Study the Influences of Electrolyte Solution on the Electrochemical and Magnetic Properties of LaNi_{4.6}Ge_{0.4} Alloys

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Abstract: In this report, we studied the effect of electrolyte concentration on the electrochemical and magnetic properties of the LaNi_{4.6}Ge_{0.4} alloys used as the negative electrode in Ni-MH rechargeable batteries. Effect of electrolyte concentration on the electrochemical and magnetic properties of the LaNi_{4.6}Ge_{0.4} alloys was investigated by the measurements of magnetization curves and charge-discharge performance of the material. The results showed that the composition electrolyte solution KOH(5.1) + LiOH(0.9), the charge-discharge performance is the highest. With this concentration of magnetization curves show superparamagnetic status and the magnetized values is the highest.

Keywords: Nano, Ni-MH batteries, LaNi5, magnetic properties, hydrogen absorption.

1. Introduction

The compounds RT_5 have been known and studied a lot because of the ability to absorb and disabsorb the very large amounts of hydrogen at atmospheric pressure and room temperature which does not damage the lattice structure [1, 2]. Hydrogen accumulation in the crystal lattice of the material creates a permanent-form hydrogen container and energy reserves [3]. This feature has been applied in many fields of science and technology, one of the applications that is built rechargeable battery cathode Ni-MH [4, 5]. The advantages of Ni-MH battery are high-capacity battery and its waste does not pollute the environment [6, 7]. On the other hand, compared with Ni-Cd or the lithium battery are familiar products in the electronics and communications handed, Ni-MH battery have longer lifetime and lower cost [8].

Currently, NiMH batteries are widely used, thus improving the quality and innovation are necessary. There are many ways to improve the battery performance has been studied as: doping 3d elements capable of absorbing hydrogen [9,10], reducing particle size which increase the surface area of the electrode in contact with the electrolyte solution to increase the level of hydrogen absorption

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[11, 12], changes capable of releasing hydrogen absorption and by acting on the electrolyte solution [13, 14]. The third way takes very few interested, earlier with NiCd batteries, the electrolyte solution has been carefully studied and selected by the 6M KOH electrolyte solution thus selected now for the same type of positive electrode is NaOH [15, 16].

2. Experimental

 $LaNi_{5-x}Ge_x$ system compounds were prepared by arc-melting method in Ar gas atmosphere from the metal components of purity at least 99.9%. Here a slight excess of La and were added to compensate for the weight loss during arc-melting. The samples were turned over and re-melted several times to attain good homogeneity. The powder samples were created by milling in agate mortar during 30 minutes to grain size about 50 µm. The crystalline structure and the phase impurity of the samples at room temperature were examined by X-ray powder diffractometer, using Cu-K_a radiation. The obtained powder XRD patterns were analyzed by means of a Rietveld refinement [9] procedure using X'pert High Score Plus in order to determine the type of structure and the lattice parameters. For the electrochemical measurements, negative electrodes were prepared by mixing LaNi_{5-x}Ge_x powder with cooper and nickel powders and binder in 70:28:2 ratio of weight. This mixture was pressed onto a Nickel mesh at a pressure of 6 tons/cm². In charge-discharge capacity measurements, the all electrodes are connected to a potential device called a Bi-Potentiostat 366A. The electrodes were fully charged at current density of 50 mA/g, and then discharged at the same current density to cut-off potential of -0.7 V (versus SCE). The data is transmitted to a computer containing the software for treatment and display of results by graphical and data files. The magnetic properties of the alloys LaNi_{5-x}Ge_x were measured on vibrating sample magnetometer (VSM) in magnetic fields up to 1.2 T.

3. Results and discussion

3.1. Crystal structure analysis



Fig. 1. The X-ray diffraction spectrum of the LaNi₅ alloys.



Fig. 2. The X-ray diffraction spectrum of the powder alloys LaNi_{4.6}Ge_{0.4} and after charge-discharge 10 cycles.

X-ray diffraction (XRD) was used to investigate the crystal structure and lattice parameters of synthesized materials. Figure 2 shows the XRD patterns of the LaNi_{4.6}Ge_{0.4} system. The data confirmed that all the samples are single phase, and crystallize in the hexagonal CaCu₅-type structure, the same structure, as does the prototype LaNi₅ in Figure 1, and no secondary phase was detected within 1% error of measurements. When replacing a part of Ni by Ge in LaNi₅ alloy, crystal characteristics of the alloy remains unchanged compared to the LaNi₅ original material. Figure 2, we show the LaNi_{4.6}Ge_{0.4} alloy, the alloys remains CaCu₅ structure. Characteristics of the sample crystal decrease, it presented in of the expanded diffraction peaks and the intensity of diffraction peaks decreased. This is because the doping process can cause the stretch lattice but not much.

3.2. The electrochemical properties



Fig. 3. Cycle performance of LaNi_{4.6}Ge_{0.4} in KOH(6M).



Fig. 5. Cycle performance of LaNi_{4.6}Ge_{0.4} in KOH (5.1M) and LiOH(0.9M).



Fig. 4. Cycle performance of $LaNi_{4.6}Ge_{0.4}$ in KOH(5M) and LiOH(1M).



Fig. 6. Cycle performance of LaNi_{4.6}Ge_{0.4} in KOH (6M) and LiOH(1M).

Electrochemical measurements were performed in a three electrodes system consisting of the working electrode (WE) was the prepared sample, the counter electrode (CE) was made from inert metal (Platinum), and the reference electrode was the saturation calomel electrode (SCE) (Hg/Hg₂Cl₂, calomel). LaNi_{4.6}Ge_{0.4} sample is charged-discharged with constant current (I = 50 mA) in the electrolyte solution has been studied. Figure 3 - 6 showed the clear influence of electrolyte

composition on the performance charge/discharge of samples. The results also indicate that the sample LaNi_{4.6}Ge_{0.4} is charged/discharge in solution KOH(5,1M) and LiOH(0,9M) gives the highest performance and most stable. The purpose of LiOH addition into the 6M KOH electrolyte is to increase electrochemical activity of the MH electrode. The existence of Li in the surface oxide layer accelerates the H₂ dissociation on the surface. Therefore, under significantly oxidizing condition the powder sample of LaNi₅ can more easily react with H₂.

These results demonstrate that when much Ni is released on the surface, it will act as a catalyst for electrochemical reactions Chemical happen, raising cycle performance of materials

3.3. The magnetic properties

The magnetization curve of bulk $LaNi_5$ and $LaNi_{4.6}Ge_{0.4}$ samples curve is a straight line passing through the origin of this is characteristic of Pauli paramagnetic with magnetic susceptibility are 3.70 and 1.72, respectively. Results are shown in Figure 7.



Fig. 7. Magnetization curve of the LaNi_{4.6}Ge_{0.4} samples in bulk and powder states.

Fig. 8. Magnetization curve of the LaNi_{4.6}Ge_{0.4} samples after 10 charge-discharge cycles.

The measured magnetization curves of powder samples after 10 charge/discharge cycles at room temperature are shown in figure 8. The magnetization curves of bulk sample shows that it is paramagnetic. In contrast to the bulk sample, the magnetization curves of all powder samples after 10 charge/discharge cycles the magnetic moment of these sample have been increase significant. It is due to during repeated charge/discharge cycling this materials were undergone volumetric deformation, broken and oxidized lead to the Ni decomposed on the surface, this amount of Ni is the main cause of magnetic properties, the larger magnetic demonstrates Ni is released more.

These results demonstrate that when much Ni is released on the surface, it will act as a catalyst for electrochemical reactions Chemical happen, raising cycle performance of materials. The obtained results showed that although measurements of magnetic characteristics is relatively simple but can give us quantitative information about the microscopic processes occurring in the material used as the negative electrode in Ni-MH rechargeable battery.

4. Conclusion

The influences of electrolyte solution on the electrochemical and magnetic properties of LaNi_{4.6}Ge_{0.4} alloys have been studied. The results show that the all LaNi_{4.6}Ge_{0.4} sample in bulk state

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and after 10 charge-discharge cycles to be single phase, and crystallize in the hexagonal CaCu₅-type structure. The sample LaNi_{4.6}Ge_{0.4} after 10 charge-discharge cycles in solution KOH(5,1M) and LiOH(0,9M) gives the highest performance and most stable. The existence of Li in the surface oxide layer accelerates the H_2 dissociation on the surface. Therefore, under significantly oxidizing condition the powder sample of LaNi₅ can more easily react with H_2 . The bulk LaNi_{4.6}Ge_{0.4} samples showed Pauli paramagnetic state, after 10 charge-discharge cycles transferred to superparamagnetic state. It is due to decomposed Ni during charging/discharging cycles. The results of magnetic measurements allow us to discuss the nature of charge-discharge process.

References

- [1] B. Sakintuna, F. Lamaridarkrim, and M. Hirscher, "Metal hydride materials for solid hydrogen storage: A review^A," Int. J. Hydrogen Energy, vol. 32, no. 9, pp. 1121–1140, Jun. 2007.
- [2] M. Pentimalli, F. Padella, L. Pilloni, E. Imperi, and P. Matricardi, "AB₅/AB₅ composite material for hydrogen storage," Int. J. Hydrogen Energy, vol. 34, no. 10, pp. 4592–4596, May 2009.
- [3] K. Chou, Q. Li, Q. Lin, L. Jiang, and K. Xu, "Kinetics of absorption and desorption of hydrogen in alloy powder," Int. J. Hydrogen Energy, vol. 30, no. 3, pp. 301–309, Mar. 2005.
- [4] W. H. Zhu, Y. Zhu, Z. Davis, and B. J. Tatarchuk, "Energy efficiency and capacity retention of Ni-MH batteries for storage applications," Appl. Energy, vol. 106, pp. 307–313, 2013.
- [5] T. Sakai, H. Miyamura, N. Kuriyama, H. Ishikawa, and I. Uehara, "Rare-earth-based hydrogen storage alloys for rechargeable nickel-metal hydride batteries," J. Alloys Compd., vol. 192, no. 1–2, pp. 155–157, Feb. 1993.
- [6] F. Cuevas, J.-M. Joubert, M. Latroche, and a. Percheron-Guégan, "Intermetallic compounds as negative electrodes of Ni/MH batteries," Appl. Phys. A Mater. Sci. Process., vol. 72, no. 2, pp. 225–238, Feb. 2001.
- [7] F. Lichtenberg, U. Köhler, A. Fölzer, N. J. Adkins, and A. Züttel, "Development of AB₅ type hydrogen storage alloys with low Co content for rechargeable Ni–MH batteries with respect to electric vehicle applications," J. Alloys Compd., vol. 253–254, pp. 570–573, May 1997.
- [8] X. Zhao and L. Ma, "Recent progress in hydrogen storage alloys for nickel/metal hydride secondary batteries," Int. J. Hydrogen Energy, vol. 34, no. 11, pp. 4788–4796, Jun. 2009.
- [9] J. C. S. Casini, F. M. Silva, Z. Guo, H. K. Liu, R. N. Faria, and H. Takiishi, "Effects of substituting Cu for Sn on the microstructure and hydrogen absorption properties of Co-free AB5 alloys," Int. J. Hydrogen Energy, vol. 41, no. 38, pp. 4–10, 2016.
- [10] T. Erika, C. Sebastian, Z. Fernando, and D. Verónica, "Temperature performance of AB₅ hydrogen storage alloy for Ni-MH batteries," Int. J. Hydrogen Energy, vol. 1, pp. 2–8, 2015.
- [11] Z. Ma et al., "Effects of size of nickel powder additive on the low-temperature electrochemical performances and kinetics parameters of AB₅-type hydrogen storage alloy for negative electrode in Ni/MH battery," J. Alloys Compd., vol. 660, pp. 289–296, 2016.
- [12] R. M. Humana, J. E. Thomas, F. Ruiz, S. G. Real, E. B. Castro, and a. Visintin, "Electrochemical behavior of metal hydride electrode with different particle size," Int. J. Hydrogen Energy, vol. 37, no. 19, pp. 14966–14971, Oct. 2012.
- [13] M. Karwowska, T. Jaron, K. J. Fijalkowski, P. J. Leszczynski, Z. Rogulski, and A. Czerwinski, "Influence of electrolyte composition and temperature on behaviour of AB₅ hydrogen storage alloy used as negative electrode in Ni-MH batteries," J. Power Sources, vol. 263, pp. 304–309, 2014.
- [14] C. Izawa et al., "Improvement of H₂ absorption of LaNi₅ by LiOH pretreatment," Int. J. Hydrogen Energy, vol. 24, no. 9, pp. 879–883, Sep. 1999.
- [15] X. Zhang, Y. Chen, M. Tao, and C. Wu, "Effect of electrolyte concentration on low-temperature electrochemical properties of LaNi5 alloy electrodes at 233 K," J. Rare Earths, vol. 26, no. 3, pp. 402–405, 2008.
- [16] C. Y. V. Li, W.-X. Weng, Z.-M. Wang, and S. L.-I. Chan, "Self-discharge behavior of LaNi₅-based hydrogen storage electrodes in different electrolytes," J. Solid State Electrochem., vol. 12, no. 7–8, pp. 935–940, Mar. 2008.