

Designing High Discharge Capacity and High-Rate Nickel Hydroxide Cathodes for Rechargeable Alkaline Nickel–Zinc Batteries

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Abstract: Energy dense, safe, rechargeable batteries are needed for a wide range of applications from portable electronics to electric vehicles. Safety concerns inherent to lithium-ion batteries make them a risk for numerous platforms including airplanes, ships, and undersea vehicles. Nickel–zinc batteries offer an energy dense, safe alternative to lithium-ion, but commercially available nickel cathodes do not match the cyclability of high-performance Zn-sponge anodes. We have developed a process to electron wire Ni(OH)₂ active material within a three-dimensional, nonperiodic cathode architecture that enables high rate performance, capacity, and cycle stability of Ni(OH)₂ in a Ni–Zn sponge cell.

Keywords: Nickel–zinc batteries, cathodes, three-dimensional architectures

Introduction

Batteries power everything ranging from portable electronics to electric vehicles (EV) and lithium-ion (Li-ion) batteries have been at the vanguard of powering these devices. With an adverse safety record that includes numerous examples of battery-related fires,^{1–4} ranging from EV crashes ejecting burning Li-ion batteries into nearby housing, grounding entire fleets of commercial airplanes, or igniting a fire on a cargo ship that burned uncontrollably for days before sinking, the military and consumer need an alternative energy dense, safe, and rechargeable battery chemistry.

Alkaline nickel–zinc (Ni–Zn) batteries use a nonflammable aqueous electrolyte but have limited rechargeability because of the Zn anode; a problem since resolved by staff scientists at the U.S. Naval Research Laboratory (NRL) who reformulated the zinc into a sponge form factor.^{5,6} At the single-cell level, Ni–Zn sponge is competitive with Li-ion's lauded energy density.⁷ A single Zn-sponge anode can outperform four commercially harvested Ni-cathodes.⁸

Commercially available Ni cathodes are fabricated using β -phase nickel hydroxide (Ni(OH)₂), which stores 0.8–0.9 electrons per Ni (relative to two electrons per Zn), limiting the energy density of the Ni–Zn cell. The α -phase of Ni(OH)₂ can store more than one electron per Ni but requires crystal-phase stabilization to access its higher theoretical capacity. We previously demonstrated that Al(III)-substituted Ni(OH)₂ stabilizes the α -phase and when formulated into a powder-composite cathode, improves the discharge, capacity, discharge voltage, and cycling stability of Ni–Zn sponge cells.⁹ We now explore the effects on battery performance of affixing α -Al-Ni(OH)₂ onto an architected cathode to enable direct electron wiring of the active material throughout the volume of a freestanding, binder-free cathode structure.

Experimental

Fabrication of Carbon Nanofiber Paper Electrodes. A beaker containing nonionic surfactant (Triton-X 100), 18 M Ω -cm water, and

as-received carbon nanofibers (CNF, Sigma) was placed in an ice-water bath and the dispersion mixed using a wand sonicator (Sonics Vibracell VC505, 40% power) for 16 min at 10-s pulse intervals (Figure 1a, step one). Carbon nanofiber paper (CNP) was fabricated by vacuum filtering the CNF dispersion (Figure 1a, step two).

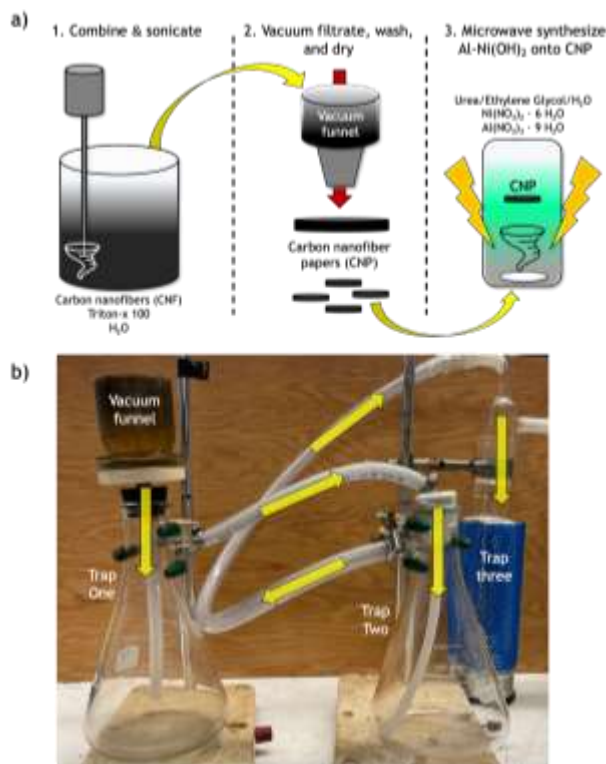


Figure 1. a) The fabrication & synthesis of Al-Ni(OH)_2 onto a freestanding carbon nanofiber paper (CNP); b) the vacuum filtration system used to fabricate a freestanding, binder-free carbon nanofiber paper (CNP) with arrows denoting flow direction.

The CNF suspension was vacuum filtered through a three-trap vacuum system: two liquid traps and one liquid nitrogen-cooled vapor trap (Figure 1b). After filtration, the CNP was rinsed with 500 mL of water and dried under vacuum at 120°C for 21 h.

Synthesis of Al-Ni(OH)_2 @CNP. Alpha-phase Al-Ni(OH)_2 nanosheets were affixed onto the fibers within CNPs by adapting our established microwave protocol.⁹ A $\frac{1}{2}$ " CNP disk and 20 mL of a Ni/Al solution (containing $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O}$, urea, ethylene glycol, and

water; Figure 1a, step three) were placed in a reaction vial within an Anton Parr microwave reactor (Monowave 450). The reaction was conducted using a two-step microwave heating protocol; the solution was heated to 80°C for 60 min, and then the temperature increased to 180°C for 3 min. The CNP was collected, rinsed with water and ethanol, and then dried under vacuum at 120°C for 21 h. The morphology of the Al-Ni(OH)_2 @CNP was investigated by scanning electron microscopy (FEI-Helios Nanolab 400). The mass of Al-Ni(OH)_2 in the CNP was determined by Atomic Absorption (Elmer PinAAcle 900f).

Testing Al-Ni(OH)_2 @CNP in Nickel–Zinc Cells. Nickel–zinc cells were assembled using alkaline-resistant cells, Zn anodes, and our previously established electrolyte/separator conditions.^{8–11} The cells were galvanostatically cycled between 1.30–1.90 V using a constant current, constant-voltage charging protocol at a charging rate of $100 \text{ mA/g}_{\text{active}}$ and variable-rate discharge at 100, 500, and $3000 \text{ mA/g}_{\text{active}}$ (Arbin battery cycler).

Results and Discussion

Carbon nanofiber papers (CNP) are fabricated from an aqueous suspension of carbon nanofibers (CNF) and surfactant mixed using a high-energy wand sonicator. The suspension is filtered through a liquid nitrogen (LN_2)-assisted three-trap vacuum system (Figure 1b) producing a CNP with randomly oriented and interwoven strands of CNFs. Vacuum filtration of the suspension generates a significant amount of surfactant bubbles; traps one and two are necessary to capture and contain the liquid bubbles (thereby protecting the vacuum system), and the third LN_2 trap condenses any liquid vapor.

The microwave synthesis of Al-Ni(OH)_2 nanosheets onto CNP uses a two-step variable temperature microwave reaction protocol. The temperature is initially set to 80°C for 1 h to equilibrate the Ni and Al at the CNF struts within the CNP; the reaction temperature is then increased to 180°C for 3 min to promote

growth of Al-Ni(OH)_2 at the fibers. Scanning electron microscopy (SEM) of the CNP after microwave reaction shows two unique Al-Ni(OH)_2 nanosheet morphologies: solution-nucleated nanosheet agglomerates and CNF-nucleated nanosheets within the CNP (Figure 2a).

Solution-nucleated nanosheets are large, 0.5–1.0 μm -sized agglomerates that are trapped within the CNP but not directly nucleated or “wired” to the CNP fibers, seen by the cluster of nanosheets in the top right of Figure 2a. By contrast, fiber-nucleated nanosheets emanate from the surface of the CNF struts within the CNP (Figure 2b).

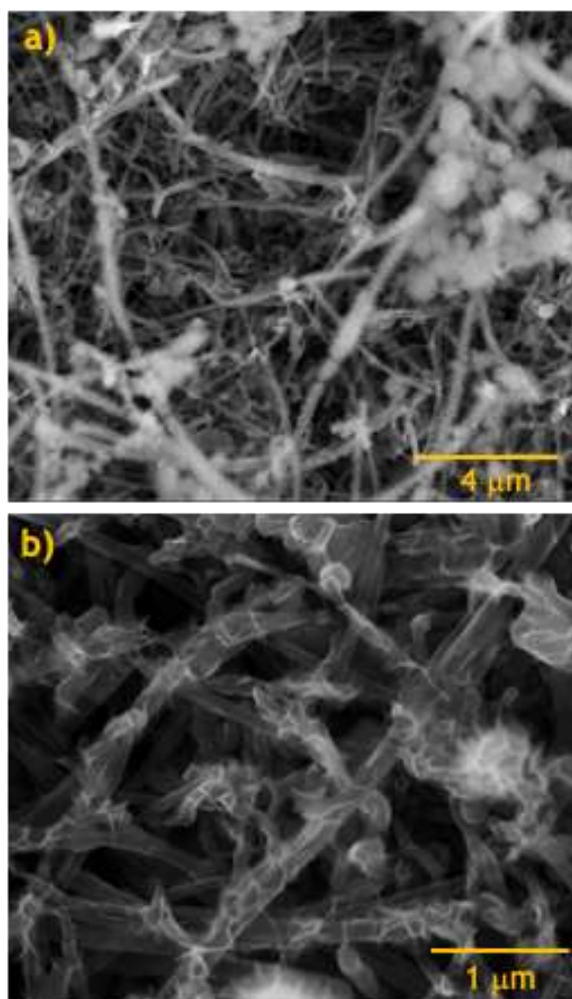


Figure 2. Scanning electron micrographs of Al-Ni(OH)_2 deposited within and onto carbon nanofiber paper (CNP).

The Al-Ni(OH)_2 @CNP is used as the Ni cathode versus the fully rechargeable Zn-sponge anode in a cathode-limiting configuration. The mass of “active” Ni(OH)_2 is deposited into the CNP at a loading of 4.0 mg cm^{-2} . The galvanostatic rate capability of the Al-Ni(OH)_2 @CNP–Zn sponge cell is determined at discharge rates of 100, 250, 500, 1000, 2000, and 3000 $\text{mA/g}_{\text{active}}$; five replicate Al-Ni(OH)_2 @CNP electrodes were run for the rate tests. The voltage vs specific capacity of the cell at 100, 500, 1000, 2000, and 3000 $\text{mA/g}_{\text{active}}$ is presented in Figure 3.

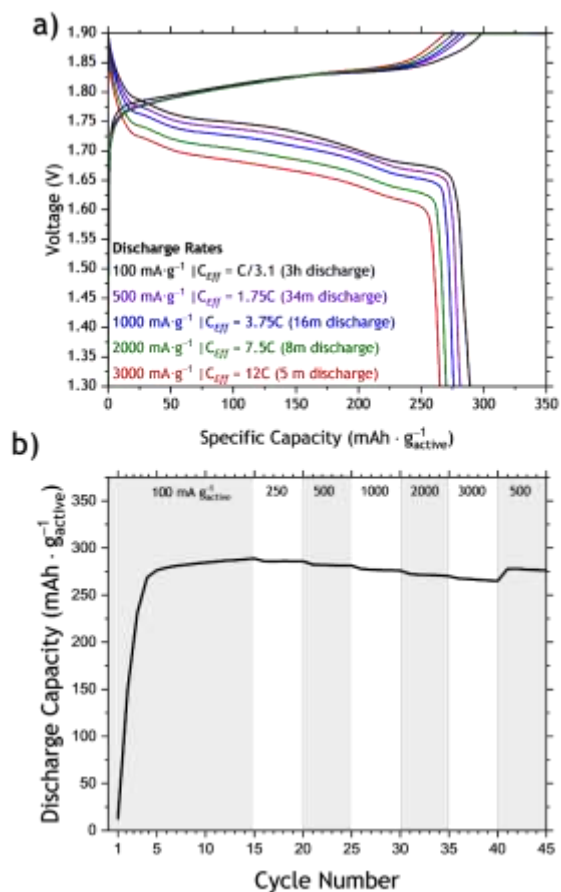


Figure 3. Galvanostatic charge–discharge of an architected Al-Ni(OH)_2 @CNP–Zn-sponge coin cell: Comparing the effect of a constant rate charge/variable rate discharge on capacity.

The Al-Ni(OH)_2 @CNP–Zn sponge cell has a discharge capacity of $280 \text{ mAh/g}_{\text{active}}$ at a discharge rate of $100 \text{ mA/g}_{\text{active}}$ with an effective C-rate (C_{eff}) of $C/3.1$ (3.1 h to full discharge). As the discharge rate increases

from 100 mA/g_{active} to 3000 mA/g_{active}, discharge capacity decreases by 18 mAh/g_{active} to 262 mA/g_{active} ($C_{eff} = 12C$ or 5-min discharge). As the discharge rate increases, the entire voltage profile decreases (Figure 3a), which we attribute to ohmic loss.

The discharge capacity and cycle stability of the Al-Ni(OH)₂@CNP-Zn-sponge cell as a function of cycle number and increasing discharge rate are presented in Figure 3b. The cell is discharged at 100 mA/g_{active} for 15 cycles to accommodate the formation cycles of Al-Ni(OH)₂@CNP; after the 15th cycle, the discharge rate is increased every five cycles from 100 to 3000 mA/g_{active} before returning to 500 mA/g_{active} at the 40th cycle (Figure 3b). The capacity fade observed when the discharge rate increases to 3000 mA/g_{active} is reversed when the rate returns to 500 mA/g_{active}.

Conclusions

Using a 3D architected carbon nanofiber paper (CNP) electrode fabricated from commercially available carbon nanofibers (CNF), we developed a synthesis that grows Al-Ni(OH)₂ nanosheets onto the CNF struts throughout the CNP. The Al-Ni(OH)₂@CNP shows remarkably high rate capabilities and cycle stability as a rechargeable Ni cathode versus the U.S. Naval Research Laboratory's fully rechargeable Zn-sponge anode. This route to an Al-Ni(OH)₂@CNP cathode is a practical approach to electron-wiring Ni(OH)₂ active material to the electrode architecture.

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