High-capacity NiAlCo Layered Double Hydroxide Cathode for Ultrafast NiZn Battery

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Rapid consumption of fossil fuels has stimulated intense research efforts on renewable energy. High-performance, low-cost, safe and environmentally friendly batteries are important to portable electronics and electric vehicles. Battery technologies provide a solution to the storage of intermittent renewable energy, playing important roles in decreasing our dependence on fossil fuels. Lithium ion batteries have high energy densities among rechargeable batteries but are insufficient for various applications and have safety problems due to flammability. The power density of lithium ion batteries are also insufficient for high power quality applications due to the limited Li^+ ion conductivity in aprotic electrolytes. The high cost and flammable nature also put constrains to various energy storage applications. On the other hand, traditional aqueous batteries are cost effective and safe, but are limited in energy density. By using inorganic/nano-carbon hybrid electrode materials, we recently developed an ultrafast rechargeable NiFe batteries. The ultra-NiFe battery can be charged in ~2 min and discharged in ~30 sec, which is almost 1,000 times faster than conventional NiFe batteries. With an operating voltage of ~1.1 V, it can deliver an energy density up to ~120 Wh/kg based on the mass of the active materials, which is high but still lower than that of lithium ion batteries.

In this exploratory work, we synthesized NiAlCo layered double hydroxide (LDH) nanoplates attached to few-walled carbon nanotubes (NiAlCo/CNT, see Figure 1 below) as the cathode material of rechargeable NiZn battery in aqueous alkaline electrolytes. The α-phase metal-hydroxide with ultrathin morphology and strong coupling to nanotubes afforded a cathode with a high capacity of ~ 354 mAh/g and ~278 mAh/g at current densities of 6.7 A/g and 66.7 A/g, respectively. Al and Co co-doping is unique in stabilizing α-phase nickel hydroxide with only a small capacity loss of ~6% over 2000 charge and discharge cycles at 66.7 A/g. Rechargeable ultra-fast NiZn batteries with NiAlCo/CNT cathode and a zinc anode can deliver a cell voltage ~ 1.75 V, energy density ~ 274 Wh/kg and power density ~ 16 kW/kg (based on active materials) with < 1 minute charging time (see Figure 2 below). The results open the possibility of ultrafast and safe batteries with high energy density.

The novel NiAlCo layered double hydroxide (LDH)/CNT hybrid is a high-capacity cathode material that enables an ultrafast nickel-zinc (ultra-NiZn) battery with both high energy and power densities (see Table 1 below). Conventional NiZn batteries are commonly prepared from β-phase $Ni(OH)_2$, and can deliver up to ~70 Wh/kg which is only ~20% of the theoretical value of ~372 Wh/kg. Comparatively, α-phase $Ni(OH)_2$ has much higher capacity by exchanging more than one electron per Ni atom during charging and discharging, but it suffers from instability in alkaline solutions due to its slow transformation to the thermodynamically more stable β-phase $Ni(OH)_2$. Many attempts have been made to stabilize α-phase $Ni(OH)_2$ by introducing +3 ions (e.g. Al, Cr, Mn and Co) to form LDH structure, but stable (e.g., over ~ 1000 cycles) α-phase $Ni(OH)_2$ electrodes with high capacity remain elusive. Our strategy is to produce α-phase $Ni(OH)_2$ with high specific capacity and overcome the instability of the α-phase by synthesizing Al and Co co-doped α-phase $Ni(OH)_2$ nanoplates on top of oxidized few-walled carbon nanotubes (NiAlCo/CNT). The Al and Co co-doping were found to stabilize the layered α-phase $Ni(OH)_2$ in LDH structure. The NiAlCo/CNT electrode measured in three-electrode configuration could deliver an ultrahigh specific capacity of ~354 mAh/g at a discharge rate of 6.7 A/g and ~278 mAh/g at a high discharge rate of 66.7 A/g based on the active metal-hydroxide mass. The Al and Co co-doping approach is superior for enhancing the stability of the LDH phase or α-phase $Ni(OH)_2$ to Al or Co doping alone. A rechargeable ultra-NiZn battery was made by pairing the NiAlCo/CNT hybrid material with a zinc anode in 1 M KOH. At a charge/discharge current of 14 A/g (~ 41 s charging and discharging time), the battery delivered a cell voltage of ~1.75 V, a specific power density of 16.6 kW/kg and a specific energy density of 274 Wh/kg (based on the mass of active materials) with ~10% capacity decay over 600 charge-discharge cycles.

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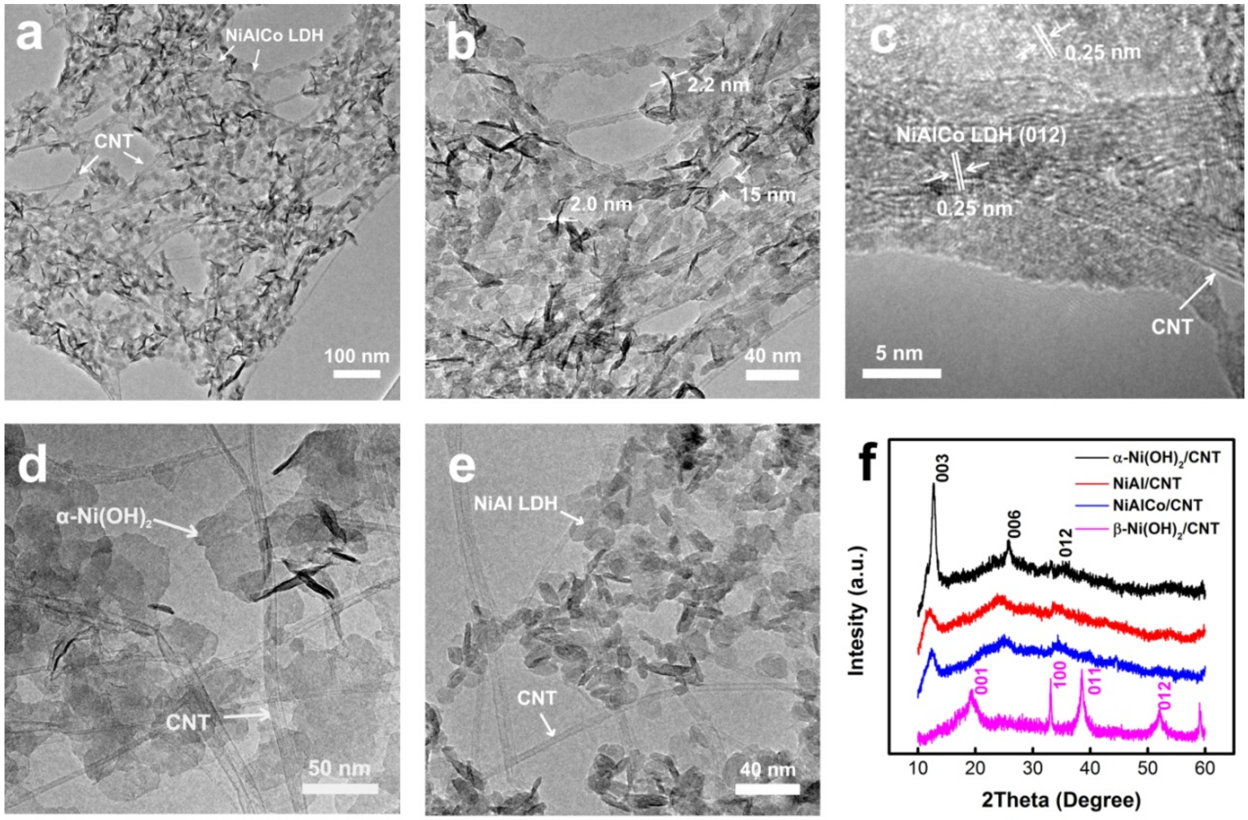

Figure 1. Characterization of size, morphology and structure of the hybrid materials. (a, b) TEM images of NiAlCo/CNT hybrid (c) HRTEM image of NiAlCo/CNT hybrid (d) TEM image of α-$Ni(OH)_2$/CNT hybrid (e) TEM image of NiAl/CNT hybrid E) XRD spectra of NiAlCo/CNT hybrid (blue), α-$Ni(OH)_2$/CNT hybrid (black), NiAl/CNT hybrid (red) and beta-$Ni(OH)_2$/CNT hybrid (purple)

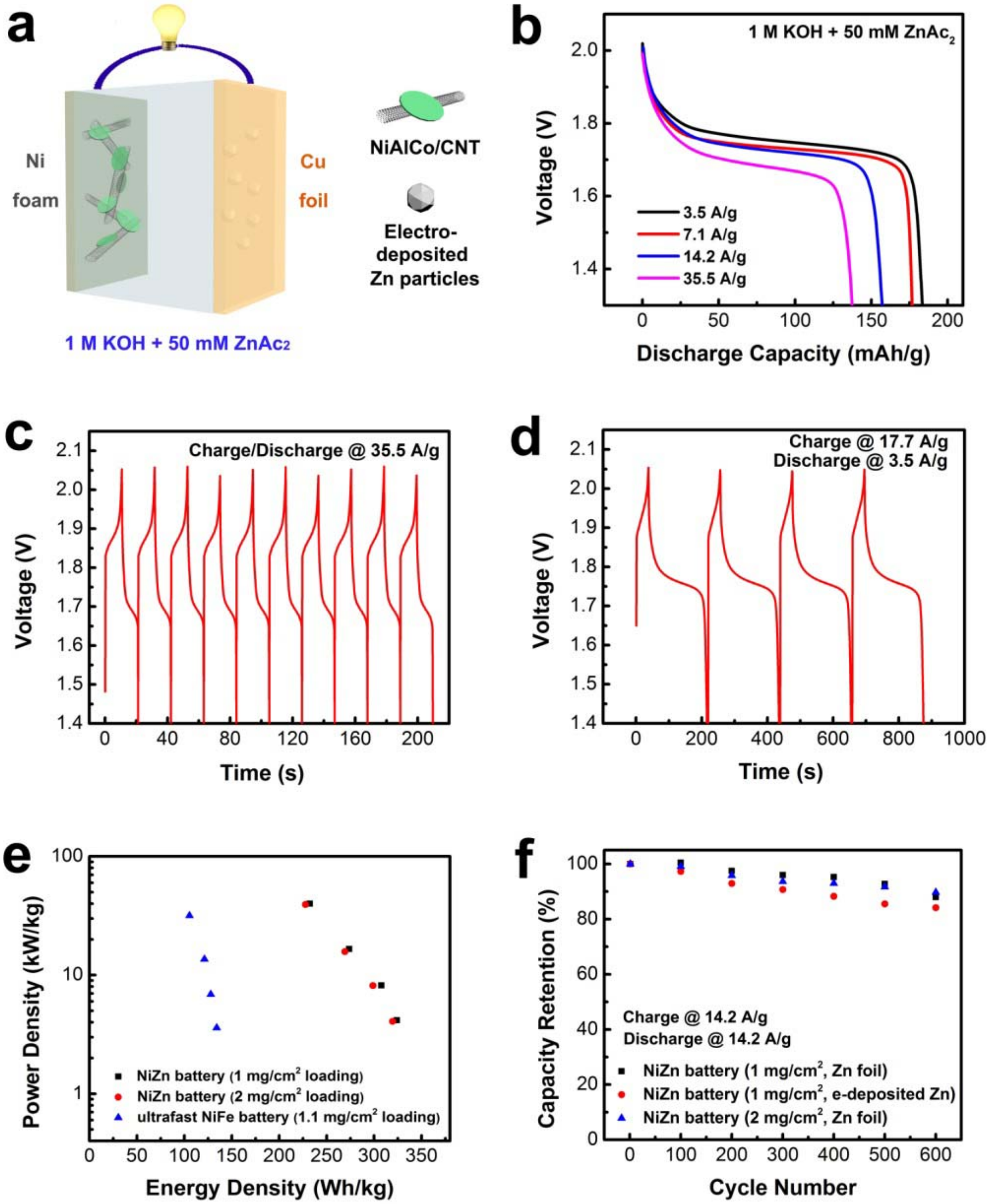

Figure 2. Electrochemical data of ultrafast NiZn cell made of NiAlCo/CNT hybrid on Ni foam and deposited Zn on Cu foam. a) Schematic diagram of the ultrafast NiZn cell. b) Galvanostatic curves of NiZn cell (~1.0 mg NiAlCo/CNT and ~0.67 mg Zn) at various current density. c) Galvanostatic charge and discharge curves of the NiZn cell at the current density of 35.5 A/g. d) Galvanostatic charge and discharge curves of the NiZn cell at a charging current density of 17.7 A/g and a discharging current density of 3.5 A/g. e) Ragone plot (masses of active materials used for calculations) of the NiZn cell (~ 1.0 mg NiAlCo/CNT and ~0.67 mg Zn), the NiZn cell (~2.0 mg NiAlCo/CNT and ~1.35 mg Zn) and ultrafast NiFe battery (~1.1 mg $Ni(OH)_2$/MWNT and 0.7 mg FeO_x/graphene) recently reported. f) Discharge capacity stability curves (capacity retention vs cycle number) of the NiZn cells with different loading at the current density of 14.2 A/g. During charge/discharge cycles, voltage was kept below the plateau at ~ 2.1 V to avoid overcharging problem and severe dendrite formation.

Table 1. Key parameters of NiAlCo/CNT cathode and ultra-NiZn cell

NiAlCo/CNT cathode		**Ultra-NiZn cell**	
Mass-specific capacity at high current density (66.7 A/g)	278 mAh/g	Peak Energy Density	324 Wh/kg
Mass-specific capacity at low current density (6.7 A/g)	354 mAh/g	Peak Power Density	40 kW/kg
Peak area-specific capacity at 10 mA/cm^2	10.5 mAh/cm^2	Cell voltage	~1.75 V
Charge/Discharge Stability	~6% decay over 2000 cycles	Charge/Discharge Stability	~10 % decay over 600 cycles