

Nanomaterial-Enhanced All-Solid Flexible Zinc–Carbon Batteries

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ABSTRACT Solid-state and flexible zinc carbon (or Lecdanché) batteries are fabricated using a combination of functional nanostructured materials for optimum performance. Flexible carbon nanofiber mats obtained by electrospinning are used as a current collector and cathode support for the batteries. The cathode layer consists of manganese oxide particles combined with single-walled carbon nanotubes for improved conductivity. A polyethylene oxide layer containing titanium oxide nanoparticles forms the electrolyte layer, and a thin zinc foil is used as the anode. The battery is shown to retain its performance under mechanically stressed conditions. The results show that the above configuration can achieve solid-state mechanical flexibility and increased shelf life with little sacrifice in performance.

KEYWORDS: battery · flexible · solid electrolyte · carbon fiber · carbon nanotubes · titanium dioxide

Energy and mobility are among the most important requirements in today's consumer electronic devices. Mobile energy is generally provided by electrochemical energy storage devices, traditionally batteries and, more recently, supercapacitors for high-power density applications. Portable devices demand increasing energy densities and decreasing footprint. Current research in battery technologies is focused on (i) exploration of anode/cathode materials with high-energy storage capacity and cyclability,¹ (ii) exploration of liquid-free electrolyte materials with higher ionic conductivities, which addresses the flammability of organic solvents and removes stringent packaging requirements,^{2,3} and (iii) optimization of the electrode/electrolyte interface to improve the cell safety and lifetime.⁴ Apart from these, simple battery fabrication methods utilizing thin, lightweight, and cost-effective materials are sought for next generation batteries. Current battery technology comprises a bulky and inflexible design, mainly as a result of protective packaging requirements due to flammability of solvents. Many modern device con-

cepts (flexible electronics, RFIDs, smart cards, intelligent clothing, etc.), however, place more importance on other figures of merit such as form factor and mechanical flexibility. In order to achieve these goals, a deviation from standard materials is necessary.

Much work has been done showing the properties of nanomaterials for charge storage. For instance, due to their promising characteristics, such as high conductivity and surface area, carbon nanotubes (CNTs) have been utilized in batteries to improve their structural and electrochemical properties and to impart mechanical flexibility. CNTs have been used as electrode additives to increase conductivity in both batteries^{5,6} and supercapacitors,^{7,8} and as thin film networks for charge collection,⁵ as the active material for intercalation electrodes in lithium-ion batteries,⁹ and more recently embedded in cellulose to produce paper-like flexible batteries and capacitors.¹⁰ The use of conventional high-energy density materials such as silicon, which in bulk form was deemed unsuitable due to its large volume expansion and cracking upon cycling, has shown much promise in nanowire form, leading to an enhancement in cyclability as well as the capacity of the electrodes.¹¹

A number of ion-conducting polymers have been studied as candidates for solid-state electrolytes.² These not only provide mechanical stability but also eliminate the problem of solvent evaporation and interfacial stability with the electrode. A number of polymers have been used as electrolytes in thin film batteries.^{2,12–14} However, these polymer electrolytes suffer from poor ionic mobility and only perform well in the amorphous state, which generally occurs around

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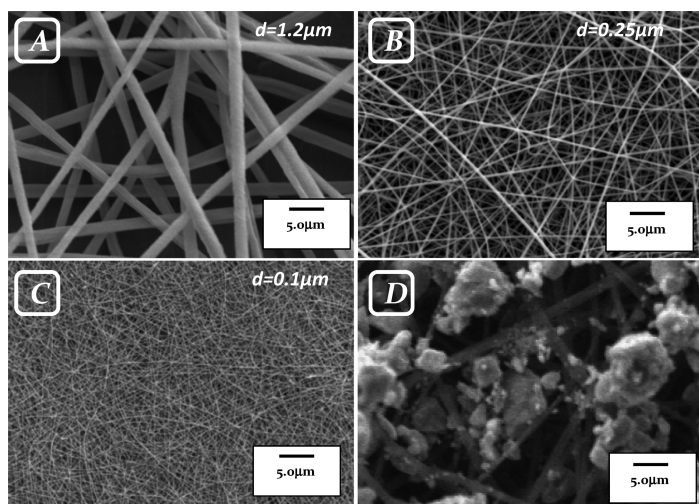


Figure 1. SEM images of (A–C) electrospun carbon fiber of varying average diameters. (D) Manganese oxide + SWCNT mixture pasted onto the fiber mat.

60–80 °C.¹ It has been observed that dispersing ceramic nanoparticles in polyethylene oxide (PEO) showed not only improved mechanical properties but also improved conductivity for Li ions by about an order of magnitude, attributed to the amorphization of the polymer structure.¹⁵ Although significant, at room temperature, improvement for dry electrolytes is not yet sufficient for that required by today's commercial Li-ion batteries ($\sim 10^{-3}$ S cm⁻¹).² PEO has been used before for transporting Zn ions;^{14,16,17} however, most work on improving ionic conductivity, including the addition of ceramic fillers, has been based around the Li system.

Here we use a standard zinc–carbon (Leclanché) battery to demonstrate the use of various nanomaterials to achieve a solid, flexible battery concept and investigate its performance under mechanical stress. Leclanché batteries are the least expensive primary batteries and are widely used in applications requiring low power drain. The anode of these batteries consists of metallic zinc, while the cathode consists of manganese dioxide (MnO₂) and active carbon powder. The electrodes are kept electrically isolated by means of a porous separator that is soaked with electrolyte, a moist

aqueous paste of zinc chloride (ZnCl₂) and ammonium chloride (NH₄Cl).¹⁸

We investigate each component of the battery with the aim of achieving performance enhancement, a tolerance to bending, and eliminating the use of liquid components. This is achieved by the use of a range of different nanomaterials, including ceramic nanoparticles, carbon nanofibers, and nanotubes. Titanium oxide (TiO₂) nanoparticles are used as ceramic fillers to improve the ionic conductivity and mechanical stability of the PEO polymer electrolyte. We show that the addition of TiO₂ nanoparticles to the Zn–PEO system enables solid battery performance to approach that of the liquid counterpart under low drain conditions. Flexible, conducting, and

high surface area carbon nanofiber mats with controllable dimensions are utilized for current collection and also provide support for cathodic MnO₂ particles (Figure 1). Single-walled carbon nanotubes (SWNTs) are intercalated with cathodic MnO₂ particles to improve electrical conductivity. This cell configuration extends shelf life and provides excellent mechanical stability with only a minor sacrifice in performance compared to the liquid counterpart. Battery performance under mechanically flexed conditions has also been investigated. The schematic and optical micrograph of the flexible battery is shown in Figure 2.

RESULTS

Following fabrication, batteries were discharged at a constant current of 0.5 mA with a computer-controlled Keithley 2400 source meter. Figure 3A shows the effect of the cathode support on the discharge characteristics of liquid electrolyte batteries. Bendable carbon nanofibers of different diameters were used. Cathode MnO₂:SWNT ratio was kept constant at 40:1. Battery capacity increases with decreasing carbon fiber diameter. The results can be understood by considering a

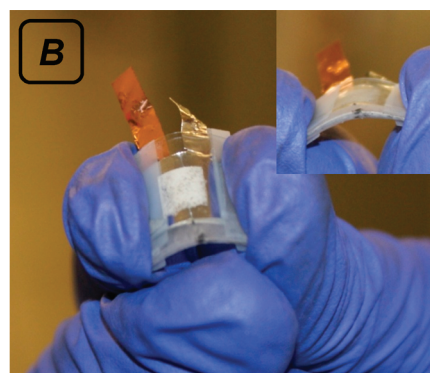
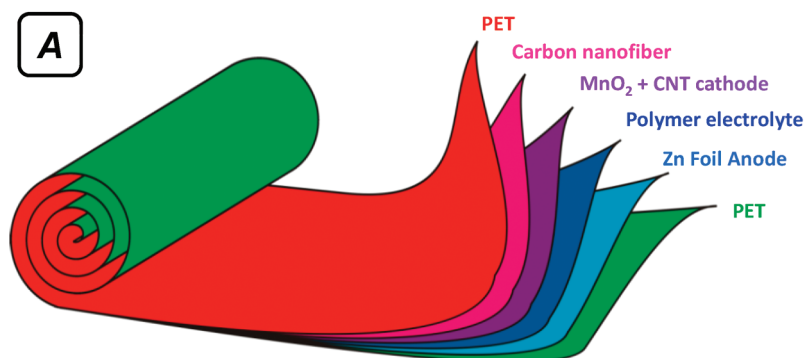


Figure 2. (A) Structure of the battery studied in this work. Each component needs to withstand flexing in order to get an overall flexible battery; (B) optical photograph of a flexible battery.

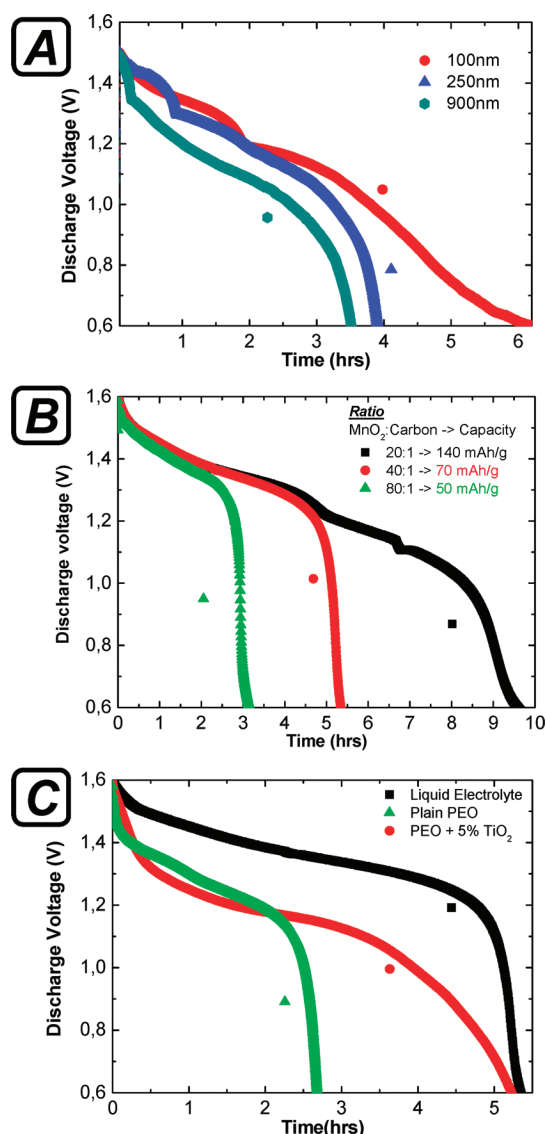


Figure 3. Constant current discharge curves showing the effect of (A) average fiber diameter on the performance of liquid electrolyte batteries. (B) Variation in battery performance as affected by a variation in MnO_2 :SWCNT ratio. (C) Different electrolytes: liquid, PEO, and ceramic enhanced PEO. All curves taken at 0.5 mA/cm^2 constant discharge.

few properties of the carbon support, sheet conductivity, surface area, and pore size (Table 1). Decreasing fiber diameter results in both a higher surface area (SA varies between 600 and $800 \text{ m}^2/\text{g}$ for the fibers used), resulting in a larger charge collection area, and higher sheet conductivity, which results in lower internal resis-

tance. Decreasing fiber diameter also decreases the average pore size. In the case of the liquid electrolyte (used in these samples), the liquid is able to penetrate between the pores together with the smaller diameter MnO_2 particles and the increased surface area is accessible. This configuration provides a very high surface area to carbon weight ratio. Figure 3B shows the effect of MnO_2 :SWCNT ratio. Rigid $500 \mu\text{m}$ thick graphite sheets (Duragraph 465) were used as charge collectors for these samples. Resulting battery capacity ranges from 50 to 140 mAh/g of MnO_2 . The discharge capacity is evaluated by discharging the battery to 0.7 V . A higher initial discharge voltage ($\sim 1.55 \text{ V}$) compared to Kiebele's nanotube work⁵ ($\sim 1.45 \text{ V}$) is noted, which may be attributed to the lower sheet resistance of the carbon fiber mat as compared to SWCNT thin films. It is also observed that increasing SWCNT concentration results in a lower voltage being reached before commencing the steep decline. We attribute this to enhanced charge transport leading to a deeper level of discharge since the $\text{Zn}-\text{MnO}_2$ cell involves a few different reactions depending on the depth of discharge.

Batteries fabricated with PEO polymer electrolyte show very poor performance compared to their liquid electrolyte counterpart, as shown in Figure 3C. Low ionic mobility makes the polymer unusable at room temperature, becoming useful only at about $60-80^\circ\text{C}$ when the amorphous stage is reached. We observe, however, in the ZnCl system, upon addition of 5 wt % TiO_2 nanoparticles, the polymer battery has a similar discharge time to the liquid case, albeit at a lower voltage due to the increased internal resistance. Fabrication in an inert atmosphere resulted in a somewhat degraded performance. Presence of both water and TiO_2 nanoparticles has some effect in preventing the crystalline phase and hence improving the ionic mobility.^{15,16} The first advantage of this type of battery comes in reduced packaging requirements. Testing of an unpackaged polymer battery left in air 1 week after fabrication still showed over 95% of its original capacity, whereas for the liquid counterpart, electrolyte evaporation occurred and the battery ceased to even provide a voltage.

Bringing all of the components of the battery together, that is, carbon fiber, $\text{MnO}_2 + \text{SWCNT}$ cathode, and the polymer electrolyte with TiO_2 nanoparticles, results in an all-solid and mechanically flexible battery.

TABLE 1. Properties of Carbon Nanofiber Sheets

average fiber diameter	thickness (μm)	sheet conductivity (S/cm)	surface area ^a (m^2/g)	mercury porosimetry	
				average pore size (μm)	porosity (%)
100 nm	15	10.26	792	0.39	66.1
250 nm	25	4.35	801	0.77	77.3
900 nm	80	1.75	607.8	5.10	89.9
graphite	500	714.29			

^aBET specific surface area.

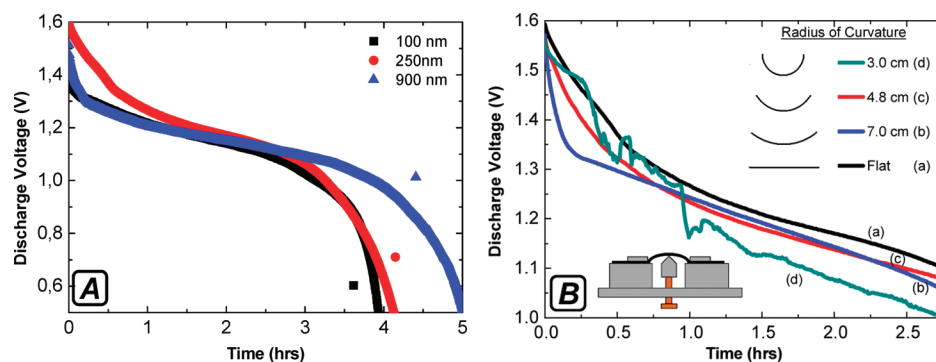


Figure 4. (A) Discharge curves of fully flexible and solid batteries and the effect of fiber diameter in performance. (B) Discharge characteristics showing performance of the solid-state battery at different bending strains. Up to 4.8 cm radius of curvature, the discharge characteristics are similar within a typical variation between samples. At 3.0 cm radius of curvature, although the battery still works, the effect of the strain on materials and contacts can be observed.

Figure 4A shows the discharge curves of the fully solid battery with different carbon fiber diameters. Although at these low discharge currents performance is similar to the liquid case, capacity increases with increasing fiber diameter, contrary to the liquid case. This may be explained, however, by taking into account the nature of the electrolyte. The solid nature means that, even though it can conform onto the surface to some extent, penetration into smaller pores is poorer than in the liquid case, and the effective surface area of the fibers becomes much reduced. The fiber with the largest pore size (Table 1) becomes more effective at reaching the electrolyte.

A paramount requirement for a flexible battery is that it should perform under mechanically stressed conditions. The mechanical properties of the individual layers are good. Figure 4B shows the initial discharge profiles of battery bending tests using a simple setup for inducing a curvature. Relatively small changes were observed in the discharge characteristics during strained measurements, up to a radius of curvature of ~ 4 cm. Beyond about 3.0 cm radius of curvature, the effect of the stress on the material and the battery construction becomes visible on the battery performance. Discharge characteristic becomes unstable and discharges sooner than in the other cases. We attribute this to the powder nature of MnO_2 , resulting in cracking and poorer

contacts. Measurements in relaxed conditions after several bending cycles actually show an improved discharge characteristic. We tentatively attribute this conditioning to bending causing better penetration of the MnO_2 particles into the fiber pores. We predict that nanosized MnO_2 for proper infiltration in the fiber pores or direct growth of nano- MnO_2 onto the fibers would circumvent the problems reported here. However, further investigations are in progress to determine the detailed reasons and to achieve better device characteristics under higher strain values.

In conclusion, we have demonstrated a low-cost, solid-state flexible battery concept that can be easily fabricated in ambient conditions. Various nanomaterials (TiO_2 nanoparticles, SWCNTs, carbon nanofibers) are exploited in a number of ways to optimize the performance of Leclanché batteries. The demonstrated concept gains importance in applications where flexibility, portability, and cost are important. These batteries would be very well suited as disposable power sources for intelligent textiles. Batteries could either be stamped/glued as a “patch” onto the power-requiring textile parts, or the individual textile fibers could be made into batteries. The use of carbon fibers is particularly promising in this respect. Further work is in progress to develop this into higher energy density, secondary Li systems.

EXPERIMENTAL SECTION

Carbon nanofibers, synthesized through an electrospinning procedure, are used as three-dimensional, high surface area, high conductivity cathode current collectors. The fibers were synthesized as reported elsewhere.¹⁹ Briefly, methanolic solution of phenolic resin and poly(vinyl butyral) (PVB) was injected through a stainless steel nozzle with an applied voltage of 15 kV. PVB was used as an additive in order to improve dimensional stability of the as-spun phenolic resin fabrics. Spinnings were carried out at ambient conditions, and fibers were collected on a grounded aluminum collector. The as-spun fibers were then cured by adding formaldehyde followed by carbonization at 900 °C for 2 h in a nitrogen atmosphere. The resulting nanofibers had the form of a self-standing mat, and their morphology is shown in Figure 1A–C. It is possible to control the average di-

ameter of the fibers from ~ 3 μm down to ~ 100 nm. We recently demonstrated that the electrospun carbon fibers (micrometer sized) can be used as a flexible current collector in dye-sensitized solar cells,²⁰ and in the current work, we are expanding the use of flexible nanofibers as electrode materials in batteries.

For the next layer, the active cathode material, MnO_2 powder (activated, Sigma Aldrich, <5 μm , 85%), is used. To enhance its low conductivity, MnO_2 is generally mixed with carbon black with MnO_2/C ratios between 11:1 and 3:1.¹⁸ In this work, we use SWNTs as an alternative to carbon black, similar to the approach taken by Kiebele and Gruner.⁵ The one-dimensional nature and the high conductivity of SWNTs allows optimum performance at MnO_2/C ratios around 40:1 to 20:1, resulting in a lighter and thinner cathode overall. The 1D structure

of SWNTs should also allow for greater tolerance to mechanical distortions. The cathode paste was produced by rigorous mixing of SWNTs (Sigma Aldrich, Arch Discharge, 50–70 vol % purity) and MnO_2 powder in the right proportion with a drop of liquid electrolyte (described later). The resulting mixture consists of typically 40 mg of MnO_2 and 1 mg of SWNTs, from which ~ 37 mg is collected and pasted onto a 1 cm^2 area over the carbon nanofiber mat and allowed to dry in ambient air. This results in a $\sim 300\text{ }\mu\text{m}$ thick film. Figure 1D shows a typical SEM image of MnO_2 paste partially covering the carbon fiber mat, giving an indication of relative particle size.

The electrolyte must allow the passage of respective ions, while blocking electronic conduction between the active components. A standard aqueous electrolyte was used to produce the cathode paste, as well as for initial tests to compare the performance of different carbon fibers. The liquid electrolyte consists of an aqueous solution of 4.4 g of NH_4Cl and 1.5 g of ZnCl in 10.5 mL of DI water. In batteries with liquid electrolyte, a cellulosic filter paper (Whatman) was used as a separator. Dry polymer electrolytes, on the other hand, do not require a separator, as the electrolyte acts as a separator itself. In our case, we use PEO (polyethylene oxide, $M_w \sim 600\,000$, Sigma Aldrich) due to ease of fabrication, good electrochemical stability, low flammability, and toxicity with the ability to form good interfacial contact with electrodes. A solution of electrolytic salts and PEO (specifically, 25 mg/mL PEO, 11 mg/mL NH_4Cl , 3.75 mg/mL ZnCl) in acetonitrile was stirred for 2–3 days; 100 μL of this solution was casted onto the electrode and allowed to dry in air at moderate temperature ($\sim 35^\circ\text{C}$), resulting in a homogeneous film. Additionally, TiO_2 nanoparticles (99.7% anatase, $<25\text{ nm}$, Sigma Aldrich) were dispersed into the same mixture in varying weight percentages with respect to PEO, which resulted in a greatly improved ionic conductivity.

Finally, to complete the batteries, a thin ($100\text{ }\mu\text{m}$) Zn foil (Advent Research Materials) was used as the anode. Batteries produced had a 1 cm^2 area. The batteries were attached to and sandwiched between two pieces of polyethylene terephthalate (PET) substrates with double-sided tape, and strips of copper foil were used as external contacts.

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