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Carbon nanotubes and carbon-coated current collector significantly improve the performance of lithium-ion battery with PEDOT:PSS binder

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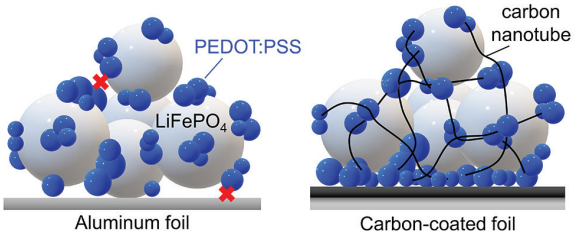
We report an approach for enhancing performance of PEDOT:PSS binder in Li-ion battery electrodes by introducing small amount of carbon additives. Coating of current collector with carbon increases adhesion and electrical contact to the binder while introduction of carbon nanotubes enhances the electrical contact between the binder particles. The combination of these factors improves rate and cycling capability of the electrode.



Keywords: Li-ion battery, cathode, binder, conducting polymer, carbon nanotubes, current collector, adhesion.

A lot of research has been recently focused on developing rechargeable Li-ion batteries for electric vehicles and stationary energy storage applications.[1–3] The increasing demand for high-power batteries requires further optimization of the battery electrode composition, including the development of efficient binding and conductive additives.[3–5] Poly-(3,4-ethylenedioxythiophene):polystyrenesulfonate composite (PEDOT:PSS) is widely considered as a promising binder for the battery electrodes[5–8] due to its eco-friendly aqueous-based processing, electrochemical stability, electronic and ionic conductivity. However, PEDOT:PSS demonstrates weak binding properties[5,8] and poor adhesion to the metal current collectors,[9,10] which result in deterioration of cycling performance of the electrodes.[9] Another issue is relatively low electronic conductivity of PEDOT:PSS causing overvoltage and poor rate capability of the electrodes.[11] Several approaches have been suggested to enhance the performance of PEDOT:PSS binders such as addition of co-binders[5,12,13] or conductive carbon black.[12,14] However, addition of these electrochemically inactive components decreases the gravimetric and volumetric energy density of the battery.

In this work, we attempted to enhance the conductive properties of PEDOT:PSS binder with small quantities of single-walled carbon nanotubes (SWCNT). Moreover, we have improved mechanical characteristics of the electrodes by applying a current collector coated with a thin layer of carbon which provides strong adhesive interaction with PEDOT:PSS binder. We especially focused on introducing the least possible amount of the carbon additives, which did not significantly affect the overall weight and specific energy of the battery.

The electrodes were based on lithium iron phosphate ($LiFePO_4$), which is one of the most recognized cathode active materials for Li-ion batteries,[1–3] and PEDOT:PSS or PEDOT:PSS/SWCNT as a binder. To prepare the PEDOT:PSS/SWCNT binder, we distributed SWCNT in PEDOT:PSS aqueous dispersions by ultrasonication; the resulted dispersions demonstrated excellent stability with no phase separation under centrifugation at 10000 rpm. The final electrode compositions were deposited from the aqueous slurries onto the aluminum (Al) or carbon-coated aluminum (Al-C) current collectors.

Adhesion of the binder films and composite electrodes to the different types of current collectors was characterized by the standard T-peel test. Carbon-coated foil (Al-C) provided an order of magnitude higher adhesion strength in comparison with conventional Al foil (Table 1). We have also compared the images of the current collectors remained after the peel-off tests (Figure S1). The Al current collector had clean metallic surface with no remained binder. On the contrary, dark layer was observed on the delaminated Al-C foil. This layer was thicker than initial carbon coating and attributed to the remained PEDOT:PSS binder particles. Therefore, Al-C foil provided cohesive delamination mechanism in peeling tests, which indicated strong affinity of Al-C to the binder.[9,15] It is due to the better wettability of Al-C foil by the aqueous electrode slurry as compared to Al foil (water contact angles 46 and 69°, respectively), that enhanced the interfacial contact of Al-C surface with the electrode.[16]

Further, we examined the effect of SWCNT on the electrical conductivity of the binder and electrodes, which was measured with a standard four probe technique. We prepared the samples with binder-to-SWCNT weight ratio of 96:4, based on preliminary data on electrical conductivity (Figure S2). The addition of SWCNT enhanced the electrical conductivity of PEDOT:PSS films by two orders of magnitude (Table 1) due to the additional conductive pathways between the PEDOT:PSS particles formed by SWCNT.[17] Similarly, the final electrode compositions demonstrated higher electrical conductivity with SWCNT added, while the peel strength of the electrodes was not affected by such a low amount of SWCNT (Table 1). It also worth noticing that the addition of SWCNT enhanced film-forming properties of PEDOT:PSS. In fact, while pristine PEDOT:PSS yielded brittle films with cracks, PEDOT:PSS/SWCNT films were dense and uniform (Figure S3). Therefore, the nanotubes connect the individual PEDOT:PSS particles, thereby improving both conductivity and mechanical integrity of the PEDOT:PSS.

Table 1 Characteristics of the binder films and $LiFePO_4$-based composite electrodes.[a]

Coating composition	Peel strength/N cm^{-1}		σ/S cm^{-1}	R/Ω	
	Al	Al-C		Al	Al-C
PEDOT:PSS	0.13 ± 0.03	0.9 ± 0.1	1.8 ± 0.4	N/A	N/A
PEDOT:PSS/SWCNT (96 : 4 w/w)	0.17 ± 0.02	> 1.0	190 ± 50	N/A	N/A
$LiFePO_4$/PEDOT:PSS (95 : 5 w/w)	0.03 ± 0.01	0.51 ± 0.05	0.21 ± 0.04	181	125
$LiFePO_4$/PEDOT:PSS/SWCNT (95 : 4.8 : 0.2 w/w/w)	0.05 ± 0.01	0.55 ± 0.04	8 ± 1	5.6	2.0

[a] σ is the electrical conductivity, Al is the aluminum current collector, Al-C is the carbon-coated aluminum current collector, R is the resistance of the composite electrodes.

Electrodes prepared under different conditions were characterized in more detail by electrochemical impedance spectroscopy. The resistance of the electrode (R, Table 1) was obtained by fitting the impedance spectra (Figure S4) to a standard Randles equivalent circuit.[18] The total resistance value is influenced by charge transfer resistance at the electrode/electrolyte interface and contact resistance at the electrode/current collector interface, however the exact resistances of these processes are difficult to separate[19]. The total resistance values were affected by the type of current collector and the presence of SWCNT. The use of carbon-coated current collector reduces the resistance by 30–65% (Table 1) by reducing the contact resistance at the electrode/current collector interface.[20,21] The introduction of SWCNT into electrodes results in a strong decrease of R value by 30–60 times (Table 1) due to the high electrical conductivity of SWCNT network.[22] The electrode with both SWCNT and carbon-coated current collector demonstrates the lowest resistance of 2 Ω.

In Figure 1 we compare the electrochemical performance of the composite electrodes in Li-ion half-cell systems. It can be seen that both the SWCNT and type of current collector affect the hysteresis between charge and discharge processes [Figure 1(*a*)]. The hysteresis between the voltage plateaus is determined by the charge transport resistance[23] and correlates well with the impedance data (R, Table 1). The lowest hysteresis between the voltage plateaus of 0.12 V corresponds to the electrode made with SWCNT and Al-C current collector [Figure 1(*a*)], which also has the lowest resistance.

Discharge capacity of the electrodes at higher rates (3C–20C) is mostly affected by the presence of SWCNT in the electrode [Figure 1(*b*)]. Note that only the electrodes made with SWCNT operates at high rates >3C. SWCNT enhances the electrical conductivity pathways in the electrode and decreases electrical resistance, which accelerates the kinetics of lithium intercalation/deintercalation.[22] The use of a carbon-coated current collector additionally increases the capacity of these electrodes at higher current densities (10C–20C) which can be explained by a further decrease in electrode resistance (Table 1).

The cycling stability of the electrodes is compared in Figure 1(*c*). The electrodes prepared with Al foil demonstrate fast capacity fading reaching zero capacity after 100 cycles. The loss of capacity is associated with poor adhesion strength of these electrodes (Table 1). During cycling, $LiFePO_4$ particles periodically shrink and expand which leads to the loss of electrical contact between the electrode and current collector surface. As a result, both interfacial resistance and electrode polarization (Figure S5) increase leading to the poorer utilization of the active material capacity. The electrode made with PEDOT:PSS binder on the Al-C foil demonstrated better but still poor capacity retention of 25% after 100 cycles [Figure 1(*c*)] due to the loss of electrical contacts between the conductive PEDOT:PSS particles during cycling. The addition of SWCNT remarkably improved the capacity retention of this electrode up to 98% [Figure 1(*c*)], because SWCNT formed robust network among the PEDOT:PSS particles with additional conductive pathways which prevented the loss of electrical contacts between particles within the electrode. Thus, we can conclude that introduction of a small amount of SWCNT enhances the electrical conductivity within the electrode active layer while the carbon coating on Al surface improves the adhesion strength of the electrode laminate. Both of these factors play a key role in the operation of the electrode and only their combination provides good electrode cyclability.

To estimate the optimal electrode composition, we tried to reduce the amount of SWCNT in the electrode composition. However, the electrode formulated with 0.1 wt% SWCNT demonstrated worse rate and cycle performance as compared to that contained 0.2 wt% of SWCNT (Figure S6). Thus, the amount of SWCNT should be at least 0.2 wt% to attain good electrochemical performance of the electrodes.

Thus, we have developed a technique for improving the electrochemical characteristics of the PEDOT:PSS binder in lithium-ion battery cathodes by introducing a small amount of carbon nanotubes. The electrodes prepared with the addition of SWCNT demonstrate significantly increased electrical conductivity, reduced resistance to charge transfer, and improved rate performance. The use of a carbon-coated current collector

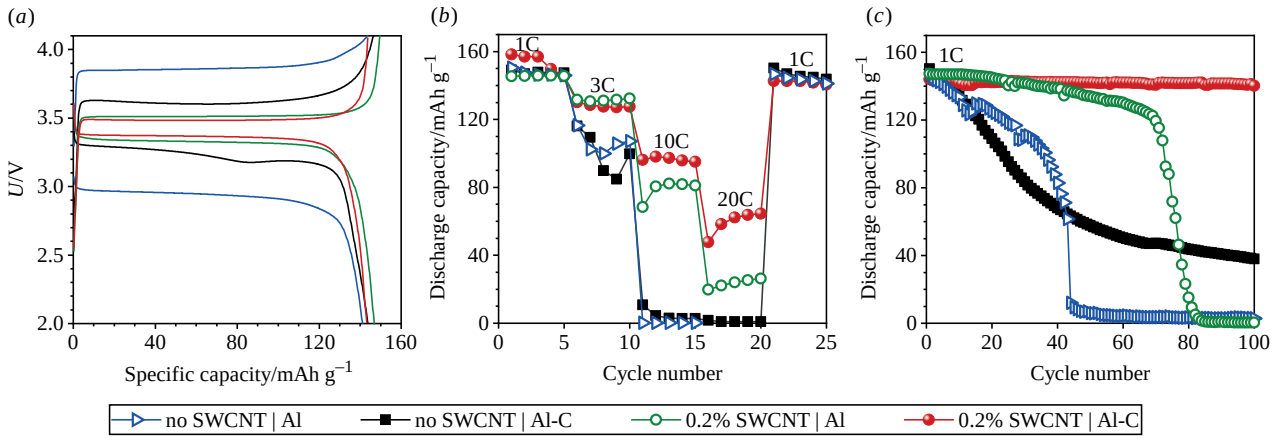


Figure 1 (*a*) Galvanostatic charge/discharge profiles (at 1C rate), (*b*) rate capability and (*c*) cycling performance (1C rate) of the $LiFePO_4$/PEDOT:PSS composite electrodes depending on the type of the current collector and the presence of SWCNT additive.

increases the adhesive strength of the electrode laminates and reduces the contact resistance at the electrode/foil interface. The carbon-coated current collector increases the interfacial stability of the electrode, and the SWCNT promotes charge transfer in the electrode volume. Both of these components are essential for good cycling performance of the battery cells.

The developed strategy requires a very small amount of carbon additives (only ~0.02 mg per cm^2 of the electrode area), so it will not limit the gravimetric and volumetric characteristics of the battery. Improved electrochemical characteristics make the developed electrode compositions promising for use in high energy batteries. More detailed studies may be required to optimize the chemical structure of the binder and the surface structure of the current collector.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.02.018.

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