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# Enhancement of the high-temperature performance of advanced nickel–metal hydride batteries with NaOH electrolyte containing NaBO<sub>2</sub>

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## ABSTRACT

In this paper, an alternative approach to improve the high-temperature performance of nickel–metal hydride (Ni–MH) batteries is proposed by introducing NaOH electrolyte with sodium metaborate (NaBO<sub>2</sub>) additives. Compared with conventional batteries using KOH electrolyte, the in-house prepared batteries with proposed electrolytes exhibit an enhanced discharge capacity, improved high-rate discharge ability, increased cycle stability and reduced self-discharge rate at an elevated temperature (70 °C). The charge acceptance of these Ni–MH batteries at 70 °C is over 96% at a charge/discharge rate of 1 C. These performance improvements are ascribed to the increased oxygen evolution overpotential, slower oxygen evolution rate and lower electrochemical impedance, as indicated by CV, steady-state polarization measurements and EIS. The results suggest that the proposed approach be an effective way to improve the high-temperature performance of Ni–MH batteries.

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## 1. Introduction

Nickel–metal hydride (Ni–MH) batteries have been intensively studied and widely used in today's power tools and portable applications due to their excellent performances and low environmental load [1–5]. Although Ni–MH batteries are commercially available, further research is still required to improve their high-temperature performance for applications in electric vehicles (EV) and hybrid electric vehicles (HEV) [6]. As is well known, the high-temperature performance of Ni–MH batteries is directly related to the behavior of the

nickel hydroxide electrode materials, which determines the cell capacity. Because of oxygen evolution readily on positive electrode at a temperature higher than 50 °C, the charge efficiency of positive electrodes is significantly degraded once the undesirable oxygen evolution reaction occurs, leading to poor performances of Ni–MH batteries at high temperatures [7,8].

In order to improve the high-temperature performances of Ni–MH batteries, considerable effort has been devoted to improving the performance of the positive electrodes, including addition of cobalt oxide (CoO) [9,10], zinc oxide [11,12], calcium fluoride [13], rare earth oxides [14–16], and

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doping of rare earth elements (Y, Er, Lu, etc.) into nickel hydroxide [17–20]. For example, with doping of yttrium, the charge acceptance of the doped nickel hydroxide increases from 41 to 82.3% at 60 °C [20]. In recent years, the high-temperature performances have been further improved through the surface modification with yttrium hydroxide [21–23], calcium phosphate [24], ytterbium hydroxide [25,26], lutetium hydroxide [27], calcium hydroxide [28] and CoOOH [29] on spherical Ni(OH)<sub>2</sub>. Although the high-temperature characteristics of Ni–MH batteries can be significantly improved by the aforementioned methods, the use of such doping or coating technology will increase the cost of Ni–MH batteries and relatively reduce the filling amount of cathode active material.

Recently, we reported a simple and economical approach of adjusting the electrolyte composition in Ni–MH batteries [30]. This approach does not affect the volume–capacity ratio of the positive electrode. Use of electrolyte additives is one of the most economic and effective methods to improve the performance of secondary batteries. However, up to now, reported literature on the effects of the electrolyte additives on the high-temperature performance of Ni–MH batteries is scarce. For sustainable commercialization of Ni–MH batteries, choosing suitable electrolyte additives and investigating the effects of the electrolyte composition on the high-temperature performance of Ni–MH batteries are of great necessity.

In this study, a cheap material sodium metaborate, which has ever been used as electrolyte additive in Zn–Ni secondary batteries to improve the cyclic performance of the negative electrode [31], was intentionally added to NaOH or KOH electrolyte as an electrolyte additive, for the first time, in Ni–MH batteries. The effects of the electrolytes on the electrochemical characteristics of Ni–MH batteries were studied.

## 2. Experimental

### 2.1. Preparation of electrodes and Ni–MH batteries

The paste nickel electrodes were prepared as follows: a mixture containing 90 wt.%  $\beta$ -CoOOH coated  $\beta$ -Ni(OH)<sub>2</sub>, 5 wt.% CoO and 5 wt.% nickel powder were mixed thoroughly through a milling procedure to ensure the uniformity of the mixture. After adding a proper amount (3 wt.%) of binders (polytetrafluoroethylene (PTFE) and carboxymethylcellulose sodium (CMC)) and distilled water, a paste with adequate rheological properties was produced by a blender through continuous stirring for 1 h. The resultant slurry was poured into a foam nickel sheet and dried at 80 °C in air. Afterward, the positive electrodes were rolled to a sheet with a thickness of 0.65 mm and cut to small pieces with dimensions of 90 mm  $\times$  41 mm  $\times$  0.68 mm. The spherical  $\beta$ -CoOOH coated  $\beta$ -Ni(OH)<sub>2</sub> used in this work was a commercial product (Henan Kelong Co., Ltd., China).

A commercial MmNi<sub>5</sub>-type hydrogen storage alloy was used for the negative electrode material. A slurry containing 96% alloy powders, 4% nickel powder and a proper amount of binders (styrene-butadiene rubber (SBR) and hydroxypropyl methyl cellulose (HPMC)) was pasted onto the nickel-coated

stainless steel strip substrates, and then dried and compressed to obtain the MH electrode. The dimensions of the pasted MH electrode plate were 125 mm  $\times$  42 mm  $\times$  0.28 mm. The capacity of the negative electrode plate was designed to be 1.5 times higher than that of the positive electrode.

A sulfonated polyolefin poriferous membrane (Vilene, Japan) with a thickness of 0.12 mm was selected as separator. After being sealed, the AA-type Ni–MH rechargeable batteries with a capacity of 1800 mAh were assembled. Four types of electrolytes were used in the experiment, which were denoted as follows—E<sub>K</sub> (for battery A): 6 M KOH + 2 wt.% LiOH aqueous solution, E<sub>Na</sub> (for battery B): 6 M NaOH + 2 wt.% LiOH aqueous solution, E<sub>K + B</sub> (for battery C): 6 M KOH + 2 wt.% LiOH aqueous solution with addition of 4 wt.% NaBO<sub>2</sub>, E<sub>Na + B</sub> (for battery D): 6 M NaOH + 2 wt.% LiOH aqueous solution with addition of 4 wt.% NaBO<sub>2</sub>.

### 2.2. Test of sealed Ni–MH rechargeable batteries and nickel electrodes

Charge/discharge measurements were conducted using a LandCT2001 battery performance testing instrument (Wuhan Jinnuo Electronics Co. Ltd, China). For activation, five charge/discharge cycles at 0.1 C were performed, and the batteries were discharged to 1.0 V. Galvanostatic charge/discharge test was carried out at 0.2 C, 0.4 C, 1 C rates under room and elevated temperatures (25 °C and 70 °C). The cut-off voltages were set at 1.0 V. In the subsequent charge–discharge cycling tests, the batteries were first charged at a 1 C rate for 1.2 h, rested for 10 min, and then discharged at a 1 C rate at 70 °C. The cut-off voltage was also set at 1.0 V. For self-discharge measurements of the Ni–MH batteries, they were initially fully charged at a 0.2 C rate for 6 h, and then stored at 70 °C for four days. The remaining capacity after storage was measured at a 0.2 C rate and compared to the discharge capacity (0.2 C) before storage.

Ex situ electrochemical tests of the nickel electrode were performed in four different electrolytes (E<sub>K</sub>, E<sub>Na</sub>, E<sub>K + B</sub>, and E<sub>Na + B</sub>) in a three-compartment electrochemical cell at 25 °C and 70 °C. Two nickel ribbon counter electrodes were placed in the side chambers and the working electrode was positioned in the center chamber. A Hg/HgO reference electrode was used via a Luggin capillary, which was made using the same alkaline solution for the working cell. CV and EIS were conducted on a Solartron SI 1260 impedance analyzer with a 1287 potentiostat interface. The CV test scan rate was 20 mV s<sup>-1</sup> and the cell potential ranged from 0.0 V to 0.8 V. For EIS, the impedance spectra were measured with the frequency range from 100 kHz to 10 mHz and an AC signal of 5 mV in amplitude as the perturbation.

### 2.3. Characterization techniques for the nickel electrodes

X-ray diffraction (XRD) was performed on a D8 diffractometer (Bruker, Germany) employing Cu K $\alpha$  radiation. The scan data were collected in a 2 $\theta$  range of 5–70°. The step size was 0.026° with a counting time of 3 s. The surface morphology of the nickel electrodes after 50 cycles at 1 C charge/discharge current rate at 70 °C was detected by the scanning electron microscopy (SEM) (SEM-6701F, JEOL, Japan).

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