

Supplementary Information

Core-shell-structured $\text{Li}_3\text{V}_2(\text{PO}_4)_3\text{-LiVOPO}_4$ nanocomposites cathode for high-rate and long-life lithium-ion batteries

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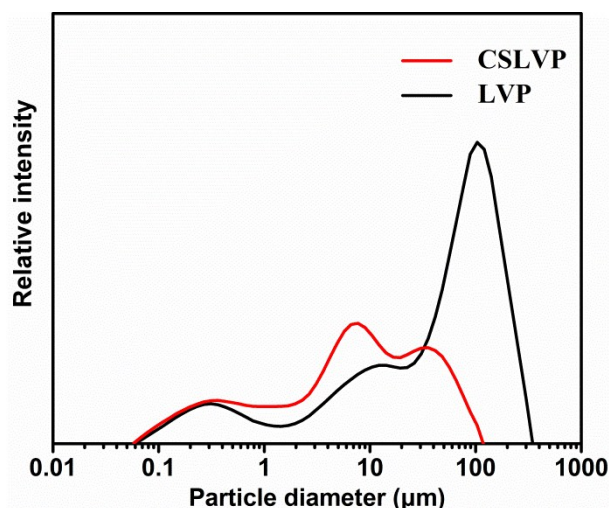


Fig. S1 Particle-size distribution of CSLVP and LVP.

Both the particle size and particle-size distribution of the samples were measured

by a laser particle-size analyzer, the results are shown in Fig. S1. Both of the samples have three peaks in particle-size distribution. The particulate size distribution of CSLVP is at a broad range of 0.06 ~ 120 μm , and the average particle size is about 6 μm . While LVP composite contains particles of size ranging from 0.06 to 258 μm , and the average value is about 53 μm , much larger than that of CSLVP.

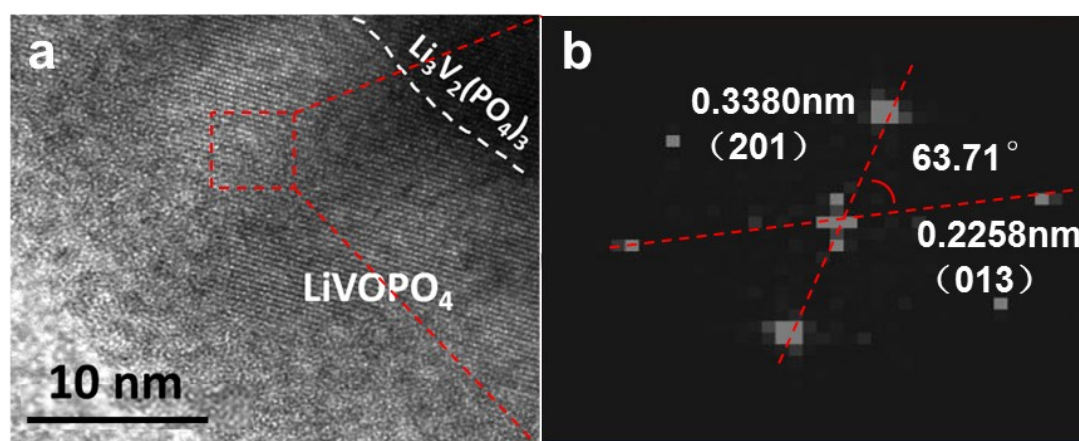


Fig. S2 (a) HRTEM of CSLVP, (b) corresponding Fast Fourier Transformation (FFT) of the region marked by the dashed rectangular.

Further, we select the HTEM image of shell region, make Fast Fourier Transformation (FFT) and measure the angle of crystal surface, and find that the measured angle (63.71°) is quite consistent with the theoretical value (64.5°) of LiVOPO_4 , as shown in Fig. S2.

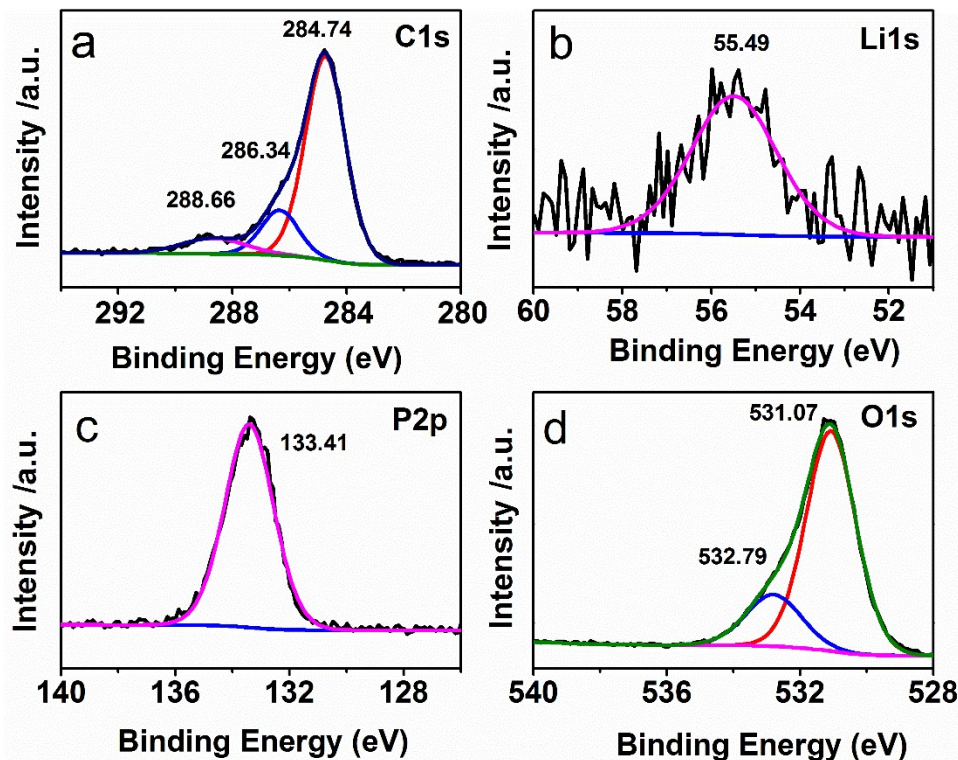


Fig. S3 XPS spectra of (a) C1s, (b) Li1s, (c) P2p, (d) O1s of CSLVP.

XPS was performed to characterize the surface composition of CSLVP. In XPS spectra of C1s for CSLVP (Fig. S3a), C=C peak at ~ 284.7 eV, C-O peak at ~ 286.3 eV and O=C-OH peak at ~ 288.6 eV are observed. The similar C1s spectra of samples CSLVP-B and LVP indicate the similar structure of residual carbon.¹ The Li1s (Fig. S3b) and P2p (Fig. S3c) binding energies in CSLVP are almost the same as those of LVP, considering the accuracy of ± 0.1 eV of XPS. This suggests that there is little influence on valence state of Li and P by high energy ball milling.¹ The binding energy of O1s (Fig. S3d) for CSLVP is a little higher than that of LVP, which is consistent with the previous reported value.² This binding energy is larger than those of oxide cathode materials such LiCoO₂ and LiNiO₂, suggesting to be more covalent which is related to the good structural and thermal stability of polyanion cathode materials. An additional O1s peak at about 532.7eV should be caused by surface O-H groups or

adsorbed water.³

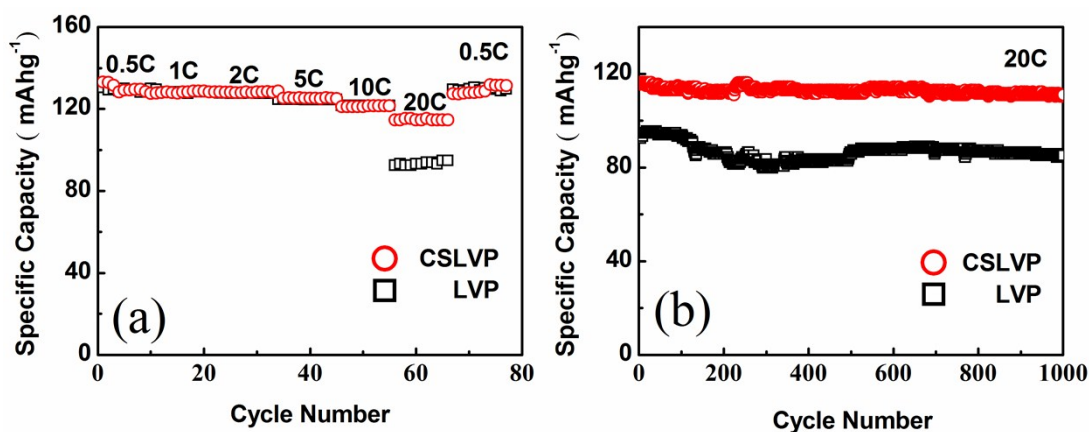


Fig. S4 (a) Rate performance, (b) Long-term cycling performance of CSLVP and LVP. The counterpart sample (without core-shell structure) has been compared with that of core-shell structure, as shown in Fig. S4.¹ The initial discharge capacity of CSLVP at the rate of 0.5 C is 131.5 mAhg⁻¹ (close to the theoretical capacity of 133.0 mAhg⁻¹ for Li₃V₂(PO₄)₃), which is higher than that of LVP (129.2 mAhg⁻¹). When the current rate increases to 20 C, the discharge capacity of 116.3 mAhg⁻¹ is still delivered for CSLVP, while the discharge capacity of 92.5 mAhg⁻¹ for LVP, as shown in Fig S4(a). Long-term cycling performance of CSLVP and LVP at a high rate of 20 C is shown in Fig. S4(b). The CSLVP cathode delivers an initial discharge capacity of 116.3 mAhg⁻¹ (only 92.5 mAhg⁻¹ for LVP) and still maintains a remarkable capacity of 111.0 mAhg⁻¹ (85.1 mAhg⁻¹ for LVP) after 1000 cycles. The CSLVP exhibited more excellent rate and long-term cycling performance.

References:

1. P. P. Sun, S. Qin, X. Z. Wang, R. Y. An, Q. Y. Xu, X. Cui, Y. M. Sun, S. B. Wang, P. Wang and Q. Fan, *J. Power Sources*, 2015, **293**, 922-928.
2. B. Zhang, C. Shen, J. -C. Zheng, Y. -D. Han, J. -F. Zhang, L. Ming, J. -L. Wang, S. Qin and H. Li, *J. Electrochem. Soc.*, 2014, **161**, A748-752.

3. M. V. Reddy, G.V. Subba Rao and B. V. R. Chowdari, *J. Power Sources*, 2010, **195**,
5768-5774.