Effect of Ambient Temperature on the Electrochemical Properties of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ Hydrogen Storage Alloy

Xin Cai¹ · Fan-Song Wei¹ · Fan-Na Wei¹ · Huan-Huan Lu¹

Received: 6 January 2016/Revised: 1 April 2016/Published online: 10 May 2016
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2016

Abstract The effect of different ambient temperatures on the electrochemical properties of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ hydrogen storage alloy was investigated. The X-ray diffraction pattern shows that the alloy consists of LaNi_5 -type phase and A_5B_{19} -type ($\text{Ce}_5\text{Co}_{19} + \text{Pr}_5\text{Co}_{19}$) phase. With the increase of the ambient temperature, the maximum discharge capacity of the alloy electrodes increases from 353.33 (283 K) to 379.25 mAh/g (308 K), and the cyclic stability (S_{100}) of the electrodes decreases from 80.19 (283 K) to 52.04% (308 K) due to the acceleration of pulverization, corrosion and oxidation at higher ambient temperature. Moreover, it is found that the increase of the temperature can accelerate the diffusion rate of hydrogen in the alloy (D) and increase the exchange current density (I_0), which are beneficial for improving the activation performance and the high-rate dischargeability (HRD) of the alloy electrodes. The activation cycles of the electrodes decrease from 4 (283 K) to 1 (308 K), and the HRD_{900} of the electrodes sharply increases from 66.36 (283 K) to 95.64% (308 K).

KEY WORDS: Hydrogen storage alloy; Ambient temperature; A_5B_{19} type; Electrochemical property

1 Introduction

With the rapid development of the science and technology, the demand for newly typed environmental Ni/MH storage battery is fast in growth [1, 2]. The negative electrode materials are the most critical aspect of the property of the Ni/MH secondary batteries [3, 4]. Rare-earth-based AB_5 -type alloys have been widely used in our daily life. However, due to the limitation of their single CaCu_5 -type structure, their maximum discharge capacity can only reach about 330 mAh/g [5, 6], which can barely meet the demand for higher energy density of Ni/MH storage battery

[7, 8]. Although the theoretical maximum discharge capacity of the Mg_2Ni alloys is up to 1000 mAh/g, the strict conditions of hydriding/dehydriding and inferior cyclic stability make them be difficult to be widely used [9–11].

In the past decades, La–Mg–Ni system alloys have been widely studied due to their higher electrochemical properties and less cost, compared with AB_5 -type alloys [12–19]. Kohno et al. [20] found that the maximum discharge capacity of La–Mg–Ni system alloys can reach to 410 mAh/g, which is 25% higher than AB_5 -type alloys. In addition, the cyclic stability and high-rate dischargeability of La–Mg–Ni system alloys are also better than AB_5 -type alloy. So La–Mg–Ni system alloys were regarded as one of the most likely negative electrode materials for the Ni/MH storage battery.

Ternary La–Mg–Ni alloys are mainly composed of PuNi_3 -type phase, Ce_2Ni_7 -type phase or $\text{Pr}_5\text{Co}_{19}$ -type phase. The types of the phase are determined by $n[\text{LaNi}_5]$ units and $m[\text{LaMgNi}_4]$ units which alternatively stack

Available online at <http://link.springer.com/journal/40195>

✉ Fan-Song Wei
zjuwei@just.edu.cn

¹ Department of Material Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

along *c*-axis in certain ratios. Systematic studies on the high-rate dischargeability of PuNi₃-type and Ce₂Ni₇-type alloys have been carried out in the past few years. Cao *et al.* [21] observed that the discharge capacity of La_{0.95}Sm_{0.66}Mg_{0.40}Ni_{6.25}Al_{0.42}Co_{0.32} alloy could reach 311.8 and 227.0 mAh/g at a high density of 2 C and 5 C. Ouyang *et al.* [22] found that the high-rate dischargeability (HRD) at 1750 mAh/g of La_{11.3}Mg_{6.0}Sm_{7.4}Ni_{61.0}Co_{7.2}Al_{7.1} alloy could increase to 89.6%. However, the cyclic stability of the PuNi₃-type alloys and Ce₂Ni₇-type alloys needs to be further improved to meet the practical application [23–26]. The alloy we studied is Pr₅Co₁₉-type phase where *n* = 3 and *m* = 2 (3AB₅ + 2AB₂ = A₅B₁₉). Among different types of La–Mg–Ni alloys, A₅B₁₉-type (Ce₅Co₁₉ + Pr₅Co₁₉, space groups are *R*-3*m* and *P*6₃/*mmc*, respectively) alloys possess preferable maximum discharge capacity, superduper high-rate discharge property and desirable cycling stability. The study on the La_{0.84}Mg_{0.16}Ni_{3.80} alloy showed that the maximum discharge capacity of the alloy reached up to 388 mAh/g and the discharge retention remained 85.3% at the 100th cycle [27]. Liu *et al.* [28] found that the HRD at the current density of 3600 mAh/g was up to 70%. Although a number of the phases have been studied, there is still no definite conclusion about the formation of the phases due to their similar compositions and formation temperatures of the superstacking phases [29]. So the alloys used to study normally have multiphase structure.

In practical application, Ni/MH storage batteries are required to work at various working conditions. That is to say, the electrochemical properties of Ni/MH storage batteries should be kept stable in a wide temperature range. As reported by Liu *et al.* [30], the maximum discharge capacity of La–Mg–Ni–Co–Mn system alloys can substantially increase from 277.5 (253 K) to 406.2 mAh/g (303 K), while it does not change a lot above 283 K. Subsequently, Li *et al.* [31] revealed that the discharge capacity of LaNi_{3.8}Co_{0.6}Mn_{0.3} alloy is the highest at 273 K and the electrochemical properties of LaNi_{3.8}Co_{0.6}Mn_{0.3} alloy could keep stable between 273 and 303 K.

In this paper, La₄MgNi_{17.5}Co_{1.5} hydrogen storage alloy was chosen to investigate the effects of different ambient temperatures on the electrochemical properties.

2 Experimental

The La₄MgNi_{17.5}Co_{1.5} alloy was melted by vacuum levitation (under high-purity argon atmosphere), and the purity of materials was above 99.9%. The alloy was turned over and remelted 3 times to ensure its high homogeneity. Then, the as-cast alloy was annealed at 1123 K for 8 h under vacuum atmosphere. The alloy samples were manually crushed into the powder of 320 mesh size for electrochemical test and XRD investigation. The crystal structure of the La₄MgNi_{17.5}Co_{1.5}

alloy was determined by XRD analysis (Rigaku D/max 2500/PC diffractometer). The pellet electrodes (Φ10 mm × 1 mm) were made by cold pressed from the mixture of carbonyl Ni powder (400 mg) and alloy powder (100 mg) at 30 MPa. Electrochemical properties were carried out in a conventional tri-electrode cell by using an automatic charge/discharge unit (LAND). The cell was composed of an alloy working electrode, a Ni(OH)₂/NiOOH counter electrode and a Hg/HgO reference electrode, and the electrolyte was 6 mol/L KOH solution. At the same time, the ambient temperatures were controlled by thermostat water bath. The alloy electrodes were charged at 120 mA/g for 4 h and discharged at 60 mA/g to test the activation performance and the maximum discharge capacity. Meanwhile, the alloy electrodes were charged/discharged at 300 mA/g to detect the cyclic stability. All the tests above were discharged to the same cutoff potential of −0.7 V (vs. Hg/HgO). The cyclic stability and high-rate dischargeability investigated after being activated fully. The capacity retention *S*₁₀₀ was defined as

$$S_{100} (\%) = C_{100} \times 100\% / C_{\max}, \quad (1)$$

where *C*₁₀₀ was the discharge capacity at the 100th cycles [32], while the high-rate dischargeability (HRD) was defined as

$$\text{HRD}_d = C_d / (C_d + C_{60}) \times 100\%, \quad (2)$$

where *d* was decided by discharge current (*d* = 300, 600, 900 mA/g). The electrodes were first charged at 120 mA/g for 4 h, discharged at (300, 600, 900 mA/g) to −0.6 V (vs. Hg/HgO) and then discharged to −0.7 V (vs. Hg/HgO) at 60 mA/g to test the HRD.

The linear polarization curves were plotted by scanning electrode potential at a rate of 0.1 mV/s from −5 to 5 mV after 50% depth of discharge (DOD). The electrochemical impedance spectroscopy (EIS) was measured from 1 mHz to 100 kHz with an amplitude of 5 mV, which is after 50% depth of discharge too. The diffusion coefficient of hydrogen was evaluated by the potentiostatic discharge technique via discharging the electrodes with the constant potential step of 600 mV for 3000 s after being fully charged. The gas storage capacity was calculated by pressure–concentration–temperature (*P*–*C*–*T*) curve.

3 Results and Discussion

3.1 Crystal Structure

Figure 1 shows the XRD pattern of La₄MgNi_{17.5}Co_{1.5} alloy. It is found that the alloy is composed of LaNi₅ phase (CaCu₅ crystal structure, space group: *P*6/*mmm*) and A₅B₁₉ phase (Ce₅Co₁₉ + Pr₅Co₁₉ crystal structure, space group: *R*-3*m* and *P*6₃/*mmc*). According to the XRD

Fig. 1 XRD pattern of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy

pattern, the phase content and lattice parameters are calculated and listed in Table 1. It is well known that A_5B_{19} phase is beneficial to the electrodes [33, 34]. It can be seen that the content of A_5B_{19} phase is up to 61.6%, which help to improve the comprehensive electrochemical properties of the alloy electrodes.

3.2 Maximum Discharge Capacity and Activation

Table 2 shows the electrochemical properties of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy at different ambient temperatures. The theoretical discharge capacity of AB_5 is below 372 mAh/g [35], while the capacity of A_5B_{19} is up to 410 mAh/g [36]. So it can be calculated that the theoretical discharge capacity of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy is about 395.36 mAh/g. From Table 2, it is found the maximum discharge capacity is 379.25 mAh/g at 308 K, which can almost reach the theoretical discharge capacity. So the $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy is suitable to be used at room temperature.

It can be seen also that the activation and the maximum discharge capacity of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy were improved as the temperature rises. For example, the activation cycles decrease from 4 cycles (283 K) to 1 cycle (308 K) and the maximum discharge capacity increases from 353.33 mAh/g (283 K) to 379.25 mAh/g (308 K). It is noted that the maximum discharge capacity of the alloys is obviously better

than the performances of $\text{LaNi}_{3.8}\text{Co}_{0.6}\text{Mn}_{0.3}\text{Mo}_{0.3}$ at all temperatures [31]. It is well known that the hydrogen evolution reaction is endothermic reaction, which means the increase of ambient temperature can promote the charge/discharge reaction. Meanwhile, the activity of the electrolyte solution is higher and the diffusion rate of ions is faster at a higher temperature. Thus, the rising temperature can enhance the instability of metal hydride, meaning that the hydrogen is easier to be oxidized into water. So the maximum discharge capacity and activation properties of alloy electrodes are improved by raising the ambient temperature.

3.3 Cyclic Stability

The cyclic stability curves of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy are shown in Fig. 2. From Fig. 2 and Table 2, it is found that the higher the temperature is, the lower the cyclic stability is. For example, the capacity retention (S_{100}) decreases from 80.19% (283 K) to 52.04% (308 K). As seen from the above analysis, the higher ambient temperature leads to higher maximum discharge capacity, increasing the lattice expansion rate and pulverization. It is well accepted that a higher degree of pulverization will lead to more surface area being exposed to corrosive electrolyte. In addition, the increasing activity of electrolyte at higher temperature can accelerate the rate of corrosion and oxidation on the alloy electrode surface. So the alloy electrodes are corroded more seriously and have poor cyclic stability.

3.4 High-Rate Dischargeability

From Table 2, it is concluded that the HRD of the alloys is improved a lot with the increase of the ambient temperature. At a lower temperature, the discharge current has great influence on the high-rate dischargeability of the electrodes. However, when elevated to a higher ambient temperature, the discharge current has just little impact on the high-rate dischargeability of the electrodes. For example, the HRD of the alloy decreases from 89.53% (HRD_{300}) to 66.36% (HRD_{900}) at 283 K, while it just decreases from 99.54% (HRD_{300}) to 95.64% (HRD_{900}) at 308 K. The HRD_{900} of the $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy is 94.83% at 293 K, which is much higher than that of AB_5 -type alloys and other La–Mg–Ni alloys under the same discharge conditions [37–39].

Table 1 Phase structure and cell parameters of $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy electrode

Phase	Space group	Phase content (wt%)	Lattice constants (nm)		Cell volume V ($\times 10^{-3} \text{ nm}^3$)
			a	c	
LaNi_5	P6/mmm (191)	38.40	5.0324	3.9861	87.401
$\text{Ce}_5\text{Co}_{19}$	R-3m (166)	43.92	5.0409	48.4299	1064.947
$\text{Pr}_5\text{Co}_{19}$	P63/mmc (194)	17.68	5.0265	32.3339	710.823

Table 2 Electrochemical properties of La₄MgNi_{17.5}Co_{1.5} alloy electrodes at different temperatures

Temperature (K)	$C_{\max}$ (mAh/g)	N_a	S_{100} (%)	HRD (%)			R_p (Ω)	I_0 (mA/g)	D (10^{-10} cm ² /s)
				HRD ₃₀₀	HRD ₆₀₀	HRD ₉₀₀			
283	353.33	4	80.19	89.53	77.53	66.36	1.41	172.95	1.663
288	362.92	3	76.20	93.85	86.91	78.79	1.36	182.48	2.280
293	371.03	2	71.66	97.89	95.05	91.97	1.30	194.21	3.096
298	375.33	2	65.52	98.72	96.78	94.83	1.03	249.30	3.504
303	375.65	2	62.21	98.81	97.06	95.27	0.71	367.74	3.937
308	379.25	1	52.04	99.54	97.85	95.64	0.68	390.30	4.445

Fig. 2 Cycle stability curves of La₄MgNi_{17.5}Co_{1.5} alloy electrodes at different temperatures

Iwakura *et al.* [40] reported that the HRD of hydrogen storage alloy electrodes is mainly decided by the electrochemical reaction rate on the surface of the alloy and the diffusion rate of hydrogen inside the alloy. The two factors above can be characterized by the surface exchange current density (I_0) and the hydrogen diffusion coefficient (D). I_0 and D can be calculated according to the linear polarization and the constant potential step technique. Compared with other types of La–Mg–Ni alloys, there are more [LaNi₅] units in A₅B₁₉-type alloy. Some studies revealed that the hydrogen in [LaNi₅] units firstly releases and the hydrogen releases firstly may act as the electrocatalyst to accelerate the electrochemical reaction on the surface of [LaMgNi₄] units [41, 42]. As shown in Table 2, the exchange current density (I_0) of the electrodes increases from 172.95 mA/g (283 K) to 390.30 mA/g (308 K) with the increase of the ambient temperature, which is consistent with the conclusion above that the rise of the ambient temperature can promote the charge/discharge reaction. At the same time, the hydrogen diffusion coefficient (D) continuously increases from 1.663×10^{-10} (283 K) to 4.445×10^{-10} cm²/s (308 K). So the combination of the exchange current density (I_0) and the hydrogen diffusion coefficient (D) promotes the increase of

Fig. 3 P–C–T curves of La₄MgNi_{17.5}Co_{1.5} alloy electrodes at different temperatures

the HRD together, which is consistent with the study reported by Liu *et al.* [30], who also found that the exchange current density (I_0) and the hydrogen diffusion coefficient (D) both increased with the rise of the temperature.

3.5 P–C–T Isotherms

Figure 3 illustrates the P–C–T isotherms of the alloys at different ambient temperatures. For the two-phase La₄MgNi_{17.5}Co_{1.5} alloy, there are two plateau regions on the curves at all temperatures, indicating two hydrogen desorption processes. As reported by Gao *et al.* [43], the LaNi₅-type phase possesses a higher plateau pressure than the A₅B₁₉-type phase. So the higher and lower plateau regions belong to the LaNi₅-type phase and A₅B₁₉-type phase, respectively. It is found that the increase of the temperature enables the storage capacities of the alloy gradually to increase from 0.78M to 0.85 H/M. Furthermore, it can be seen that the effect of the ambient temperature on the plateau pressures is limited from 288 to 303 K (all around 0.025 MPa). The plateau pressures only increase at 283 and 308 K, which is different from the results of Cao *et al.* [44], who found the plateau pressures increased with the rise of

the temperature. This means that each kind of alloy has the most suitable temperature to be used.

4 Conclusions

The $\text{La}_4\text{MgNi}_{17.5}\text{Co}_{1.5}$ alloy consists of LaNi_5 phase (CaCu_5 crystal structure) and A_5B_{19} phase ($\text{Ce}_5\text{Co}_{19} + \text{Pr}_5\text{Co}_{19}$ crystal structure). The phase content of A_5B_{19} is up to 61.6%, which is beneficial to improve the electrochemical properties of the alloy electrodes. With the increase of ambient temperature, the activation and the maximum discharge capacity of the alloy electrodes are both improved due to the increase of instability of metal hydride and the promotion of the charge/discharge reaction. The cyclic stability of the electrodes decreases a lot with the rise of the temperature. It is because of the increase of the lattice expansion rate and pulverization and the acceleration of the rate of corrosion and oxidation on the alloy electrode surface. It is shown that the HRD of the alloy electrodes becomes more satisfactory at a higher temperature, which is proposed to be the combination of the exchange current density (I_0) and the hydrogen diffusion coefficient (D).

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (No. 50901036), Graduate Science and Technology Innovation Project of Jiangsu University of Science and Technology (No. YCX15S-18) and Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

- [1] L.H. Zhang, L.J. Zhang, *Ind. Focus* **1**, 6 (2012). (in Chinese)
- [2] W.H. Zhu, Y. Zhu, Z. Davis, J. Bruce, *Appl. Energy* **106**, 307 (2013)
- [3] M.A. Fetcenko, S. Venkatesan, S.R. Ovshinsky, *Batter. Electrochem.* **92**, 141 (1992)
- [4] L. Pei, Ph.D. Dissertation, Guangdong University of Technology, 2008. (in Chinese)
- [5] S.K. Zhang, Y.Q. Lei, L.X. Chen, G.Y. Shu, Y. Zhang, Q.D. Wang, G.L. Lv, *Trans. Nonferrous Met. Soc. China* **11**, 183 (2001)
- [6] Y. Chen, H.G. Pan, R.G. Xu, S.Q. Li, L.X. Chen, C.P. Chen, Q.D. Wang, *J. Alloys Compd.* **293–295**, 648 (1999)
- [7] Y.Q. Lei, *New Energy Materials* (Tianjin University Press, Tianjin, 2000), p. 44
- [8] W.C. Zhang, S.M. Han, J.S. Hao, Y. Li, T.Y. Bai, J.W. Zhang, *Electrochim. Acta* **54**, 1383 (2009)
- [9] Y.H. Zhang, Z.M. Yuan, T. Yang, Z.H. Hou, D.L. Zhao, *Acta Metall. Sin. (Engl. Lett.)* **28**, 826 (2015)
- [10] L.Z. Ouyang, X.S. Yang, M. Zhu, J.W. Liu, H.W. Dong, D.L. Sun, J. Zou, X.D. Yao, *J. Phys. Chem. C* **118**, 7808 (2014)
- [11] Y.H. Zhang, H.T. Wang, X.P. Dong, W.G. Bu, Z.M. Yuan, G.F. Zhang, *Acta Metall. Sin. (Engl. Lett.)* **27**, 1088 (2014)
- [12] Y. Li, Y. Tao, D.D. Ke, Y.F. Ma, S.M. Han, *Appl. Surf. Sci.* **357**, 1714 (2015)
- [13] S.M. Balogun, Z.M. Wang, H.G. Zhang, Q.R. Yao, J.Q. Deng, H.Y. Zhou, *J. Alloys Compd.* **579**, 438 (2013)
- [14] Y.H. Zhang, B.W. Li, H.P. Ren, Z.W. Wu, X.P. Dong, X.L. Wang, *Rare Met. Mater. Eng.* **38**, 941 (2009)
- [15] G. Capurso, M. Naik, S.L. Russo, A. Maddalena, A. Saccone, F. Gastaldo, D.S. Negri, *J. Alloys Compd.* **580**(Suppl 1), S159–S162 (2013)
- [16] Y. Li, S.M. Han, Z.P. Liu, *Int. J. Hydrog. Energy* **35**, 12858 (2010)
- [17] T. Yang, T.T. Zhai, Z.M. Yuan, W.G. Bu, S. Xu, Y.H. Zhang, *J. Alloys Compd.* **617**, 29 (2014)
- [18] R.H. Tang, S. Zhou, F.M. Xiao, Y. Wang, T. Sun, *Mater. Rev.* **22**, 48 (2015). (in Chinese)
- [19] A.Q. Deng, Y.Q. Luo, J.B. Fan, *Rare Met.* **44**, 99 (2015). (in Chinese)
- [20] T. Kohno, H. Yoshida, F. Kawashima, T. Inaba, I. Sakai, M. Yamamoto, M. Kanda, *J. Alloys Compd.* **311**, 5 (2000)
- [21] Z.J. Cao, L.Z. Ouyang, L.L. Li, Y.S. Lu, H. Wang, W. Liu, D. Min, Y.W. Chen, F.M. Xiao, T. Sun, R.H. Tang, M. Zhu, *Int. J. Hydrog. Energy* **40**, 451 (2015)
- [22] L.Z. Ouyang, Z.J. Cao, L.L. Li, H. Wang, J.W. Liu, D. Min, Y.W. Chen, F.M. Xiao, R.H. Tang, M. Zhu, *Int. J. Hydrog. Energy* **39**, 12765 (2014)
- [23] Z.X. Li, W. Zhu, C. Tang, B.H. Chong, X.B. Yang, *Rare Met. Mater. Eng.* **44**, 397 (2015). (in Chinese)
- [24] L.C. Pei, S.M. Han, J.S. Wang, L. Hu, X. Zhao, B.Z. Liu, *Mater. Sci. Eng. B* **177**, 1589 (2012)
- [25] J. Zhang, G.Y. Zhou, G.R. Chen, M. Latroche, A. Percheron-Guegan, D.L. Sun, *Acta Mater.* **56**, 5388 (2008)
- [26] T.Z. Si, Q.A. Zhang, G. Pang, D.M. Liu, N. Liu, *Int. J. Hydrog. Energy* **34**, 1483 (2009)
- [27] Y.M. Zhao, S.M. Han, Y. Li, J.J. Liu, L. Zhang, S.Q. Yang, *Electrochim. Acta* **152**, 265 (2015)
- [28] Z.Y. Liu, X.L. Yan, N. Wang, Y.J. Chai, D.L. Hou, *Int. J. Hydrog. Energy* **36**, 4370 (2011)
- [29] R.V. Denys, V.A. Yartys, *J. Alloys Compd.* **509**, S540 (2011)
- [30] Y.F. Liu, H.G. Pan, W.Q. Jin, R. Li, S.Q. Li, H.W. Ge, Y.Q. Lei, *Chin. J. Nonferrous Met.* **14**, 802 (2004). (in Chinese)
- [31] S. Li, H.Y. Zhou, W.P. Liu, H.G. Zhang, J.Q. Deng, Z.M. Wang, *Rare Met. Mater. Eng.* **44**, 1591 (2015)
- [32] Y.G. Tang, *Ni/MH Storage Battery* (Chemical Industry Press, Beijing, 2007), p. 132
- [33] J.J. Liu, S.M. Han, Y. Li, X. Zhao, S.Q. Yang, Y.M. Zhao, *Int. J. Hydrog. Energy* **40**, 1116 (2015)
- [34] J.B. Fan, A.Q. Deng, G.J. Xia, K.N. Qian, Y.C. Luo, *Rare Met. Mater. Eng.* **39**, 2142 (2010)
- [35] J.J.G. Willems, *Philips J. Res.* **39**, 54 (1984)
- [36] M. Li, L. Zhu, H.J. Wei, X.Y. Jian, *Chin. J. Rare Met.* **36**, 236 (2012). (in Chinese)
- [37] B.Z. Liu, A.M. Li, Y.P. Fan, M.J. Hu, B.Q. Zhang, *Trans. Nonferrous Met. Soc. China* **22**, 2730 (2012)
- [38] B.P. Wang, Y.Z. Chen, Y.N. Liu, *Int. J. Hydrog. Energy* **37**, 9082 (2012)
- [39] L. Zhang, S.M. Han, Y. Li, J.J. Liu, J.L. Zhang, J.D. Wang, S.Q. Yang, *Int. J. Hydrog. Energy* **38**, 10431 (2013)
- [40] C. Iwakura, T. Oura, H. Inouse, M. Matsuoka, *Electrochim. Acta* **41**, 117 (1996)
- [41] H.L. Chu, S.J. Qiu, Q.F. Tian, L.X. Sun, Y. Zhang, F. Xu, Y.Y. Liu, Y.N. Qi, M.Q. Fan, *Int. J. Hydrog. Energy* **32**, 4925 (2007)
- [42] Q.A. Zhang, M.H. Fan, T.Z. Si, F. Fang, D.L. Sun, L.Z. Ouyang, *J. Phys. Chem. C* **114**, 11686 (2010)
- [43] J. Gao, X.L. Yan, Z.Y. Zhao, Y.J. Chai, D.L. Hou, *J. Power Sources* **209**, 257 (2012)
- [44] Z.J. Cao, L.Z. Ouyang, H. Wang, J.W. Liu, D.L. Sun, Q.A. Zhang, M. Zhu, *J. Alloys Compd.* **608**, 14 (2014)