCr}_{0.6}\text{Mn}_{0.20}\text{Ni}_{1.2}$	303	290
$\text{ZrCr}_{0.6}\text{Mn}_{0.30}\text{Ni}_{1.1}$	303	320
$\text{ZrCr}_{0.6}\text{Mn}_{0.40}\text{Ni}_{1.0}$	303	270
$\text{ZrCr}_{0.40}\text{Mn}_{0.10}\text{V}_{0.20}\text{Ni}_{1.3}$	298	309
$\text{ZrCr}_{0.50}\text{Mn}_{0.50}\text{V}_{0.10}\text{Ni}_{1.3}$	298	216
$\text{ZrCr}_{0.40}\text{Mn}_{0.40}\text{V}_{0.20}\text{Ni}_{1.0}$	298	251
$\text{ZrCr}_{0.25}\text{Mn}_{0.60}\text{V}_{0.05}\text{Ni}_{1.3}$	298	315
$\text{ZrCr}_{0.30}\text{Mn}_{0.20}\text{V}_{0.20}\text{Ni}_{1.3}$	298	310
$\text{ZrCr}_{0.20}\text{Mn}_{0.20}\text{V}_{0.30}\text{Ni}_{1.3}$	298	278
$\text{ZrCr}_{0.20}\text{Mn}_{0.40}\text{V}_{0.10}\text{Ni}_{1.3}$	298	295
$\text{Zr}_{0.70}\text{Ti}_{0.30}\text{Cr}_{0.40}\text{Mn}_{0.20}\text{V}_{0.10}\text{Ni}_{1.3}$	298	295
$\text{Zr}_{0.90}\text{Ti}_{0.10}\text{Cr}_{0.40}\text{Mn}_{0.20}\text{V}_{0.10}\text{Ni}_{1.3}$	298	305
$\text{ZrCr}_{0.40}\text{Mn}_{0.20}\text{V}_{0.10}\text{Ni}_{1.3}$	298	324
$\text{ZrCr}_{0.40}\text{Mn}_{0.20}\text{V}_{0.10}\text{Ni}_{1.2}\text{Fe}_{0.1}$	298	315
$\text{ZrCr}_{0.40}\text{Mn}_{0.20}\text{V}_{0.10}\text{Ni}_{1.2}\text{Co}_{0.1}$	298	320

### 3.2 Effect of mischmetal addition on activation process

Fig. 3 presents the activation process of hydrogen storage alloys designated as  $\text{ZrCr}_{0.4}\text{Mn}_{0.4}\text{V}_{0.2}\text{Ni}_{1.0}$  and  $\text{Zr}_{0.9}\text{La}_{0.1}\text{Cr}_{0.36}\text{Mn}_{0.36}\text{V}_{0.18}\text{Ni}_{1.4}$ . The first alloy needs 15 full charge-discharge cycles to fulfill its highest discharge capacity of  $250 \text{ mAh} \cdot \text{g}^{-1}$  at 298 K, while the other releases 90% ( $210 \text{ mAh} \cdot \text{g}^{-1}$ ) of its maximum charge during the second cycling at the same test condition.

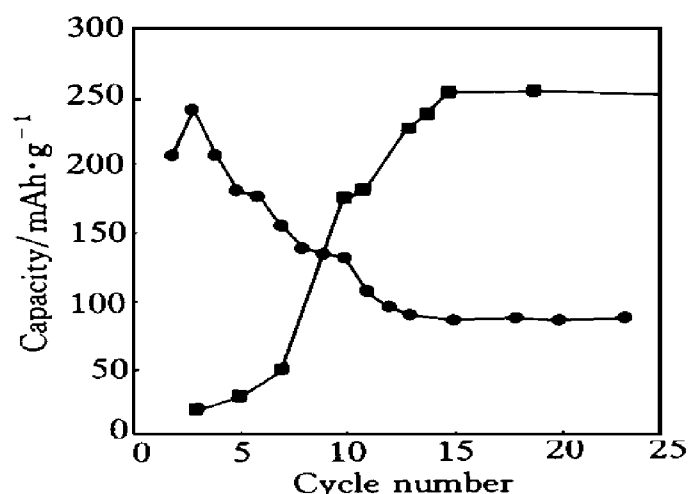


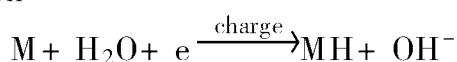
Fig. 3 The activation process of hydrogen storage alloys

■ —  $\text{ZrCr}_{0.4}\text{Mn}_{0.4}\text{V}_{0.2}\text{Ni}_{1.0}$ ;

● —  $\text{Zr}_{0.9}\text{La}_{0.1}\text{Cr}_{0.36}\text{Mn}_{0.36}\text{V}_{0.18}\text{Ni}_{1.4}$ ;

Discharge current  $50 \text{ mA} \cdot \text{g}^{-1}$  at 298 K

The La alloying reduces dramatically its activating cycles for the segregation and oxidation of La on the alloy particles, which modify the outer layer of oxides to be penetrative easily for  $\text{H}_2\text{O}$  molecular. But generally the reformed oxide layer was regarded to be permeable for H atoms during electrochemical reaction. However it is a fact that hydrogen desorbing-absorbing reaction



occurs at the Ni-rich sublayer instead of on the surface. The producing hydrogen atoms are directly absorbed by the bulk alloy or recombined with hydroxide ions to form  $\text{H}_2\text{O}$  molecular, which needs to be transferred through outlayer into electrolyte meanwhile the  $\text{OH}^-$  moves ad-

versely. Therefore it is justified that the outlayer of alloy particles is penetrable for  $\text{H}_2\text{O}$  molecular instead of H atoms.

By XRD analysis, it is found that both are multiphase, and that C15 and C14 coexist in the  $\text{Zr}_{0.9}\text{La}_{0.1}\text{Cr}_{0.36}\text{Mn}_{0.36}\text{V}_{0.18}\text{Ni}_{1.4}$  alloy by about the same partial ratio, however mainly C14 for  $\text{ZrCr}_{0.4}\text{Mn}_{0.4}\text{V}_{0.2}\text{Ni}_{1.0}$ . La with a larger atomic size replacing Zr in the A site brings forth the large  $r_A/r_B$  ratio to form C15 structure fairly.

Also it is not to be denied that the improvement in activity of  $\text{Zr}_{0.9}\text{La}_{0.1}\text{Cr}_{0.36}\text{Mn}_{0.36}\text{V}_{0.18}\text{Ni}_{1.4}$  alloy certainly is due to the higher Ni concentration in the composition and the superstoichiometry.

In order to improve the activation behavior of Zr-based electrode materials, several pretreatments have been proposed. As an attempt to make it easier for hydrogen to penetrate the dense Zr-oxide, stable monoclinic Zr-oxide has been changed to the permeable tetragonal oxide by annealing the Zr-based alloy at  $250 \sim 300^\circ\text{C}$  at low oxygen pressure<sup>[12]</sup>, or immersing the electrode materials in hot KOH solution or HF,  $\text{NH}_4\text{F}$  solution<sup>[13]</sup>. In the as-cast sample of  $\text{Zr-CrNiLa}_{0.05}$ , it was found that spherical La rich phase is evenly distributed in the alloy matrix and La-rich phase is swelled by expansion owing to hydrogen absorption and induced cracks around them during activation process<sup>[14]</sup>. The aim of these attempts is to improve the actual reaction surface area and to modify the particle surface of the electrodes.

### 3.3 Cyclic life

Fig. 4 depicts the relation of discharge capacity *versus* cycle number of  $\text{Zr}(\text{Cr}_x\text{Ni}_{1-x})_2$  ( $x = 0.35, 0.50$ ). Both electrodes were charged at  $360 \text{ mA} \cdot \text{g}^{-1}$  for 1 h and discharged at  $180 \text{ mA} \cdot \text{g}^{-1}$  for 1 h, with a depth of discharge (DOD) around 60% ~ 70% (*i. e.*  $C_{\text{max}} = 300 \text{ mAh} \cdot \text{g}^{-1}$ ). The discharge capacity was measured at a discharge rate  $50 \text{ mA} \cdot \text{g}^{-1}$  every 50 cycles. The figure shows that after 250 cycles both electrodes degrade only slightly. The excellent cycle stability is probably due to the good resistance of Cr and Zr against KOH solution.

Fig. 5 shows the electrochemical charging-discharging cycling lives of Zr-Cr-Ni multicomponent alloy electrodes. In the  $(\text{Zr}_{1-y}\text{Ti}_y)\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$  ( $y = 0.0, 0.1, 0.3$ ) series alloys, the capacity of electrode with higher Ti content decays by 30% after 50 cycles (DOD=65%). However, the capacity retention of electrode with low and no Ti is about 86% after 820 cycles under the test condition. They have excellent cycling stability. Small amount of Fe substituting brings forth attractive effect on improving the cycling stability, which is in good agreement with that reported by Sawa<sup>[12]</sup>, who believed that the dissolution of other metals was inhibited by Fe, but its mechanism is expected to be further discussed.

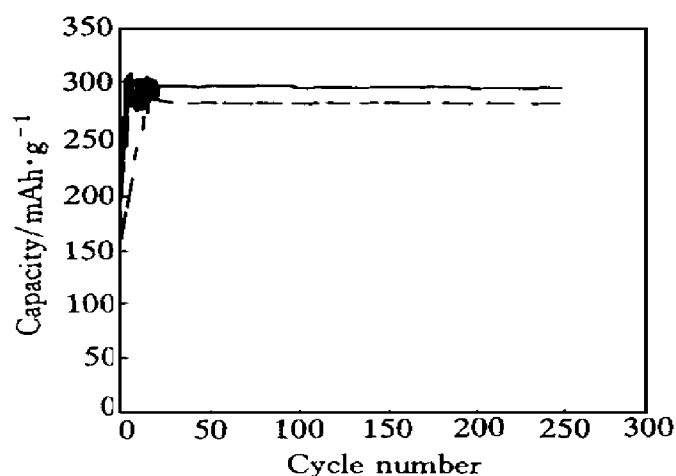


Fig. 4 Capacity changes with number of cycle at  $50 \text{ mA} \cdot \text{g}^{-1}$ , 303 K

Solid line  $\text{Zr}(\text{Cr}_{0.35}\text{Ni}_{0.65})_2$ ; dotted line  $\text{Zr}(\text{Cr}_{0.5}\text{Ni}_{0.5})_2$

### 3.4 Charge retention

Charge retention ( $CR$ ) is represented as follows:

$$CR = \frac{C_1}{C_2} \times 100\%$$

where  $C_1$  is rest discharge capacity of the electrode being fully charged and then stored in the KOH solution for a long time,  $C_2$  is the discharge capacity during the next regular cycle ( $50 \text{ mA} \cdot \text{g}^{-1}$  charge for 8 h and then discharge at  $50 \text{ mA} \cdot \text{g}^{-1}$  to  $-0.6 \text{ V}$  respect to  $\text{Hg}/\text{HgO}$ ) of the corresponding electrode.

Table 3 lists the  $CR$  of Zr-based alloy elec-

trodes after different storage times and under different temperatures. The  $CR$  values of  $\text{ZrCr}_{0.7}\text{Ni}_{1.3}$ ,  $\text{ZrCr}_{0.25}\text{Mn}_{0.60}\text{V}_{0.05}\text{Ni}_{1.3}$  and  $\text{ZrCr}_{0.15}\text{Mn}_{0.50}\text{Ni}_{1.3}$  electrodes, which have been stored for 24 d at 277 K, are 88%, 67% and 71% respectively. In the above three electrodes, there is all  $1.3/AB_2$  formula of Ni, and only Zr in an A site,  $CR$  decreases obviously as the Mn content increases and the superstoichiometric alloy displays low  $CR$  as well.

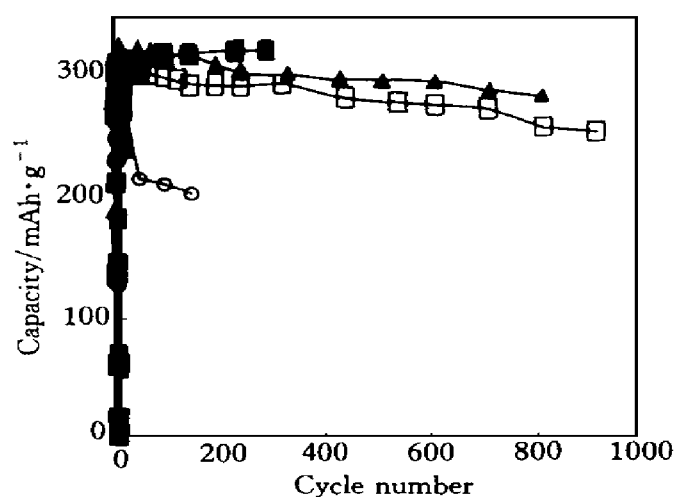


Fig. 5 The electrochemical charging-discharging cycling lives of Zr-Cr-Ni multicomponent alloy electrodes,  $50 \text{ mA} \cdot \text{g}^{-1}$  and 298 K

○  $\text{Zr}_{0.7}\text{Ti}_{0.3}\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$ ;  
□  $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$ ;  
▲  $\text{ZrCr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$ ;  
■  $\text{ZrCr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.2}\text{Fe}_{0.1}$

Table 3 The charge retention of the Zr-based alloy electrodes

Alloy	$t$ / d	$\theta$ / °C	$\frac{C_1}{C_2}$ / $\text{mAh} \cdot \text{g}^{-1}$	$CR$ / %
$\text{ZrCr}_{0.7}\text{Ni}_{1.3}$	24	4		81
$\text{ZrCr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$	23	4	273	89
	5	15	250	84
$\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$	23	4	258	86
	5	15	225	75
$\text{Zr}_{0.7}\text{Ti}_{0.3}\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$	23	4	230	79
	5	15	148	51
$\text{ZrCr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.2}\text{Fe}_{0.1}$	23	4	282	92
$\text{ZrCr}_{0.25}\text{Mn}_{0.6}\text{V}_{0.05}\text{Ni}_{1.3}$	23	4	250	67
$\text{ZrCr}_{0.15}\text{Mn}_{0.50}\text{Ni}_{1.3}$	23	4	189	71

In the  $(\text{Zr}_{1-y}\text{Ti}_y)\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$  ( $y = 0.0, 0.1, 0.3$ ) series alloys, when  $y = 0.0$ , the Ti-free alloy exhibits the best  $CR$  of 86%, and only 79% for  $y = 0.3$ ; It is worthy to note that a small Fe alloying effectively retains more charge with a  $CR$  of 92%. We also have analyzed the effect of storing temperature on  $CR$ . The  $CR_s$  of the above-mentioned  $(\text{Zr}_{1-y}\text{Ti}_y)\text{Cr}_{0.4}\text{Mn}_{0.2}\text{V}_{0.1}\text{Ni}_{1.3}$  ( $y = 0.0, 0.1, 0.3$ ) series electrodes stored at 288 K for 5 d decrease as the Ti content increase, and remain relatively lower values of 81%, 75% and 51% respectively.

More substitution of Ti for Zr and Mn for Cr, and high superstoichiometric degree and storing temperature as well are deteriorate the  $CR$  property of hydride electrodes using Zr-based hydrogen storage alloys. These factors have been known to be related to intrinsic property of alloys, which is interpreted in  $P$ - $C$ - $T$  (Pressure-Concentration-Temperature isotherm) characteristics. The  $CR$  of hydride electrode is believed to reduce as the hydrogen desorbing pressure plateau raises. Meanwhile the lost charge during storing process can be explained in terms of hydrogen releasing from bulk alloy (or hydride). The mobile hydrogen atoms dissolved in the host lattice move to particle surface where the hydrogen concentration is lower, and recombine to form  $\text{H}_2$  molecular steadily and then diffuse throughout into atmosphere.

#### 4 CONCLUSIONS

(1) The alloys  $\text{Zr}(\text{Cr}_x\text{M}_y\text{Ni}_{2-x-y})$  ( $\text{M} = \text{V}$  or  $\text{Mn}$ ) with  $x + y = 0.7 \sim 1.0/AB_2$  formula have larger hydrogen storage and electrochemical discharge capacities.

(2) When substitution of Ti for Zr partly in  $\text{Ti}_y\text{Zr}_{1-y}\text{M}_2$  ( $y = 0.0 \sim 0.3$ ) alloys, the plateau pressure of the hydride tends to increase with increasing  $y$ , however its electrochemical capacity and electrochemical stability decrease with increasing Ti content. Electrodes with no Ti or

very low Ti content preserve 86% of their discharge capacities after 820 cycles under 65% depth of discharge, exhibit excellent electrochemical stability.

(3) The activation of  $\text{Zr}_{0.9}\text{La}_{0.1}\text{Cr}_{0.36}\text{Mn}_{0.36}\text{V}_{0.18}\text{Ni}_{1.4}$  electrode is improved with  $\text{LaNi}_5$  synthesized by arc-melting, but its cyclic stability are deteriorated severely.

(4) The charge retention of hydride electrodes is related to the hydrogen pressure plateau, therefore more Mn substituted for Cr, Ti for Zr and higher superstoichiometric degree and storing temperature will decline its self-discharge property.

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