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Effect of Rare Earth Oxide on Electrochemical behaviors of Ni-MH Battery on New Energy Vehicle

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Ni-MH Battery used in New Energy Vehicle (NEV) often presents poor electrochemical behaviors under high temperature condition. In view of this gap, this paper explores electrochemical behaviors of such Ni-MH battery that contains rare-earth elements (Y, Er, Tm, Yb, and Lu) oxides at room and high temps, and discusses the impact of rare earth elements on its charge and discharge voltage, discharge efficiency, volt-ampere characteristics and service life. The results show that the rare earth oxides change the electrochemical behaviors of the surface of the Ni-MH battery crystallites, leading to a concurrent increase in both oxygen evolution overpotential and positive electrode charge efficiency. After rare earth oxides are added, the high rate discharge efficiency of Ni-MH batteries at room temperature significantly worsens. When the discharge is greater than 3C, the Ni-MH batteries with Lu element have the lowest discharge efficiency. Ni-MH batteries containing Ni element show the oxygen evolution potential and oxidation/reduction potential difference all increase at room temperature, and the gas evolution amount of batteries containing rare earth oxides when the potentials exceed the range of oxygen evolution peak is far less than that of common Ni-MH batteries. The Ni-MH batteries perform reversely under high temperature vs. normal temperature conditions. The addition if rare earth elements can effectively improve the service life of Ni-MH batteries.

1. Introduction

Owing to the constant development of society, the non-renewable energy resources such as petroleum and natural gas are sharply consumed, resulting in the looming depletion of fossil fuels. The renewable, pollution-free green energy resources as a hotspot in the world energy field require a full development now and in the future.

NEVs are highly admired by various countries in the world because of its zero emission of exhausts and unused fossil fuels. Ni-MH Batteries, as a type of power source with high specific energy, safety and pollution-free, can well fit the bill for NEVs. However, the electrochemical behaviors of Ni-MH Batteries decreases significantly under high temperature conditions. as most part of energy power stored in Ni-MH Batteries under high temperature conditions consumes for maintaining the positive potential, the charge reaction efficiency of the positive electrode significantly decreases (Feng and Northwood, 2005; Do and Tsai, 2011). Some studies suggest that positive oxygen evolution reaction in Ni-MH batteries can ensure the normal working efficiency of them.

Ambient temperature, electrolyte concentration and pressure are the main factors that affect the positive oxygen evolution of Ni-MH Batteries, especially the temperature, which as a parameter plays the most important impact on it (Qiu et al, 2015). Some studied that metal (Zn, Cd, Ti) and non-metallic elements (alkaline earth, rare earth) were added to the positive electrode of Ni-MH Batteries in attempt to improve electrochemical behaviors of Ni-MH Batteries with the high-temperature resistance of the above elements (Inoue et al,2013). Rare earth is an ideal element that can improve the chemical properties of Ni-MH Batteries. It also contains some heavy rare-earth oxides such as Er, Tm, Yb, and Lu which greatly contribute to charge-discharge efficiency (Hong, 2001). Due to the lack of pertinent literature, there is no clear standard for the content of rare earth elements added in Ni-MH Batteries. It is of great significance to explore how the impact of the rare earth element on the electrochemical behaviors of Ni-MH batteries is subjected to change with its multiple dosages in high temperature environment (Pan et al., 2002; Xie, 2008).

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In this paper, Ni-MH Batteries containing rare earth elements (Y, Er, Tm, Yb, and Lu) oxides are investigated at room temperature and at high temperature in order to fill the gap of pure Ni-MH Batteries which presents poor electrochemical behaviors in new energy vehicles under high temperature conditions. In addition to this, here also discusses about what the impact of rare earth elements on the charge-discharge voltage, discharge efficiency, volt-ampere characteristics, and service life of Ni-MH Batteries in details.

2. Test material and method

Test materials: Nickel hydroxide, rare earth oxides, deionized water, CMC and HPMC binders.
Test method: weigh a certain amount of nickel hydroxide and rare earth, mix them for abrasive powder; add ground powder to a solution containing CMC and HPMC binder, and stir them for 2-3 h using a stirrer. The stirred mixed solution is extracted, and smeared on the surface of prefabricated foamed nickel laminated to 0.6 mm. Two pieces of cadmium are placed on both sides of the foamed nickel as a negative electrode, insert the prepared electrode into an electrolyte solution of NaOH+LiOH.
The electrochemical behaviors of the prepared Ni-MH Batteries are tested in the following four cases:
(a) charge and discharge it at 0.2C at room temperature (25°C), discharge it to 0.8V after charging for 7h, and this cycle shall be repeated 6 times in total, measure the battery capacity; charge and discharge it at 0.2C cycle at high temperature (60°C), repeat the above steps for cycles.
(b) charge and discharge it at 1C at room temperature (25°C) and high temperature (60°C), the charge time shall be set to 2h, discharge time to 0.8V, measure charge and discharge efficiency at 1C;
(c) Charge it at 0.2C for 7h at room temperature (25°C), and discharge it at 1C, 2C, 3C, 5C, 10C discharge rate to 0.8h, measure the battery performance;
Compare the test results of (a) and (b), the charge and discharge efficiency at high magnification is obtained. The batteries in this paper are added with oxides of rare earth elements such as Er, Tm, Yb, and Lu.

3. Test results and analysis

3.1 What is impact of temp on charge-discharge property of Ni-MH Batteries

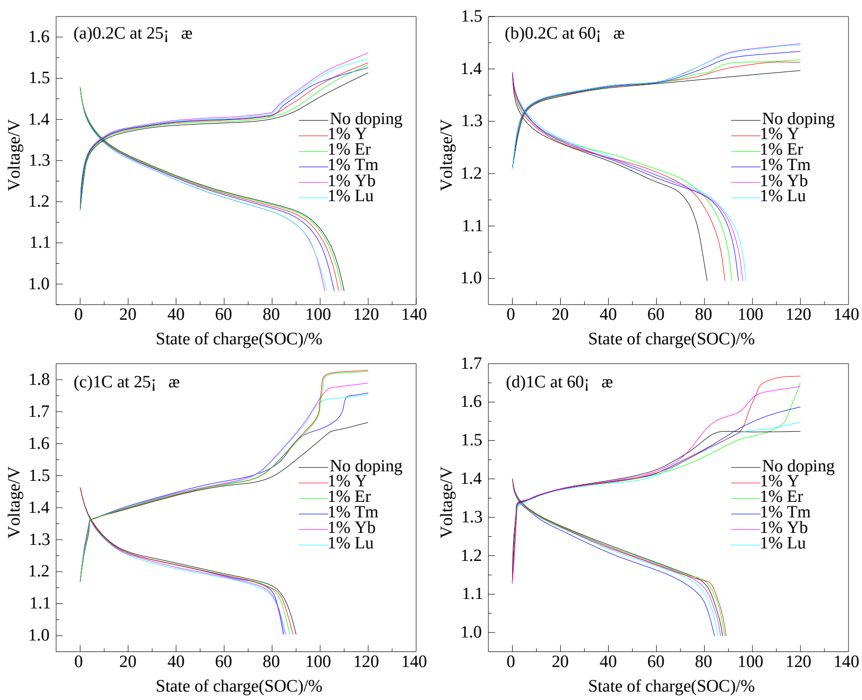

Figure 1: Charge-discharge curve of Ni-MH Batterie with REOs

As shown in Figure 1, it is the curve of the charge-discharge of Ni-MH Batteries with additives of the rare earth oxides Y, Er, Tm, Yb, and Lu at room temperature and at high temperatures. The discharge efficiencies of the electrodes under four conditions in four cases are given in Table 1. With charge-discharge at 0.2C, the discharge plateaus of common Ni-MH Batteries and Ni-MH Batteries with five rare-earth oxides at 25°C have no evident distinction, when the ambient temperature rises to 60°C, the discharge capacity of Ni-MH Batteries added with rare earth oxides presents a significant growth trend, and the charging voltage maintains a continuous increase after SOC >90%. It is suggested that the rare earth oxides improve the electrochemical behaviors of the Ni-MH Batteries crystallites, resulting in an increase in both oxygen evolution overpotential and positive electrode charge efficiency.

Table 1: Discharge efficiency of Ni-MH Batteries with REOs

Charge/discharge condition	No doping	Y	Er	Tm	Yb	Lu
25℃,0.2C / mA·h	97.2	96.3	97.3	96.0	92.7	91.7
60℃,0.2C / mA·h	74.1	79.5	84.0	86.4	86.5	88.4
$\eta_{0.2}$(60℃) / %	75.0	83.3	86.7	90.7	93.3	95.0
25℃,1C / mA·h	80.8	80.4	80.1	79.2	79.6	78.6
60℃,1C / mA·h	76.9	79.2	79.6	77.9	78.5	77.9
η_{1}(60℃) / %	95.6	98.7	98.5	96.8	99.2	99.8

It can also be seen from Table 1 and Figure 1 that after the rare earth oxide is added to the Ni-MH Batteries at 60°C, the discharge efficiency is proportional to the atomic number. Under proper conditions, rare earth oxides can be dissolved in alkaline solution to form hydroxides, and films evenly distributed on the surface of Ni-MH Batteries that has a poor conductivity. When the oxygen evolution reaction occurs on the electrode of Ni-MH batteries, the movement of electrons can be effectively suppressed, further reducing the rate of oxygen evolution reaction.

3.2 What is impact of REOs on rate discharge property of Ni-MH Batteries

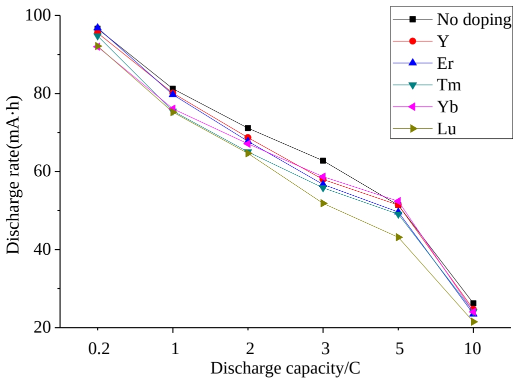

Figure 2: Discharge capacity of different types of Ni-MH Batteries at 0.2~10C at room temp

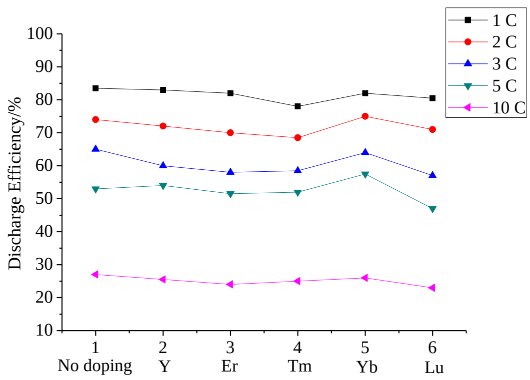

Figure 3: Discharge efficiency of different types of Ni-MH Batteries at 0.2~10C at room temp

Table 2: Median voltage of different types of Ni-MH Batteries at 0.2~10C

Discharge condition	Middle discharge voltages/V					
	No doping	Y	Er	Tm	Yb	Lu
0.2(60℃)	1.2423	1.2453	1.2426	1.2307	1.2308	1.2445
1(60℃)	1.2288	1.2209	1.2039	1.2032	1.2279	1.2215
0.2	1.2479	1.2416	1.2475	1.2517	1.2547	1.2419
1	1.2150	1.2084	1.2147	1.2246	1.2246	1.2108
2	1.1862	1.1817	1.1809	1.1925	1.1964	1.1726
3	1.1527	1.1529	1.2624	1.1638	1.1605	1.1483
5	1.0809	1.0936	1.1005	1.0963	1.0941	1.0788
10	1.1024	1.1083	1.0614	1.0544	1.0562	1.0549

As shown in Figure 2, the discharge capacities of common Ni-MH Batteries and Ni-MH Batteries with REOs at 0.2C-10C are given. Table 2 lists the corresponding median voltage. In Figure 3, there are discharge efficiencies of different types of Ni-MH Batteries at 1C-10C at room temperature. From Figure 2, Figure 3 and Table 2, we learn that after the rare earth oxides are added to the Ni-MH batteries, the discharge of the battery is greatly vulnerable. In terms of the median voltage, at the room temperature, except the Y element which has a low median voltage, the median voltages of Ni-MH batteries added with Er, Tm, Yb, and Lu are all higher than those of pure Ni-MH Batteries; the electrodes at the high temperature perform basically same behaviors.

3.3 What is the impact of REOs on volt-ampere characteristics of Ni-MH Batteries

As shown in Figure 4 and 5, there are the curves of volt-ampere characteristics of different types of Ni-MH batteries under normal and high temperature conditions, respectively. In Table 3, the parameters of oxidation/reduction peak potential and oxygen evolution potential of Ni-MH Batteries are counted up. From Figure 4, Figure 5 and Table 3, it can be seen that after the addition of rare earth oxides, various indicators of Ni-MH batteries (oxidation/reduction peak potential, oxygen evolution potential, charge-discharge cyclic voltammetry curves, etc.) all change significantly. At room temperature, Ni-MH batteries containing Ni element exhibit higher potentials for oxygen evolution and the oxidation/reduction, and the gas evolution amount of the battery containing a rare earth oxide in the region where the potential exceeded the oxygen evolution peak is far less than that of pure Ni-MH Batteries. It is much smaller than ordinary Ni-MH Batteries. The behaviors of Ni-MH batteries at high temperature is opposite to that at room temp.

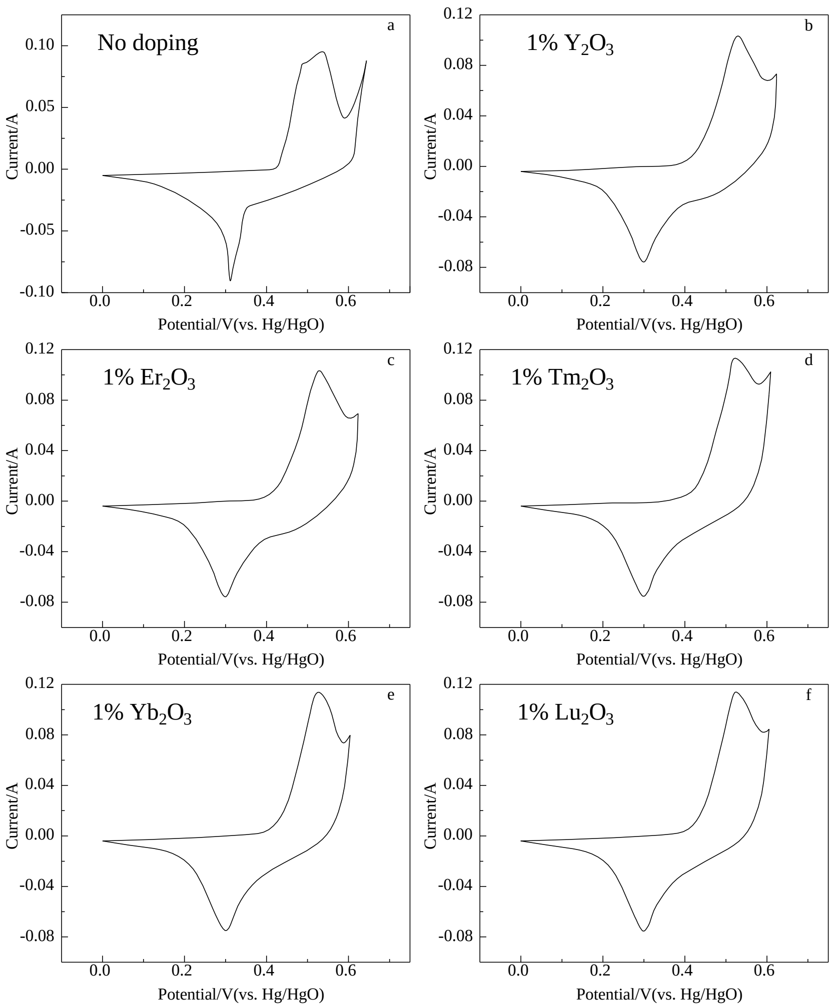

Figure 4: Curve of volt-ampere characteristics of different types of Ni-MH Batteries at room temp.

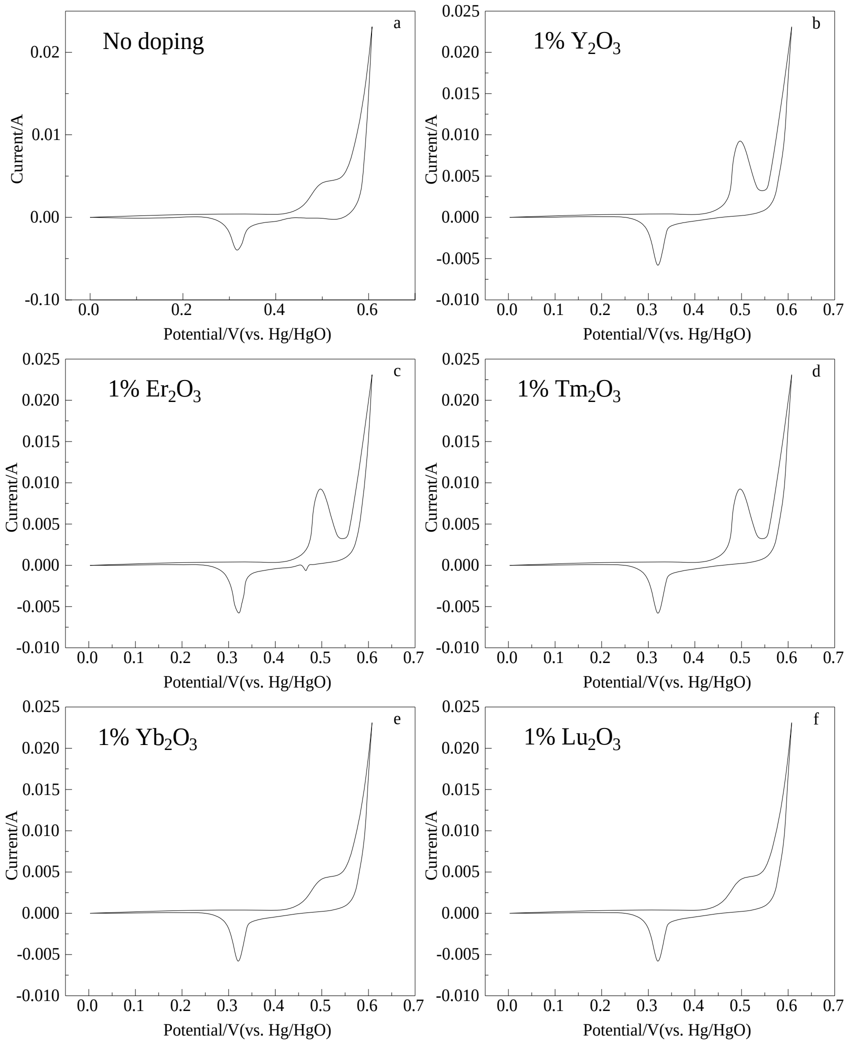

Figure 5: Curve of volt-ampere characteristics of different types of Ni-MH batteries at high temp

Table 3: Volt-ampere characteristics of different types of Ni-MH Batteries at high and room temp.

Temperature/℃	Additive	E_{pa} /V	E_o /V	E_{pc} /V	E_o–E_{pa} /mV	E_{pa}–E_{pc} /mV
25	No doping	0.534	0.596	0.321	74	212
	Y_2O_3	0.547	0.639	0.298	75	270
	Er_2O_3	0.562	0.645	0.299	79	265
	Tm_2O_3	0.574	0.642	0.287	60	276
	Yb_2O_3	0.564	0.638	0.289	74	268
	Lu_2O_3	0.571	0.643	0.285	66	274
60	No doping	/	/	0.317	/	/
	Y_2O_3	0.478	0.545	0.322	68	161
	Er_2O_3	0.480	0.551	0.312	68	170
	Tm_2O_3	0.490	0.563	0.317	58	183
	Yb_2O_3	0.488	0.552	0.313	53	190
	Lu_2O_3	0.495	0.549	0.297	53	202

The service life of different types of Ni-MH Batteries under high temperature conditions is shown in Figure 6. It is obvious that the pure Ni-MH Batteries decrease rapidly after 50 cycles of charging and discharging; after the rare earth oxides are added to the Ni-MH Batteries, after undergoing 50 cycles of charge-discharge, the capacity remains at a relatively high level, it is suggested that the addition of rare earth elements can effectively prolong the service life of Ni-MH batteries.

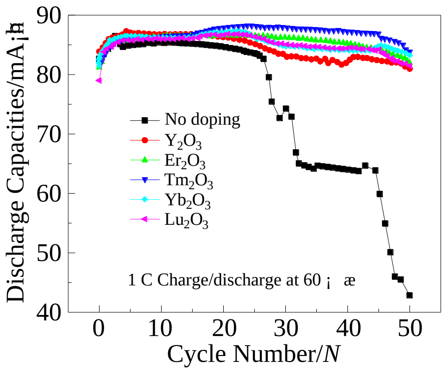

Figure 6: Service life of different types of Ni-MH Batteries at high temp

4. Conclusions

In view of the poor electrochemical behaviors of Ni-MH Batteries at high temperatures, the Ni-MH batteries containing rare earth elements (Y, Er, Tm, Yb, and Lu) oxides at room and high temperatures are explored for any higher electrochemical behaviors. Here also discusses about what is the impact of rare earth elements on the charge-discharge voltage, discharge efficiency, volt-ampere characteristics and service life of Ni-MH batteries. The findings are listed as follows

(1) The Ni-MH batteries doped with rare earth oxides significantly increase discharge capacity in high temperature environment and maintains sustained growth in charge voltage after SOC>90%. It is suggested that the rare earth oxides improve the electrochemical behaviors of the crystallites of Ni-MH batteries, resulting in double up of oxygen evolution overpotential and positive electrode charge efficiency.

(2) After the addition of rare earth oxides, the high-rate discharge efficiency of Ni-MH Batteries at room temperature swoops. When the discharge is greater than 3C, the discharge efficiency of Ni-MH batteries with Lu element is the lowest. At room temperature, Ni-MH Batteries containing Ni element exhibit an increase in the oxygen evolution potential and the oxidation/reduction potential difference, and the gas evolution amount of the battery containing a rare earth oxide in the region where the potential exceeded the oxygen evolution peak is far less than that of pure Ni-MH batteries. The behaviors of Ni-MH batteries under high temperature condition is opposite to that under normal temperature condition. The addition of rare earth elements can effectively extends the service life of Ni-MH batteries.

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Reference

Do J.S., Tsai R.L., 2011. Optimization for the formation of metal hydride electrode used in ni/mh batteries, Advanced Materials Research,306-307, 151-154, DOI: 10.4028/www.scientific.net/amr.306-307.151

Feng, F., & Northwood, D. O., 2005. Self-discharge characteristics of a metal hydride electrode for ni-mh rechargeable batteries, International Journal of Hydrogen Energy, 30(12), 1367-1370, DOI: 10.1016/j.ijhydene.2005.06.013

Hong K. 2001. The development of hydrogen storage electrode alloys for nickel hydride batteries, Cheminform, 96(1), 85-89, DOI: 10.1016/s0378-7753(00)00678-9

Inoue H., Kotani N., Chiku M., Higuchi E. 2013. Electrochemical Characterization of Rare Earth-Free Negative Electrodes for Nickel-Metal Hydride Battery Applications, ECS Meeting, 58, 19-23, DOI: 10.1149/05836.0019ecst

Pan Y.H., Srinivasan V., Wang C.Y. 2002. An experimental and modeling study of isothermal charge/discharge behavior of commercial ni–mh cells, Journal of Power Sources, 112(1), 298-306, DOI: 10.1016/s0378-7753(02)00450-0

Qiu S., Huang J., Chu H., Zou Y., Xiang C., Zhang H., 2015. Influence of zr addition on structure and performance of rare earth mg-based alloys as anodes in ni/mh battery, Metals, 5(2), 565-577. DOI: 10.3390/met5020565

Xie Q. 2008. Intelligent control technology of charge and discharge for ni-mh battery of electric vehicles, Journal of Mechanical Engineering, 44(8), DOI: 10.3901/jme.2008.08.185