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Fabrication of bipolar nickel metal hydride batteries with nanometer copper oxide as anodic additive

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Abstract

The bipolar nickel metal hydride batteries were fabricated with a novel anodic additive of nanometer copper oxide. Cycle voltammetry indicated that the nanometer copper oxide in the anode electrode was reduced to copper in the first charge, and SEM and EDS proved the sphere copper particles deposited on the alloy surface and stably existed in the next cycles. EIS results revealed the lower contact resistance and charge transfer resistance of the nanomaterial added anode electrode. Moreover, the bipolar battery with the nanometer additive displayed excellent electric performance and increased specific energy and power in electrochemical tests, which made it better meet the requirement of power sources for electric and hybrid vehicles. The present work has provided a novel additive of the anode electrode to effectively improve the performance of the bipolar Ni/MH batteries.

Keywords: Nanometer additive; Bipolar battery; Electric vehicle

1. Introduction

With ever increasing concerns over global environmental considerations such as air pollution, green house effect and acid rain, research and development of electric vehicles (EV) and hybrid electric vehicles (HEV) are being actively conducted [1–3]. The bottleneck of the development of EV or HEV technologies is the hysteretic development of the batteries used on vehicles [4–6]. Bipolar Ni/MH battery is a promising battery system for electric and hybrid electric vehicles, which has more compact structure and lower resistance than monopolar battery (Fig. 1), and possesses many advantages such as high specific energy and power, excellent high rate discharge capability and less inert materials [7].

As for the power sources of EV or HEV, the high specific power and energy are the most important properties of the batteries. Currently, there are mainly two ways to increase the specific power and energy of the battery: one is to enhance the performance of the electrodes; and the other is to reduce the weight of the battery. Current researches most concern on the first aspect of increasing the performance of the electrodes. In the past, various methods have been introduced to improve the performance of the anode and cathode electrode, such as mixture of various additive, alkaline or acid etching, ball-milling and micro-encapsulation [8–15]. Feng and Northwood have studied the properties of the MH electrode microencapsulated Cu, and they found that the microencapsulated electrode had higher exchange current density and better high-rate dischargeability compared with the untreated one [16,17]. However, little attention has been paid to the second aspect of reducing the weight of the battery, and the main study of this aspect is improving the battery design, such as fabrication bipolar batteries. Furthermore, it is expected that the specific power and energy of the battery will be greatly increased if the above two aspects can be combined. Therefore, great efforts have been made to find new methods to combine the two aspects and improve the performance of the battery.

Recently, copper oxide (CuO) is explored to be used as a new class of electrode materials for rechargeable lithium-ion batteries [18–20]. Tarascon et al. studied the discharge mechanism of a CuO electrode and demonstrated that the final reduction product was metallic copper grain dispersed in the matrix. The unusual electrochemical reduction product of copper oxide and

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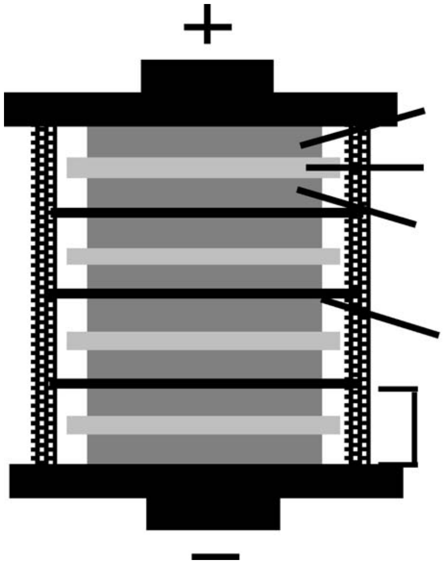

Fig. 1. Schematic diagram of a bipolar battery: (1) positive electrode; (2) separator; (3) negative electrode; (4) bipolar plate; (5) a single cell in bipolar battery.

its large specific capacity attract us and motivate us to use the nanometer CuO as a novel anodic additive for the bipolar Ni/MH batteries.

In this paper, we report this novel anodic additive of nanometer CuO for bipolar Ni/MH batteries. The reaction mechanism of the nanometer CuO additive in the anode electrode is probed and its influences on the weight of the anode and the bipolar battery are investigated. Moreover, the electrochemical resistance of the anode electrode is studied and the electrochemical performance of the bipolar battery is tested.

2. Experimental

2.1. Preparation of nanometer CuO

The nanometer CuO was prepared by solid-state reaction at room temperature [21]. Eight grams of NaOH and 17.1 g $CuCl_2{\cdot}2H_2O$ was separately pretreated in the agate mortar to mill for 10 min. Then the two powders were mixed and keep on milling for 30 min at room temperature. After the mixture changed from shallow green to entirely black, it was put into the distill water of 200 mL and imposed into ultrasonic for 20 min. At last, the product was washed with distilled water and methanol and then dried in vacuum at 50 °C.

2.2. Preparation of anode electrode

The $LaNi_5$-type hydrogen storage alloy (La is 13.25 wt.%, Ni is 69.37 wt.%, Co is 7.14 wt.%, Mn is 4.86 wt.%, Ce is 3.15 wt.%) was sieved and only particle size between 300 and 400 mesh was used. The alloy power was mixed with the prepared CuO of 5 wt.% and a small amount of PTFE (0.5 wt.%) and CMC (1 wt.%) to form a mixture. The mixture was pasted into porous foamed nickel substrates (5 cm × 5 cm), followed by rolling to form the electrode. At last the electrodes were dipped into the mixed solution of PTFE (1 wt.%) and CMC (2 wt.%), and dried in vacuum at 50 °C for 12 h.

2.3. Assemble of bipolar battery

The positive electrodes were made with the same process as the anode electrodes. The nickel hydroxide was mixed with a small amount of PTFE (0.5 wt.%) and CMC (1 wt.%) to form a mixture. The mixture was pasted into porous foamed nickel substrates (5 cm × 5 cm), followed by rolling to form the electrode.

The bipolar plates were made by welding the positive and negative electrodes on both sides of a thin steel plate (0.08 mm), which was nickel coated. The edges of bipolar plates were sealed with frames made of ABS polymer to prevent the leakage of the electrolyte. The bipolar battery was assembled with bipolar plates and separators by compression and adhesion.

2.4. Electrochemical measurement of the anode electrode

The electrochemical impedance (EIS) and cycle voltammogram (CV) measurements were performed in a glass cell with three compartments separated by sintered glass tubes. The MH electrode was placed in the central compartment and a nickel hydroxide electrode with the larger capacity was placed in the compartment of one side as counter electrode, and a porous sintered glass was placed in the center of the glass tube connecting the two compartments. A Hg/HgO electrode was placed in another compartment as reference electrode and a luggin capillary tube was placed close to the working electrode in order to minimize the ohmic drop across the electrolyte solution. The EIS and CV measurements were both carried out with Solartron 1280 electrochemical analysis system. The voltage perturbation of EIS was 5 mV and the frequency was swept from 20 kHz to 5 mHz. The scan range of CV was −1.2 to 0.2 V, and the scan rate was $5\ \mathrm{mV\,s^{-1}}$.

2.5. Electrochemical tests of bipolar battery

Electrical testing of the bipolar batteries was carried out with a computer-controlled cycling equipment. The batteries were activated by charge/discharge cycling at a low rate. High-rate constant current pulse discharge and charge were performed with electric and hybrid electric vehicle battery testing system made by Arbin.

2.6. Examination of morphology, composition and particle size

Surface morphology of the hydrogen storage alloy power was observed with a scanning electron microscope (SEM) linking with an energy dispersive spectrum (EDS). The lattice structure of the CuO powder was confirmed by X-ray diffraction (XRD) with Cu Kα radiation. The morphology of the CuO was examined by transmission electron microscope (TEM) with an accelerating voltage of 100 kV.