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Effects of different electrolytes containing Na_2WO_4 on the electrochemical performance of nickel hydroxide electrodes for nickel–metal hydride batteries

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ABSTRACT

To improve the high-temperature performance of the nickel hydroxide electrodes in nickel–metal hydride batteries, sodium tungstate (Na_2WO_4) used as an electrolyte additive has been added into two types of binary electrolytes (KOH–LiOH and NaOH–LiOH) in this study. The effects of electrolyte composition on the electrochemical performance of nickel electrodes have been systematically investigated via a combination of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM), energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and charge/discharge tests. It is found that by adding (1.0 wt.%) Na_2WO_4 , the performance of nickel electrodes is significantly improved in both NaOH and KOH electrolytes at 70 °C. The improved performance can be attributed to the deposition of $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ solid film on the surface of nickel electrode, which is beneficial to the increase in oxygen evolution overpotential, the slow-down of oxygen evolution rate and the decrease in charge-transfer resistance.

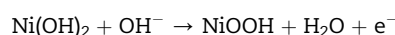
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1. Introduction

As a result of its excellent electrochemical properties, nickel hydroxide ($\text{Ni}(\text{OH})_2$) has been intensively studied and widely used as a cathode material in all nickel-based commercial rechargeable alkaline batteries, especially for nickel–metal hydride (Ni–MH) batteries [1–6]. Ni–MH power battery has been widely used for electric vehicle (EV) and hybrid electric

vehicle (HEV) applications [7,8]. 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 [9].

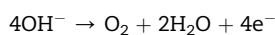
It is well known that the oxidation reaction of Ni(II) to Ni(III) occurs in an earlier period of the charging process.



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However in the subsequent period, oxygen evolution reaction (OER) on Ni(OH)₂/NiOOH electrode as a side reaction gradually dominates.



Because the oxygen evolution overpotential on Ni(OH)₂/NiOOH electrode drops rapidly at an elevated temperature, the competition between the charging of Ni(OH)₂ and OER becomes more serious [10]. Therefore, at elevated temperatures, because the charge efficiency of the electrode significantly declines, the prosperities of Ni–MH batteries are adversely affected, resulting in capacity fading, increased internal resistance and decreased cycle life [10,11].

In order to enhance the high-temperature characteristics of nickel electrode, considerable efforts have been made on researching in spherical Ni(OH)₂ powder with various additives such as cobalt, zinc, calcium, or rare-earth-based oxides and hydroxides [12–19]. On the basis of these studies, rare-earth-based additives show great influence on the high-temperature performance of the batteries. It was found that the doping of rare earth elements (Y, Yb, Lu, etc.) into nickel hydroxide can significantly improve the performance of nickel hydroxide at an elevated temperature [20–23]. In recent years, the method of surface coating with yttrium hydroxide [24–26], calcium phosphate [27], ytterbium hydroxide [28,29], lutetium hydroxide [30], calcium hydroxide [31,32] and CoOOH [33] on nickel hydroxide powders has been developed to further improve the high-temperature performances of nickel hydroxide.

Nevertheless, although numerous studies have been carried out to enhance the characteristics of nickel hydroxide electrodes, the results are still not satisfying. For EV applications, the cost is a very important factor to be considered. The use of the aforementioned rare earth elements doping or coating technology will increase the cost of Ni–MH batteries. Therefore, for sustainable commercialization of Ni–MH batteries, a simpler and more economical method to increase the high-temperature charge acceptance of the positive electrode is desirable.

Recently, a novel economical approach to increase the high-temperature charge acceptance of the positive electrode through the use of sodium tungstate (Na₂WO₄) as an electrolyte additive has been reported [34]. It was found that Na₂WO₄ can be an effective electrolyte additive to improve the high-temperature performance of Ni–MH batteries. Especially, the results proved that the high-temperature discharge capacity of Ni–MH batteries could be greatly affected by the chemical composition of the electrolyte. In our previous work [34], we have studied the effect of Na₂WO₄ on the electrochemical characteristics of Ni–MH cells with KOH electrolyte. However, how the tungstate ion functions is not clear. Moreover, it is necessary to further investigate the effect of Na₂WO₄ in different electrolytes on the performance of Ni(OH)₂ electrodes before it can be used in commercial batteries. Hence, the goal of this work is to further investigate the effect of different electrolytes containing Na₂WO₄ on the electrochemical performance of nickel electrodes with a focus on exploring its mechanisms of action.

On the basis of our previous work [34], sodium tungstate as an electrolyte additive has been added into two types of binary KOH–LiOH and NaOH–LiOH electrolytes in this study. The effects of electrolyte composition on the electrochemical performance of nickel electrodes have been systematically investigated via a combination of cyclic voltammetry, electrochemical impedance spectroscopy, scanning electron microscope, energy-dispersive X-ray analysis, X-ray diffraction and charge/discharge tests.

2. Experimental

2.1. Electrolyte preparation and cell assembly

Nickel electrodes were fabricated as follows. The nickel hydroxide powders were mixed with CoO and nickel powder in a weight ratio of 88:5:5 together with a small amount (2 wt.%) of polytetrafluoroethylene (PTFE) aqueous solution as a binder and then the mixture was forced into a nickel foam to form a 2 cm × 2 cm electrode. After drying at 80 °C for 5 h in air, the nickel hydroxide electrode was pressed at a pressure of 20 MPa for 3 min to assure good electrical contact between the nickel foam and the active material.

Test cells were assembled using the prepared nickel hydroxide electrode as the cathode, two pieces of hydrogen storage alloy electrodes made from commercial AB₅ hydrogen storage alloys as the anode, and a sulfonated polyolefin porous membrane as separator to separate the cathode and anode. Four types of electrolytes were used in the experiment, which were denoted as follows—E_{Na} contains NaOH, E_K contains KOH, E_{K+W} contains KOH + Na₂WO₄ and E_{Na+W} contains NaOH + Na₂WO₄.

The wt.% values for Na₂WO₄ were calculated using the ratio of the addition weight of Na₂WO₄ to the total weight of electrolyte.

In all the above experiments, the reagents used were of A.R. grade and the electrolyte was prepared with deionized water.

2.2. Electrochemical tests

Galvanostatic charge/discharge measurements were conducted using a Land CT2001A battery tester (Wuhan Jinnuo Electronics Co. Ltd. China). For activation, five charge–discharge cycles at 0.1C were performed, and the batteries were discharged to 1.0 V. Actual galvanostatic charge/discharge test was carried out at 0.2C, 1C, 2C charge/discharge current rates at 25 °C and 70 °C. The cut-off voltages were set as 1.0, 1.0, 0.9 V, respectively. In the subsequent charge–discharge cycling tests, the batteries were charged at a 1C rate for 1.2 h, rested for 10 min, and then discharged at 1C discharge current rate to a limited voltage of 1.0 V at 25 °C and 70 °C. The discharge capacity of the nickel hydroxide in the positive electrode was calculated based on the amount of active material Ni(OH)₂ without taking into account the additives in the electrode.

Ex situ electrochemical tests of nickel electrode were performed in four different electrolytes (E_K, E_{Na}, E_{K+W}, and E_{Na+W}) in a three-compartment electrochemical cell at 25 °C and

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