# Supporting information

## Modified Secondary Lithium Metal Batteries with the Polyaniline/Carbon Nanotube Composite Buffer Layer

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### Experimental

#### The fabrication of the $LiCoO_2$/CNT cathodes.

The carbon nanotubes used in this work were harvested from the superaligned CNT arrays on the silicon wafers grown by the chemical vapour deposition method.[S1] CNTs and $LiCoO_2$ were simultaneously dispersed in ethanol and treated by ultrasound for 10 min to form a uniform suspension. Then, the suspension was filtrated through a micro porous membrane with the aid of vacuum to form a thin $LiCoO_2$/CNT film. We peeled off the film from the micro membrane and dried it in a vacuum oven at 80 °C for 12 h. Finally, we cut the film into a disk electrode with a suitable size which can be put into a button cell. The average mass is 13 mg and the weight percentage of the $LiCoO_2$ in the composite is 85%.

#### The fabrication of the PANI/CNT electrodes.

First, like the fabrication of $LiCoO_2$/CNT, we obtained a thin CNT film also by ultrasonic dispersion, vacuum filtration and evaporation. Then the CNT film was immersed in 0.2 M aniline solution with 1 M HCl as the solvent. After that, an equal volume of precooled 0.2 M ammonium persulfate solution was added to the aniline solution through drop-by-drop way. After that, we kept the mixture at 0-5 °C for 12 h for complete reaction. Finally, the obtained PANI/CNT was washed by the deionized water, acetone and ethanol, and dried in a vacuum oven at 80 °C for 12 h. And then we cut the PANI/CNT film into samples which is a little smaller in size than the abovementioned $LiCoO_2$/CNT electrodes. The PANI/CNT samples have the average mass of 2 mg, which is 15.4% of the mass of the $LiCoO_2$/CNT electrodes. The PANI is 1 mg in weight, so the weight percentage of the PANI in the PANI/CNT is 50%.

**Assembly of the cells.**

Coin-type (CR 2016) cells were assembled in an argon filled glove box with the composites mentioned in this paper as the positive electrode and Li metal foil as the negative electrode. Polymer film (Celgard 2400, USA) was used as the separator and 1 M $LiPF_6$ solution in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed at weight ratio of 1:1 was used as the electrolyte.

**Characterization and Electrochemical Measurement.**

The cells were tested with galvanostatic charge-discharge measurement (Land Battery Testing System, China). The range of voltage is 3.5 V-4.2 V. The microstructure of the PANI/CNT film was characterized by the scanning electron

microscope (SEM) (Sirion 200, resolution 1.0 nm).

**The surface area and pore volume of porous PANI/CNT film** can be calculated as follows.

The porosity of the PANI/CNT film is calculated by

$$P = 1 - \frac{\rho_f}{\alpha\rho_c + \beta\rho_p}, \quad (1)$$

where $\rho_f$ is the density of PANI/CNT film, $\rho_c$ and $\rho_p$ are the true density of CNT and PANI molecular respectively, and $\alpha$ and $\beta$ are the CNT and PANI proportion of the composite respectively. $\rho_f$ was calculated by

$$\rho_f = \frac{m}{S_f d}, \quad (2)$$

where $m$, $S$, and $d$ are the mass, area, and thickness of PANI/CNT film. Through the formula 2, the $\rho_f$ is calculated as 0.31 g cm$^{-3}$. By calculating a single CNT model, $\rho_c$ was obtained as about 1.85 g cm$^{-3}$. By experimentally measuring the mass and volume of polyaniline obtained from the rest of reacted solution, $\rho_p$ was calculated as about 1.3 g cm$^{-3}$. By comparing the mass of film before and after polymerization of PANI, we get $\alpha = \beta = 50\%$. So the PANI/CNT film has a porosity of 80%. Then the pore volume $P_V$ can be calculated as

$$P_V = \frac{P}{\rho_f}. \quad (3)$$

So the PANI/CNT film has the pore volume of 2.58 cm$^3$/g.

From the SEM image of PANI/CNT film, we regard the film to be a long wire winded as a mesh, we assume the wire have a diameter as 2$r$, a length of $l$, so the surface area can be calculated as

$$S = \frac{2\pi r l}{m}, \quad (4)$$

m is the mass of PANI/CNT film, and can be calculated as

$$m = \pi r^2 l \rho_a, \quad (5)$$

$\rho_a$ is the average density of this wire and can be get by

$$\rho_a = \alpha \rho_c + \beta \rho_p \quad , \quad (6)$$

$\alpha$, $\beta$, $\rho_c$, $\rho_p$ are the same with which mentioned above. So formula 4 can be reduced to

$$S = \frac{2}{r(\alpha \rho_c + \beta \rho_p)}. \quad (7)$$

From the SEM image, the $r$ is about 50 nm. So the $S$ is 25.4 $m^2/g$.

**References**

S1 X. Zhang, K. Jiang, C. Feng, P. Liu, L. Zhang, J. Kong, T. Zhang, Q. Li and S. Fan, *Adv. Mater.*, 2006, **18**, 1505.