## Electronic Supplementary Information for

## Polyaniline Nanofiber/Vanadium Pentoxide Sprayed Layer-by-Layer Electrodes for Energy Storage

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**Figure S1.** Sample A was prepared with a blow-drying time of 30 sec; Sample B was prepared with a blow-drying time of 1 min. Both samples have 50 layer pairs.



PANI NF:0.5 mg/mL PANI NF:1 mg/mL

**Figure S2.** Images of PANI NF/V<sub>2</sub>O<sub>5</sub> LbL electrodes prepared by spray process with different PANI NF concentrations. The numbers on top of the images are the number of layer pairs.



Figure S3. Image of PANI NF/V<sub>2</sub>O<sub>5</sub> LbL electrodes after optimization of parameter settings.



**Figure S4.** (a) UV-Vis spectra of (PANI NF/V<sub>2</sub>O<sub>5</sub>)<sub>30</sub> LbL films at 2.0 V (black curve) and at 3.5 V vs  $\text{Li/Li}^+$  (red curve).



Figure S5. Galvanostatic cycling data based on volume.



**Figure S6.** Ragone plot of (PANI NF/V<sub>2</sub>O<sub>5</sub>)<sub>30</sub> spray-assisted LbL electrodes and (PANI NF/V<sub>2</sub>O<sub>5</sub>)<sub>16</sub> dip-assisted LbL electrodes, which is based on volume.

30 BL	3 5V	2 75V	2V
JUBE	5.5 1	2.134	21
Y <sub>0CPE2</sub>	8.57e-6	6.147e-6	3.383e-6
a <sub>CPE2</sub>	0.8345	0.8497	0.84
$R_2/\Omega$	228.2	285	350.3
Y <sub>0W</sub>	134.1e-3	356.6e-6	200.0e-6
$B_W$	0.3841	0.9514	0.06651
Y <sub>0CPE1</sub>	214.2e-12	222.3e-12	214.1e-12
a <sub>CPE1</sub>	0.958	0.9566	0.9586
$R_1/\Omega$	956.9	957.1	959.7
Y <sub>CPE3</sub>	0.02343	0.02653	0.05103
a <sub>CPE3</sub>	0.9335	0.9434	0.8979

 Table S1. Parameters used for fitting of the equivalent-circuit model to the data

The impedance of a CPE has the form:

## $Z = (1/Y_o)/(j\omega)^{\alpha}$

When this equation describes a capacitor, the constant  $Y_0 = C$  (the capacitance) and the exponent a = 1. For a constant phase element, the exponent a is less than one.

The equation for the Warburg impedance can be written as:

$$Z = (1/Y_o)/\sqrt{j\omega}$$

where

$$Y_o = 1/(\sqrt{2} \cdot \sigma)$$

If the diffusion layer is bounded, the impedance at lower frequencies no longer obeys the equation above. Instead, we get the form:

$$Z = [(1/Y_o)/\sqrt{(j\omega)}] \tanh [B\sqrt{j\omega}]$$

with

$$B = \delta / D^{1/2}$$

d = Nernst diffusion layer thickness (cm) D = an average value of the diffusion coefficients of the diffusing species (cm<sup>2</sup>/s)