JOURNAL OF
POWER
SOURCES

Electrochemical performance of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ Laves phase alloy electrode

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Abstract

The electrochemical performance of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ ($x = 0.05, 0.1, 0.15, 0.2$) system alloys, based on $ZrMn_{0.5}V_{0.4}Ni_{1.1}$, are investigated intensively. With the increase in Co content, the maximum capacity, high-rate dischargeability (HRD) and CL of the alloy electrode decreases, and the self-dischargeability increases. Electrochemical activities of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes are worse than that of the matrix alloy. While, the alloy electrodes are heat-treated by hot alkaline solutions, their activities improve greatly, and there are not more than four cycles to reach the maximum capacity. However, the maximum capacities show a small decrease. The reversible capacity loss mainly results from desorption of hydrogen from hydride, and is affected by the stability of hydrides. E of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes agrees well with their reversible capacity loss. In all the investigated alloy electrodes, $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrode has the most excellent properties in capacity, CL, HRD and self-dischargeability. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy is a favorable alloy for use as an active electrode if its temperature property will be improved. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Laves phase; Electrochemical performance

1. Introduction

In our laboratory, we had shown that $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ alloy is the most favorable alloy for use as an active electrode in the $ZrMn_{0.9-x}V_xNi_{1.1}$ ($x = 0.1$–0.8) system. The highest capacity was 342 mAh/g (50 mA/g of discharging current), high-rate dischargeability $C_{200}/(C_{200} + C_{50})$ (HRD) was 75%, the capacity retention was 85% after 100 charging–discharging cycles under the condition of 100% DOD and self-discharge rate was 7.1% per day [1].

Cobalt is an active element in Laves phase electrode alloy [2], and can improve the catalytic properties of alloy electrode. Nonstoichiometric alloys have excellent general electrochemical property [3,4], such as higher capacity and HRD. In this work, we report intensive study results of the electrochemical performance of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ ($x = 0.05, 0.1, 0.15, 0.2$) nonstoichiometric alloys as an active electrode material. The phase composition, electrochemical capacity, activation property, temperature-dependence on capacity, HRD, cycle life and self-dischargeability are investigated.

2. Experimental

The alloys were prepared by arc melting in an argon atmosphere using the pure constituent metals with purity >99.9%. The as-cast alloys were crushed and grounded mechanically to 360 mesh for making electrodes and examination of the XRD pattern.

X-ray diffraction (XRD) pattern was performed on a Rigaku D/max-III'B diffractometer using Cu Kα radiation. The electrode was prepared as described in the previous paper [1,6]. Electrochemical measurements were carried out at room temperature except for the temperature-dependence tests. A Hg/HgO reference electrode and a nickel sheet counter electrode were employed. Activity property test was performed at 100 mA/g of charging current for 4 h, setting up 15 min, and at 50 mA/g of discharging current to −0.6 V versus Hg/HgO at 25°C. High-rate dischargeability (HRD) was defined as $C_{200}/(C_{200} + C_{50})$ [5]. A HDV-7B potentiostat was adopted to obtain the polarization curves in the vicinity of the rest potential, including charging state

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(SOC) and discharging state (SOD) [6]. The apparent exchange current density J_0 (mA/g) of the hydrogen electrode reaction was determined by calculating the slope of the polarization curve by

$$J_0 = \frac{RTJ}{F\eta}$$

The electrode cycle life tests were carried out by charging 1 h at 400 mA/g and discharging to -0.6 V (versus Hg/HgO) at 400 mA/g. The self-dischargeability tests were referred in [7]. The electrode temperature effect examination was carried out by charging 4 h at 100 mA/g and discharging at 50 mA/g to -0.6 V (versus Hg/HgO) at 10, 25 and 40°C.

3. Results and discussion

3.1. Phase structure

Fig. 1 represents XRD patterns for alloy $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ ($x = 0.05, 0.1, 0.15, 0.2$) (a) and alloy $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ (b). All alloys are multiphase structures. According to the qualitative analysis methods of XRD, secondary phases are determined by the three most intensive peaks from XRD patterns. The main phase is C15 Laves phase, identical to the matrix alloy [8,9]. The lattice parameters of main phase and secondary phase component are listed in Table 1. With the increase in Co content, the lattice parameter decreases first, but increases between $x = 0.15$ and 0.2. There exists C15, C14, Zr_9Ni_{11}, Zr in every alloy, and there exists Zr_7Ni_{10} in alloy at $x = 0.05$ and 0.15 (see Fig. 1). Comparing the result from [8], we can conclude that adding Co in alloy $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ induces the appearance of Zr, and the appearance of Zr_7Ni_{10} at $x = 0.05$ and 0.15.

3.2. Activity property

Fig. 2 shows the activity property of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ ($x = 0.05, 0.1, 0.15, 0.2$) alloy electrodes. The maximum

Table 1
Lattice parameters of main phase and secondary phase component of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ system alloys

Alloy	a (nm)	Secondary phase
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$	0.7095	C14, Zr_7Ni_{10}, Zr_9Ni_{11}, Zr
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$	0.7086	C14, Zr_9Ni_{11}, Zr
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$	0.7065	C14, Zr_7Ni_{10}, Zr_9Ni_{11}, Zr
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$	0.7069	C14, Zr_9Ni_{11}, Zr

capacities and activity numbers of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrode and listed in Table 2. With the increase in Co content, the maximum capacity decreases; except that there is little increase between $x = 0.15$ and 0.2. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrode has the largest capacity, 363.3 mAh/g, which is larger than that of $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ alloy electrode, 342 mAh/g. However, the maximum capacities of other alloy electrodes are less than that of $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ alloy electrode. There are more than 18 cycles of electrochemical activity for all alloy electrodes, which are worse than that of matrix alloy electrode (18 cycles).

Zuttel pretreated the alloy powder of $Zr(V_{0.25}Ni_{0.75})_2$ with concentrated KOH solution to improve the electrode activity [10]. We immersed alloy electrodes in 6 mol/dm^3 KOH solution at 65°C for 4 h. The treating effect on electrode activity is listed in Table 2. We can find the activity property improving greatly. It needs not more than four cycles for activity. However, the maximum capacity has a minor decrease (Table 2).

3.3. Exchange current density and high-rate dischargeability

Table 3 lists the high-rate dischargeability (HRD) and apparent exchange current density J_0 of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ system alloy electrodes. With the increase in Co content, HRD decreases from 88.8 to 62.7%. The HRD of matrix alloy electrode is 75%. The exchange current density J_0 at
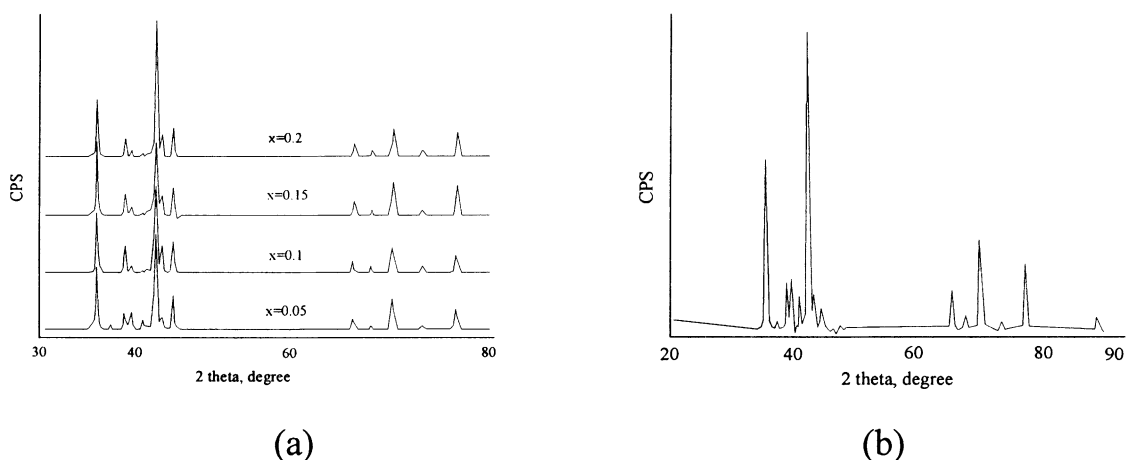

(a)

(b)

Fig. 1. XRD patterns for alloys $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_i$ (a) and alloy $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ (b).
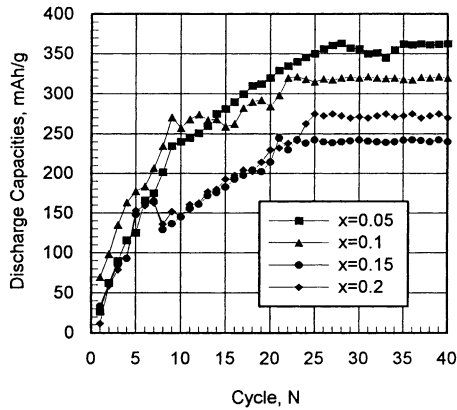
Fig. 2. Electrochemical activity property of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes (charging at 100 mA/g for 4 h and discharging at 50 mA/g to −0.6 V vs. Hg/HgO).

SOC ($-E_{eq} > 0.94$ V) is larger than that at SOD for each alloy electrode. J_0 at SOC and SOD has similar change trend. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$ alloy electrode has the largest J_0 at SOC and SOD in the alloy system. J_0 does not correlate well with HRD, this is different from other researchers' results [7,12]. Wang et al. concluded that HRD related to J_0, D_α (surface hydrogen diffuse coefficient in α phase) and I_l (limited diffuse current density) [15]. HRD correlated well with J_0 only at the limited states.

3.4. Temperature effect on capacity

Table 4 and Fig. 3 show the discharge capacities and the discharge curves of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ at 10, 25, and

Table 2
Maximum capacities, activity numbers of hot alkaline treated (later) and untreated (former) $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes[a]

Alloy	Capacity (mAh/g)	Activity number (cycles)
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$	363.3/359.6	22/4
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$	321.5/320.1	18/4
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$	245.0/240.2	21/3
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$	275.0/257.2	25/3

[a] Electrochemical capacity and activity number of $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ alloy electrode is 342 mAh/g and 18, respectively.

Table 3
HRD and J_0 of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrode[a]

Alloy	HRD(%)	J_0 (mA/g)	$-E_{eq}$ (V)
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$	88.8	7.459	0.9433
		4.705	0.8808
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$	76.7	9.835	0.9496
		5.569	0.8796
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$	75	6.432	0.9410
		2.609	0.8830
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$	62.7	6.419	0.9451
		2.525	0.8639

[a] HRD of $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ alloy electrode is 75%.

Table 4
Temperature-dependence of discharge capacity of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes

Alloy	Capacity, C_e at 10°C (mAh/g)	Capacity at 25°C (mAh/g)	Capacity, C_e at 40°C (mAh/g)
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$	254.7/70%	363.3	288.5/79.3%
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$	256.9/79.9%	321.5	276.1/85.9%
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$	241.6/98.6%	245	261.6/106.8%
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$	196.3/71.4%	275	252.2/91.7%

40°C. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$ alloy electrode has the largest capacity at 40°C, but the other alloy electrodes have the largest capacity at 25°C. Assuming the capacity at 25°C for C_0, the discharge efficiency ($C_e = C/C_0$) at 10 and 40°C are listed in Table 4. The discharge capacities of all the electrodes show a maximum with respect to the temperature. The decrease in the capacity at higher temperature may be due to the decrease in the hydrogen storage capacity and the high self-discharge rate in the open cell, while the decrease at lower temperature may be due to the decrease in the diffusivity of hydrogen in the metal hydride [11]. The alloy electrode at $x = 0.15$ has the most excellent temperature stability and that at $x = 0.05$ has the worst temperature stability.

3.5. Cycle life

Fig. 4 shows the discharge capacity versus cycle number curve for $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrode. As the cobalt content increases, the capacity retention of alloy electrode decreases. After 200 charging–discharging cycles, the capacity retention decreases from 86.3 to 66.5%. All alloys have better cycle stability than matrix alloy $ZrMn_{0.5}V_{0.4}Ni_{1.1}$, 85% after 100 cycles.

The cycle life (CL) is defined as the cycle number at which the discharge capacity decreases to half of the maximum capacity [13]. CL decreases with the increasing Co content, i.e. CL = 650 for $x = 0.05$; CL = 435 for $x = 0.1$; CL = 386 for $x = 0.15$ and CL = 284 for $x = 0.2$.

3.6. Self-dischargeability

Iwakura proposed that self-dischargeability of alloy electrode can be divided into two parts, i.e. reversible (C_3-C_2) and irreversible (C_1-C_3) ones [7]. For $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrode, as the Co content increases, the self-dischargeability increases, but there is little decrease from $x = 0.1$ to 0.15 (refer to Table 5). Their self-discharge rates are lower than that of matrix alloy, 7.1% per day, except for alloy $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$. The reversible capacity loss shows a similar trend with the self-discharge rate, however, the irreversible capacity loss has little decrease from $x = 0.05$ to 0.1. Iwakura proposed that reversible capacity loss resulted from desorption of hydrogen from hydride. When the hydrogen pressure P_{H_2} associated with the hydride
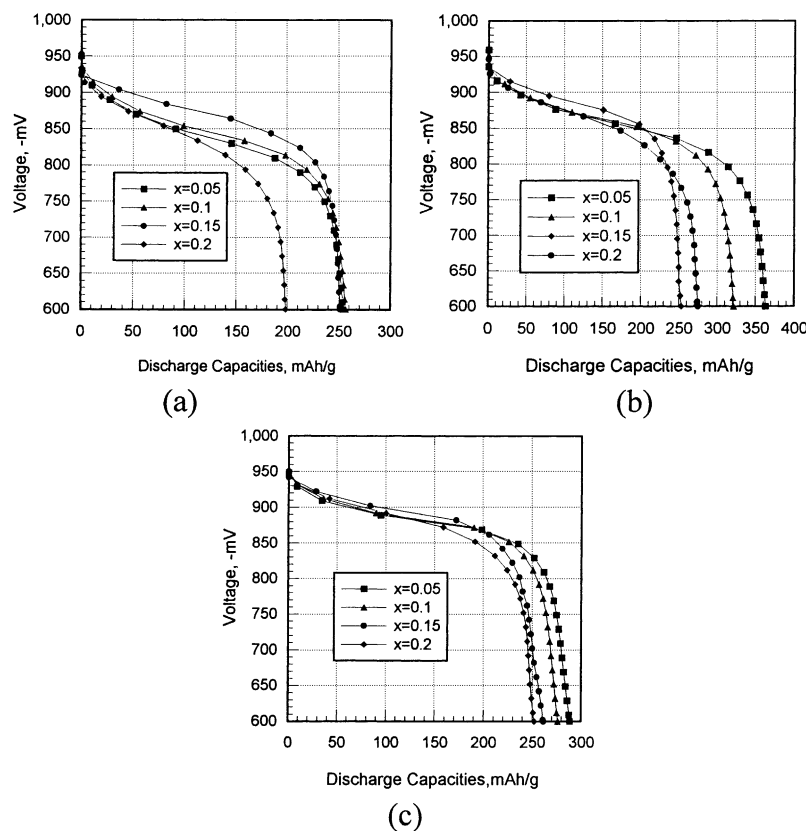
Fig. 3. Discharge curve of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes at $10°C$ (a), $25°C$ (b) and $40°C$ (c). Charging at 100 mA/g for 4 h and discharging at 50 mA/g to -0.6 V vs. Hg/HgO.

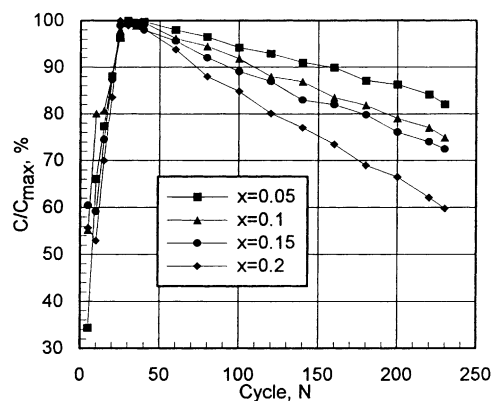Fig. 4. Discharge capacity vs. cycle number of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes. Charging 1 h at 400 mA/g, discharging at 400 mA/g to -0.6 V vs. Hg/HgO, $25°C$.

anode at SOC exceeds 1 atm, the metal hydride will be easily released from the anodes. The open-circuit potentials observed are about -0.94 V versus Hg/HgO for all alloy electrodes (refer to Table 3), however, from [14] it is concluded that $E_{eq}^0 = -0.9285$ V at $P_{H_2} = 1$ atm and $25°C$. This means that P_{H_2} exceeds 1 atm at the end of the charge for all alloy electrodes. The relation of E_{eq} with reversible capacity loss is shown in Fig. 5. We find that a higher E_{eq} indicates larger reversible capacity loss, and that only $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$ alloy electrode has the highest E_{eq}, but the reversible capacity loss is lower than that of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$ alloy electrode. We supposed that $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$ hydride has higher stability. From Fig. 3(b), we can detect the voltage of various electrodes at 10, 50 and 90% SOD (listed in Table 6). Here $E_{0.1}$,

Table 5
Self-discharge property of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes[a] (mAh/g as capacity unit)

Alloy	C_1	C_2	C_3	C_1-C_3	C_3-C_2	Self-discharge rate (%/day)
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$	363.3	334.2	354.2	9.1	20	3.4
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$	277.5	249.2	273.3	4.2	24.1	4.8
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$	243.3	214.5	228.7	16.6	14.2	4.55
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$	276.7	218.3	249.2	27.5	30.9	8.5

[a] Self-dischargeability rate of $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ alloy electrode is 7.1%/day.
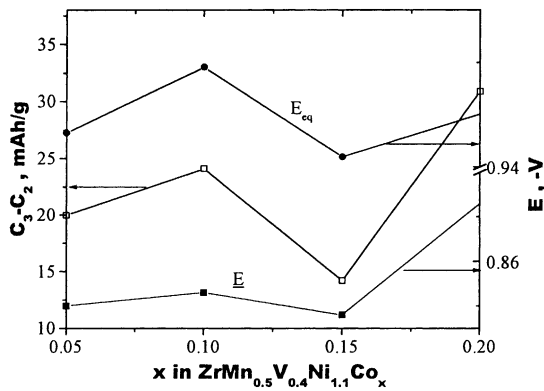
Fig. 5. Relation between E_{eq} and reversible capacity loss ($C_3 - C_2$) of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes.

Table 6
Discharge voltage at some SOD of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes (unit: $-V$ versus Hg/HgO electrode)

Alloy	$E_{0.1}$	$E_{0.5}$	$E_{0.9}$	E
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$	0.91	0.861	0.789	0.85
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$	0.913	0.868	0.794	0.853
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$	0.914	0.868	0.782	0.848
$ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$	0.926	0.89	0.82	0.873

$E_{0.5}$, $E_{0.9}$ represent 10, 50 and 90% SOD of various electrodes, respectively. E represents the average value of $E_{0.1}$ and $E_{0.9}$. $E_{0.5}$ regarded as the plateau voltage, indicates the stability of hydride. From Tables 5 and 6 and Fig. 5, we find that the $E_{0.5}$ values are the same as that for $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$ and $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$ alloy electrode, but the latter has lower reversible loss. However, E agrees well with reversible capacity loss for $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrode.

We suppose that E, combined $E_{0.5}$ with E_{eq}, determines the reversible capacity loss of electrode.

4. Conclusion

The crystal structure and electrochemical properties of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy, based on $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{1.1}$ alloy, are investigated. The studied results can be concluded as follows:

1. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloys are multiphase alloys; their main phase is C15 Laves phase, similar to the matrix alloy $ZrMn_{0.5}V_{0.4}Ni_{1.1}$.
2. With the increase in Co content, the maximum capacities of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrode decreases. The maximum capacity of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrode is 363.3 mAh/g, which is larger than that of matrix alloy electrode, 342 mAh/g. The capacities of other alloy electrodes are lower than that of matrix alloy electrode. The activity property of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes are worse than matrix alloy; activity numbers are not less than 18. Their activities improve greatly by soaking the alloy electrode in concentrated KOH solution. However, the maximum capacities have a small decrease.
3. With the Co content increases, HRD of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes decrease from 88.8 to 62.7% except for $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$, the other alloy electrodes have higher HRD than that of matrix one, 75%. The apparent exchange current density J_0 does not correlate well with the high-rate dischargeability. J_0 of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrode is larger than that of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrode.
4. The electrode cycle life decreases from 650 to 284 with the increase in Co content. All alloys have better cycle stability than $ZrMn_{0.5}V_{0.4}Ni_{1.1}$ alloy.
5. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.15}$ alloy electrode has larger capacity at 40°C, and the other alloy electrodes have larger capacity at 25°C. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.1}$ alloy electrode shows excellent temperature stability, however, $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrode shows the worst temperature stability.
6. Except for $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.2}$ alloy electrode, the other electrodes have lower self-discharge rate than that of matrix alloy. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrode has least self-discharge rate, including reversible and irreversible capacity loss. The reversible capacity loss results mainly from desorption of hydrogen from hydride, and is affected by the hydride stability. E of $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ alloy electrodes agrees well with their reversible capacity loss.

Generally, with the increase in cobalt content in the $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_x$ ($x = 0.05, 0.1, 0.15, 0.2$) system, maximum capacity, HRD and CL of alloy electrodes decrease, and self-dischargeability increases. $ZrMn_{0.5}V_{0.4}Ni_{1.1}Co_{0.05}$ alloy electrodes has the most excellent comprehensive electrochemical property, which includes the largest capacity, largest high-rate dischargeability, maximum CL, most excellent self-dischargeability, and all these performances exceed those of matrix alloy electrode. If its temperature stability can be improved, it should be a promising electrode alloy.

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