GCEP Report
Ultra-Fast Rechargeable Nickel/Zinc Batteries

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Abstract

High-performance, low-cost and environmentally friendly batteries are important to portable electronics, stationary grid storage and electric vehicles. Since starting this project, we explored the synthesis of β-phase $Ni(OH)_2$ and Al, Co-codoped α-phase $Ni(OH)_2$ (NiAlCo) nanoplates covalently attached onto oxidized few-walled carbon nanotubes (β-$Ni(OH)_2$/CNT and NiAlCo/CNT). These hybrid materials were investigated as the cathode material of rechargeable Ni/Zn batteries. They exhibited high specific capacity of ~220 and ~350 mAh/g for β-$Ni(OH)_2$/CNT and NiAlCo/CNT respectively, and long cycling stability with < 20 % capacity loss after 1,000 charge-discharge cycles. Due to delayed start of the project, we will request an extension to use the synthesized materials to develop fully rechargeable Ni/Zn batteries with an ultrahigh power density and fastest charging and discharging time in seconds.

Background

Battery technologies provide a solution to the storage of intermittent renewable energy, playing important roles in decreasing our dependence on fossil fuels[1]. Li-ion batteries are taking the leading role currently[1-3]. They have high energy density, but suffer from insufficient power density, their high cost and flammable nature[1-3]. On the other hand, traditional aqueous batteries are often cost effective and relatively safe, but are limited in energy density[3-4]. Nickel/zinc (Ni/Zn) batteries are one type of alkaline rechargeable with an open circuit voltage of ~1.7 V and a high theoretical energy density of 372 Wh/kg[3-4]. They have higher working voltage than other alkaline systems (*e.g.* Ni/Cd or Ni/MH). Considering their lower cost and non-flammable nature, Ni/Zn batteries are one promising candidate to power future electric vehicles. However, practical Ni/Zn batteries have limited performance with energy density of 55~85 Wh/kg and power density of ~0.2 kW/kg, constrained by available battery electrode materials up to now, for both Ni and Zn sides[3-5].

Results thus far

a. Successful preparation of α- or β-phase $Ni(OH)_2$ nanoplates on carbon nanotubes (CNTs)

We developed a multi-step solution method to synthesize α- or β-phase $Ni(OH)_2$ nanoplates on few-walled CNTs. The method enlists controlled hydrolysis of metal salts at a low temperature (~80^oC) in a DMF/H_2O mixed solvent, followed by solvothermal treatment at a higher temperature (~120-150^oC) to afford the desired phase and crystallinity of metal hydroxide and the simultaneous reduction of oxidized carbon nanotubes. Introduction of a small fraction of Al and Co precursors (~20 at% in total) induced the formation of layered double hydroxide (LDH), which has an equivalent structure to α-phase $Ni(OH)_2$.

Transmission electron microscopy (TEM) images in Figure 1b-c show that the typical β-$Ni(OH)_2$/CNT and NiAlCo/CNT we obtained. The resulting β-$Ni(OH)_2$/CNT hybrid contain ~100 nm β-$Ni(OH)_2$ nanoplates with irregular shapes interconnected by CNTs, while co-doping of trivalent Al and Co cations not only converts the chemical structure, but also transforms the

final hydroxide product to much smaller oval-shaped thin nanoplates (~15 nm in width and ~2 nm in thickness). X-ray diffraction (XRD) (Figure 1d) confirm the formation of brucite β-$Ni(OH)_2$ (black) and LDH with large interlayer spacing of 0.71 nm (red).

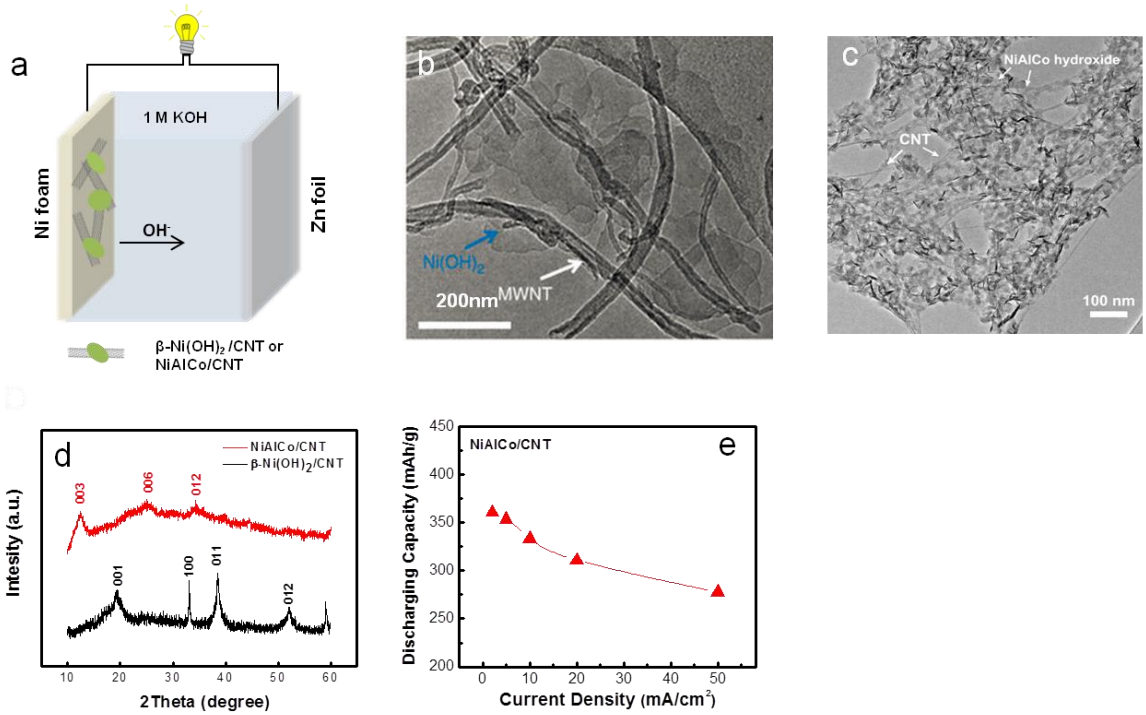

Figure 1: Rechargeable Ni/Zn batteries based on inorganic-CNT hybrid electrode materials. (a) A schematic showing the battery configuration, (b) SEM image of β-$Ni(OH)_2$/CNT, (c) SEM image of NiAlCo/CNT. (d) XRD of β-$Ni(OH)_2$/CNT and NiAlCo/CNT, (e) dependence of specific capacity on discharge current density for NiAlCo/CNT tested in a three electrode system.

b. Detailed electrochemical assessment of $Ni(OH)_2$/CNT hybrid materials in alkaline solutions

We investigated the electrochemical properties of both hybrid Ni electrode materials through cyclic voltammetry (CV) and galvanostatic charge-discharge measurements using a standard three electrode system in 1 M KOH. All the CV curves exhibited a pair of redox peaks in the voltage range of 0 - 0.6 V (*vs.* Ag/AgCl electrode), corresponding to the active redox conversion between Ni^{II} and $Ni^{III/IV}$ in this potential range. When assessed under galvanostatic charge-discharge measurements, they exhibited high specific capacity of ~220 and ~350 mAh/g for β-$Ni(OH)_2$/CNT and NiAlCo/CNT respectively at 5 mA/cm^2 (based on the mass of active materials, Figure 1e), among the highest capacities of all Ni-based electrode materials reported to date. Both electrode materials demonstrated high cycling stability with <30 % capacity loss after 2,000 charge-discharge cycles at 50 mA/cm^2. Our next step is to maximize the loading of the Ni materials for electrode construction, and pair it with a Zn electrode for full battery demonstration.

Conclusions

In this investigation, we prepared β-$Ni(OH)_2$/CNT and NiAlCo/CNT as novel electrode materials for rechargeable Ni/Zn batteries. They exhibited large specific capacity and good cycling stability. As a next step, full Ni/Zn batteries will be made with these hybrid materials to demonstrate high energy density and ultrahigh power density Ni/Zn cells.

Publications and Patents

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