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ORIGINAL PAPER

Effect of metal oxides on electrochemical performances of La–Mg–Ni-based alloys

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Abstract Metal oxides (TiO_2, Er_2O_3 and ZnO) were added to La–Mg–Ni-based hydrogen storage alloy electrodes and their effects on the structural and electrochemical properties were studied. The charge efficiency, especially at high charge current density was greatly ameliorated, and the high rate charge capability at 1440 mA g^{-1} increased from 85.1% (blank) to 94.1% (TiO_2), 93.3% (Er_2O_3) and 90.5% (ZnO). The high temperature dischargeability was also improved in case of TiO_2, Er_2O_3 and ZnO additives. These additives suppressed formation of $Mg(OH)_2$ and $La(OH)_3$ during charge/discharge process and therefore the cycling stability was improved. The discharge capacity retention at the 200th cycle increased from 72.9% (blank) to 79.6% (TiO_2), 87.5% (Er_2O_3) and 77.9% (ZnO).

Keywords Hydrogen storage alloys · Metal oxides · High temperature · Cycling stability

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1 Introduction

Nickel/Metal hydride (Ni/MH) batteries have been widely used in portable electronic devices, electric hand tools and even electric vehicles owing to their good performances and excellent environmental friendliness [1]. The commercial AB_5-type rare earth-based hydrogen storage alloys, however have been suffering from low discharge capacity as negative electrode materials, not favorable for further development of Ni/MH batteries [2, 3]. So it is urgent to develop new types of alloys with higher capacity and other electrochemical properties. Some recent research showed that La–Mg–Ni-based AB_3-type alloys were promising negative electrode materials for their comparatively higher discharge capacity; however, this type of alloys should be improved in their overall electrochemical properties, especially the cycling stability for practical application [4–7].

It was found that some 3d transition metal oxides showed noticeable catalytic effect on hydrogen absorption/desorption properties of hydrogen storage alloys [8]. It was claimed that transition metals (TMs) combined with oxygen played an important role during the sorption process, which was probably related to the improved charge exchange reactions with hydrogen molecules [9, 10]. Nb_2O_5 was added to MgH_2, partially reduced upon milling process and improved the hydrogen sorption/desorption kinetics for its 5+ less valence [11]. Iron oxides, Fe_3O_4 and Fe_2O_3, were believed to increase H-absorption rate by facilitating nucleation [10, 12]. As for use of metal oxides as additives to negative electrodes of Ni/MH batteries, CuO and ZnO were reported to form a protective layer to inhibit oxidation of lanthanide, and therefore prolong cycle life of the electrodes [13, 14]. The heavy rare earth oxides facilitate to improvement in discharging properties of Ni/MH batteries either as an additive to the $Ni(OH)_2$ electrode, or as an additive to MH electrode using AB_5-type alloys as main materials [15]. However, most of addition was applied onto the AB_5-type, and the exact mechanism on hydriding/dehydriding was not clear yet.

In order to improve electrochemical properties of the La–Mg–Ni-based alloy electrodes, some 3d transition metal oxides (TiO_2 and ZnO) and heavy rare earth oxide (Er_2O_3) were added to the electrode. Effects of these metal oxides on electrochemical properties of La–Mg–Ni-based alloy electrodes were studied.

2 Experimental

The La–Mg–Ni-based $La_{0.88}Mg_{0.12}Ni_{2.90}Mn_{0.10}Co_{0.50}Al_{0.10}$ alloy was prepared by inductive melting under argon atmosphere, followed by annealing treatment at 1,173 K for 8 h. The chemical composition of annealed ingots was examined by ICP. Then the ingots were mechanically pulverized and ground in the air. X-ray diffraction (XRD) patterns were obtained on a D/Max-2500/PC X-ray diffractometer (Cu K_α radiation), and then analyzed using a Jade-5.0 software.

0.34 g alloy powders of 200–400 meshes with 2 wt% additives (TiO_2, Er_2O_3 and ZnO) and 0.06 g carbonyl nickel powders were mixed well with two drops of 3 wt% PVA solution. The slurry was pasted onto both sides of a foamed nickel (1.8 × 1.8 cm), dried completely in vacuum at 333 K, and finally cold pressed under a pressure of 10 MPa. Electrochemical tests were performed in a system consisting of metal hydride as working electrode, $Ni(OH)_2$/NiOOH as counter electrode and 6 mol/l KOH solution as electrolyte on a DC-5 battery testing instrument at 298 K. The electrodes were fully charged (~50% over-charge rate) at 72 mA g^{-1}, and then discharged at the same current density to cut-off voltage of 1.0 V. The intervals between charge and discharge are 10 min. The full discharge capacities were measured after the electrodes were charged at different charge current densities (72, 144, 360, 720, 1080, 1,440 and 1,800 mA g^{-1}) when high rate charge ability (HRC) was measured. The high temperature characteristics of electrodes were measured at 313, 323 and 333 K.

3 Results and discussion

Capacities of the electrodes with and without additives during activation are shown in Fig. 1. It can be noticed that the electrode without additive needs 8 cycles to achieve the maximum discharge capacity, 334 mAh g^{-1}. ZnO additive reduces the activation cycle number to 4, and increases the discharge capacity slightly to 338 mAh g^{-1}. TiO_2 and Er_2O_3 decrease the discharge capacity slightly from 334 to 326 and 333 mAh g^{-1}, respectively.

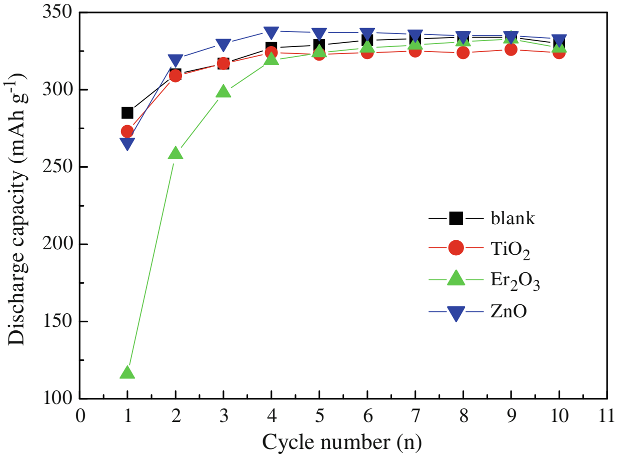

Fig. 1 Activation curves of electrodes with and without additives

The Ni/MH batteries will be more widely used if they can be rapidly charged, and therefore the charge acceptance capability, especially for the negative electrodes, should be improved [16]. The high rate charge capability (HRC) at different current density is shown in Fig. 2. It can be seen that the electrodes with metal oxides have higher HRC values, and the difference is obviously seen when the current density increases to more than 360 mA g^{-1}. When the charge current density increases to 1,440 mA g^{-1}, the HRC increases from 85.1% (blank) to 94.1% (TiO_2), 93.3% (Er_2O_3) and 90.5% (ZnO).

The effect of temperature on the electrochemical characteristics is investigated by charging/discharging the electrodes at 60 mA g^{-1} current density in the temperature range of 298–333 K. The high temperature dischargeability

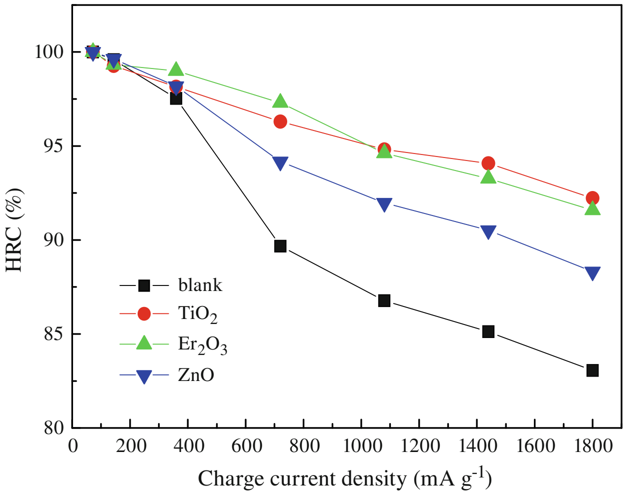

Fig. 2 HRC of electrodes with and without metal oxides

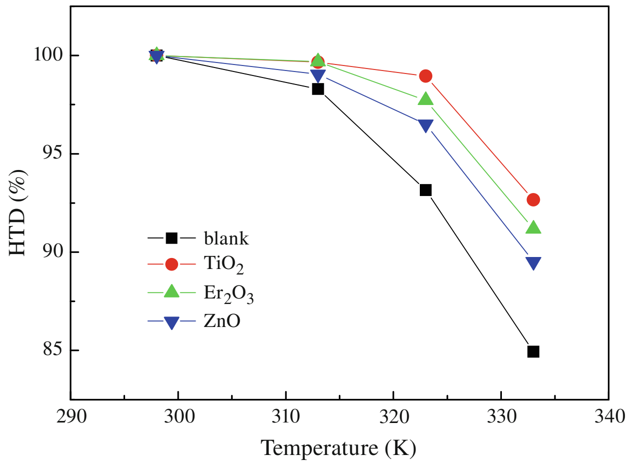

Fig. 3 High temperature discharge characteristics of electrodes with and without additives

(HTD) at different temperature is calculated according to Eq. 1 and is shown in Fig. 3.

$$\mathrm{HTD}(\%) = \frac{C_T}{C_{298}} \times 100, \tag{1}$$

where C_T is the discharge capacity at a certain temperature, mAh/g; C_{298} is the discharge capacity at 298 K. It can be seen that the discharge capacity of blank electrode is very sensitive to temperature and decreases sharply with increasing temperature when the temperature is higher than 323 K. When metal oxides, TiO_2, Er_2O_3 and ZnO are added, the decrease in discharge capacity is slow down. It should be pointed out that TiO_2 addition help to keep capacity when the temperature is below 323 K, and the electrode with TiO_2 addition keeps 99.0% of its capacity at room temperature. When the temperature increases to 333 K, the discharge capacity of all the four electrodes decreases sharply, but the capacity of electrode with additives is higher than that of the blank one. The high temperature dischargeability increases from 84.9% (blank) to 92.7% (TiO_2), 91.2% (Er_2O_3) and 89.5% (ZnO).

The *i*–*V* polarization curves for hydrogen evolution reaction (HER) are provided in Fig. 4. As shown, hydrogen evolution over-potential increases as TiO_2, Er_2O_3 and ZnO are added to the electrodes. The increase in hydrogen evolution over-potential suppress auxiliary hydrogen evolution at last charging stage, improving charge efficiency, even at high charge current density and at high temperature. Therefore, high rate charge capability and high temperature dischargeability are improved after metal oxides, TiO_2, Er_2O_3 and ZnO are added.

In order to analyze effect of additives on cycling stability of the electrodes further, capacity retention rate S_n is defined as the following equation.

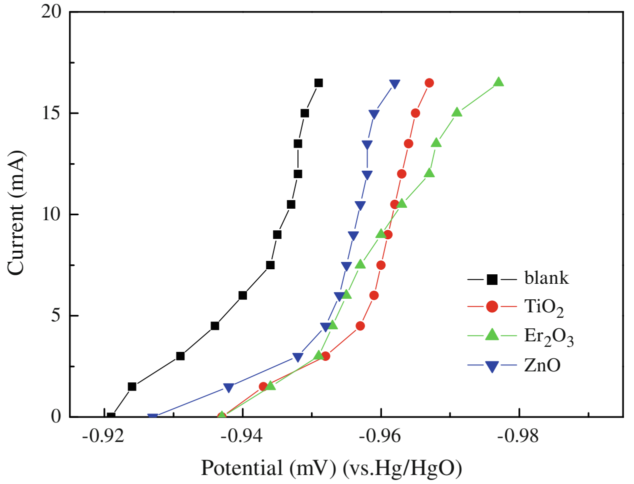

Fig. 4 Galvanostatic polarization measurement for the electrodes with and without additives

$$S_n(\%) = \frac{C_n}{C_{\max}} \times 100, \tag{2}$$

where S_n is the capacity retention at Cycle n, C_n is the discharge capacity at Cycle n, and $C_{\max}$ is the maximum discharge capacity. From Fig. 5 it can be clearly seen that the discharge capacity retention rate of electrode with additives is higher than that of the blank electrode, indicating the cycling stability is improved by adding metal oxides, TiO_2, Er_2O_3 and ZnO. The discharge capacity retention rate at the 200th cycle increases from 72.9% (unmodified) to 79.6% (TiO_2), 87.5% (Er_2O_3) and 77.9% (ZnO), respectively. Among the metal oxides, Er_2O_3 is the most effective additive to improve the cycling stability.

It is generally believed that oxidation and pulverization of alloy are the mainly reason for discharge capacity decay of metal hydride electrodes. In order to see changes in

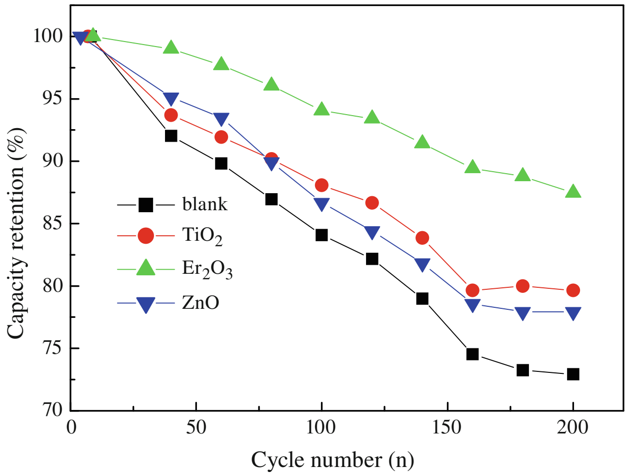

Fig. 5 Cycling stability of electrodes with and without additives

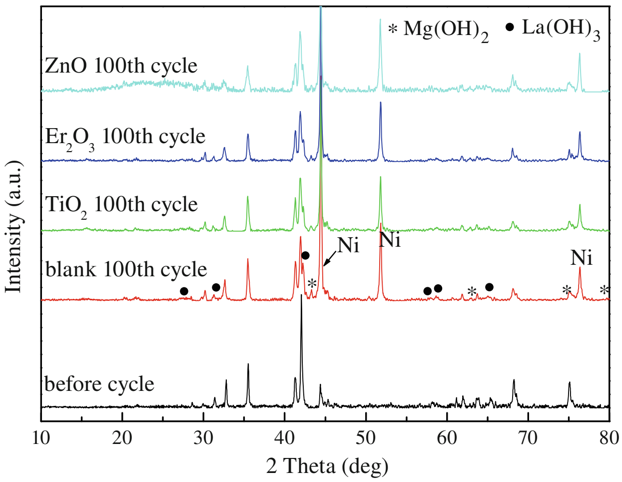

Fig. 6 XRD patterns of electrodes before and after 100 charge/discharge cycles

phase structure after cycling, the XRD patterns are measured and shown in Fig. 6. It can be seen that the main crystal structure remained even after 100 charging/discharging cycles. Compared with the pattern for alloy before cycling, some new peaks appear corresponding to $Mg(OH)_2$ and $La(OH)_3$ which are formed during the charging/discharging process. In the four patterns for alloys after cycling, the intensity for peaks corresponding to $Mg(OH)_2$ and $La(OH)_3$ varies for alloy electrodes with and without additives. The XRD patterns have weaker peak intensity of $Mg(OH)_2$ and $La(OH)_3$ for electrodes with metal oxide additives. This indicates that the alloy electrode with additives suffers from less serious corrosion during charging/discharging process, which contributes to a better cycling stability.

In light of small difference in XRD patterns, FESEM images of electrodes with and without additives after cycling are shown in Fig. 7. In Fig. 7a, surface of the electrode without additive is covered with tiny needle-like substance. EDS shows that elemental oxygen increases remarkably, that is the substance covered on the surface is $Mg(OH)_2$ and $La(OH)_3$. In Fig. 7b–d scattered needle-shaped hydroxide distribute on surface of the alloy particles, indicating that the oxide additives (TiO_2, Er_2O_3 and ZnO) are helpful to suppress oxidation of the alloy in aqueous alkali, contributing to less serious degradation in discharge capacity.

4 Conclusions

2 wt% TiO_2, Er_2O_3 and ZnO were added to AB_3-type hydrogen storage alloy electrodes and their effects on the electrochemical properties were investigated. The electrochemical measurements showed that high rate charge capability, cycling stability and high temperature dischargeability increased in case of using metal oxide additives. The high rate charge capability The HRC at

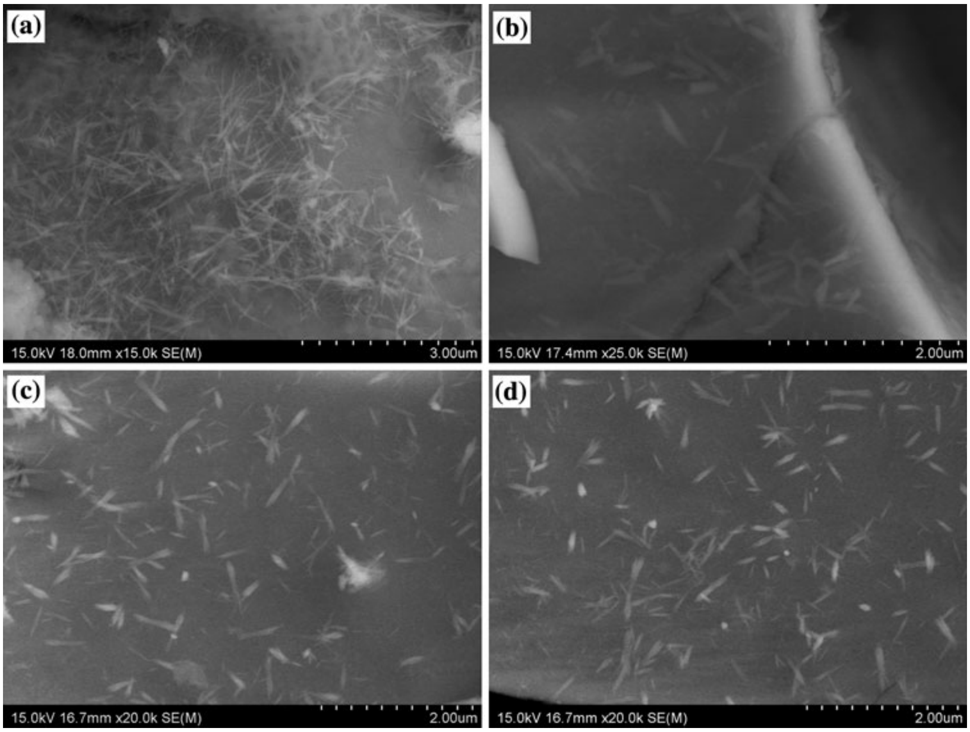

Fig. 7 SEM images of electrodes after 100 charge/discharge cycles. **a** Blank electrode; **b** TiO_2; **c** Er_2O_3; **d** ZnO

1440 mA g^{-1} increased from 85.1% to 94.1% (TiO_2), 93.3% (Er_2O_3) and 90.5% (ZnO) owing to the catalytic effect of the 3d transition metal oxides (TiO_2 and ZnO) and the heavy rare earth oxides (Er_2O_3) on hydriding of the alloy electrodes. These oxides addition suppressed oxidation of the alloys in alkaline electrolyte during charging/discharging cycles, and therefore cycling stability of the electrodes was ameliorated. The discharge capacity retention rate at the 200th cycle mounted up from 72.9% (unmodified) to 79.6% (TiO_2), 87.5% (Er_2O_3) and 77.9% (ZnO). The high temperature dischargeability was also improved, increasing from 84.9% to 92.7% (TiO_2), 91.2% (Er_2O_3) and 89.5% (ZnO) at 333 K.

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