Electronic Supplementary Information

# LISICON structured $Li_3V_2(PO_4)_3$ with high rate and ultralong life for low-temperature lithium-ion batteries

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**Table S1** Structure parameters of the r-LVP/C determined by Rietveld refinement.

| Atom | Wyckoff position | Occupancy | x | y | z |
|---|---|---|---|---|---|
| Li1 | 18f | 0.94 | 0.2 | 0.0064(1) | 0.4505(2) |
| Na1 | 3a | 0.03 | 0.0749(6) | 0.0289(7) | 0.0013(6) |
| Na2 | 3b | 0.03 | 0.0749(6) | 0.0289(7) | 0.4986(4) |
| V1 | 6c | 1 | 0 | 0 | 0.1461 |
| V2 | 6c | 1 | 0 | 0 | 0.6528 |
| P1 | 18f | 1 | 0.2923 | 0.0019 | 0.2513 |
| O1 | 18f | 1 | 0.1915 | -0.0096 | 0.1919 |
| O2 | 18f | 1 | 0.7656 | 0.9126 | 0.6990 |
| O3 | 18f | 1 | 0.2434 | 0.8007 | 0.2659 |
| O4 | 18f | 1 | 0.5006 | 0.8796 | 0.7556 |

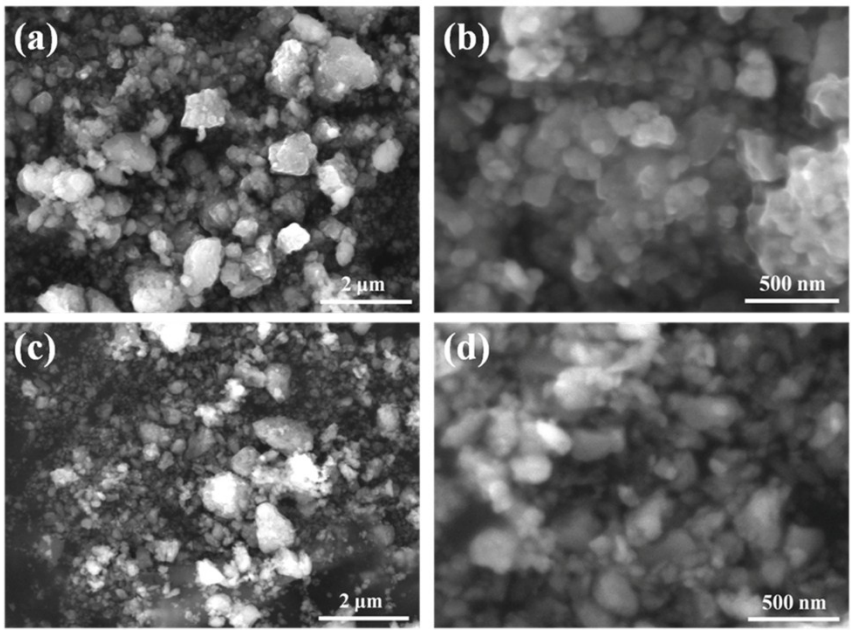


**Fig. S1** SEM images of the r-NVP/C precursor (a, b) and the r-LVP/C product (c, d).

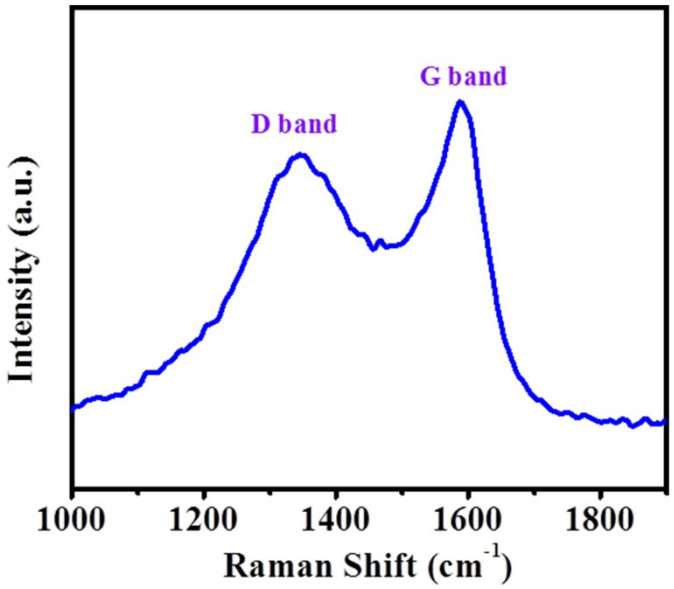


**Fig. S2** Raman spectrum of the r-LVP/C.

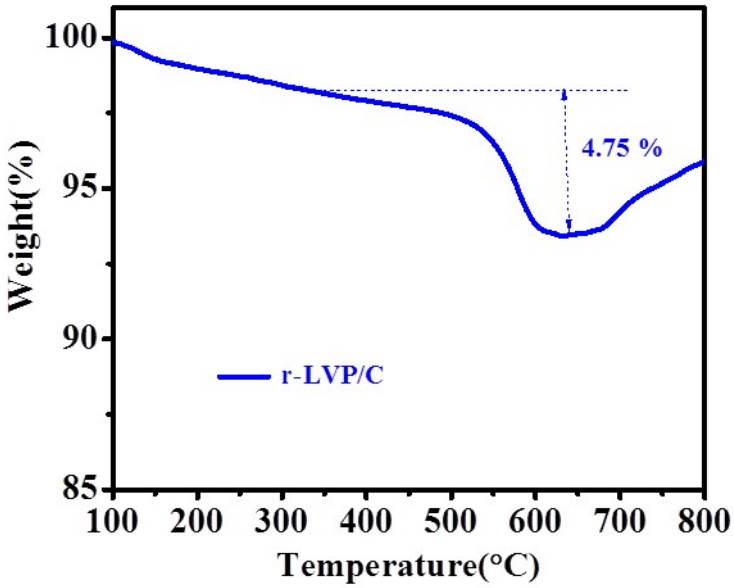


**Fig. S3** TG curves of r-NVP/C and r-LVP/C under flow air atmosphere.

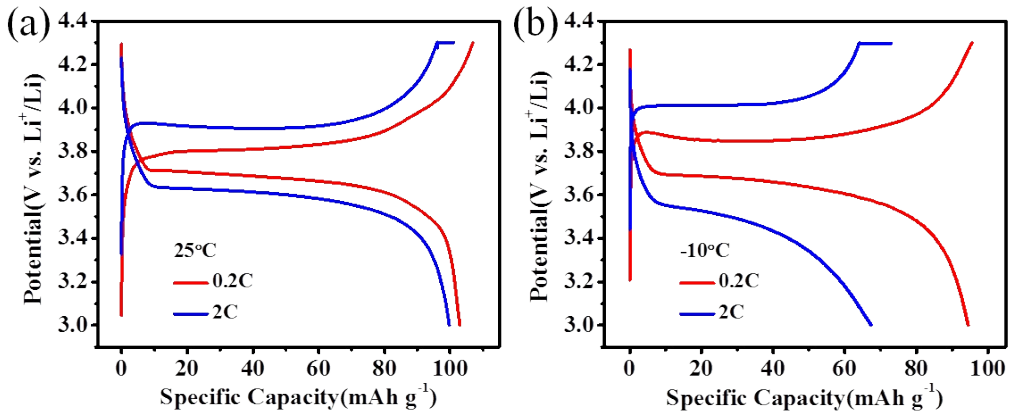


**Fig. S4** Galvanostatic charge/discharge curves of the r-LVP/C at 25 °C (a) and -10 °C (b) at a higher mass loading of ~6 mg/cm$^2$.

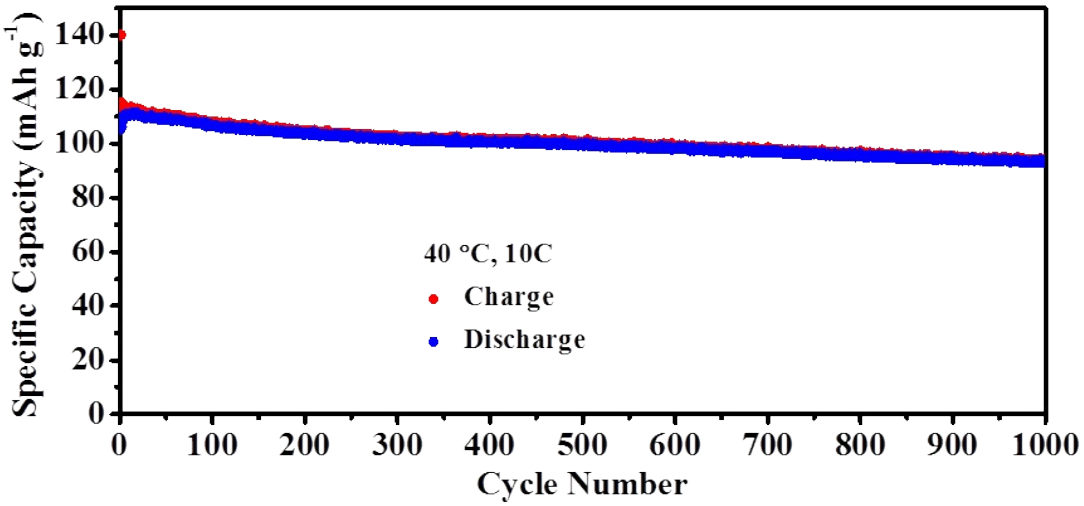


**Fig. S5** Cycling performance of the r-LVP/C at 40 °C with a high rate of 10C.

**Table S2** The comparison of the low temperature electrochemical performance of the r-LVP/C and the reported cathodes for LIBs.

| Electrode Materials | Temperature (°C) | Capacity Retention LT/RT (Rate) | Reference |
|---|---|---|---|
| **r-LVP/C** | -20 | 87.0 % (0.2 C) | This work |
| **m-LVP/C** | -20 | 95.3 % (0.1 C) | Ref. S1 |
| **m-LVP/C** | -20 | 86.7% (0.3 C) | Ref. S2 |
| **m-LVP/C** | -20 | 85.5 % (5 C) | Ref. S3 |
| **LFP/C** | -25 | 71.4 % (0.2 C) | Ref. S4 |
| **LFP/C** | -20 | 31.5% (0.3 C) | Ref. S2 |
| **LFP/C** | -20 | 66.7 % (1 C) | Ref. S5 |
| **LFP/C** | -20 | 78.3 % (0.1 C) | Ref. S6 |
| **LFP/C** | -20 | 66.9 % (1 C) | Ref. S7 |
| | -40 | 51.3 % (1 C) | |
| **$LiMn_{0.8}Fe_{0.2}PO_4/C$** | -15 | 64.7 % (0.1 C) | Ref. S8 |
| **$Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O_2$** | -20 | 39.4 % (0.1 C) | Ref. S9 |
| **$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$** | -20 | 72 % (0.2 C) | Ref. S10 |
| **$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$** | -20 | 82.9 % (0.2 C) | Ref. S11 |

**Table S3** Electrode kinetic parameters obtained from equivalent circuit fitting for the r-LVP/C measured at various temperatures.

| | 25°C | 0°C | -10°C | -20°C |
|---|---|---|---|---|
| **Rct (Ω)** | 101 | 208 | 637 | 1493 |
| **$D_{Li+}$ ($10^{-13}$ $cm^2$ $s^{-1}$)** | 3.3 | 2.2 | 1.3 | 0.9 |

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