Research Article

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Carbon Nanotubes Coated Paper as Current Collectors for Secondary Li-ion Batteries

https://doi.org/10.1515/ntrev-2019-0002
Received Nov 26, 2018; accepted Dec 19, 2018

Abstract: We developed a surfactant-free spray coating process to coat commercial cellulose-based paper with carbon nanotubes (CNTs) and prepared paper-CNTs current collectors for Li-ion batteries (LIBs). The paper-CNTs were used as current collectors for replacing conventional aluminum foil. Li-ion batteries assembled using paper-CNTs were coated with LiFePO₄ as the active material and used as cathodes with Li as the anode, and the assembled LIBs showed a high energy density of 460 Wh kg⁻¹ at a power density of 250 W kg⁻¹. These electrodes were stable even at a current density as high as 600 mA g⁻¹, and showed cycling stability for ~450 cycles at 150 mAh g⁻¹. Furthermore, paper-CNTs based electrodes showed ~17% improvement in areal capacity compared to commercial aluminum-based electrodes suggesting that paper-CNTs can readily displace Al foils as current collectors.

Keywords: LiFePO₄; Carbon nanotubes; Paper; Li-ion batteries

There has been a growing interest in displacing relatively-heavy metallic current collectors in Li-ion batteries (LIBs) with lightweight paper/cellulose based substrates for efficient energy storage. In addition to lightweight and flexibility, the use of paper-based cathodes for LIBs has many advantages such as the low cost of raw materials, ease of availability, biodegradability, and convenient integration into the existing manufacturing lines and safety [1–12]. A critical roadblock, however, is that paper is electrically insulating unlike traditional metallic current collectors such as Al and Cu used in LIBs. In this regard, many researchers have endeavored to make cellulose fiber-based conducting composites, or coat papers with different conducting materials (e.g., activated carbon) using binders [13–16]. These processes invariably involve the use of additives, such as insulating binders (e.g., butyl rubber) and surfactants [13–20], which result in a lower gravimetric capacity due to the compromised electrical conductivity and increased amount of inactive material present in the electrode. Herein, we developed an additive-free roll-to-roll spray coating technique to prepare highly-conducting multi-walled carbon nanotubes (CNTs) coated paper which can be used as current collectors. Our method doesn’t involve heat for drying since we used ethanol for spray coating which can be easily evaporated at room temperature, thus making paper-CNTs based current collectors more economically viable. Given that the average diameter of cellulose fibers is on the or-
order of few tens of microns, CNTs are ideal for achieving a conformal conductive coating on these fibers. Specifically, we demonstrate that roll-to-roll spray coated paper-CNTs substrates can be used as current collectors for LiFePO$_4$ (LFP)-based LIBs. The as-prepared paper-CNTs current collectors exhibited a low sheet resistance (~243 ohm/m$^2$) even at a low CNT mass loading ~0.3 mg cm$^{-2}$. A full cell containing a graphite anode and a 90 wt.% LFP coated paper-CNTs cathode showed a gravimetric capacity of ~150 mAh g$^{-1}$ at 0.5C rate (75 mA g$^{-1}$). At the material level, the paper-CNTs based LIBs prepared in this study exhibited an energy density of 460 Wh kg$^{-1}$ at a power density of 250 W kg$^{-1}$. Furthermore, the LFP coated paper-CNTs cathodes exhibited a ~17% improvement in areal capacity compared to the Al-based LFP cathodes with excellent stability for ~450 cycles at 150 mA g$^{-1}$, and robust performance at high rates up to ~600 mA g$^{-1}$.

1 Methods

1.1 Spray coating paper with CNTs

CNTs: The MWCNTs (diameter < 8 nm, 10 - 30 µm long, > 95 wt.% purity, and > 500 m$^2$/g specific surface area) used in this study were purchased from Cheap Tubes Inc. (Catalog Number: 030101). A Branson Sonifier 250 (200 Watt, operated at 40% duty cycle) was used to sonicate the CNTs for two cycles, wherein each cycle lasted for 15 minutes with a 10-minute break between consecutive cycles.

Paper: Regular copy paper (8 ½” x 11”) purchased from Staples was used as the substrate.

Spray coating process: An entire (8 ½” x 11”) sheet of paper was spray coated twice (each lasting for 5 s) using a mobile spray gun (Iwata 5095 WS400 with 1.3 mm nozzle and 29 psi ambient air pressure) that was placed at a distance of 40 cm from the paper. The spray coated paper was allowed to dry at room temperature after each coating cycle.

Foils: The activated carbon coated aluminum foils were purchased from MTI Inc. (Catalog Number: EQ-CC-Al-18u-260).

1.2 Electrode slurry preparation

The LFP cathodes were prepared by dispersing carboxymethylcellulose (CMC) (1 wt.%, MTI Corp.), styrene-butadiene rubber (SBR) (4 wt.%, MTI Corp.), timcal graphite & carbon super P (5 wt.%, MTI Corp.), and LiFePO$_4$ (90 wt.%, MTI Corp.) in DI water (18 MΩ). CMC was first dissolved completely in water at 85°C, and subsequently, SBR was added to this solution at room temperature. Carbon super P and LFP powders were dried, mixed and added to the above solution with continuous stirring. The resulting slurry was stirred overnight, and a doctor blade set to 100 µm was used to coat bare paper and paper-CNTs current collectors. Next, the coated papers were dried at room temperature, and subsequently, oven dried at 100°C for 6 h in a precision compact oven. The LFP mass loadings in these coatings was ~3.4 mg cm$^{-2}$.

1.3 Coin cell preparation

Cathodes (dia. ~10 mm) were stamped, weighed and soaked in an electrolyte of 1M lithium hexafluorophosphate (LiPF$_6$) in ethylene carbonate and dimethyl carbonate (w/w = 1:1, Sigma-Aldrich) before assembling them into 2032 type coin cells with a lithium chip (15.6 dia. x 0.45 mm thick, MTI Corp.) as the counter electrode. Here we used a lithium chip which is bigger than the cathode in size and capacity, hence the anode is not the limiting electrode. These electrodes were separated by a Celgard 2325 separator (Celgard, LLC) that was presoaked in the electrolyte. The coin cells were assembled inside a glove box where oxygen and moisture contents were below 0.1 ppm. Full cells were assembled with commercial graphite coated on copper foils (MTI Corp.) as the counter electrodes.

1.4 Galvanostatic charge-discharge (GCD) measurements

The electrochemical characterization was carried out using an MTI multi-channel battery analyzer. LFP cells were initially conditioned by charging and discharging over a potential range of 2.0 to 4.2 V at a C/4 rate (1C = 150 mA g$^{-1}$). Subsequently, GCD studies were performed at varying current rates (0.5C to 4C) to compare their electrochemical performance. At the material level, gravimetric energy and power densities were calculated based on the weight of the active material, i.e., LFP.

1.5 Electrochemical Impedance Spectroscopy (EIS)

After conditioning, EIS was conducted on the cells from 1 MHz to 0.1 Hz, at 0 V vs. OCV with an AC amplitude of 20 mV.
2 Results and Discussion

As shown in Figure 1a, scanning electron microscopy (SEM, Hitachi S4800) revealed a network of micron-sized fibers with high porosity in uncoated paper. Figure 1b shows that the paper retained its fibrous structure and porosity even after it was spray coated with CNTs. Thermogravimetric analysis revealed a very low mass loading of CNTs (~0.3 mg cm\(^{-2}\)) on the paper; and at this mass loading, the paper-CNTs exhibited a sheet resistance ~240 ohm per square. As described in the methods section, LFP was deposited on paper-CNTs and uncoated paper, and assembled into a half-cell using Li metal anodes to evaluate their electrochemical performance. Representative SEM images of LFP coating on paper-CNTs (top and cross-sectional view) are shown in Figures 1c and 1d.

![Figure 1: Representative scanning electron micrographs of (a) uncoated paper, (b) paper coated with carbon nanotubes (CNTs), (c) top view and (d) cross-sectional view of LiFePO\(_4\) coated on paper-CNTs.](image)

We employed cyclic voltammetry to monitor the intercalation/de-intercalation of Li\(^+\) in cells assembled using uncoated paper/LFP (paper/LFP) and paper-CNTs/LFP cathodes at a scan rate of 0.1 mV s\(^{-1}\) as presented in Figure 2a [21]. Paper-CNTs/LFP electrodes showed an oxidation peak current density of 0.179 A g\(^{-1}\) at ~3.8 V and a reduction peak current density of ~0.136 A g\(^{-1}\) at ~3 V. On the other hand, uncoated paper/LFP has negligible peaks as evident in the inset of Figure 2a due to poor electrical conductivity of paper.

These cells were further characterized to elucidate the changes in charge transfer resistance values (R\(_{ct}\)) using electrochemical impedance spectroscopy (EIS) [22] (Figure 2b). The Nyquist plots for paper-CNTs/LFP, and paper/LFP exhibited a classical single time-constant behavior, which was modeled using Randles circuit analysis [23] (inset in Figure 2b). The characteristic semicircle in the mid- to high-frequency regions, which corresponds to R\(_{ct}\), is relatively lower (~69.3 \(\Omega\)) in the case of paper-CNTs/LFP electrodes compared to that in paper/LFP electrodes (~239 \(\Omega\)). Given that all the cells have the same electrolyte, the three-fold reduction in R\(_{ct}\) for the paper-CNTs/LFP is attributed to the presence of CNTs.

The GCD responses of the paper-CNTs/LFP half and full cells at 0.5C rate (75 mA g\(^{-1}\)) are shown in Figure 3a. All gravimetric capacities were determined at the material level by dividing the total capacity with the active material (i.e., LFP) weight. Gravimetric capacities (~140 mAh/g) reported for commercial LFP powders coated on Al foils (MTI Corp.) [24, 25] have been achieved with our paper based current collectors due to the coating of CNTs. As discussed in the methods section, we assembled full cells using a graphite anode and a paper-CNTs/LFP cathode. These cells showed a gravimetric capacity value of ~150 mAh g\(^{-1}\). However, a slight reduction in the discharge voltage was observed in the response of the full cell due to the presence of the graphite anode instead of the Li metal anode. The performance of paper-CNTs/LFP electrodes was further evaluated at different C-rates of 0.5 – 4C (75 – 600 mA g\(^{-1}\)) between 2.0 – 4.2 V and the results are presented in Figure 3b. These cells showed high capacity values of ~74 mAh g\(^{-1}\) even at a very high current density of 600 mA g\(^{-1}\) (4C rate). The decrease in the capacity values at higher C-rate is expected as the gravimetric capacity of LIBs decreases at higher power/current densities. Nevertheless, after the 4C cycling, the paper-CNTs/LFP electrodes were cycled again at 0.5C rate and the initial capacity values were recovered showing that the loss of capacities at high C-rates are reversible (Figure 3b). We also fabricated cells using activated carbon coated Al (Al/C) current collectors (MTI Corp.) coated with LFP (active material mass loading ~34 mg cm\(^{-2}\)) to compare the performance of paper-CNTs/LFP with conventional cells [21]. The areal capacity values of paper-CNTs/LFP and Al/C/LFP electrodes are comparable as seen in Figure 3c with the former exhibiting slightly improved values. At the 2C rate, paper-CNTs/LFP...
Figure 2: (a) Cyclic voltammograms (0.1 mV s$^{-1}$) and (b) Nyquist plots for LiFePO$_4$ electrodes (with paper and paper-CNTs current collectors). The inset in Figure 2b shows the Randles circuit for single time-constant behavior observed in the Nyquist plot.

Figure 3: (a) Gravimetric charge-discharge curves, (b) C-rate cycling, (c) Areal capacities, and (d) Cycling performance of paper-CNTs/LiFePO$_4$ electrode. Inset in panel (b) depicts the representative galvanostatic discharge curves for the 5$^{th}$ cycle of each C-rate series. Inset in panel (d) is the Ragone plot and the numbers in the legend in the inset of Figure 3d denote references for other works that used paper-based electrodes.
This simple method of electrode fabrication didn’t comeelectroactive materials of our modified current collectors.
images. We also adopted a water-based slurry for coating of the commercially available paper as evidenced by the SEM images. We used a water-based slurry to coat active materials on paper-CNTs current collectors, which is greener, economical, and sustainable. Using a water-based slurry, it is difficult to achieve uniform coating of the active material on Al/C current collectors - cracks often develop which results in a poor overall resistance of the electrode. Unlike Al, paper has a high affinity for water, which allows it to easily wick the slurry resulting in a homogenous coating even with 90% active materials. This ability led to the improved performance presented in Figures 2 and 3. Although previous reports demonstrated the possibility of using paper-based electrodes, they achieved an active material loading of only 70 – 80% in their electrodes [1, 3, 13, 15, 16]. In our case, the paper-CNTs allowed for ~90% active material loading. As discussed in our previous work (ACS Omega 2018, 3, 4502-4508), the presence of CNTs reduces the resistance at the cathode current collector and active material interface (CCAMI) and thus provides access to the capacity of most of the active material, resulting in high energy density values. The robustness of our paper-CNTs/LFP electrodes was tested by cycling them at 1C rate for 450 cycles (Figure 3d). As evident from Figure 3d, the paper-CNTs/LFP electrodes exhibited excellent coulombic efficiency and cycling stability. Paper-CNTs/LFP electrodes were found to have an energy density of 460 Wh kg⁻¹ at a power density of 250 W kg⁻¹, which is superior to previously reported paper-based electrodes (inset of Figure 3d) [1–3, 16].

3 Conclusion

We successfully coated LIB cathode material on a CNTs modified paper based current collector. We used a surfactant-free conformal coating of CNTs on the fibers of the commercially available paper as evidenced by the SEM images. We also adopted a water based slurry for coating of electroactive materials of our modified current collectors. This simple method of electrode fabrication didn’t come promise on the performance of the LIBs assembled from these electrodes. Full cells made from these LFP based electrodes showed high capacity values of ~150 mAh g⁻¹. Paper-CNTs/LFP electrodes had excellent stability and cyclability for over 500 cycles. They exhibited a high energy density of 460 Wh kg⁻¹ at a power density of 250 W kg⁻¹ (150 Wh kg⁻¹ at a power density of 80 W kg⁻¹ at the battery level).

Acknowledgement: This work was financially supported by NASA-EPSCoR project “Nanomaterials-based Hybrid Energy Storage Devices” #2022438. The authors would like to sincerely thank Prof. Joseph Thrasher for his help with TGA analysis, Mr. Prakash Parajuli for help with spray coating, Ms. Divya T. Vedullapalli for her help with the analysis of GCD data, Dr. Srirparna Bhattacharya and Dr. Longyu Hu for resistivity measurements.

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