

## Supporting Information for

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**“An integrated core-shell structured  $\text{Li}_3\text{V}_2(\text{PO}_4)_3@C$  cathode material of LIBs prepared by a momentary freeze-drying method” by**

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## Experimental

### Material synthesis

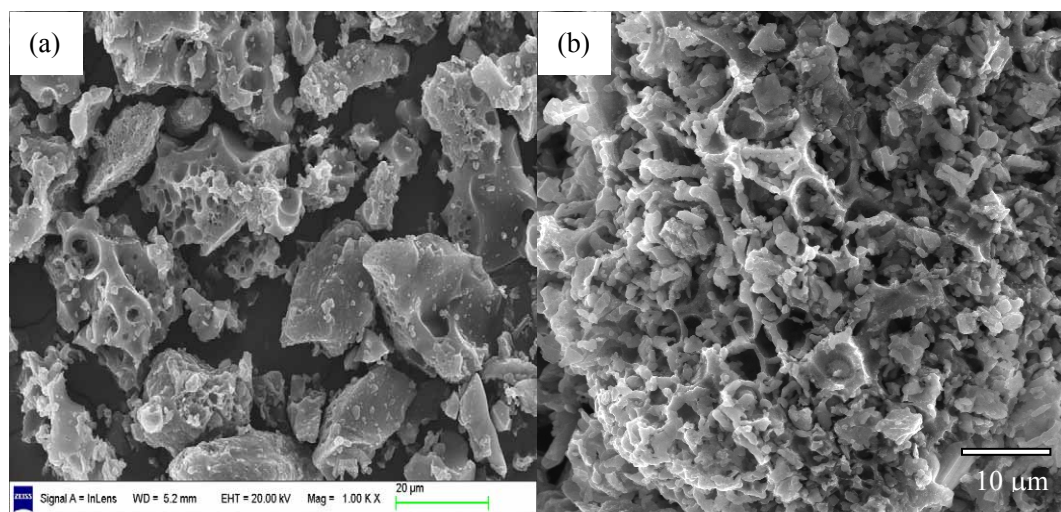
All chemicals used in this work were of analytical grade and used without any purification. The samples were synthesized by the sol-gel method using  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{NH}_4\text{VO}_3$ ,  $\text{H}_3\text{PO}_4$  and citric acid as raw materials in the molar ratio of 3.05:2:3:2. Citric acid was used both as a chelating agent and carbon source. First, citric acid was dissolved in deionized water under magnetic stirring at room temperature, and then the  $\text{NH}_4\text{VO}_3$  was added at 55 °C. Until a clear yellow solution was formed, stoichiometric  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  were added into the solution in sequence under continuously stirring. The mixture was heated at 80 °C for about 8h under active stirring to evaporate the water until a dark blue sol was obtained. The obtained sol was divided into two parts: one part was drop-by-drop frozen under liquid nitrogen (momentary freeze-drying method), and another part was frozen naturally in a refrigerator (normal freeze-drying method) as controlled samples. Then they were subjected to the vacuum drying process for about 24h at -40 °C in a freeze-drying machine. The obtained powders were ground and pre-heated at 300 °C in the air for 4 h. Finally, the pre-heated material was ground and sintered at 850 °C for 10h under  $\text{N}_2$  atmosphere to yield the  $\text{LVP}@C$  composite.

### Material characterization

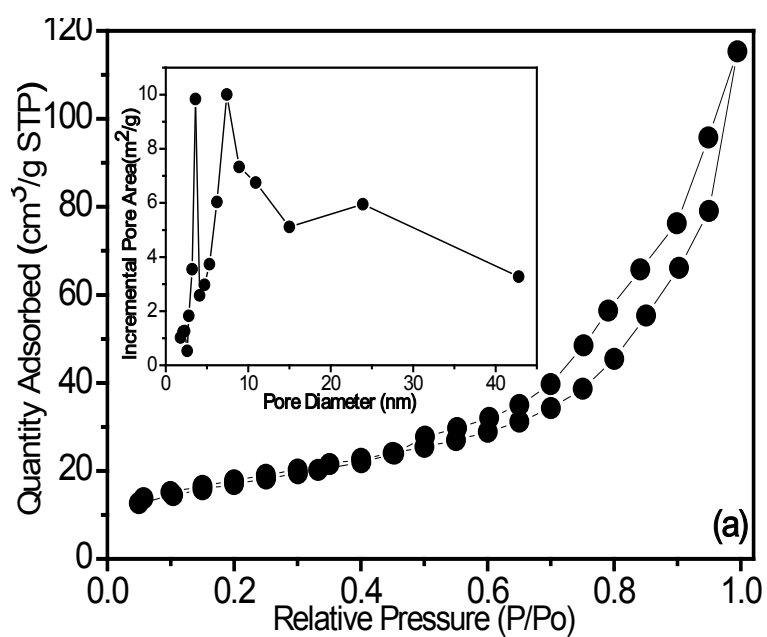
The carbon content of the sample was confirmed by organic element analyzer (Vario EL cube), and the carbon amount of the  $\text{LVP}@C$  composite is 3.98%. The phase composition and crystalline structure of the samples were studied by X-ray diffraction, using a D/max-Ultima III Diffractometer at 40kV, 40mA with  $\text{Cu } K\alpha$  radiation ( $\lambda=0.154\text{nm}$ ) and the samples were step-scanned in the  $2\theta$  range from 10 to 60°. The morphology and particle size of the sample were detected by field emission scanning electron microscope (FE-SEM, Zeiss Supra 55). The nanoscale microstructure was examined by a high resolution transmission electron microscope (HR-TEM, Hitachi H-800).

### Electrochemical testing

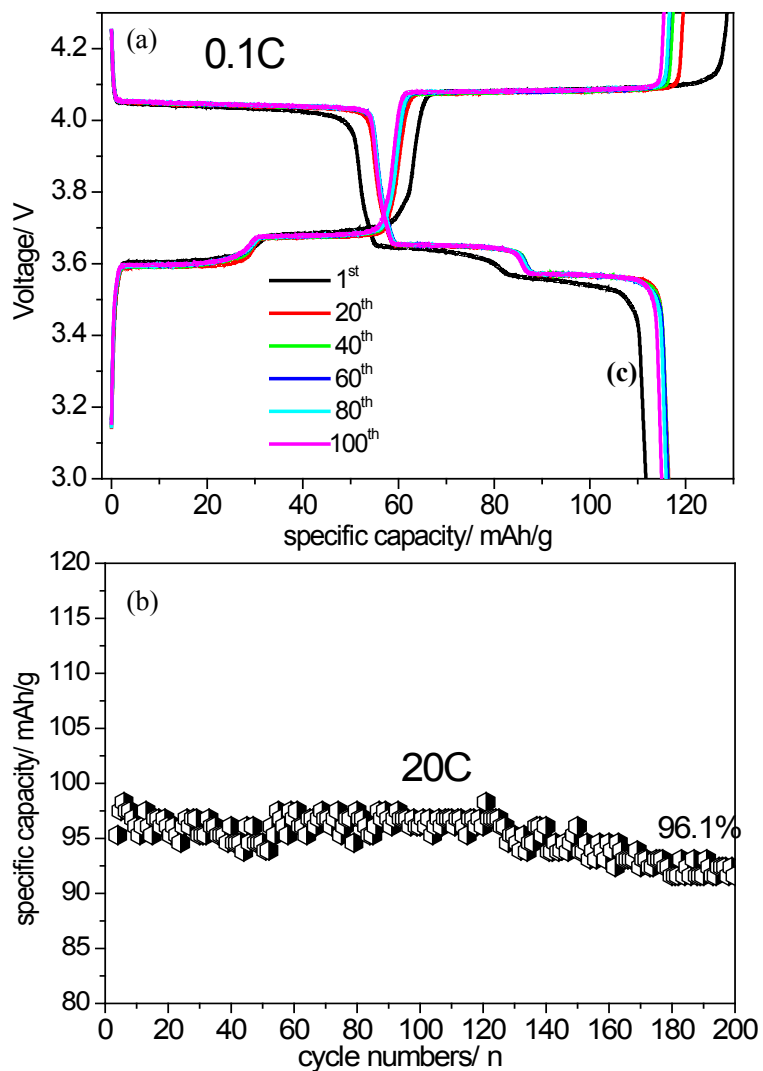
The electrochemical properties of the LVP@C composite were characterized using CR2032 coin cells. The cathode consisted of 80wt.% as-prepared samples, 10wt.% acetylene black and 10wt.% polyvinylidene fluoride (PVDF) in an appropriate amount of N-Methyl Kelopyrrolidide on aluminum foil. Then the electrodes were dried at 120°C for 12h. The coin-type cells were assembled in a glove box filled with high purity argon. The lithium metal foil was served as the counter and reference electrode. Cellgard 2400 as the separator, and 1M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC) /dimethyl carbonate(DMC)/ethylene methyl carbonate(EMC) with the volumetric ratio of 1:1:1 as the electrolyte. The galvanostatic charge-discharge tests are conducted on LAND CT2001A test system (Wuhan, China) at different current densities within the potential range of 3.0-4.3V and 3.0-4.8V (vs.Li/Li<sup>+</sup>) at room temperature. Cyclic voltammetry (CV) measurements were performed on CHI650D (Chenhua, Shanghai) electrochemical workstation. The specific capacity and current density were based on the active material only. When the rate performances of our coin cells were tested at different current densities (1C, 2C, 5C, 10C, 20C and 30C, respectively), the discharge currents were 0.273mA, 0.546mA, 1.365mA, 2.73mA, 5.46 mA and 8.19 mA, respectively. On the other hand, the geometric area of electrode is a fixed value, which is ca. 0.785cm<sup>2</sup>, therefore, 1C=0.3478mA/cm<sup>2</sup>, 2C=0.6955 mA/cm<sup>2</sup>, 5C=1.7389 mA/cm<sup>2</sup>, 10C=3.478 mA/cm<sup>2</sup>, 20C=6.956 mA/cm<sup>2</sup> and 30C=10.434 mA/cm<sup>2</sup>, respectively.



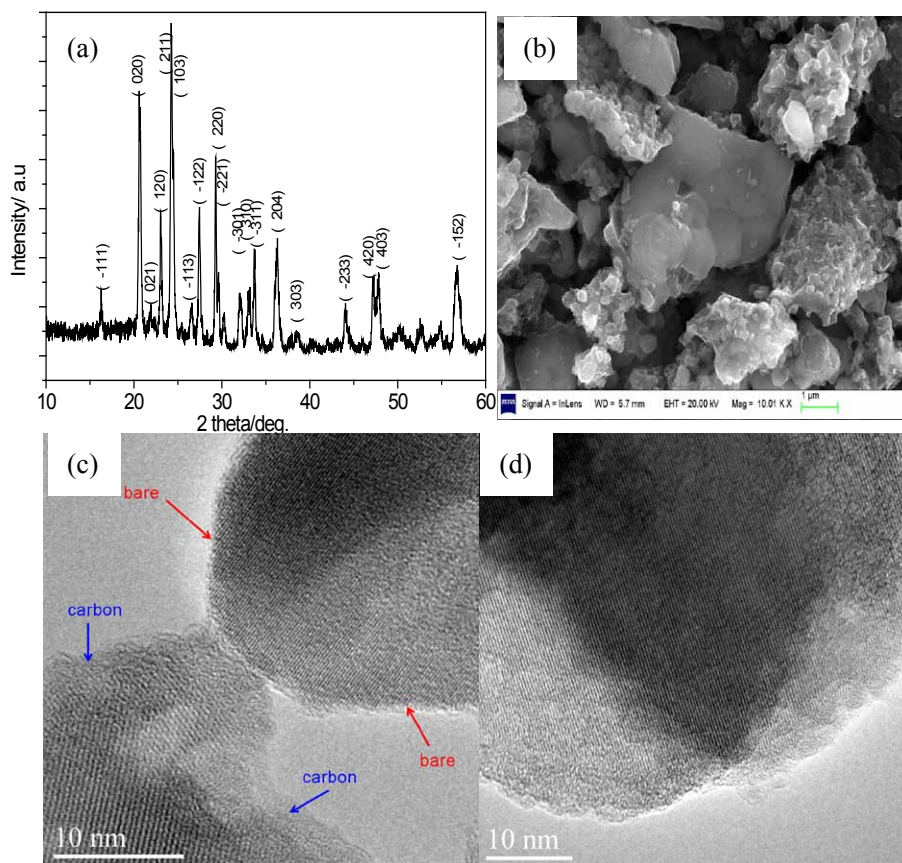
**Figure S1:** SEM pictures of the Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@C material indicating quite a porous morphology in a large scale.



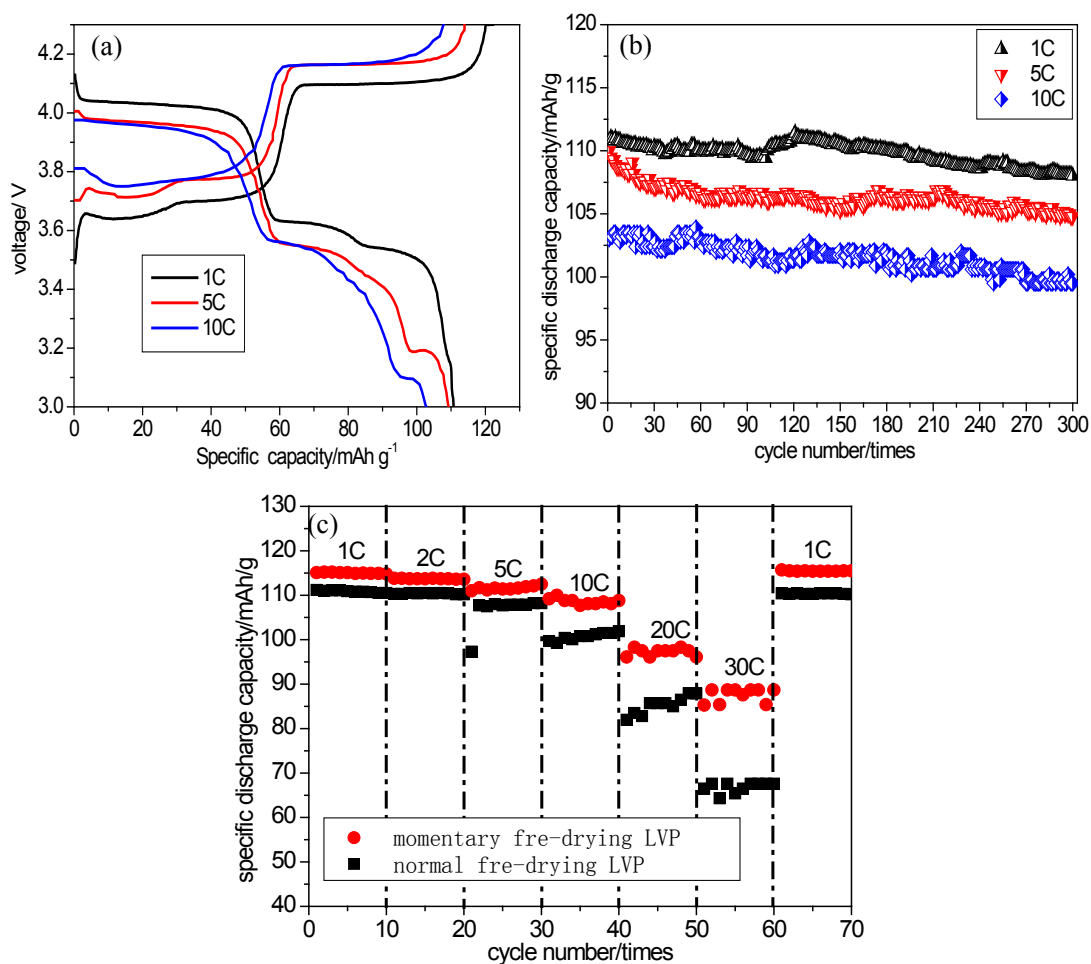
**Figure S2:** N<sub>2</sub> adsorption/desorption isotherms and pore-size distribution curves of LVP@C.



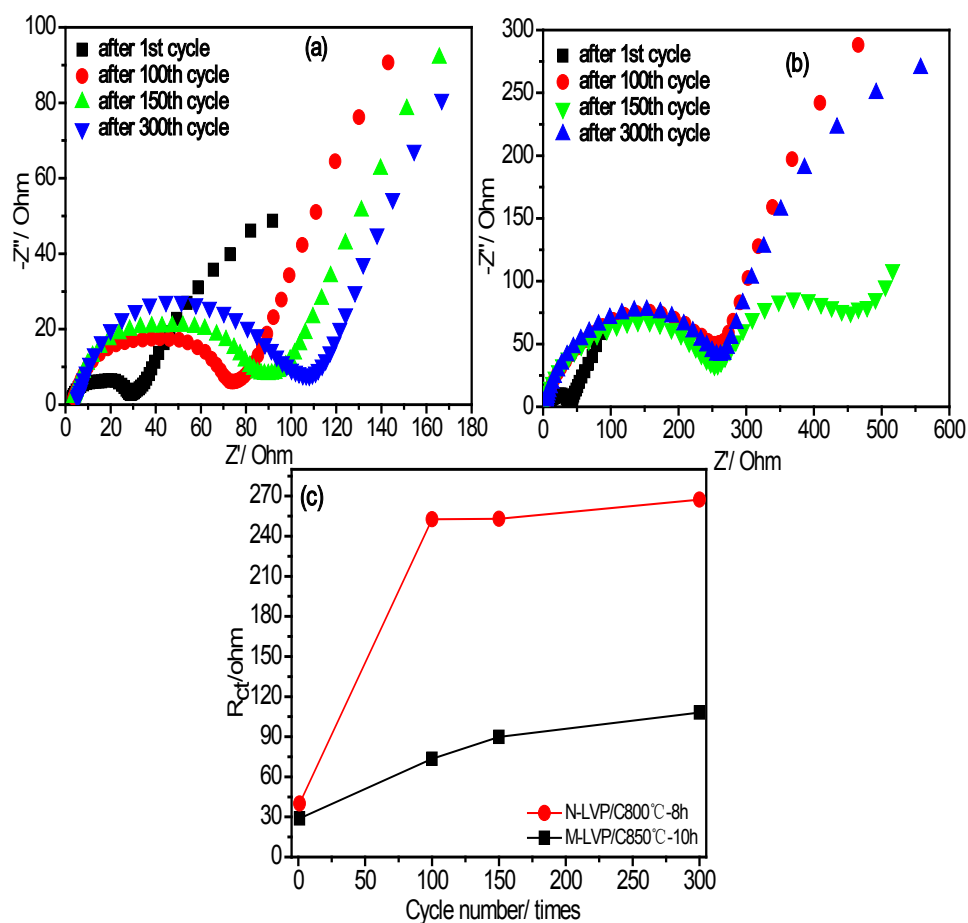
**Figure S3:** (a) The charge-discharge curves of the  $\text{Li}_3\text{V}_2(\text{PO}_4)_3@C$  material at various cycles under a current density of 0.1C; (b) cycle performance at a current density of 20C.



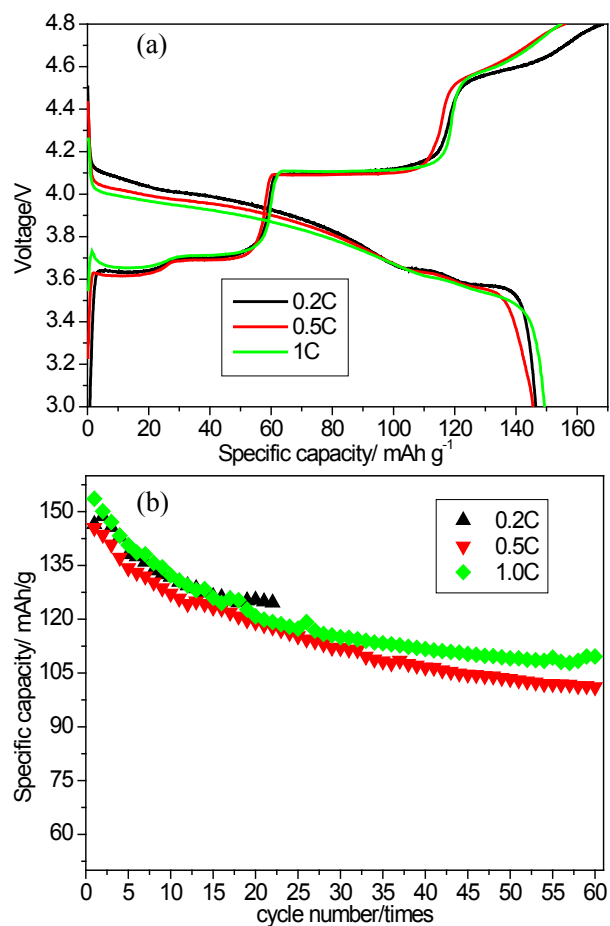
**Figure S4:** Characterizations of the controlled  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  materials prepared by a normal freeze-drying method, (a) XRD patterns; (b) SEM picture; (c, d) TEM images.



**Figure S5:** The electrochemical properties of the controlled  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  material, (a) the first cycle profiles of charge-discharge at various current densities; (b) cycle performances at various current densities; (c) a comparison of the rate capability between momentary fre-drying core-shell  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  and normal fre-drying controlled  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  sample. All the tests were worked in the potential window of 3.0 – 4.3 V (vs.  $\text{Li}/\text{Li}^+$ ).



**Fig.S6** Nyquist plots of (a) core-shell  $\text{Li}_3\text{V}_2(\text{PO}_4)_3@C$  material and (b) the controlled LVP at the charge potential of 4.3V with the current density of 5C after different charge-discharge cycles test, (c) The change trends in charge transfer resistance of core-shell  $\text{Li}_3\text{V}_2(\text{PO}_4)_3@C$  material and the controlled sample.



**Figure S7:** The electrochemical properties of the core-shell  $\text{Li}_3\text{V}_2(\text{PO}_4)_3@\text{C}$  material within the potential window of 3.0-4.8V, (a) the first cycle profiles of charge-discharge at various current densities; (b) cycle performances at various current densities.