



Calcium metaborate as a cathode additive to improve the high-temperature properties of nickel hydroxide electrodes for nickel–metal hydride batteries

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HIGHLIGHTS

- $\text{Ca}(\text{BO}_2)_2$ is proposed as a cathode additive to improve the Ni–MH cell performance.
- $\text{Ca}(\text{BO}_2)_2$ facilitates a more uniform distribution of Ca than other calcium additives.
- The cells with $\text{Ca}(\text{BO}_2)_2$ show excellent electrochemical performance at 25 and 70 °C.

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ABSTRACT

In this paper, a novel additive, calcium metaborate (CMB), is proposed to improve the high-temperature characteristics of the nickel electrodes for nickel–metal hydride batteries. As a soluble calcium salt, CMB can easily and uniformly be dispersed in the nickel electrodes. The effects of CMB on the nickel electrode are investigated via a combination of cyclability, capacity retention, electrochemical impedance spectroscopy, scanning electron microscope and X-ray diffraction. Compared with conventional nickel electrodes, the electrode containing 0.5 wt.% CMB exhibits superior electrode properties including enhanced discharge capacity, improved high-rate discharge ability and excellent cycle stability at an elevated temperature (70 °C). The improved cell performance of the nickel electrode containing CMB additives can be attributable to the increased oxygen evolution overvoltage and slower oxygen evolution rate. Compared with insoluble calcium salts, such as $\text{Ca}(\text{OH})_2$, CaCO_3 , and CaF_2 , CMB is more effective as a cathode additive 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 its high rate charge/discharge capability, flexible design capability for demands, and environmentally friendly nature [1–6]. 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 hydride electric vehicles (HEV) [7,8]. As is well known, the high-

temperature and high power performance is one of the key requirements for a Ni–MH power battery, and is strongly affected by the high-temperature performance of nickel hydroxide electrodes. At elevated temperatures, the undesirable oxygen evolution reaction on the positive electrode, which results in lower charge efficiency, is the main factor that restricts the high-temperature performance of the positive electrode at a high charge/discharge rate. Consequently, the capacity of Ni–MH batteries quickly fades with increased internal resistance and decreased cycle life [7,8].

To enhance the high-temperature characteristics of Ni–MH batteries, considerable attempts have been made to improve the performance of nickel electrodes, which are classified as follows:

- 1) cobalt and its compounds, such as metallic Co [9,10], $\text{Co}(\text{OH})_2$ [11,12], and CoOOH [13,14], which are the indispensable

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components in the positive electrodes of Ni–MH batteries to achieve high electrochemical efficiency.

- 2) rare earth elements (Y, Er, and Lu, *etc.* [15–18]), rare earth oxides (Y, Er, and Lu oxides, *etc.* [19,20]) and rare earth hydroxides (yttrium hydroxide [21–24], ytterbium hydroxide [25], and lutetium hydroxide [26]), which have remarkable properties that can shift the oxygen evolution potential of nickel electrodes to positive values.
- 3) calcium compounds, such as CaF₂ [27], CaCO₃ [28], Ca(OH)₂ [29,30], and Ca₃(PO₄)₂ [31], which are effective additives to raise the oxygen evolution potential of nickel electrodes, suppressing the formation of γ-NiOOH that leads to the harmful expansion of β-Ni(OH)₂ electrodes.

Nevertheless, although the high-temperature characteristics of Ni–MH batteries can be significantly improved by the aforementioned methods, the results are still not satisfying. For EV applications, the cost is a very important factor to be considered. The use of rare earth elements doping or coating greatly increases the cost of Ni–MH batteries. Thus, the cheap calcium compounds are more promising as cathode additives for Ni–MH batteries. To date, calcium compounds used in the nickel electrodes are usually insoluble calcium salts, such as CaF₂, CaCO₃, Ca(OH)₂, and Ca₃(PO₄)₂. For example, Derek et al. [27] have studied the effect of CaF₂ on the high-temperature charge acceptance of Co(OH)₂-coated Ni(OH)₂ electrode for Ni–MH batteries and concluded that the use of CaF₂ additive in the positive electrode could significantly reduce gas evolution and improve the high-temperature stability. However, the small amounts (0.5–5 wt.%) of such additives with submicron sizes are not easily and uniformly mixed with a mass of nickel hydroxide powder with a particle size of 5–15 μm in an agglomeration. As is well known, the uniformity of additives in active materials greatly affects the physical and electrochemical performance of the electrode. Therefore, a simpler and more economical method of improving the dispersancy of calcium compounds in the positive electrode is desirable.

Soluble calcium salts, which can dissolve in the slurry during the mixing process and result in a homogeneous dispersal in the active materials, may be a good choice to solve the problem. When the alkaline electrolyte is added into the assembled battery with the nickel electrode containing soluble calcium salts, Ca²⁺ of the soluble calcium salts can react with OH[−] in the alkaline electrolyte. The reaction equation is as follows:



Therefore, soluble calcium salts act similar to Ca(OH)₂, which raises the oxygen evolution potential of the nickel electrode, and minimizes the shape change of the nickel electrode. Especially, one of the advantages of using soluble calcium salts is that additives can be easily mixed with active materials and the distribution of Ca²⁺ can be greatly improved.

Up to now, few studies have been reported on the application of soluble calcium salts as cathode additives in nickel electrodes for Ni–MH batteries. This is because that the use of common soluble calcium salts, such as CaCl₂, and Ca(NO₃)₂, introduces harmful anions, which are detrimental to the properties of Ni–MH batteries. For instance, it was found that NO₃[−] could bring about so called “shuttle reactions” and result in a capacity drop of the battery during storage [32]. So, selection of suitable soluble calcium salts and investigation of their effects on the high-temperature performance of Ni–MH batteries are of great interest.

In our previous work, we have reported a novel economical approach to increase the high-temperature charge acceptance of the positive electrode through the use of sodium metaborate

(NaBO₂) as an electrolyte additive [33]. It was found that BO₂[−] could effectively improve the high-temperature performance of Ni–MH batteries. In this work, on the basis of the above research calcium metaborate (CMB), a soluble calcium salt, was selected as cathode additives in an attempt to improve the high-temperature electrochemical performance of Ni–MH batteries. The effects of CMB on the electrochemical performance of the Ni–MH battery were investigated. For comparison, other calcium additives of submicron Ca(OH)₂, CaCO₃, and CaF₂ were also included in the test.

2. Experimental

2.1. Preparation of nickel electrodes and cell assembly

The pasted nickel electrodes (*E_A*) were prepared as follows: 84.5 wt.% spherical β-Ni(OH)₂, 5.0 wt.% CoO, 5.0 wt.% nickel powder, and 0.5 wt.% CMB were thoroughly mixed with a certain amount of 5.0 wt.% hydroxypropyl methylcellulose (HPMC) and polytetrafluoroethylene (PTFE) solution as a binder to obtain a homogeneous slurry possessing adequate rheological properties. The mixed slurry was poured into a foam nickel sheet (2 cm × 2 cm) and dried at 80 °C for 5 h. Subsequently, the pasted electrodes were pressed at a pressure of 20 MPa for 3 min. For comparison, the conventional electrode without CMB additives (*E_B*) and electrodes with other calcium additives (0.5 wt.% of submicron Ca(OH)₂(*E_C*), CaCO₃(*E_D*), and CaF₂(*E_E*)) were prepared using the same method. The spherical β-Ni(OH)₂ used in this work is a commercial product (Henan Kelong Co., Ltd., China).

2.2. Electrochemical measurements

Galvanostatic charge–discharge tests were conducted using a Land CT2001A battery performance testing instrument (Wuhan Jinnuo Electronics Co. Ltd, China). For activation, five charge/discharge cycles at 0.2 C were performed, and the cells were discharged to 1.0 V. The batteries were then charged at a 1 C rate for 72 min and separately discharged at respective 0.2, 1, 2 C and 5 C discharge current rates under room and an elevated temperature (25 °C and 70 °C). The cut-off voltages were set as 1.0 V, 0.9 V, 0.7 V, respectively. In the subsequent charge–discharge cycling tests, the batteries were charged at a 1 C rate for 72 min, rested for 10 min, and then discharged at respective 1 and 5 C discharge current rates. The cut-off voltages were set as 1.0 and 0.7 V, respectively.

Cyclic voltammogram (CV), electrochemical impedance spectroscopy (EIS), and steady-state polarization measurements were conducted in a three-electrode model cell at 25 °C and 70 °C, respectively, using a Solartron SI 1260 impedance analyzer with a 1287 potentiostat interface. The test cell comprised a working electrode (the positive electrode), a counter electrode (nickel ribbon), an Hg/HgO reference electrode, and 6 M KOH + 15 g L^{−1} LiOH solution as electrolyte. For CV test, the scanning rate was between 1 mV s^{−1} and 8 mV s^{−1} over a potential range from 0.0 V to 0.8 V. For EIS measurement, the impedance spectra were recorded at an AC signal of 5 mV in amplitude as the perturbation with a sweep frequency range of 100 kHz–10 mHz. Steady-state polarization measurements were performed as follows: after the nickel electrode was fully charged at a rate of 0.2 C, it was polarized at constant potentials in 25 mV steps from 0.45 to 0.65 V vs. Hg/HgO. At each potential, the electrodes were polarized for 10 min and steady state currents were recorded.

2.3. Characterization techniques for the nickel electrodes

The morphology of the nickel electrodes were determined by scanning electron microscopy (SEM) (JEOL-JSM-6701F). The phase

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