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Effects of rare earth elements on properties of AB_5-type electrode materials at different temperature

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Abstract: Discharge property is an important factor to evaluate electrode materials. The discharge capacity of the hydrogen-storing alloys are not only influenced by its thermodynamic property but also closely related to its dynamic property. When the temperature changes, the degrees of influence of the above-mentioned two factors on the discharge performance vary accordingly. As a consequence, adjusting compositions of the alloys to make them have good discharge performance under a relatively wide range of temperature is of great significance. On the basis of great deal of experimental investigation, the optimum combination of rare earth elements in hydrogen-storing electrode materials using at-30-55℃ is determined and the relationships between the cell parameters and discharge performance of alloys at －30℃ are discussed. Additionally, the DFEC calculation method has been improved to predict the discharge capacities, which is in good agreement with the experimental ones. This is of theoretical significance in investigating new hydrogen-storing alloys of the AB_5 type.

Key words: AB_5-type hydrogen-storing alloy; discharge performance; rare earth elements; cell parameters

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1 Introduction

The hydrogen-storing alloy is a key negative-electrode material used in MH/Ni battery, and it is crucial for the capacity, cycling life, high-rate discharge, high and low temperature performance, and self-discharge. At present, the negative-electrode material used in second MH/Ni battery is mainly the AB_5 type of hydrogen-storing alloys, the parent material of which is $LaNi_5$. However, the $LaNi_5Hx$ is not suitable for using as a negative-electrode material, because it has a high hydrogen-equilibrium pressure (about 0.17 MPa at 25℃) and a very short cycling life. In 1984, Willems[1] gave a good solution to above-mentioned two problems by pseudo-binary alloying which is characterized by using other appropriate metal atoms substituting the La or Ni located at the lattices of the alloy. Since then, the relationship between the elemental substitute and electro-chemical properties of hydrogen-storing alloys has long been a subject to be dis-

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cussed[2,3], and the MH/Ni batteries, in which AB_5 type alloy is used as negative-electrode material, have been greatly advanced. In later 1980s, high-quality and cheap mixed RE-Ni system of hydrogen-storing materials were successfully developed and massively produced, and MH/Ni batteries were industrialized in several countries, such as Japan, Netherlands and China. Currently, further development of the MH/Ni batteries should be characterized by high power, low cost, high capacity, and wide-range temperature. The theoretical discharge capacity of the AB_5-type hydrogen-storing alloy is about 380 mAh/g, but the discharge capacity of mixed RE system hydrogen-storing alloys commercially used is, nevertheless, generally less than 320 mAh/g. Moreover, it is affected by temperature. It is stable under a temperature between 10℃ and 40℃, but considerably deteriorated when temperature is greater than 45℃ or less than −18℃. To meet the wide-range temperature demand, improving the negative-electrode materials used in the batteries would be crucial. In this paper, the alloy compositions are optimized by using Uniform Design Theory, and the relations between the cell parameters, DFEC values, and the electro-chemical properties are discussed. These are of great assistance in producing AB_5-type hydrogen storing alloys with high capacities in wide-range temperature.

2 Experimental method

According Uniform Design Theory, 15 AB_5 hydrogen-storing alloys, Mm(NiCoMnAl)5, were designed. The raw materials were based on purified metals, of which the purities of the RE are 99.5% (mass ratio) and those of Ni, Co, Mn and Al are all greater than 99% (mass fraction) and the alloys were prepared by arc melting method under an Ar atmosphere. The alloys were melted into button forms, which were re-melted 4 times in order to improve the homogeneity. The resulting ingots were pulverized mechanically into powder below 200 mesh. And the average diameter measured by using a laser particle size analyzer is 53 μm.

The alloy crystallographic structure was investigated by using X-ray diffraction (XRD) with the diffraction power of 36 kV×20 mA and Kα Cu anticathode. The scan manner was step scanning with a step of 0.02° and a scan rate of 2°/min. The scan scope is between 10℃ and 90℃.

The electrode pellets were prepared by using the cool-pressure method, that is, 0.4 g alloy powder and 1.6 g Ni powder were evenly mixed and rapped by Ni foams, and then pressed under a pressure of 10 MPa to be a pellet of 18 mm×18 mm×1.5 mm. The "sandwich" method was used to examine the electro-chemical properties, and the measured temperatures were −30℃, −20℃, 20℃, and 55℃, respectively.

3 Results and discussion

3.1 Relationships between discharge capacity and [DFEC] value

The compositions of the 15 AB_5-type alloys designed are listed in Table 1. It is worthy to note that contents and proportions of the elements in side B are constant whereas contents of the three elements La, Ce and Pr in side A evenly vary between 0 and 1 (atomic fraction), and $C_{La}+C_{Ce}+C_{Pr}=1$.

Although the relationships between the RE compositions and the electro-chemical properties in AB_5-type alloys have been studied by many researchers[4,5], the quantitative relations are difficult to be determined because of complex interactions among the REs of the alloys. Bernauer *et al*.[6] have proposed that the hydrogen-absorbing abilities of the transition metals are related to the electronic concentrations in their d-orbits:

$$H/M = 5-DEC \quad (1)$$

Where H/M is atomic ratio of the hydrogen and metal elements in the hydride, and DEC is the electronic concentration in the d-orbit. In order to make this model suitable for multi-RE system hydrogen-storing alloys, equation (1) can be adjusted as:

$$H/M=5X+7Y-DFEC \quad (2)$$

$$DFEC=\sum e_{di}X_i+\sum e_{fi}Y_i \quad (3)$$

Where X represents atomic fraction of elements that may provide un-full d-orbit electrons, Y is that of elements provided un-full f-orbit electrons, e_{di} and e_{fi} are the un-full d- and f-orbit electron numbers provided by element i, respectively, and X_i and Y_i are the atomic fractions of the elements that provide un-full d and f electrons. It has been illustrated that the DFEC value has a linear relation to the hydrogen-equilibrium pressure of alloys, that is, the larger the DFEC value the higher the hydrogen-equilibrium pressure[7,8].

Table 1 Compositions of the alloys

No.	La	Ce	Pr	Ni	Co	Al	Mn
1	0.82	0.06	0.12	3.7	0.6	0.25	0.45
2	0.68	0.18	0.14	3.7	0.6	0.25	0.45
3	0.59	0.34	0.07	3.7	0.6	0.25	0.45
4	0.52	0.05	0.43	3.7	0.6	0.25	0.45
5	0.45	0.21	0.34	3.7	0.6	0.25	0.45
6	0.39	0.38	0.23	3.7	0.6	0.25	0.45
7	0.34	0.59	0.07	3.7	0.6	0.25	0.45
8	0.29	0.12	0.59	3.7	0.6	0.25	0.45
9	0.25	0.33	0.42	3.7	0.6	0.25	0.45
10	0.20	0.56	0.24	3.7	0.6	0.25	0.45
11	0.16	0.81	0.03	3.7	0.6	0.25	0.45
12	0.12	0.20	0.68	3.7	0.6	0.25	0.45
13	0.09	0.46	0.45	3.7	0.6	0.25	0.45
14	0.051	0.73	0.22	3.7	0.6	0.25	0.45
15	0.02	0.03	0.95	3.7	0.6	0.25	0.45

For the AB_5-type hydrogen-storing alloys, the REs in side A are hydrogen-absorbing. It has been believed that the higher La content the higher charge and discharge capacity of the alloy[9]. In case of La substituted by Ce, Pr and Nd, the discharge capacity would decrease. However, this is only a qualitatively description, because the discharge capacity of an alloy is influenced by not only alloy's thermodynamic performance but also its kinetic property. Especially, when the temperature changes, these two properties would have different effects. Therefore, according to the physical meaning of the DFEC value, we can give minor modification for equation (3) to make it better in predicting the relationships between the compositions of the REs in side A and the electrochemical capacity of AB_5-type alloys. The modified equation is as:

$$[DFEC]=C_{La}+2C_{Ce}+3C_{Pr}/K_1+4C_{Nd}/K_2-K\,C_{La}C_{Ce}C_{Pr}\,C_{Nd}/T \quad (4)$$

Here coefficients of C_{La}, C_{Ce}, C_{Pr} and C_{Nd} are 1, 2, $3/K_1$ and $4/K_2$, respectively, of which 1, 2, 3 and 4 are the sums of d-electrons in layer O and f-electrons in layer N for elements La, Ce, Pr, and Nd, respectively, and K_1 and K_2 are constants determined by the influences of elements Pr and Nd on the cell volumes and hydrogen-absorbing abilities of alloys, respectively, with $K_1=2.5$ and $K_2=3$; K is a constant defined by the interaction of REs, and T represents the measuring temperature (℃).

Table 2 lists the calculated [DFEC] values at different temperatures for the 15 alloys studied, and the co-variations between [DFEC] and discharge capacity at different temperatures are shown in Fig. 1(a—c).

Table 2 Calculated [DFEC] values for the 15 alloys at different temperatures

Tem./℃	Sample No.							
	1	2	3	4	5	6	7	8
−30℃	1.1123	1.2903	1.4214	1.1897	1.4322	1.5896	1.6714	1.3366
20℃	1.0415	.0846	1.2529	1.0555	1.0467	1.1806	1.5029	1.0902
55℃	1.0684	1.1628	1.3169	1.1065	1.1932	1.3360	1.5669	1.1838

Tem./℃	Sample No.						
	9	10	11	12	13	14	15
−30℃	1.58032	1.7370	1.8347	1.4143	1.63942	1.8143	1.2227
20℃	1.16452	1.4145	1.7880	1.2185	1.41586	1.7160	1.2159
55℃	1.32252	1.5370	1.8057	1.2929	1.50082	1.7534	1.2185

As illustrated in Fig. 1, although the discharge capacities of the materials are essentially linearly correlated to the [DFEC] value at the temperatures of −30℃ and 55℃, the situations, however, are different. At the temperature of −30℃ the discharge capacity has a positive linear correlation to the [DFEC] value (Fig. 1(a)) whereas at the temperature of 55℃ it has a negative one (Fig. 1(c)). It also can been seen from Fig. 1(b) that at 20℃ the correlation between the discharge capacity and [DFEC] value of the alloys is not so apparent as those at −30℃ and 55℃. Additionally, the discrepancy between the maximum (335 mAh/g), and minimum (290 mAh/g) of the discharge capacity of the 15 alloys at this temperature is not significant.

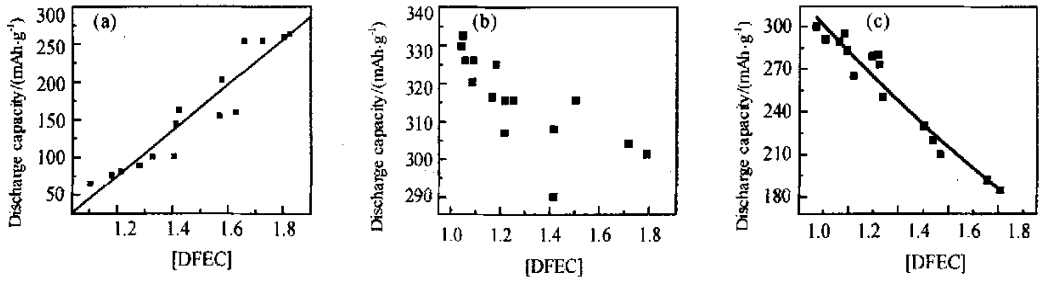

Fig. 1 Relationships between [DEFC] values and discharge capacities of alloys at different temperatures
(a)−30℃; (b)−20℃; (c)−55℃

3.2 Relationships between cell parameter and discharge capacity

The XRD analyses were made on the 15 alloys, and the results are listed in Table 3 and are shown in Fig. 2. The analyses indicate that all the 15 alloys can be indexed as AB_5-type phase with $CaCu_5$ structure, and no other second phases have been detected (Fig. 2). Importantly, when there are more than two kinds of REs in the side A of the alloys, the cell volume is not simply decreased with the reduction of La content. At the temperature of −30℃ the discharge capacity of the electrode alloys is, as shown in Figs. 3(a) and (b), negatively lineated with the cell volume (V) and axis ratio (a/c), except for a little irregular variation when the cell volume (V) is between 0.08750 nm^3 and 0.08825 nm^3 and the axis ratio (a/c) is about 1.24.

The electrochemical capacity of AB_5-type electrode alloys is closely related to its cell volume. This is

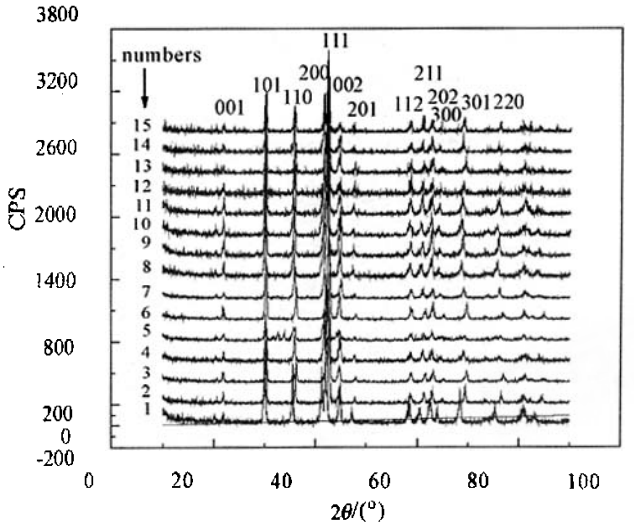

Fig. 2 Spectrum of XRD analyses on the alloys

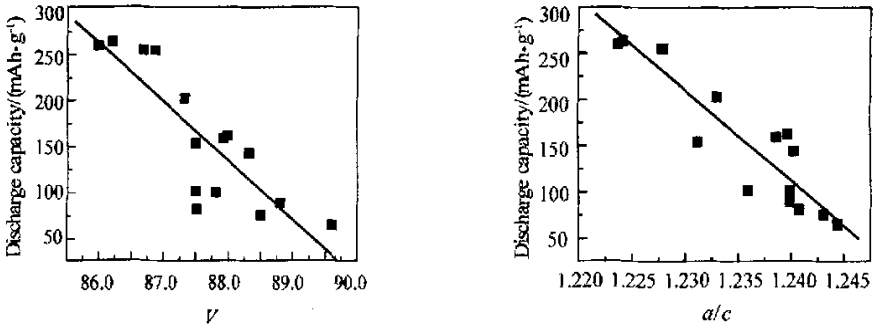

Fig. 3 Relationships between discharge capacity and the cell volume V (a) and axis ratio a/c (b) of the alloys at the temperature of −30℃

because that the bigger cell volume the larger dimension among the lattices, which would accommodate more hydrogen atoms. Nevertheless, the discharge capacity of an electrode at low temperatures, especially lower than −20℃, is mainly controlled by dynamic processes of the electrode reaction[10,11]. In this case, the smaller the cell volume the higher hydrogen-equilibrium pressure of the metal hydride, which would accelerate the diffusion rate of hydrogen in the metal matrix, therefore favorite to discharge[12]. According to the data of Table 1 and 3, when the composition of the side B of the alloy is constant, the cell volume (V) and axis ratio (a/c) would be controlled by the compositions of the REs, of which elements La and Ce have the most important effects. Since the cell volume of La is relatively large whereas that of Ce relatively small, according to Vegard principle, when there are only two REs in an alloy, increase of La content would lead to increase of the cell volume, but increase of Ce would reduce it. The effect of element Pr on the cell volume is generally at between those of La and Ce. When an alloy contains more than two REs, the influences of them on the cell volume would be very complex. In this case, it is difficult to evaluate the changing trend by using contents of individual elements.

Table 3 Cell parameters of the alloys

Lattice parameter	Sample No.							
	1	2	3	4	5	6	7	8
c	4.0578	4.0554	4.0471	4.0441	4.0434	4.0475	4.0493	4.0402
a	5.0494	5.0284	5.0196	5.0271	5.0124	4.9907	4.9721	5.0097
a/c	1.2444	1.2399	1.2403	1.2431	1.2397	1.2330	1.2279	1.2399
V	89.597	88.802	88.310	88.509	87.977	87.304	86.692	87.813

Lattice parameter	Sample No.						
	9	10	11	12	13	14	15
c	4.0546	4.0519	4.0498	4.0442	4.0450	4.0477	4.0338
a	4.9919	4.9750	4.9574	4.9985	5.0101	4.9527	5.0052
a/c	1.2312	1.2278	1.22410	1.2359	1.2386	1.2236	1.2408
V	87.499	86.853	86.191	87.503	87.929	85.985	87.517

3.3 Relationships between discharge capacity and RE compositions

The discharge capacities of the 15 alloys studied are shown as those listed in Table 4. They do not simply increase at 20℃ and 55℃ or decrease at −20℃ and −30℃ with the increase of La content. In general, to make the alloy have a relatively high discharge capacity at room temperature the atomic fraction of element La should not be less than 0.2 but and greater than 0.5 at −20℃. The fraction of element Ce should be greater than 0.2 at −20℃ and be not less than 0.5 at −30℃. In addition, the alloys No. 5 and 9 (Table 4) have discharge capacities of 335 mAh/g and 318 mAh/g at room temperature, 255 mAh/g and 260 mAh/g at −20℃, and 283 mAh/g and 273 mAh/g at 55℃, respectively. Therefore, these two alloys can meet the demand of using in a wide-range temperature. Both alloy No. 7 and No. 10 have discharge capacities of 255 mAh/g at −30℃, and 300 mAh/g and 290 mAh/g at −20℃, 317 mAh and 309 mAh/g at 20℃, and 210 mAh/g and 220 mAh/g at 55℃, respectively. So, these two alloys have good normal- and low-temperature properties and can be used as materials of low-temperature-type electrodes. Alloys No. 1 and 2 have discharge capacities of 332 mAh/g and 322 mAh/g, 300 mAh/g and 289 mAh/g at temperatures of 20℃ and 55℃, respectively, and thus can be used as materials of normal- and high-temperature-type electrodes.

Table 4 Discharge capacity of the 15 alloys at different temperatures

Tem. /℃	Sample No.							
	1	2	3	4	5	6	7	8
−30℃	65	89	144	76	163	203	255	101
−20℃	80	99	162	130	255	238	300	189
20℃	332	322	317	328	335	327	317	328
55℃	300	289	280	291	283	250	210	295
−30℃	155	255	264	102	160	260	81	

Tem./℃	Sample No.							
	1	2	3	4	5	6	7	8
−20℃	260	290	273	161	203	281	159	
20℃	318	309	302	317	290	305	308	
55℃	273	220	185	279	230	192	265	

4 Conclusions

(1) [DFEC] values can be used to predict discharge capacities of electrode materials, especially at low- and high-temperature conditions, and the predicted results are in good agreement with experimental ones.

(2) Both the cell volume (V) and axis ratio (a/c) of the alloys are negatively proportioned with the discharge capacity at a temperature of −30℃.

(3) The discharge capacity of alloy (LaCePr)$Ni_{3.7}Co_{0.6}Mn_{0.45}Al_{0.25}$ at room temperature (20℃) is not significantly decreased with the reduction of La content. If the RE compositions are properly proportioned, the alloy can have relatively high discharge capacity (>310 mAh/g) when the atomic fraction of La in the alloy is greater than 0.2. The low-temperature discharge capacity of the alloy is closely related to its Ce content. When the compositions of REs are appropriate, as long as the atomic fraction of Ce is greater than 0.2, the discharge capacity at −20℃ will be high, and if the Ce atomic fraction is between 0.2 and 0.4, the discharge capacities even at temperatures between −20℃ and 55℃ would be satisfactory; in case of a temperature of −30℃, a higher discharge capacity can be obtained if the Ce fraction is greater than 0.5. The high-temperature discharge capacity of the alloy is closely correlated with its La content. At a temperature of 55℃ the alloy would have relatively high discharge capacity (>290 mAh/g) when the La atomic fraction is greater than 0.25.

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