



Hydrogen storage alloys/reduced graphite oxide: an efficient hybrid electrode with enhanced high-rate dischargeability



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ARTICLE INFO

Article history:

Received 27 November 2015
Received in revised form 28 March 2016
Accepted 29 March 2016
Available online 29 March 2016

Keywords:

Hydrogen storage alloy
Reduced graphite oxide
High-rate dischargeability
Nickel metal hydride battery

ABSTRACT

The main challenge of applications of nickel metal hydride batteries in high power fields, new-energy vehicles, power tools, military devices, etc., originates from poor high-rate dischargeability of their negative electrode material—hydrogen storage alloys (HSAs). Here we report the design and synthesis of a composite by coating HSAs with reduced graphite oxide (RGO) via a top-down route. The capacity retention rate of the fabricated HSAs/RGO hybrid electrode reaches 51.25% at a discharge current density of 3000 mA g^{-1} , which is almost 4 times that of bare HSAs electrode (13.51%). Such an enhanced high-rate dischargeability performance is caused by (1) high specific surface area of RGO to increase active sites; (2) high conductivity of RGO to accelerate the charge transfer rate; and (3) unique interconnected RGO sheets among HSAs to reduce the internal resistance.

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1. Introduction

Clean and efficient energy storage devices are vigorously pursued due to rising concerns about the limited global energy supply, environment pollution and climate change [1–3]. Among these devices, nickel metal hydride (Ni-MH) batteries still represent the state-of-the-art technology in the market owing to their inherent safety, excellent temperature flexibility and environmental benefit [4–6]. Ni-MH batteries have already been widely used in portable electric devices, power tools and some new-energy vehicles, such as Honda Insight and Toyota Prius, which play an important role in reducing the fossil fuel consumption and CO_2 emission [7–9]. However, the power density of Ni-MH batteries, which is dominated by the high-rate dischargeability (HRD) of their negative electrode materials—hydrogen storage alloys (HSAs) [10], needs further enhancement in order to meet the growing market requirements [11]. Thus, numerous efforts have been implemented to investigate the HRD properties of HSAs recently.

Nowadays, AB_5 -type HSAs, which own CaCu_5 -type hexagonal structure (P6/mmm), are the most universally adopted negative electrode materials for Ni-MH batteries [12]. Typically, MH electrode pellets for electrochemical tests are prepared by pressing the mixture of active materials (HSAs) and binding materials (such

as polytetrafluoroethylene, graphite, metal powders etc. [13,14]). The HRD performance of the electrode is determined by the electrochemical kinetics on the electrode surface and the diffusion rate of hydrogen atoms in the active material [15,16]. Following this principle, a number of novel strategies have been developed to improve HRD properties of AB_5 -type HSAs in recent years. The additives with high conductivity and specific surface area, e.g. carbon nanotubes, are added into HSAs to enhance the HRD performance of electrodes [17,18]. Mechanical milling the mixtures of HSAs and graphite, transition metals, carbon nanotubes, etc., has also been introduced by bringing excellent electric catalytic agents [19,20]. Moreover, surface modifications like fluoridation treatment, electroless plating (Ni, Ni-P coatings) and alkaline treatment have been performed to increase the surface conductivity of electrodes [21–23]. These approaches have been demonstrated to be effective, but the improvements of HRD performance are limited [21,23]. Furthermore, the deformation and amorphization of HSAs is detrimental to the electrode for the mechanical milling, and elaborate control of the coating thickness is necessary for the electroless plating [19,21,23]. Thus, the development of novel electrode materials for applications in high-power Ni-MH batteries is still on the way.

Graphene, an amazing two-dimensional material with large surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), has shown superior electrical conductivity and thermal conductivity, chemical stability, structural flexibility and reassembly properties [24,25]. These merits enable graphene to hold strong promise in incorporating with metals and metal oxides to improve their electrochemical performance.

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Recently, SnO₂/graphene, Co/graphene, Co₃O₄/graphene, and graphene/nanosized silicon composites have been fabricated and utilized as anode materials in lithium ion batteries and lithium-sulfur batteries, exhibiting excellent cycle stability and rate capability [26–30]. Graphene-based hybrid nanocomposites (SbS₂/graphene, SnO₂/graphene) have also shown enhanced electrochemical performance as electrodes of sodium ion batteries [31,32]. In addition, graphene oxide/MnO₂ nanocomposites are utilized to improve the electrochemical properties of supercapacitors [33]. All these superior performances primarily result from high conductivity and large surface area of graphene, leading to faster electrochemical reaction rate, as well as charge and ion transfer rates in the electrodes [28,29,32]. Moreover, graphene sheets could act as bridges to connect active particles, significantly decreasing the internal resistance and polarization [33,34]. Thus, graphene as a promising material has been incorporated in energy storage devices to improve their HRD performance, and this is also applicable for Ni-MH batteries [34].

Here we present a rational design and synthesis of a novel material as the negative electrode of Ni-MH batteries composed of HSAs and reduced graphene oxide (RGO) i.e. HSAs/RGO composite. Such a hybrid electrode possesses superior HRD performance. The electrochemical capacity retention could reach 51.25% at a discharge current density of 3000 mA g⁻¹, which is almost 4 times that of bare HSAs electrode (13.51%). The large surface area and high electrical conductivity of RGO enabled the composite faster surface electrochemical reaction, which boosts the enhanced HRD properties.

2. Experimental

The procedure to prepare HSAs/RGO hybrid electrodes involves the synthesis of RGO and the incorporation of HSAs as depicted in Fig. 1a. Briefly, GO is prepared by a modified Hummers' method [35–37] and sonication. Then, HSAs are incorporated into the above GO dispersion, followed by the co-reduction treatment of GO with hydrazine [38–40]. Subsequently, the HSAs/RGO composites are annealed to further reduce GO to RGO and also to increase the interactions between HSAs and RGO [29]. After that, the composites are rinsed with ultrapure water and ethanol, and then dried. The details are given below.

The (LaCeY)(NiMnCoAl)₅ alloy was prepared by radio-frequency inductive melting of rare earth elements (99.5%) and other metallic elements (99.9%) in a copper crucible under a protective Ar atmosphere. The sample was re-melted for five times to ensure its homogeneity, and then the ingot was annealed at 1000 °C for 5 h under an Ar atmosphere. The annealed ingot was ground mechanically to fine powders with an average particle diameter of 50 ± 10 μm measured by Malvern particle analyzer Mastersizer 2000.

The graphite oxide was synthesized by a modified Hummers' method. A mixture of graphite flakes (3.0 g) and KMnO₄ (18.0 g) was added into the concentrated H₂SO₄/H₃PO₄ (360:40 ml) solution. The as-prepared graphite suspension was heated to 50 °C and stirred for 12 h. The suspension was then cooled to room temperature (25 °C) and poured onto ice (400 ml), followed by addition of 30% H₂O₂ (9 ml). After that, the suspension was filtered by utilizing a 0.2-μm (pore size) polytetrafluoroethylene (PTFE) membrane and washed with 30% HCl and ultrapure water. The purified graphite oxide suspension was then dispersed in water to create the dispersion liquid with a concentration of 0.5 mg ml⁻¹. Exfoliation of the graphite oxide to GO was achieved by sonicating the above dispersion liquid for 30 min.

The HSAs/RGO composite was fabricated by a top-down method described as follows. The above homogeneous GO dispersion (100 ml) was mixed with 100 ml ultrapure water and 0.5 g (LaCeY)(NiMnCoAl)₅ alloy in a flask. After sonicating for 30 min, 43.75 μl hydrazine solution (35 wt% in water, Aladdin) and 700 μl ammonia solution (28% in water) were added into the mixture. The flask was then vigorously shaken or stirred for several minutes at room temperature. After that, the flask was put into a water bath (95 °C) for 1 h. Subsequently, the dark mixture was filtered through an Anodisc membrane filter (0.2-μm pore size) and rinsed with ultrapure water and ethanol for several times and then dried in a vacuum oven. The fabricated composite was annealed in a tube furnace at 400 °C for 5 h under an Ar/H₂ atmosphere. The weight percent of HSAs in the composite was determined by inductively coupled plasma (ICP) measurements.

The morphological and structural characteristics of the HSAs/RGO composite and (LaCeY)(NiMnCoAl)₅ alloy were performed by using a field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL, 15 keV) and a transmission electron microscope (TEM,

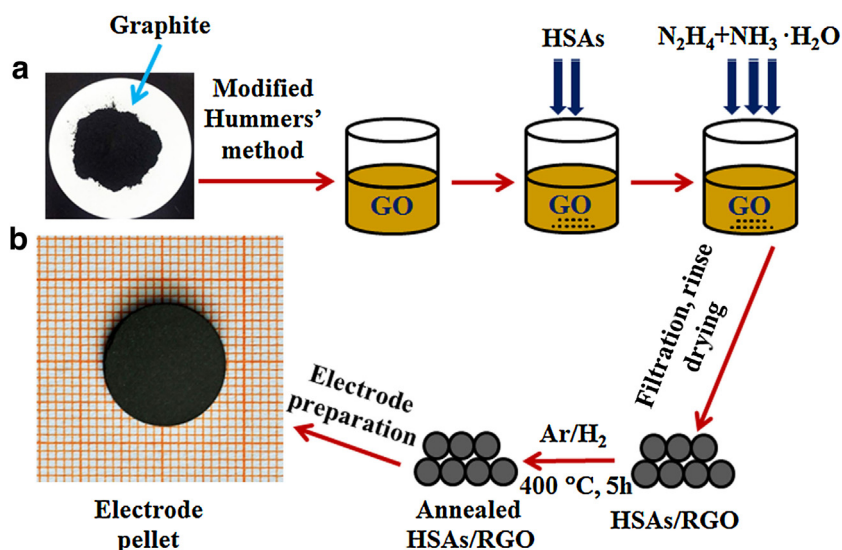


Fig. 1. A schematic illustration of the fabrication of HSAs/RGO composite and electrode pellets. (a) The synthesis route of HSAs/RGO composite. (b) The photograph of an electrode pellet for electrochemical measurements.

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