

Supplementary Information

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a cathode additive for the over-discharge protection of lithium ion batteries

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Experimental

Synthesis of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$

The $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ composite was synthesized by the carbon thermal reduction method.¹ Stoichiometric amounts of Li_2CO_3 , V_2O_5 , $\text{NH}_4\text{H}_2\text{PO}_4$ and sucrose were dispersed into an appropriate amount of ethanol. Then the mixture was ball milled for 7 h. After the ball milling, the mixture was dried at 80 °C in a vacuum oven to evaporate ethanol and then preheated at 400 °C in Ar atmosphere for 3 h to expel H_2O and NH_3 . Finally, the precursor was reground and sintered at 800 °C for 8 h in Ar atmosphere to obtain the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

Preparation of electrodes and batteries

A 2025-size coin cell was manufactured by the conventional method. Commercial LCO and graphite electrodes were provided by Xiongtao Power Co. Limited (Shenzhen, China). 7 wt.% LVP was added to LCO electrode through a “layer to layer” mode to make a composite cathode. At the same time, pre-lithiated graphite anode was used to provide the lithium source for LVP in the voltage range of 1.6~2.0 V. The pre-lithiation process was based on the method provided by Jin Zhang *et al.*² And the pre-lithiation capacity was 67.3 mAh/g. An ethylmethyl carbonate (EMC)/ethylene carbonate(EC)/propylene carbonate(PC) (1:1:1,v/v)-based solution containing 1 mol/L LiPF_6 was used as an electrolyte. Additionally, aluminum foil and copper foil were used as a cathode collector and an anode collector, respectively.

Physical characterization and electrochemical testing

The X-ray diffraction (XRD) pattern collected on sample was recorded with a D/max- γ B X-ray diffractometer (Rigaku Corporation, Japan) using nickel-filtered $\text{Cu K}\alpha$ radiation. The surface morphology for the sample was characterized by a Philip XL 30 scanning electron microscopy (SEM; Philips, Netherlands).

Galvanostatic charge-discharge of LCO/graphite and LVP:LCO(7:93)/graphite cell were tested on Neware Battery Test System (Shenzhen, China). At first, the cells were cycled in voltage range of 3~4.2 V for several times. Then over-discharge tests were performed by applying constant current of 0.2 C to 2 V, and 0.013 mA to 0 V. At last the cells were kept at 0 V for 7 weeks. After a series of over-discharge damage, the cells were cycled in voltage range of 3~4.2 V again.

Cyclic voltammograms curves (CV) were recorded for LVP:LCO(7:93), LCO or LVP electrode using Li metal foil as reference and counter electrode in cell configuration. CV was conducted on a CHI660e electrochemical workstation (Shanghai Chenhua, China). The CV curves for the test cell were recorded in a potential range of a 1.4~4.4 V (vs. Li^+/Li) at a scan rate of 0.2 mV/s. and electrochemical impedance spectroscopy (EIS) results for LCO/graphite and LVP:LCO(7:93)/graphite cell were recorded on this electrochemical workstation with the frequency ranging from 10 kHz to 10 mHz and an AC signal of 5 mV in amplitude as the perturbation. The parameters of the equivalent circuit were calculated and analysed by the ZVIEW software.

S1. XRD results for LVP

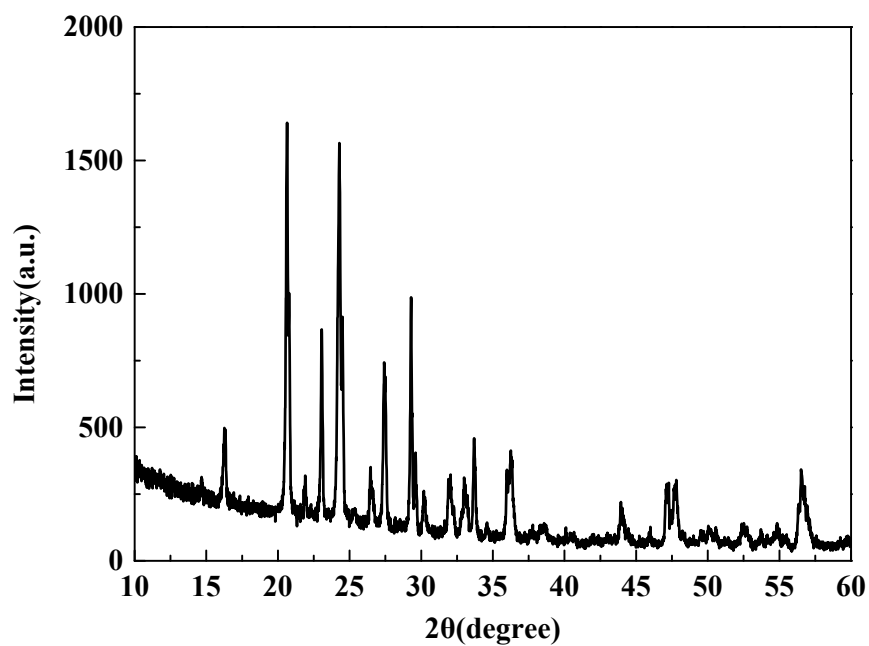


Fig. S1† XRD pattern for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The diffraction peaks of the sample are assigned to monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ ^{3, 4}, and no other secondary phases were detected; indicating that samples produce are well crystallized and the pure LVP cathode material was obtained by carbon thermal reduction method.

S2. Morphology information of LVP

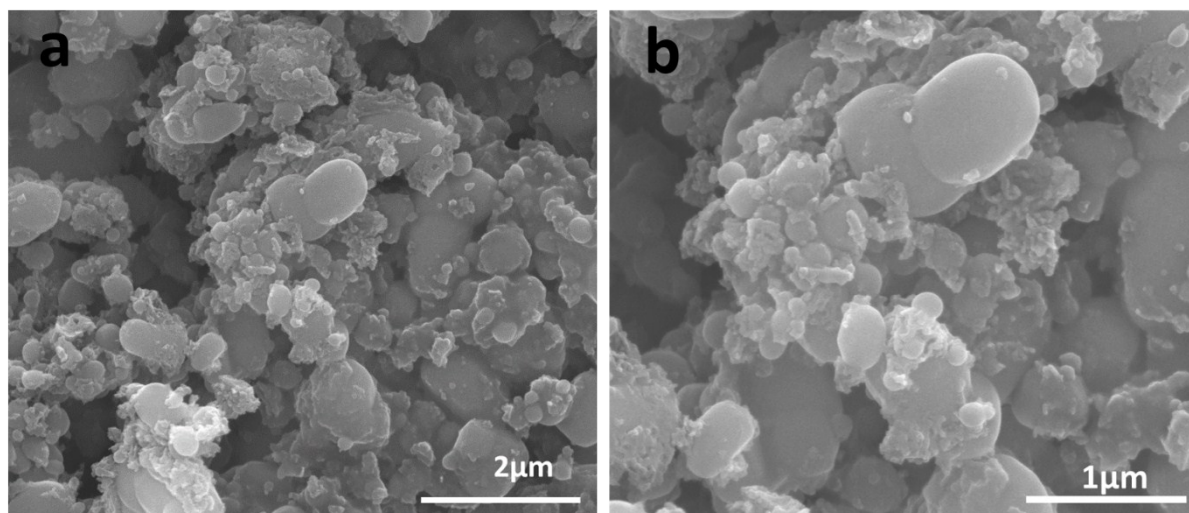


Fig. S2† (a) Low- and (b) high-magnification SEM images of LVP. The particle size of the sample is not very uniform and the particles are slightly agglomerated. But most of the sample size is about 0.5 μm, which clearly indicates the formation of micron sized particles.

S3. Charge and discharge curves of LVP:LCO(5:95), LVP:LCO(7:93) and LVP:LCO(9:91) before and after kept at 0V for 7weeks

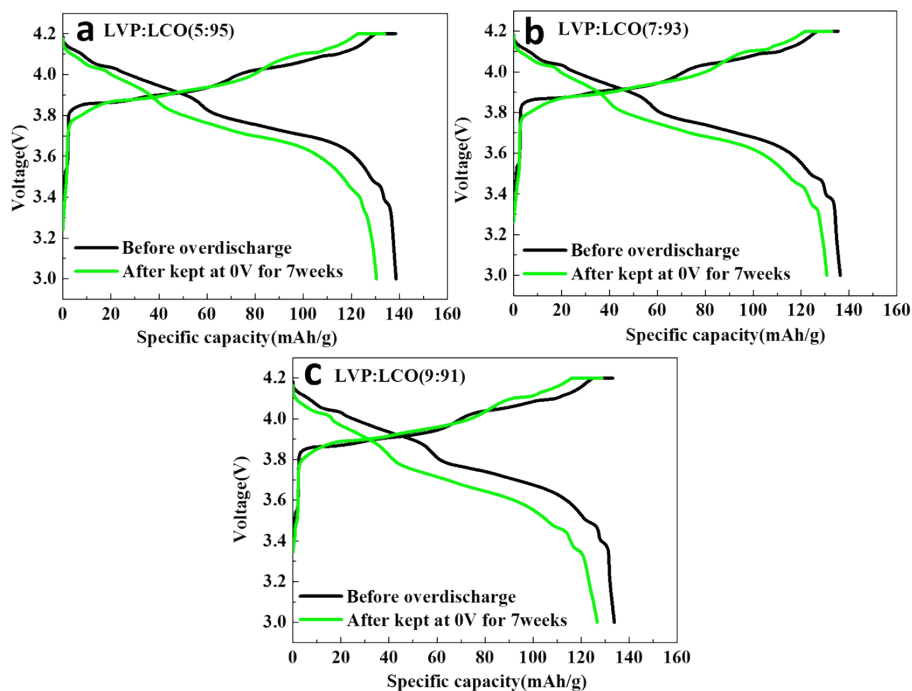


Fig. S3† Charge and discharge curves before and after kept at 0V for 7weeks for (a) LVP:LCO(5:95); (b) LVP:LCO(7:93); (c) LVP:LCO(9:91). It can be seen that all the charge/discharge curves of the composite electrode maintain well with the addition of LVP.

S4. Photograph of separator for LCO/graphite cell and LVP:LCO(7:93)/graphite cell

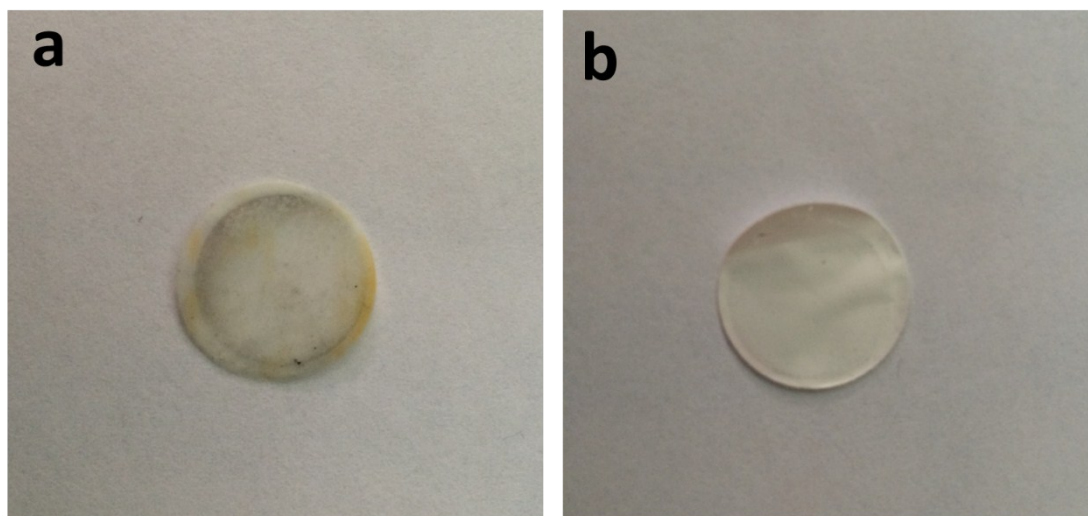


Fig. S4† Photographs of separator for (a) LCO/graphite cell; (b) LVP:LCO(7:93)/graphite cell after kept at 0 V for 7 weeks. It can be seen, after kept at 0 V for 7 weeks, some substance whose color is yellow and black is appeared on the surface of the separator for LCO/graphite cell, which may be related to the corrosion of the Cu foil and the exfoliation of graphite. Compared with that, the separator for LVP:LCO/graphite cell is still clean when it is kept at 0 V for 7 weeks.

S5. XRD pattern for LCO electrode and LVP:LCO(7:93) electrode

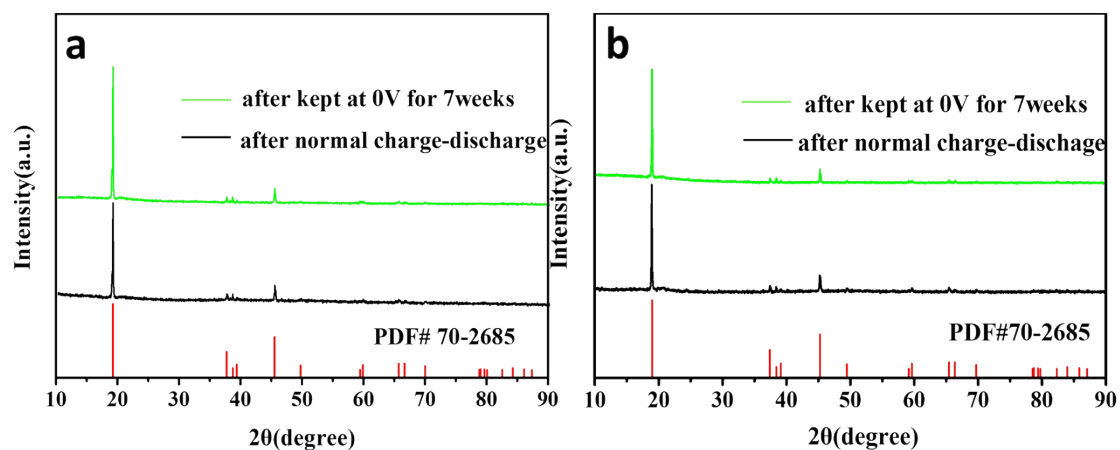


Fig. S5† XRD pattern for (a) LCO electrode; (b) LVP:LCO(7:93) electrode after normal charge-discharge cycles and after kept at 0 V for 7weeks. It can be seen that the crystal structure of LCO maintains very well no matter with or without LVP after kept at 0V for 7weeks, suggesting the LCO component was relatively stable under the tested condition.

Table S1† The difference of electrochemical performance among LVP:LCO(5:95), LVP:LCO(7:93) and LVP:LCO(9:91).

samples	LVP:LCO(5:95)	LVP:LCO(7:93)	LVP:LCO(9:91)
capacity retention ratio	94.12%	95.91%	94.69%
Specific capacity before over-discharge (mAh/g)	138.59	136.33	133.81
Specific capacity after kept at 0V for 7weeks (mAh/g)	130.45	130.75	126.70

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2. J. Zhang, Z. Shi and C. Wang, *Electrochim. Acta*, 2014, **125**, 22.
3. D. Li, M. Tian, R. Xie, Q. Li, X. Fan, L. Gou, P. Zhao, S. Ma, Y. Shi and H. T. Yong, *Nanoscale*, 2014, **6**, 3302.
4. D.-W. Han, S.-J. Lim, Y.-I. Kim, S. H. Kang, Y. C. Lee and Y.-M. Kang, *Chem. Mater.*, 2014, **26**, 3644.