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Synthesis of Carbon Nanotube Incorporated Metal Oxides for the Fabrication of Printable, Flexible Nickel-Zinc Batteries

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Abstract

The development of printable composite electrodes embedded with multiwalled carbon nanotubes (CNTs) for flexible nickel-zinc batteries is presented. The cathode and the anode comprised of $\text{Ni}(\text{OH})_2$ -CNT and ZnO -CNT respectively are prepared by coprecipitation of the metal oxides on CNTs. High loading ratio of electroactive materials increases the amount of active materials in electrode, but causes a lower material utilization efficiency due to decrease in overall electrode conductivity. The direct loading of active materials onto CNTs enhances contact where the CNTs serve the pathways for electron transport leading to higher performance than physical mixing of active ingredients. The cells show good performance even under bending conditions and the overall technology is scalable by printing methods.

Keywords

carbon nanotubes; flexible nickel-zinc batteries; nickel hydroxide; precipitations; zinc oxide

Flexible batteries are promising power sources for the next generation of electronics such as wearable sensors, implanted medical devices, bendable screens, and smart cards.^[1–3] The two most common designs for flexible batteries are the thin-film and cable batteries.^[4–13] In the former, the electrodes are painted or cast to form thin layers with a separator in between.^[4,7,14,15] This type of cells can be fabricated with commercially available printing techniques such as roll-to-roll printing and inkjet printing. Flexible batteries based on textiles or carbon cloths as matrix where the active materials are loaded/doped onto the scaffold have also been fabricated.^[6,16,17]

Different flexible batteries have been studied and major efforts have gone into the development of both primary and secondary batteries including zinc-carbon,^[7,8,13] alkaline,^[15,18–20] zinc-air,^[11,21] nickel-iron,^[22] and lithium-ion systems. Primary flexible batteries that focus on low costs and toxicity have mostly used zinc as anode, with a metal oxide such as MnO_2 as the active cathode material. Most of them have also used aqueous electrolytes, which are safer than the flammable organic electrolytes. However, rechargeable batteries are longer lasting, ecofriendly, and are often preferable to primary batteries. The most widely

Conflict of Interest

The authors declare no conflict of interest.

studied is the lithium-ion battery using lithium metal oxides and carbon electrodes. [5,9,10,23–28]

Nickel-zinc batteries typically use $\text{Ni}(\text{OH})_2$ cathode, Zn/ZnO anode, and an alkaline aqueous electrolyte. They show a higher output voltage of 1.6 V compared to Ni-MH cells that have an open-circuit voltage of 1.2 V. Besides, nickel-zinc batteries use aqueous electrolytes and are relatively safer. While flexible lithium batteries have been studied extensively, to the best of our knowledge there is only one published paper on a flexible nickel-zinc cell,^[16] where active materials were deposited on 3D hierarchical carbon cloth/ nanofiber substrates via atomic layer deposition of ZnO from Zn and water to form the anode, and immersion deposition of NiO from ammonia and nickel (II) sulfate to form the cathode. Other flexible substrates such as cotton textile,^[29–32] nylon,^[33] and polyester^[34] have also been used as substrates for flexible power sources. Here, the fabrics were soaked with solutions of active material for coating.

Highly electrically conductive, inert materials with high surface area are often important components of flexible electrode formulations. Promising materials include graphene,^[22,35–37] CNTs,^[26,38] carbon microfiber,^[6,39] carbon black,^[40] porous materials from plant,^[41,42] and even organic conductive polymers.^[43] Each material has its own benefits and limitations. Porous carbons derived from plants tend to have high surface area as well as particle size. While reduced graphene oxides have good conductivity they tend to be less soluble. Both these are more suitable for supercapacitors and lithium-ion batteries. CNTs have been found to be excellent components of diverse electroactive composites.^[36,38,44,45] Similar to carbon fibers, the CNTs are highly conductive and can serve as the matrix or scaffolds for active materials. The 1D shape allows them to form a wide network within the matrix. Embedded in a composite, the CNTs serve as channels for electrons and electrolytes transport even with large amount of active materials loaded onto them. Such composites can be used to prepare electrode inks for flexible batteries. Thin-film techniques such as atomic layer deposition,^[16] chemical vapor deposition,^[46] and chemical approaches such as microwave-induced reactions^[45,47] have been used to load metal oxides on CNTs. Coprecipitation is a simple approach that can be effective in loading relatively large concentration of metal oxides on CNTs. Binders can be added to such formulations to provide the necessary cohesiveness, flexibility, and the ability to hold electrolytes for the electrodes.^[8,15,20,21] Such formulations can be converted into an ink and are amenable to mass production via techniques such as roll-to-roll printing.

The objective of this paper is to develop electrodes using CNT embedded metal oxides for flexible Ni-Zn batteries. Yet, another goal is to develop simple precipitative techniques to synthesize CNT-metal oxide composites that are suitable to form electrode inks that can be cast/printed directly onto flexible substrates to form electrode films.

The electrode inks, flexible electrodes, and the battery are shown in Figure 1. The flexible separator was placed between the electrodes.

Flexible $\text{Ni}(\text{OH})_2$ -CNT cathode: $\text{Ni}(\text{OH})_2$ had poor electrical conductivity and hence conductive additives were needed to be added to the ink. $\text{Ni}(\text{OH})_2$ -CNT composites were

prepared through a reaction between NaOH and $\text{Ni}(\text{NO}_3)_2$. The CNT percentages in the composites were varied. The scanning electron microscopy (SEM), X-ray diffraction (XRD), thermal gravity analysis (TGA), and energy-dispersive X-ray spectroscopy (EDS) characterizations of the $\text{Ni}(\text{OH})_2$ -CNT composites are shown in Figure 2. It could be seen from the SEM images that CNTs were embedded into the $\text{Ni}(\text{OH})_2$. Unless carboxylated, the CNTs tended to agglomerate. The EDS showed that the composite was mainly composed of nickel, carbon, and oxygen (Figure 2c). TGA of the $\text{Ni}(\text{OH})_2$ -CNT composites (Figure 2d) was used to calculate the amount of CNTs and $\text{Ni}(\text{OH})_2$ in the composites. The $\text{Ni}(\text{OH})_2$ -CNT composites prepared here contained 40.8, 29.8, 24.0, and 18.7% CNTs, respectively, which are referred to as $\text{Ni}(\text{OH})_2$ -CNT_{40.8}, $\text{Ni}(\text{OH})_2$ -CNT_{29.8}, $\text{Ni}(\text{OH})_2$ -CNT_{24.0}, and $\text{Ni}(\text{OH})_2$ -CNT_{18.7}. During TGA analysis, the decrease in weight between 200 and 230 °C was due to the decomposition of $\text{Ni}(\text{OH})_2$ to NiO, while the decrease between 350 and 500 °C was attributed to the oxidation of CNTs to carbon dioxide. $\text{Ni}(\text{OH})_2$ exist mainly under two polymorphs, namely, α and β . The α - $\text{Ni}(\text{OH})_2$ is relatively unstable and turns to β in alkaline media, and β turns into γ upon overcharging.^[48,49] XRD patterns of $\text{Ni}(\text{OH})_2$ -CNT did not show any obvious crystalline pattern although a couple of peaks were indexed at 33.34° (100), 38.3° (101), and 59.21° (110) (ICCD Reference code 00–014–0117, ref. [48]). The sample was mostly amorphous (Figure 2e).

Cyclic voltammetry (Figure 2f) of $\text{Ni}(\text{OH})_2$ -CNT showed an anodic peak at 0.35–0.4 V versus Ag/AgCl electrode from the oxidation of nickel (II). Oxygen generation caused distortion of the curve and even covered the anodic peak at higher potential. This was particularly true at higher scan rates. The cathodic peaks at 0.15 and 0.05 V were attributed to the reduction of different nickel (III) forms to nickel (II), which was in line with what has been reported before.^[50]

The different $\text{Ni}(\text{OH})_2$ -CNT composites were used to fabricate nickel-zinc batteries in fixed Swagelok-type electrochemical cells described before.^[8,15,20] In each cycle, a cell was charged to 2 mAh using constant current (1 mA)–constant voltage (1.9 V), and then discharged under constant current of 0.8 mA until 1.1 V. The cycling data of cells with different $\text{Ni}(\text{OH})_2$ -CNT composites are shown in Figure 3. It also shows delivered cell capacity during each discharge as a function of cycle numbers.

Generally, as the amount of $\text{Ni}(\text{OH})_2$ increased (Figure 2b), the overall conductivity of composite and electrode decreased (Table 1), and so did the overall battery performance. High amount of CNTs caused cracking and disintegration of electrodes, leading to an increase in electrical resistance. It was found that the $\text{Ni}(\text{OH})_2$ -CNT_{29.8} provided the optimum performance (Figure 3 and Table 1). Higher amount of CNTs (or lower loading of $\text{Ni}(\text{OH})_2$) in electrodes enhanced the electrode conductivity but would occupy the limited space in the battery, thus reducing the mass of electroactive materials. In general, the cell performance tended to increase as the amount of CNTs reached 29.8%, beyond which the performance dropped. However, as seen from Table 1, a specific capacity based on active material and material utilization was the highest for the composite with 40.8% CNTs ($\text{Ni}(\text{OH})_2$ -CNT_{40.8}). The material utilization reached 85% but lowered the total capacity because of the lower availability of $\text{Ni}(\text{OH})_2$. Loading a lower amount of $\text{Ni}(\text{OH})_2$ would further improve material utilization but at the cost of lowering the overall battery capacity.

Flexible ZnO-CNT anode: The ZnO in the anode was also loaded onto CNTs via coprecipitation to form a composite as shown in Figure 4. A reaction between ZnCl_2 and NaOH was used to synthesize Zn(OH)_2 , which was then reduced to ZnO by heating at 200 °C. The EDS results from the final composite showed the presence of C, Zn, and O. The concentration of ZnO in the composite could be varied by varying the amount of the reactants during precipitation. When simply mixed together, flexible zinc anodes tended to crack at high CNT concentration and during bending. This has also been reported before.^[15] It was found that when CNTs were embedded into the $\text{Zn(OH)}_2/\text{ZnO}$ during precipitation such cracking was prevented. TGA results of ZnO-CNT composites were used to calculate the amount of CNTs and ZnO in the composites. ZnO-CNT composites contained 31.9, 28.3, 25.2, 20.7, and 15.6% of CNTs, respectively, which are referred to as ZnO-CNT_{31.9}, ZnO-CNT_{28.3}, ZnO-CNT_{25.2}, ZnO-CNT_{20.7}, and ZnO-CNT_{15.6}. Figure 4e showed the XRD pattern of ZnO-CNT sample, where peaks were indexed as 31.81° (100), 34.45° (002), 36.32° (101), 47.62° (102), 56.63° (110), 62.86° (103), 67.95° (112), and 89.72° (203), respectively, which corresponded to the characteristic hexagonal wurtzite structure of zinc oxide particles (Reference code 01-089-7102). Unlike the Ni-based cathode, the peaks in ZnO-CNT showed crystal structure of zinc oxide.

Cyclic voltammetry analysis of ZnO-CNT composites is shown in Figure 4g. Redox couple of Zn/ZnO was observed between -1.35 and -1.2 V. Significant hydrogen evolution was observed at the lower potential end (-1.35 V). Because of the relatively high amount of CNTs in the composites, these metal oxide-CNT composites also showed capacitive behavior, especially in the case of ZnO-CNT.

These ZnO-CNT composites were used to make anodes for nickel-zinc cells (Figures 5 and 6). A certain amount of metallic Zn was added to the electrode formulation to enhance conductivity and discharge performance. Since the anode now was the limiting reagent, a different charge-discharge cycle was used for evaluation. For the first two cycles the cell was charged to 4 mAh using constant current (4 mA)-constant voltage (1.9 V) method, and then discharged under constant current of 4 mA until discharged to 1.4 V for electrode activation. From the third cycle, a typical cell was charged to 4 mAh using constant current (2 mA)-constant voltage (1.9 V) method, and then discharged under constant current of 1.6 mA till 1.2 V. Figure 5 shows data comparing cells made with the ZnO-CNT_{15.6} composite (a total of 10% CNTs in electrode) and commercial ZnO (4% CNT in electrode). The ZnO-CNT composite showed better performance, which could be attributed to higher CNT amount. A 10% CNT electrode was also prepared by physical mixing of ingredients, however it cracked and materials peeled off upon bending.

Composites with different CNT percentages were tested (Figure 6a). The anode ink contained 64% of the ZnO-CNT composite and 22% of zinc metal and rest were binders and additives (all weights expressed on a dry basis). Low amount of CNTs led to high electrode resistance (Table 2), and lower performance. ZnO-CNT_{28.3} was the optimum composition and an increase of CNT concentration in ZnO-CNT_{31.9} led to lower performance. Higher CNT concentrations increased the viscosity of the paints, while decreasing flexibility and leading to cracks formation. Hence, the amount of CNTs in the composite is an important consideration.

Morphology of CNTs has impact on properties like dispersibility. Among these, surface functional groups tend have a more significant impact than length or diameter.^[51] We have reported that the treatment of CNTs before using them as electrode ingredients could alter the physical and electrochemical properties.^[20,52,53] Based on these data, the CNTs were functionalized for 10 min (FCNT-10) and 40 min (FCNT-40), respectively. The resulted carboxylated CNTs containing different levels of carboxylation (Table 3) were tested as an alternate to raw CNTs to form an equivalent ZnO-CNT_{28.3} composite with two different levels of carboxylation. It could be seen from Figure 6 that the carboxylated CNTs showed lower performance that decreased with the degree of carboxylation. Results were similar when CNT-Ni(OH)₂ composites were synthesized with carboxylated CNTs and the data were not presented here for brevity.

In an effort to enhance anode performance, Ca(OH)₂ was added as an additive where calcium zincate served as a rechargeable anode material, which has been known to reduce dendrite and morphology changes associated with pure Zn-ZnO anode.^[54–56] Anodes containing 14% of Ca(OH)₂ were prepared and tested, however these electrodes showed lower performance (Figure 7). Zn metal, which could improve both conductivity and discharge performance, was also added along with ZnO-CNT_{28.3} and its optimum concentration was determined. Three concentrations, namely, 20, 30, and 38% of Zn in the ink formulation were tested, and 30% showed the best performance.

Flexible cells: In the fabrication of flexible cells, the evolution of hydrogen gas appeared to pose a problem. This was also expected from the cyclic voltammogram. This was greatly inhibited when the steel current collector was coated with materials with higher overpotential such as Zn (Figure 8).^[57] Two flexible cells were connected in series to power LED lights as shown in Figure 1d. The specific capacity of the flexible cell was 42 mAh g⁻¹, which could be significantly enhanced by improving the packaging. The performance of the flexible cell under bending conditions is shown in Figure 8. Cells were attached to cylinder substrate with certain radii and then tested. During bending, parts of the electrodes and separator can stack together and enhance contact in some sections while other parts may separate to lose contact. In the cells fabricated here, no drop in performance was observed under bending conditions in terms of capacity or voltage. Cycle numbers could also be significantly improved by advanced packaging methods.

In summary, printable ink formulations for flexible electrodes were developed by synthesizing metal oxide-CNT composites, which were used to fabricate flexible Ni-Zn batteries. With the increase in CNT incorporation into the active materials, the composites showed relatively higher electrical conductivity. CNT carboxylation improved dispersion but did not show performance enhancement. The resulting electrode inks were suitable for conventional printing methods such as screenprinting, and there was flexibility as far as loading of electroactive materials and additives was concerned.

Experimental Section

The Ni(OH)₂-CNT composites were prepared by stoichiometric reaction between prepared 2 m NaOH (Sigma Aldrich, 97%) solution and 0.194 m Ni(NO₃)₂ (Sigma Aldrich,

hexahydrate, 99%), in presence of multiwalled CNTs (purity 95%, diameter 20–30 nm, length 10–30 μm , Cheap Tubes Inc. Brattleboro, VT). The purification and functionalization of CNTs were performed in a Microwave Accelerated Reaction System (Mode: CEM Mars) using experimental procedures previously reported.^[52] CNTs were dispersed in $\text{Ni}(\text{NO}_3)_2$, stirred and sonicated (Omni Sonic Ruptor 250) for 30 min each, before 2 M NaOH was added at the rate of 0.8 mL min^{-1} . Resulted samples were filtrated and dried at 90 $^\circ\text{C}$ under vacuum for 12 h. Typical cathode slurry was prepared by adding 90% $\text{Ni}(\text{OH})_2$ -CNT composite and 10% polyethylene oxide (PEO, Sigma Aldrich, $M_v \approx 400\,000$) binder, into deionized (DI) water. 0.05 g of such electrode slurry was also pasted onto 12 m $\times$ 10 mm polyethylene terephthalate (PET) film to measure the electrical resistance between the distances of 12 mm. After mixing the components in DI water, the paste was sonicated for 30 min, and then stirred for 20 h to form a homogeneous slurry. During cathode optimization, the anode was made with 4% PEO binder, 4% CNTs, 1% methylcellulose (Sigma Aldrich, $M_n \approx 40\,000$), 2% bismuth (III) oxide (Sigma Aldrich, 90–210 nm particle size, 99.8%), 35% zinc oxide (Sigma Aldrich, 99%), and 54% zinc powder (Sigma Aldrich, 10 μm , 98%). The anode was stoichiometrically in excess.

Similar to cathode $\text{Ni}(\text{OH})_2$ -CNT composite, anode ZnO-CNT composites were also prepared from stoichiometric coprecipitation method, with 82.25 g L^{-1} zinc chloride (Sigma Aldrich, 98%) aqueous solution added into 2 M NaOH solutions at the rate of 0.4 mL min^{-1} in presence of CNTs. Resulted samples were filtrated and dried at 200 $^\circ\text{C}$ under vacuum for 12 h to get the ZnO-CNT composites. Equal amounts (0.05 g) of ZnO-CNT composite slurries containing 10% PEO were painted onto PET films and dried like $\text{Ni}(\text{OH})_2$ -CNT, before electrical resistance was measured between the distances of 2 mm. The battery anode paste contained zinc powder, PEO binder, methyl cellulose, and bismuth (III) oxide. In some of the formulations, zinc oxide, calcium hydroxide (Sigma Aldrich, 95), and CNTs were also included. The powders were mixed with DI water and then stirred to form a homogeneous anode paste. Attempts were made to optimize the amount of zinc, zinc oxide, ZnO-CNT composites, and $\text{Ca}(\text{OH})_2$. During anode optimization, cathode was typically fixed with 10% binder and 90% $\text{Ni}(\text{OH})_2$ -CNT_{2.353} composite, which was also abundant.

Swagelok-type cells using graphite rod current collectors and glass fiber separator (Grade GF/A: 1.6 μm , Whatman) were assembled to optimize the electrode formulation.^[15] The electrolyte was 8.5 M KOH solution saturated by ZnO, and contained 0.5 M sodium tetraborate (decahydrate, 99.8%). For flexible cells, electrodes were prepared by casting the electrode slurry onto the stainless steel 316 current collector on the adhesive side of PET film coated with ethylene vinyl acetate (EVA) resin. The typical electrode area was 3 $\times$ 2 cm. In some flexible cells, current collectors for anode were electroplated with thin layer of zinc. After applying the slurries onto the current collectors, the electrodes were allowed to dry under room temperature for 4 h. The last 5 minutes of drying was under vacuum (9.893 kPa). The typical weights of the cathode and anode after drying were 0.038 and 0.064 g, respectively. The battery was thermally sealed with a glass fiber separator and a PTFE separator (5.0 μm , ANOW) sandwiched between electrodes. Flexible electrodes after drying are shown in Figure 1.

SEM with EDS were collected on a LEO 1530 VP scanning electron microscope. TGA was done on PerkinElmer Pyris 1. XRD patterns were taken on a PANalytical Empyrean XRD. During the CV) analysis, the working electrodes contained 90% Ni(OH)₂-CNT and 80% ZnO-CNT, respectively, with the rest being PEO. CV was carried out on a Homiangz 320C electrochemical analyzer versus a standard Ag-AgCl electrode in 8.5 m KOH electrolyte. The electrochemical performance of the cells was measured using a MTI Battery Analyzer (Richmond, CA). The Ni-Zn cells were charged using constant current–constant voltage method and discharged under constant current. The flexible batteries were firmly attached to solid cylinder substrates of certain radii and tested to examine electrochemical performance under bending conditions.

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Figure 1.

a) Electrode inks from synthesized metal oxide-CNT composites; photograph of b) flexible cathode, c) flexible anode, d) an assembled cell, and e) two cells powering up LED lights.

Figure 2.

a,b) SEM images of Ni(OH)₂-CNT composites; c) EDS results showing the major elements in Ni(OH)₂-CNT composite; d) TGA analysis of Ni(OH)₂-CNT composites with different amounts of CNTs; e) XRD analysis of Ni(OH)₂-CNT_{29.8} composite; f) cyclic voltammetry of composite Ni(OH)₂-CNT_{29.8} versus Ag/AgCl electrode.

Figure 3. Capacity as a function of cycle numbers for Swagelok cells with electrodes containing different Ni(OH)_2 -CNT composites.

Figure 4.

a,b) SEM images of ZnO-CNT composites; c) SEM images of pure ZnO; d) EDS results showing the major elements in ZnO-CNT composite; e) TGA analysis of ZnO-CNT composites with different amounts of CNTs; f) XRD analysis of ZnO-CNT_{28.3} composite; g) cyclic voltammetry of ZnO-CNT_{28.3} versus Ag/AgCl electrode.

Figure 5. Anodes made from ZnO-CNT_{15.6} composite, and mixture of ZnO and CNT composite. Each anode also contained 1% cellulose, 4% binder, 2% Bi₂O₃, and 54% zinc metal.

Figure 6. Performance of ZnO-CNT composite anodes (each anode contained 64% by weight of the ZnO-CNT composite and 22% zinc metal): a) composites containing different amounts of CNTs; b) anode with ZnO-CNT_{28.3} composites synthesized from carboxylated CNTs.

Figure 7. Anode with and without Ca(OH)_2 , and different amount of zinc metal (all electrodes also contained $\text{ZnO-CNT}_{28.3}$).

Figure 8.
Flexible Ni-Zn cells under flat and bending conditions ($r = 5.5$ cm).

Table 1.

Performance of different cathode composites (taken from tenth cycle).

CNT percentage in Ni(OH) ₂ -CNT composite	Specific energy [mWh g ⁻¹ cathode]	Specific capacity [mAh g ⁻¹ cathode]	Specific capacity [mAh g ⁻¹ Ni(OH) ₂]	Ni(OH) ₂ utilization [%]	Resistance of composite film [kΩ]
40.8%	213.91	129.82	243.58	84.28	0.73
29.8%	215.18	138.36	219.07	75.80	0.65
24.0%	172.91	109.91	160.66	55.59	4.74
18.7%	2.18	1.55	—	—	8.96

Table 2.

Performance of different anode composites (taken from 11th cycle).

CNT percentage in ZnO-CNT composite	Specific energy [mWh g ⁻¹ anode]	Specific capacity [mAh g ⁻¹ anode]	Resistance of composite film [kΩ]
31.9%	165.00	99.69	3.7
28.3%	189.53	115.31	1.2
25.2%	195.78	116.88	2.4
20.7%	165.63	98.60	34
15.6%	44.29	25.94	75

Table 3.

EDS results for CNTs.

Element (weight %)	Raw CNTs	FCNT-10	FCNT-40
C	92.67	87.88	86.34
O	6.10	11.25	13.55
Ni	1.23	0.87	0.11