

Full paper

Molecule-confined FeOx nanocrystals mounted on carbon as stable anode material for high energy density nickel-iron batteries

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ABSTRACT

Nickel-iron (Ni-Fe) rechargeable batteries are attractive as sustainable solutions for large-scale electrical energy storage because of their low cost, eco-friendliness and safety, but their iron anodes always suffer from low capacity and poor stability, which greatly limits their wide applications. We present here a molecular confinement strategy to fabricate ultrasmall iron oxide nanocrystals firmly mounted on carbon (mc-FeOx/C) that works as stable anode material for high energy density Ni-Fe batteries. Compared with conventional iron oxide on carbon synthesized without molecular confinement (FeOx/C), the mc-FeOx/C exhibits a much higher capacity (370.2 vs 159.5 mAh g⁻¹ at a current density of 2 A g⁻¹) and better stability (capacity retention of 93.5% vs 61.2% after 1000 charge/discharge cycles). When to further combine with a nickel cathode, the mc-FeOx/C based Ni-Fe battery delivers an energy density up to 173.7 Wh kg⁻¹, among the highest value for Ni-Fe batteries reported so far. The mc-FeOx/C based Ni-Fe battery also offers excellent rate capability (e.g., 112.6 Wh kg⁻¹ at 28.9 kW kg⁻¹) and good stability (capacity retention of 91.6% after 1000 cycles), retaining their applications for large-scale electrical energy storage.

1. Introduction

Large-scale electrical energy storage highly requires rechargeable batteries that can deliver high energy efficiency and also are safe, cost-efficient and environment-friendly [1–5]. Rechargeable batteries such as lithium-ion and lead-acid batteries are commercially available but almost none of them are sufficiently robust, environment-friendly or cost-effective to respond to the growing demand of large-scale electrical energy storage with load leveling, peak shaving and micro-grids [6–9]. On the other hand, nickel-based rechargeable batteries such as nickel-iron (Ni-Fe) and nickel-air batteries using aqueous electrolytes are attractive as a sustainable solution for large-scale electrical energy storage owing to their safety, low cost and eco-friendliness [10–12]. In particular, Ni-Fe batteries could provide high energy density and both Ni and Fe are abundant on earth [13,14], holding great promise for large-scale electrical energy storage devices. However, iron anodes in currently developed Ni-Fe batteries always suffer from relatively low energy density and poor stability, which might be caused by the large particle size of active iron materials and their weak coupling with supporting matrix/current collector [15]. Additionally, passivation of the iron anode by iron hydroxide that is produced during the discharge

process always occurs [16], preventing further anodic utilization and leading to poor rate capability.

Considerable efforts have been devoted to improving the electrochemical properties of iron anodes for Ni-Fe batteries, and a popular way is to synergistically combine active iron-based nanoparticles and carbon materials, which not only improve electrical conductivity but also help to reduce particle size and passivation of the iron anodes [17–19]. However, most of currently fabricated iron anodes comprising iron nanoparticles and carbons still face challenges such as relatively slow reaction kinetics of active iron nanoparticles and weak coupling between the two materials. For example, an iron anode consisting of Fe nanoparticles wrapped with graphitic shells was obtained by pyrolysis of polymeric complexes containing iron salts, exhibiting improved cycling stability [18]. Nevertheless, the graphitic shell wrapped Fe nanoparticles showed an energy density of 136.7 Wh kg⁻¹ at a power density of 0.7 kW kg⁻¹ and only retained around 52% of the energy density (71.4 Wh kg⁻¹) at 11.7 kW kg⁻¹. This poor rate capability should be caused by the restrained reaction kinetics of Fe nanoparticles resulted from graphitic shell wrapping. Another way to utilize carbon materials in iron anodes is to deposit iron-based nanoparticles on surface of carbon nanomaterials. As an example, an iron anode comprising

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iron oxide nanoparticles (nanoparticle size in the range of 5–10 nm) grown on reduced graphene oxide (FeOx/rGO) was synthesized by a solution phase reaction followed by a thermal annealing step [19]. The FeOx/rGO anode exhibits a high initial capacity of around 300 mAh g^{-1} , which should benefit from the small particle sizes for high active site density. In addition, the FeOx/rGO anode shows a good rate capability, indicating that the small FeOx nanoparticles grown on carbon can reduce passivation of the iron anode. Nevertheless, the FeOx/rGO anode quickly decays to be around 200 mAh g^{-1} (capacity loss of 33.3%) after 200 cycles. It is found that the weak coupling of the FeOx nanoparticle with the underlying rGO is the reason for the poor stability. By using glucose during the thermal annealing step to increase the coupling, the stability of the FeOx/rGO was improved but still loss around 20% capacity after 300 cycles. Therefore, exploration of effective approaches to fabricate small size iron-based nanoparticles on carbon with strong coupling is critical to build high performance iron anodes, eventually benefiting the development of high energy density and stable Ni-Fe batteries.

We present here a molecular confinement approach to fabricate ultrasmall iron oxide nanocrystals that are firmly mounted on carbon (mc-FeOx/C). The molecular confinement is realized by conformation matching of organic molecules of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) with graphitic carbon. After molecular assembly and thermal annealing, ultrasmall FeOx nanocrystals are uniformly formed and mounted on carbon materials, enabling strong bonding between the two components. Morphology and structures of the mc-FeOx/C were investigated, followed by exploring its electrochemical performance using control sample of conventional FeOx nanoparticles on carbon (FeOx/C) that were prepared without molecular confinement. The mc-FeOx/C was further demonstrated as active material of iron anode for Ni-Fe battery together with a nickel complex-based nickel cathode.

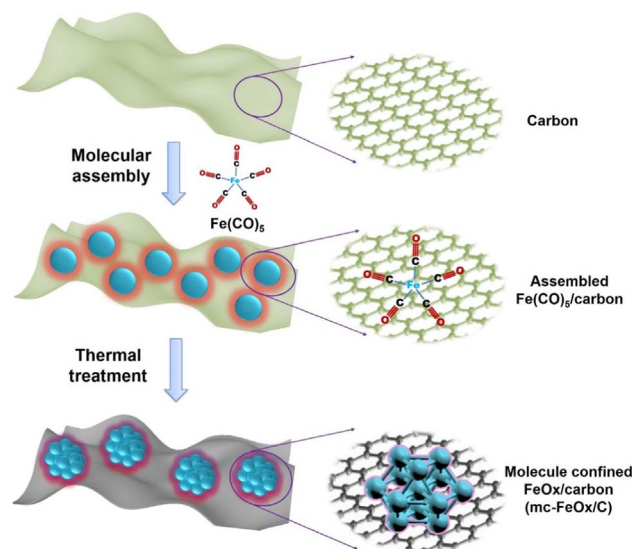
2. Materials and methods

2.1. Material synthesis

Carbon material was synthesized through a blowing route using glucose as carbon precursor and NH_4Cl as blowing agent. 2.0 g of glucose was mixed with NH_4Cl with a molar ratio of 1:1, and the mixture was thermally treated at a rate of $5 \text{ }^\circ\text{C min}^{-1}$ up to $950 \text{ }^\circ\text{C}$ for 3 h in a tubular furnace under a nitrogen atmosphere. Once cooling to room temperature, the obtained samples were treated with hot water to remove excess NH_4Cl . The mc-FeOx/C was synthesized by a molecular confinement approach using organic molecule of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and as-prepared carbon. In details, 0.2 g of as-prepared carbon was dispersed in 0.2 L of acetonitrile under sonication for 60 min, followed by slowly adding 1.0 g $\text{Fe}(\text{CO})_5$ into the above solution and sonicated for another 60 min. Subsequently, the assembled $\text{Fe}(\text{CO})_5/\text{C}$ was collected by centrifugation, washed with acetonitrile to remove excess $\text{Fe}(\text{CO})_5$. Then, the $\text{Fe}(\text{CO})_5/\text{C}$ sample was treated at a rate of $5 \text{ }^\circ\text{C min}^{-1}$ up to $800 \text{ }^\circ\text{C}$ for 2 h under a nitrogen atmosphere, producing mc-FeOx/C. For comparison, a control sample of iron oxide particles on as-prepared carbon (FeOx/C) was synthesized by mixing FeCl_3 and carbon, which was treated using the same procedure as that of the mc-FeOx/C. Nickel complex that was used for nickel cathode was fabricated as reported [20]. 32.0 ml of N, N-dimethylformamide, 2.0 ml of ethanol and 2.0 ml of water were mixed in a glass bottle, followed by adding 0.75 mmol benzenedicarboxylic acid. Subsequently, 0.75 mmol nickel chloride and 0.8 ml triethylamine was added to the above solution. Afterwards, the colloidal solution was ultrasonicated for around 6 h, followed by centrifugation and drying.

2.2. Material characterizations

Morphology and structure of the materials were investigated by transmission electron microscopy (TEM, JEM-2010F), and field



Scheme 1. Scheme showing the use of molecular confinement approach to fabricate mc-FeOx/C from organic molecules of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and carbon.

emission scanning microscopy (SEM, JSM-6700F). Compositions were determined by energy dispersive X-ray spectroscopy (EDS, JSM-6700F) and thermogravimetry (TGA)-differential thermal analysis (DTA) (Shimadzu DTG-60). During the TGA measurement, the samples were heated from room temperature up to $800 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$ in a dynamic atmosphere of air using α -alumina crucibles. The crystal structure was characterized by powder X-ray diffraction (XRD, Bruker AXS X-ray Diffractometer). Nitrogen adsorption-desorption experiments were carried out at 77.3 K by means of an Autosorb analyzer. X-ray photoelectron spectroscopy (XPS) characterizations were performed on a PHI Quantera X-ray photoelectron spectrometer with a chamber pressure of 5×10^{-9} Torr, a spatial resolution of $30 \text{ } \mu\text{m}$ and an Al cathode as the X-ray source to determine compositions.

2.3. Electrochemical measurements

Material inks were prepared by mixing active material and PTFE (60 wt% water suspension) in a ratio of 50:1 by weight, and then dispersed in ethanol under stirring for 2 h, resulting in a concentration of 1 mg ml^{-1} with respect to the active material. The material ink was drop-casted into a piece of carbon foam with a loading of around 1 mg cm^{-2} with respect to the active material. The ink coated carbon foam were dried at $100 \text{ }^\circ\text{C}$ under vacuum for 12 h. All the working electrodes in this work were prepared following the above procedures unless otherwise noted. A typical three-electrode cell with a platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode was used to study electrochemical behaviors of the materials. Impedance spectroscopy spectra were recorded with an amplitude of 5 mV from 0.1 Hz to 100 kHz under open circuit potentials. Ni-Fe batteries were measured in a two-electrode configuration with mc-FeOx/C (or FeOx/C) based iron anode and a Ni complex based nickel cathode. The two electrodes were separated by a filtration membrane, and 1 M KOH was used as the electrolyte. All the measurements were conducted at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$).

2.4. Calculations

Charge-discharge specific capacity (C , mAh g^{-1}) was calculated from discharge profiles at different current densities using equation of $C = I \times \Delta t / m$, where I , Δt and m are the discharge current density, discharge time, and mass of the active material mass. Energy density E

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