

## Supporting Information

### VGCF-sheath@LiMn<sub>0.4</sub>Fe<sub>0.6</sub>PO<sub>4</sub>-shell Heterostructure Nanowire for High Rate Li-ion Batteries

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#### Experimental

##### Materials:

LiNO<sub>3</sub> (0.2 mol dm<sup>-3</sup>), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.08 mol dm<sup>-3</sup>), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.12 mol dm<sup>-3</sup>), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (0.2 mol dm<sup>-3</sup>) and poly acrylic acid (0.8 g) were dissolved into a mixed solution (20 ml) of water, methanol and nitric acid (10:9:1). After stirring for an hour, VGCF (Vapor Grown Carbon Fiber, 0.1 g) was ultrasonically dispersed into the solution using a sono-horn. The resultant precursor solution was poured into a syringe connected to a metal needle. A direct current electric field of 25 kV was applied between the needle and the Al foil target used for collection. The as-spun materials were then dried in a vacuum for an hour at 100 °C. The dried materials separated from the Al foil were heated at 800 °C for 10 hours under Ar flow condition.

##### Characterization:

The crystallographic structural characterization was performed by X-ray powder diffraction (XRD) and Rietveld refinement. The XRD analysis was carried on a Rigaku SmartLab X-ray diffractometer using Cu K $\alpha$  radiation. The morphology was observed by means of field-emission scanning electron microscopy (FESEM) and bright-field transmission electron microscopy (bright-field TEM) using a Carl Zeiss Gemini and a JEOL JEM-2010F (200 kV

accelerating voltage), respectively.

Electrochemical measurements were taken by a three-electrode cell. The prepared active materials were mixed and ground with 5 wt % polytetrafluoroethylene powder. The mixture was spread and pressed on the SUS-304 mesh. A  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4$  in EC/DEC was used as an electrolyte. Cell assembly was carried out in a glove-box in an atmosphere. The weight in specific capacity and current rate were calculated only for active materials. Cathode performance was tested five times at five charge/discharge rates (0.05, 0.1, 0.2, 0.5 and 1.0 C rate), respectively.

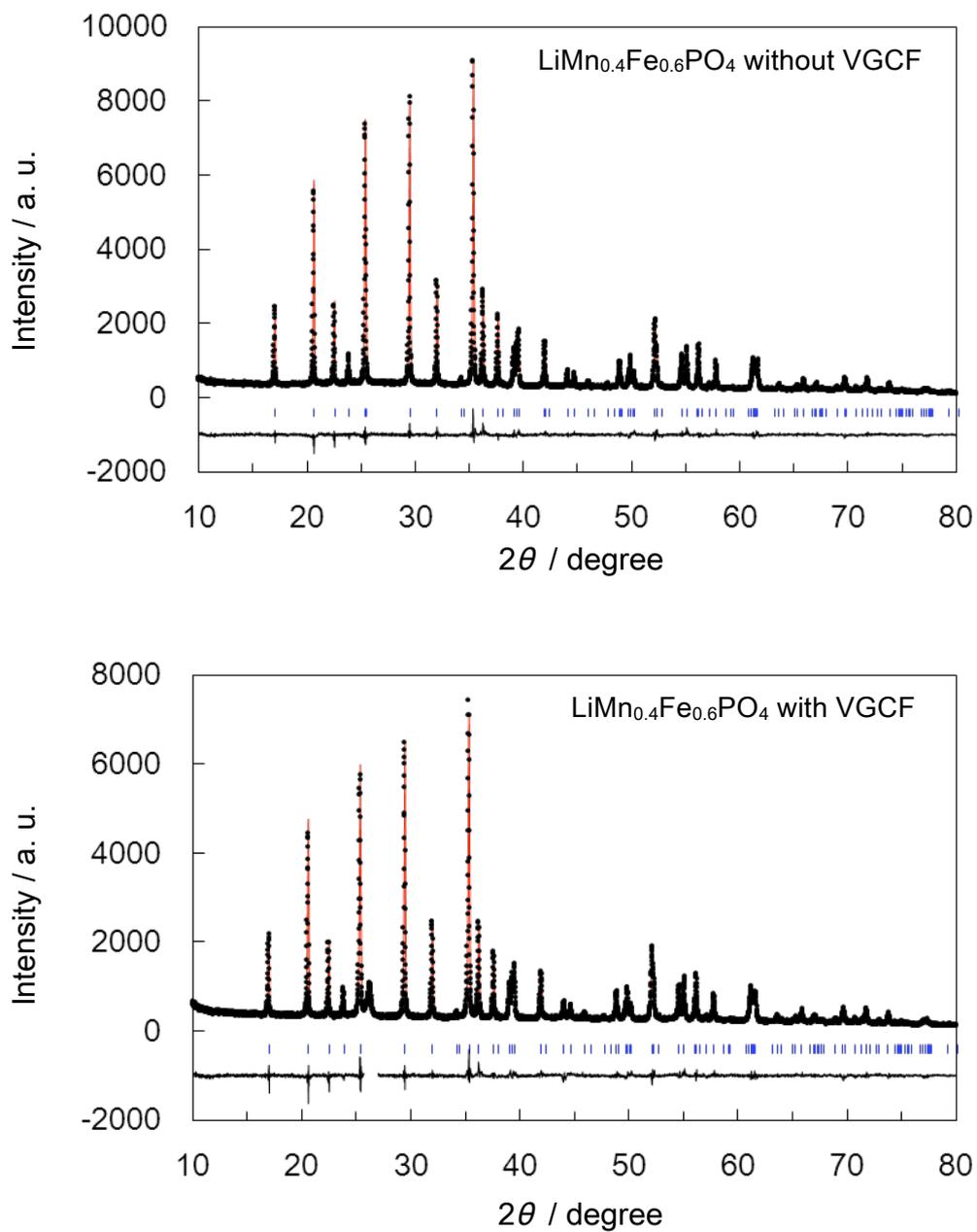


Figure S1. Rietveld refinement pattern of the X-ray diffraction data for **1** and **2** (space group *Pnma*). The observed intensity data are shown by dots; the solid lines overlying them are the calculated intensity. Vertical marks below the diffraction patterns indicate position of possible Bragg reflections. Differences between the observed and calculated intensity are plotted as  $D_{yj}$  at the same scale.



Table S1(a). Reitveld refinement results for **1**.

atom	site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å)
Li	4a	1	0	0	0	1.0
Mn, Fe	4c	1	0.2828(6)	0.25	0.9724(4)	2.05(5)
P	4c	1	0.0944(8)	0.25	0.4199(4)	2.52(7)
O1	4c	1	0.0897(1)	0.25	0.7468(5)	2.24(5)
O2	4c	1	0.4544(4)	0.25	0.2377(8)	2.24(5)
O3	8d	1	0.1595(3)	0.0473(3)	0.2743 (2)	2.24(5)

$$a = 10.388(4) \text{ \AA}, b = 6.0499(8) \text{ \AA}, c = 4.7184(5) \text{ \AA}. R_{\text{wp}} = 6.234, R_{\text{p}} = 4.804, S = 1.2863.$$

Table S1(b). Reitveld refinement results for **2**.

atom	site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å)
Li	4a	1	0	0	0	1.0
Mn, Fe	4c	1	0.2827(5)	0.25	0.9723(2)	1.61(6)
P	4c	1	0.0949(4)	0.25	0.4196(7)	2.2(3)
O1	4c	1	0.0900(9)	0.25	0.7415(2)	1.90(8)
O2	4c	1	0.4532(7)	0.25	0.237(9)	1.90(8)
O3	8d	1	0.159 (4)	0.0472(7)	0.2731(2)	1.90(8)

$$a = 10.398(1) \text{ \AA}, b = 6.0559(3) \text{ \AA}, c = 4.723(2) \text{ \AA}. R_{\text{wp}} = 6.744, R_{\text{p}} = 5.235, S = 1.3519.$$

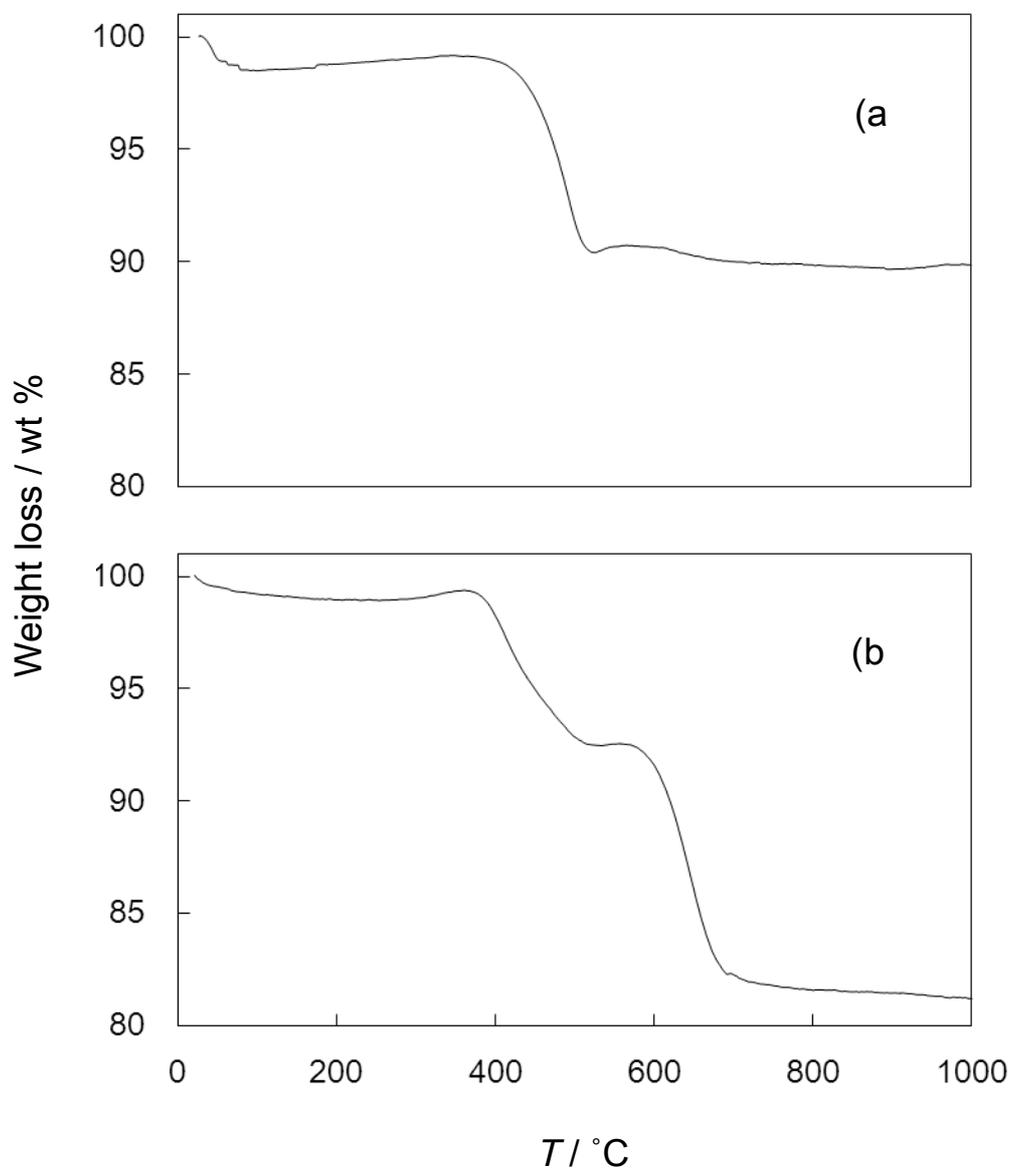


Figure S2. TG measurement of (a) **1** and (b) **2**.