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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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1. Experimental details

Materials

3,4-ethylenedioxythiophene (EDOT, Sigma Aldrich), poly(4-styrenesulfonate) (PSS, M_w = 75,000, 18 wt.% aqueous solution, Sigma Aldrich), ammonium peroxodisulfate ($(NH_4)_2S_2O_8$, Panreac), and carbon-coated $LiFePO_4$ particles ("T2", BTR New Energy Materials) were used as received. Single-walled carbon nanotubes (SWCNT, "Tuball", OCSiAl) were purified from metal catalysts in concentrated HCl prior use. Aluminum foil (Al, Gelon LIB) and carbon-coated aluminum foil (Al-C, Gelon LIB) current collectors were used as received.

Synthesis of PEDOT:PSS

PEDOT:PSS was prepared by oxidative polymerization of EDOT in aqueous solution of PSS. EDOT (265 μL) and PSS solution (4.72 mL, molar ratio EDOT : PSS = 1 : 2) were blended with distilled water (total volume 90 mL). The mixture was stirred for 3 h, then $(NH_4)_2S_2O_8$ dissolved in 10 mL of distilled water was added (molar ratio $(NH_4)_2S_2O_8$: EDOT = 1 : 1.2). The polymerization was carried out under vigorous stirring in a closed flask for 24 h. The polymerization product was separated by centrifugation (6000 rpm, 3 min). Excess PSS was removed from the resulting PEDOT:PSS by washing several times with ethanol, after that the polymer was dried under dynamic vacuum at 110 °C.

Preparation of the electrodes

PEDOT:PSS powder was mixed with SWCNT in the desired weight ratio (the SWCNT content was varied in the range 1 – 6 wt.%). The mixture was dispersed in distilled water in a concentration of 20 mg mL^{-1} using a Vibra-Cell VCX 750 ultrasonic processor (Sonics Materials, 20 kHz). The dispersion was thoroughly mixed with $LiFePO_4$ powder until completely homogenous (the fraction of $LiFePO_4$ was 95 wt.% with respect to the total solids content). The resulting slurry were spread on the surface of either Al or Al-C foil using a doctor blade applicator (Novotest AU-823) with a 250 μm gap. After being dried in air for 1 day, the coatings were roll-pressed. The disc shaped electrodes were cut out of the resulting laminates (the area of each electrode was 2 cm^2), weighed on a high precision balance (0.01 mg accuracy), and after that dried under dynamic vacuum at 130 °C for 4 h. The surface loading of $LiFePO_4$ was ca. 3–4 mg cm^{-2}.

Characterization

DC electrical conductivities of PEDOT:PSS/SWCNT films were measured by four probe method using a Loresta-GP MCP-T610 resistivity meter (Mitsubishi Chemical).

Peel strengths of the electrode laminates were measured according to the standard T-peel test using an EZ-LX universal testing machine (Shimadzu), the detailed experimental procedure has been reported by us earlier.[9]

The electrodes were tested in electrochemical half-cells with lithium metal foil as anode, glass fiber separator (Schleicher & Schuell MicroScience) and 1M $LiPF_6$/EC:DMC (1:1 v/v) electrolyte (Sigma Aldrich). The potentiostatic charge/discharge experiments were performed using a P-20X8 potentiostat-galvanostat (Electrochemical Instruments, Russia) within the potential range of 2.0–4.1 V vs Li/Li^+. The capacity values were normalized by the weight of $LiFePO_4$ material. The electrochemical impedance spectra of the cells were measured at 50% state-of-discharge using an Autolab PGSTAT302N potentiostat/galvanostat at open circuit potential within the frequency range of 10 kHz to 1 Hz (5 points per decade) with a voltage amplitude of 5 mV. The data were fitted using Nova 2.1 software.

2. Optical microscopy images of the current collectors

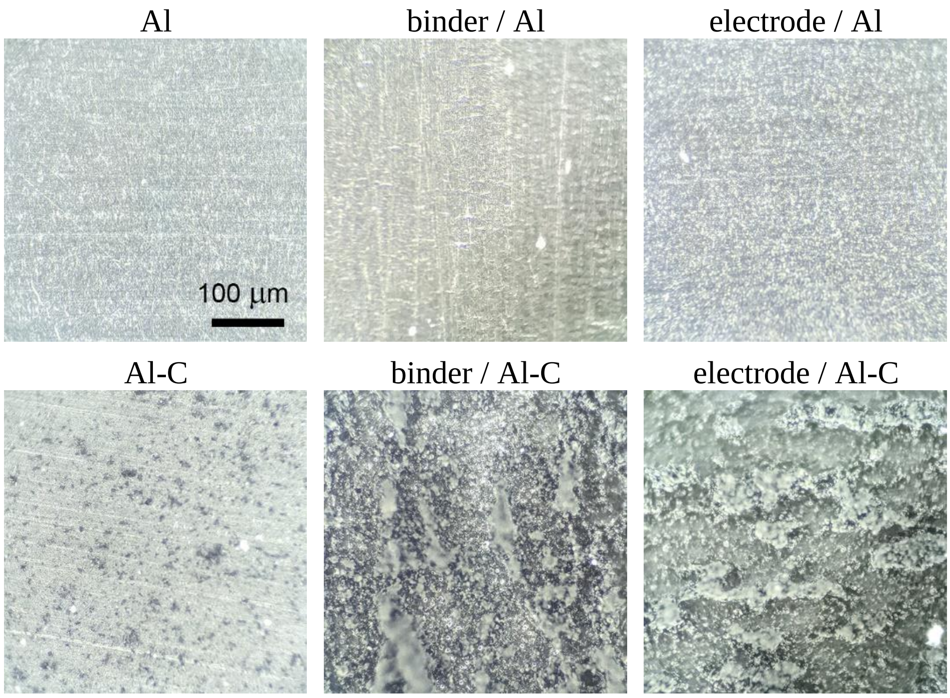

Figure S1 Optical microscopy images of the pristine aluminum (Al) and carbon-coated aluminum (Al-C) current collectors and the current collectors peeled off from the PEDOT:PSS binder films and electrodes laminates. The composition of the electrodes was $LiFePO_4$/PEDOT:PSS/SWCNT (95 : 4.8 : 0.2 w/w/w).

3. Characteristics of the binder films

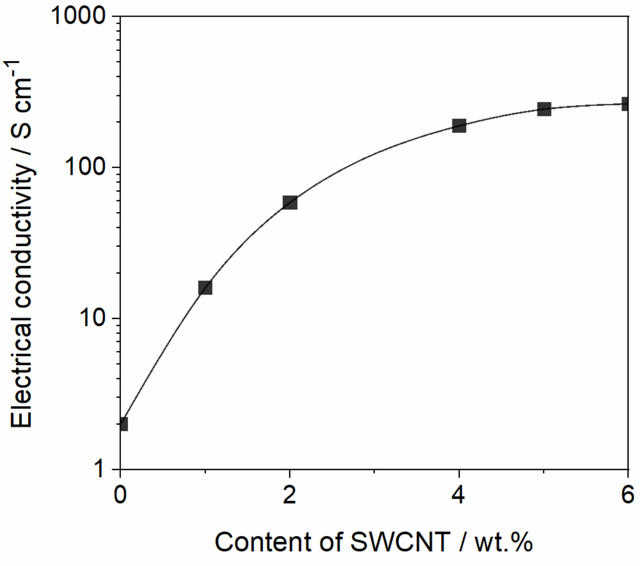

Figure S2 Electrical conductivity of dried PEDOT:PSS/SWCNT composite films as a function of the weight fraction of SWCNT.

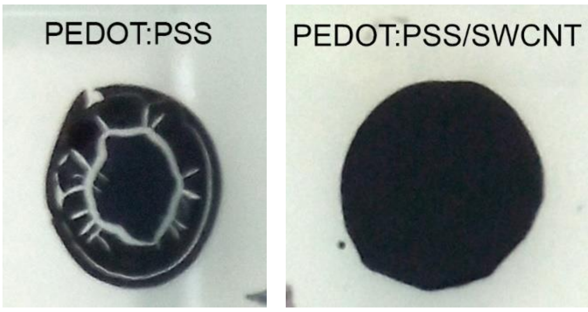

Figure S3 Images of the PEDOT:PSS and PEDOT:PSS/SWCNT (96:4 w/w) composite films.

4. Impedance spectra of the electrochemical cells

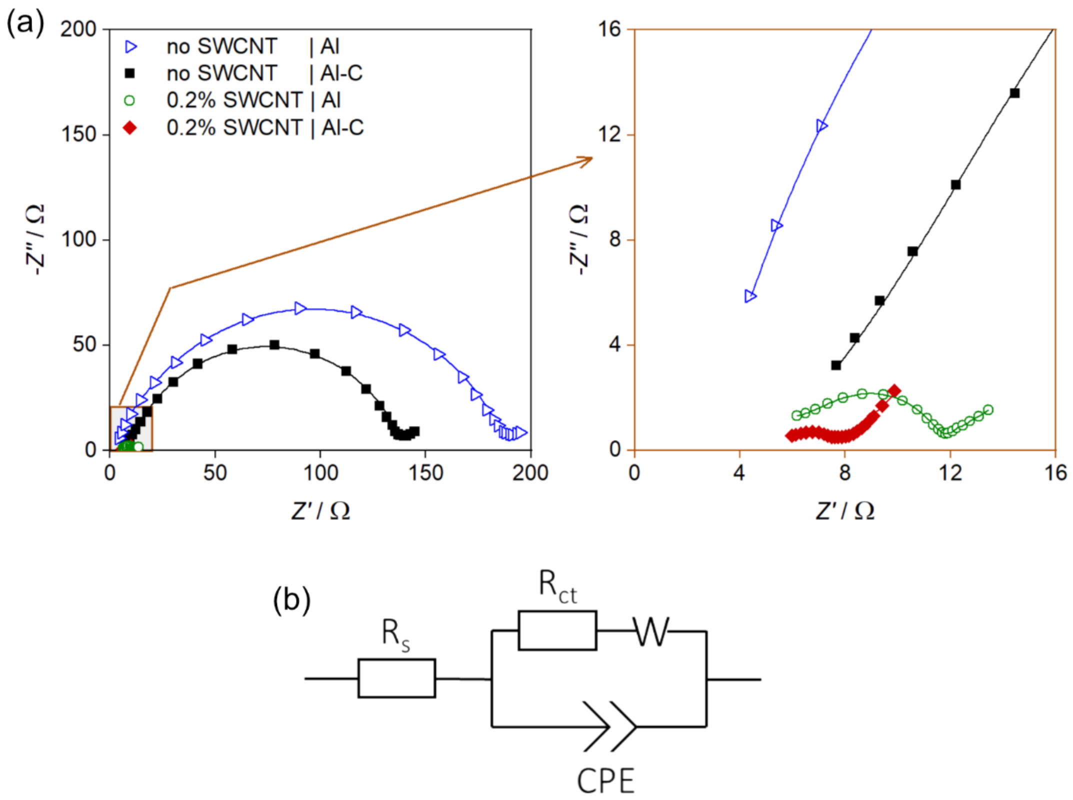

Figure S4 (a) Electrochemical impedance spectra of the electrodes at 50% state-of-discharge depending on the type of the current collector and the presence of SWCNT additive. Data points are marked with symbols while fittings with equivalent circuit are shown by lines. (b) Randles Equivalent circuit used to fit the impedance spectra of the cathodes. R_s – bulk resistance (including the resistances of the electrolyte, current collector and separator), R_{ct} – charge transfer resistance, W –Warburg element related to the ionic diffusion in the bulk LFP particles, CPE – constant phase element.

5. Galvanostatic profiles of the electrodes

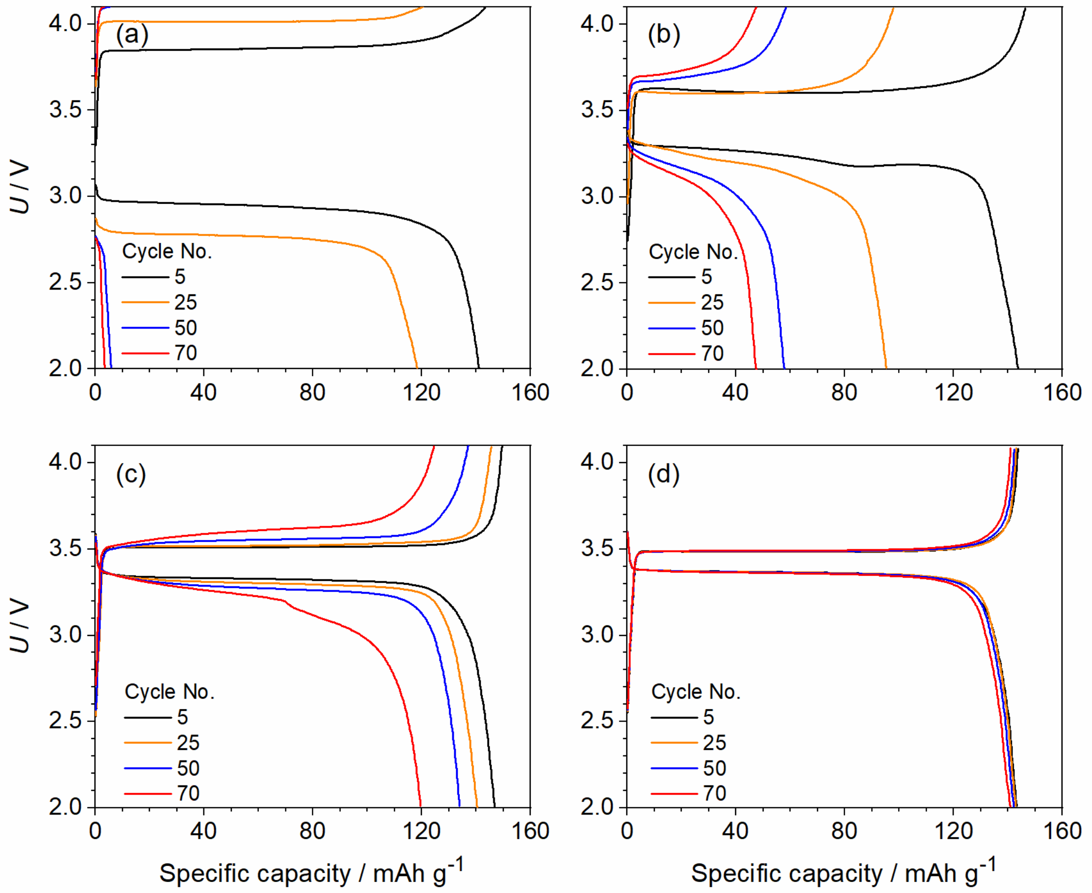

Figure S5 Galvanostatic charge/discharge curves (1C rate) of the $LiFePO_4$/PEDOT:PSS composite electrodes depending on the type of the current collector and the presence of SWCNT additive: (a) Al current collector, no SWCNT added; (b) Al-C current collector, no SWCNT added; (c) Al current collector, 0.2 wt.% SWCNT; (d) Al-C current collector, 0.2 wt.% SWCNT.

6. Electrochemical performance of the electrodes with different SWCNT contents

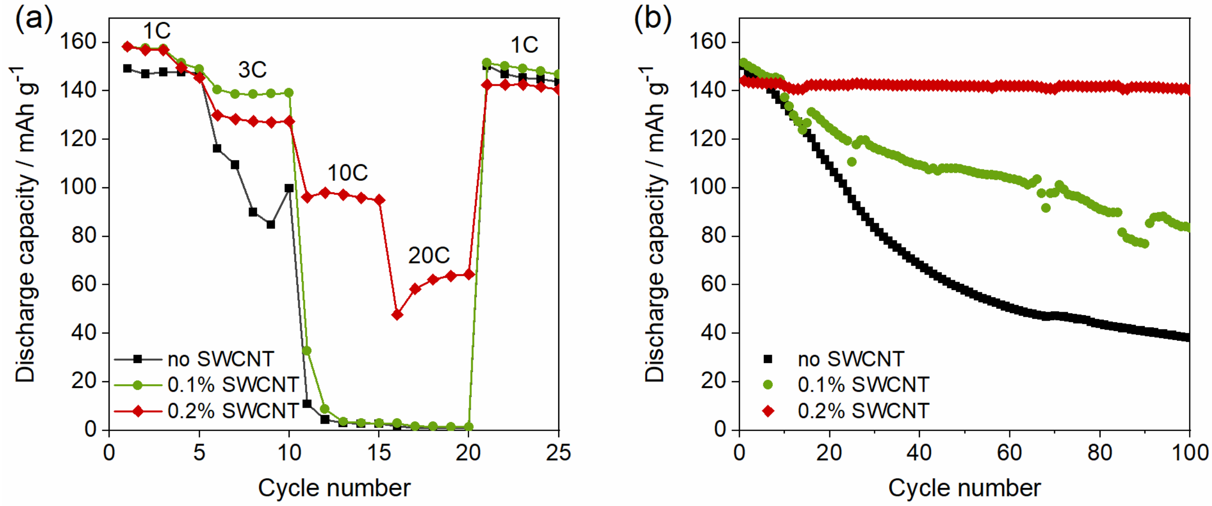

Figure S6 (a) Rate capability and (b) cycling stability of the $LiFePO_4$/PEDOT:PSS composite electrodes prepared on the Al-C current collector depending on the weight content of SWCNT.