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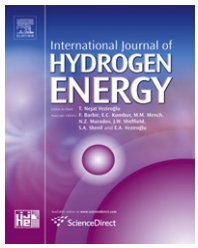

Short Communication

Sodium tungstate as electrolyte additive to improve high-temperature performance of nickel–metal hydride batteries

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ARTICLE INFO

Article history:
Received 25 December 2012
Received in revised form
9 February 2013
Accepted 11 February 2013
Available online 14 March 2013

Keywords:
Nickel–metal hydride battery
High-temperature performance
Sodium tungstate
Cycle stability

ABSTRACT

Sodium tungstate (Na_2WO_4) used as new electrolyte additive to enhance the high-temperature performance of Nickel–metal hydride (Ni–MH) battery is investigated in this paper. The effects of Na_2WO_4 on nickel hydroxide electrodes are investigated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and a charge/discharge test. It is found that the Ni–MH cell with the conventional KOH electrolyte containing 1 wt.% Na_2WO_4 additive exhibits higher discharge retention and better cycling performance than the cell without Na_2WO_4 additive at both 25 °C and 70 °C. These performance improvements are ascribed to the enhancement of oxygen evolution overvoltage and lower electrochemical impedance, as indicated by CV and EIS. The results suggest that the proposed approach be an effective way to improve the high temperature performance of Ni–MH batteries.

1. Introduction

Nickel–metal hydride (Ni–MH) batteries have been widely used in today's power tools and portable applications due to their advantages such as flexible design, excellent power, long cycle life and environmental friendliness, etc [1–5]. As is well known, as power sources for electric vehicles (EV) and hybrid electric vehicles (HEV), the Ni–MH batteries are required to work at high discharge rates in a high-temperature environment of over 60 °C in which a number of cells are connected in series to provide a high system voltage [6]. Although Ni–MH batteries are commercially available, their high-temperature performance still needs to be improved by further research.

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. Due to oxygen evolution readily on positive electrode at a temperature higher than 50 °C, the charge efficiency of positive electrodes is significantly diminished once the undesirable oxygen evolution reaction occurs, leading to poor performances of Ni–MH batteries at high temperatures [7,8].

In order to enhance the high-temperature characteristics of the positive electrodes, considerable efforts are put in to

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0360-3199/$ – see front matter
http://dx.doi.org/10.1016/j.ijhydene.2013.02.047

improve the performance of the spherical $Ni(OH)_2$ electrodes, including addition of cobalt oxide (CoO) [9,10], zinc oxide [11,12], calcium fluoride [13], rare earth oxides [14–16], doping of rare earth elements (Y, Er, Lu, etc.) into nickel hydroxide [6,17–19] and coating of rare earth hydroxide [20–25], calcium phosphate [26], calcium hydroxide [27] and CoOOH [28] on spherical $Ni(OH)_2$ powders. On the basis of these studies, the high-temperature performance of Ni–MH batteries has been significantly improved by the aforementioned methods. However, the use of such doping or coating technology, involving complex synthetic process and high cost, will increase the cost of Ni–MH batteries and relatively reduce the filling amount of cathode active material. Hence, for sustainable commercialization of Ni–MH batteries, novel economical approach of increasing the high-temperature charge acceptance of the positive electrode is desirable.

Use of electrolyte additives is one of the most economic and effective methods to improve the performance of secondary batteries, which does not affect the volume-capacity ratio of the positive electrode [29]. However, to the best of our knowledge, reported literature on the effects of the electrolyte additives on the high-temperature performance of Ni–MH batteries is very few [30].

In this paper, sodium tungstate (Na_2WO_4) was used as a novel electrolyte additive to improve the high-temperature performance of Ni–MH batteries with KOH electrolyte. The effects of the Na_2WO_4 on the electrochemical characteristics of Ni–MH cells were studied via a combination of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and a charge/discharge testing. It was found that the Ni–MH cell using KOH electrolyte with the addition of Na_2WO_4 showed excellent performance at an elevated temperature.

2. Experimental

Na_2WO_4 used in this work was of analytical grade and was used in the as-received condition without further purification. Nickel hydroxide cathode materials were purchased from Henan Kelong Co. Ltd, China.

The nickel electrodes were prepared by mixing the $Ni(OH)_2$ powder (85 wt.%), 5 wt.% CoO, 5 wt.% nickel powder and a certain amount of 5 wt.% PTFE solution. The mixed slurry was poured into a foam nickel sheet and dried at 80 °C for 5 h. Afterward, the dried electrodes were pressed at 20 MPa for 3 min to assure good electrical contact between the foam nickel and the active material.

Test cells were assembled using the prepared nickel hydroxide electrode as the cathode, a hydrogen storage alloy electrode as the anode, and a sulfonated polyolefin poriferous membrane as separator to separate the cathode and anode. For cell A, the electrolyte (E_{K+W}) used was a 6 M KOH + 2 wt.% LiOH aqueous solution with addition of 1 wt.% Na_2WO_4. For comparison, cell B was also assembled with a conventional electrolyte (E_K) composition of a 6 M KOH + 2 wt.% LiOH aqueous solution.

Charge/discharge measurements were conducted using a LandCT2001A 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, and 2 C discharge current rates under room and elevated temperatures (25 °C and 70 °C). The cut-off voltages were set as 1.0 V, 1.0 V, 0.9 V, respectively. In the subsequent charge–discharge cycling tests, the cells 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 25 °C and 70 °C. The cut-off voltage was set at 1.0 V.

Electrochemical tests of nickel electrode were performed in a three-compartment electrochemical cell at 25 °C and 70 °C. CV and EIS were conducted on a Solartron SI 1260 impedance analyzer with a 1287 potentiost interface. The CV test scan rate was 5 mV s^{-1} and the cell potential ranged from 0.0 V to 0.8 V, with nickel ribbon as the counter electrode and a Hg/HgO electrode as the reference electrode. 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.

3. Results and discussion

To evaluate the effect of the Na_2WO_4 on the high temperature performances of Ni–MH cells, the discharge curves of Ni–MH cells with the different electrolytes at 25 °C and 70 °C were

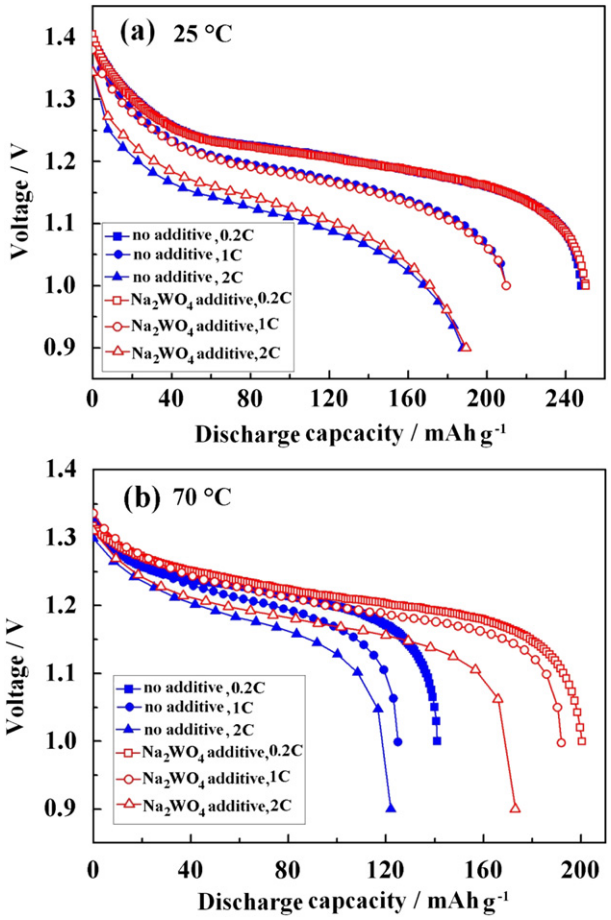

Fig. 1 – Discharge curves of Ni–MH cells using KOH electrolyte with and without 1 wt.% Na_2WO_4 additive at different discharge rates at (a) 25 °C and (b) 70 °C.