# Supporting information

# Homologous V<sub>2</sub>O<sub>3</sub>/C box-in-box and V<sub>2</sub>O<sub>5</sub> box for lithium-ion full cells

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#### **1. Experimental Section**

*Synthesis of*  $V_2O_3$  *NPs.* The VO<sub>x</sub> precursors were firstly synthesized according to Balkus' work with a minor revision.<sup>1</sup> In a tipical synthesis, 0.3 g of ammonium metavanadate and 0.5 g of P123 (EO<sub>20</sub>P<sub>70</sub>E<sub>20</sub>) were dispersed into 30 mL of deionized water containing 2 mL of 1 M HNO<sub>3</sub> under stirring for 7 h at room temperature, and then transferred into an autoclave and maintained at 200 °C for 12 h. Finally, the V<sub>2</sub>O<sub>3</sub> NPs can be obtained by treating as-obtained hydrothermal products at 600 °C for 10 h in argon.

*Synthesis of*  $V_2O_3$  *HNSs.* The synthesis of  $V_2O_3$  HNSs was according to Lou's work with a minor revision.<sup>2</sup> In a tipical synthesis, 3 mL of 0.33 M VOC<sub>2</sub>O<sub>4</sub> and 30 mL of isopropanol were mixed in a 50 mL autoclave under stirring for 1 h and then heated at 200 °C for 10 h. The  $V_2O_3$  HNSs can be obtained by annealing the precursor in argon at 600 °C for 10 h.

## 2. Figures



Figure S1. TEM image of the carbon box-in-box.



Figure S2. XRD pattern of the V<sub>2</sub>O<sub>3</sub>/C box-in-box.



Figure S3. TGA curves of  $V_2O_3/C$  box-in-box and  $V_2O_3$  NPs.



**Figure S4.** (a) Raman spectrum and (b) N<sub>2</sub> adsorption-desorption isotherms of the V<sub>2</sub>O<sub>3</sub>/C box-in-box (the insert of part b shows the corresponding pore-size distribution curve).



Figure S5. (a) CV curves at 0.2 mV s<sup>-1</sup>, (b) charge-discharge curves at 100 mA g<sup>-1</sup> of the  $V_2O_3/C$  box-in-box for the initial 3 cycles.



Figure S6. Rate performance of the pure carbon box electrodes.



**Figure S7.** (a) SEM image of V<sub>2</sub>O<sub>3</sub> NPs, (b) SEM image of V<sub>2</sub>O<sub>3</sub> HNSs (the inset showing the corresponding TEM image), (c) XRD patterns of V<sub>2</sub>O<sub>3</sub> HNSs (red line) and V<sub>2</sub>O<sub>3</sub> NPs (blue line).



Figure S8. High-resolution V2p XPS spectra of the V<sub>2</sub>O<sub>3</sub>/C box-in-box (a) before cycling and (b) after cycling.



Figure S9. SEM images of the  $V_2O_3/C$  electrode (a) before cycles and (b) after cycles.



**Figure S10.** XRD pattern of the  $V_2O_5$  box.



Figure S11. Charge-discharge curves at 100 mA g<sup>-1</sup> of the full cell for the initial 3 cycles.

#### 3. Table

Cathode	Anode	Rate capability	Cycling behavior	Ref.
Ni <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub>	Si/RGO	-	77 mAh g <sup>-1</sup> (70%) 1/4C for 15 cycles	S3
LiMn <sub>2</sub> O <sub>4</sub>	MnO <sub>x</sub> /C	85 mAh g <sup>-1</sup> (0.2C) 25 mAh g <sup>-1</sup> (5C)	-	S4
LiCoPO <sub>4</sub>	$Li_4Ti_5O_{12}$	-	93 mAh g <sup>-1</sup> (76%) 0.1 C for 20 cycles	S5
$LiNi_{0.5}Mn_{1.5}O_4$	CuO-MCMB	125 mAh g <sup>-1</sup> (1C) 95 mAh g <sup>-1</sup> (5C)	-	S6
$LiMn_2O_4$	$Mn_2O_3$	-	80 mAh g <sup>-1</sup> (81%) 1C for 40 cycles	S7
LiMn <sub>2</sub> O <sub>4</sub>	TNSTs	100 mAh g <sup>-1</sup> (0.2 A g <sup>-1</sup> ) 58 mAh g <sup>-1</sup> (1.6 A g <sup>-1</sup> )	-	S8
$V_2O_5$	V <sub>2</sub> O <sub>3</sub> /C	130 mAh g <sup>-1</sup> (2/3 C) 43 mAh g <sup>-1</sup> (33 C)	81 mAh g <sup>-1</sup> (80%) 3.3 C for 100 cycles	This work

Table S1. A summary table for recent reports on lithium-ion full cells.

The specific capacities of all those full cells shown in the table are based on the cathode material weight. For this work,  $1 \text{ C}=0.15 \text{ A g}^{-1}$ .

### 4. References

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