

## Supporting Information

### **Over-lithiated NCM through $\text{Li}_5\text{FeO}_4$ for high energy silicon-based lithium-ion batteries**

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## **Experimental section**

### **Materials**

Commercial Si/C (theoretical capacity 950 mAh/g) powder purchased from Guangdong Canrd New Energy Technology Co., Ltd. was treated at 120°C in a vacuum oven for 12 h before use. NCM85E was obtained from a commercial vendor and also treated at 120°C in a vacuum oven for 12 h before use. The Super P (SP) carbon was used as the conductive additive. Polyacrylic acid (PAA) in water and poly(tetrafluoroethylene)(PTFE) powder were used as the binder. The synthesis and handling of LFO powder was performed inside an argon atmosphere glovebox. Fe<sub>2</sub>O<sub>3</sub> was thoroughly mixed with Li<sub>2</sub>O with a molar ratio of 1:5.5 using mortar and pestle for 30 mins. Extra Li<sub>2</sub>O was used to compensate for the lithium loss during the extended high-temperature treatment during synthesis. The mixture was first heated at 600°C for 12 h, and then at 800°C for 48 h with a subsequent grinding step to obtain a homogeneous powder. The final LFO powder was stored inside an argon atmosphere box to prevent its reaction with H<sub>2</sub>O and CO<sub>2</sub>.

### **Characterizations**

The powder X-ray diffraction (XRD) and in-situ XRD results were conducted by Bruker D8 Advance with Cu K $\alpha$  radiation ( $\lambda=0.154$  nm). The micro morphology and element distribution were characterized by scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) (FESEM, Hitachi SU8010). The electrochemical mass spectrometry (DEMS) measurements were performed by a quadrupole mass spectrometer (PrismaPro QMG 250 M2) with a turbomolecular pump (Pfeiffer Vacuum). The cyclic voltammetry (CV) tests were performed on an electrochemical workstation (CHI740E, Chenhua Co., Shanghai, P.R. China) at a rate of 0.5 mV s<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) were performed on a Thermo Fisher Scientific Model K-Alpha instrument configured with Al K $\alpha$  radiation (1486.6 eV) and XPS data was corrected with 284.8 eV as the basis.

### **Battery assembly and electrochemical measurements**

Si/C slurry was made by mixing Si/C, SP carbon and PAA in a weight ratio of 90:5:5 using a mixer at 1200 rpm until the slurry appeared uniform without apparent

aggregates. The Si/C slurry was then coated onto a copper foil. The laminates were dried in 80°C vacuum oven for overnight drying.

Due to the sensitivity of LFO to moisture, the fabrication of both the NCM85E-LFO blend laminate and the LFO laminate were performed in the glovebox. To fabricate NCM85E-LFO blend cathode electrodes, NCM85E, SP carbon and LFO were first mixed with a weight ratio of 40:5:4 using mortar and pestle in the glovebox. PTFE was then added to achieve a weight ratio of NCM85E-LFO: SP carbon: PTFE = 44:5:5. The mixture was then hand mixed with mortar and pestle until a uniform film was obtained. The resulting film was then cast onto an Al mesh. To fabricate the LFO laminate, LFO, SP carbon and PTFE with a weight ratio of 50:8:7 were hand mixed in the glovebox using mortar and pestle to obtain a uniform film. The film was then cast onto an Al mesh. The NCM85E cathode electrodes, with a weight ratio NCM85E: SP carbon: PTFE = 8:1:1, the film preparation process was the same as before. To assemble coin cells, 12 mm-diameter Si/C electrodes were used as the anode, and 10mm-diameter LFO, or NCM85E or NCM85E-LFO blend electrodes were used as the cathode. The electrolyte contains 1.0 M LiPF<sub>6</sub> in the 3:7 w/w mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC).

The half-cell and full-cell testing were performed in a temperature controlled chamber at 28°C. Half-cell testing was used to obtain the initial voltage profiles for each electrode. The SiC950 electrodes were cycled between 0.01 V and 1.5 V at 0.1 C rate, the NCM85E and NCM85E-LFO electrodes were cycled between 3.0 V and 4.3 V at 0.1 C rate. The LFO electrodes were cycled between 1 V and 4.5 V at 0.025 C rate. Full-cell testing was performed to evaluate the impact of LFO on the electrochemical performance of the cells. The cells were first cycled 2 times between 2.5 V and 4.3 V at 0.1 C rate as the initial formation cycles. After formation cycles, the cells underwent cycle test where the cells were cycled in the same voltage window at 0.2 C rate. The N/P ratios of the full cells were about 1.2.

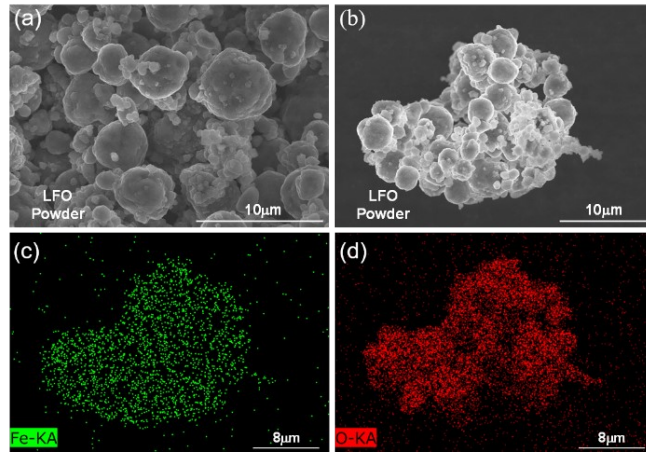
### **Calculation process of pre-lithium agent amount**

The initial discharge and charge specific capacity of SiC950 half-cell are 977.4 and 777.9 mAh/g, respectively. It can be calculated that the first cycle irreversible specific capacity is  $977.4 - 777.9 = 199.5$  mAh/g. In our manuscript, the active material of the SiC950 electrode is 5.5 mg.

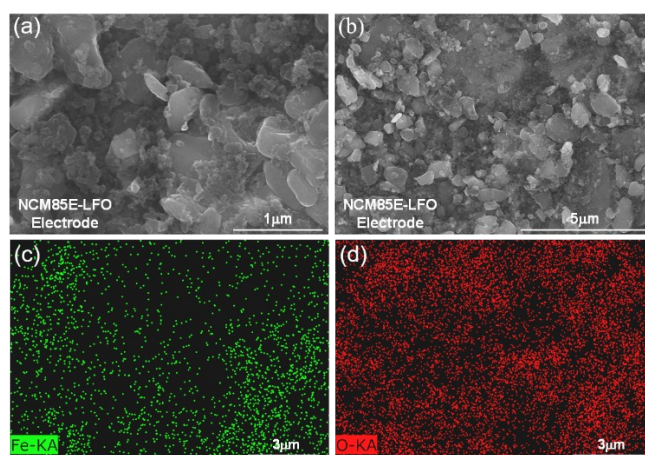
The initial charge capacity of the LFO is 620.7 mAh/g. It can be calculated that if the loss of lithium is exactly replenished,  $199.5 * 5.5 / 620.7 = 1.77$  mg of LFO is required.

According to the SiC950 half-cell stable cycle specific capacity of 800 mAh/g, the NCM85E half-cell stable cycle specific capacity of 200 mAh/g and NP ratio = 1.2, it can be calculated that the mass of NCM85E active material is  $5.5 * (800 / 200) / 1.2 = 18.33$  mg.

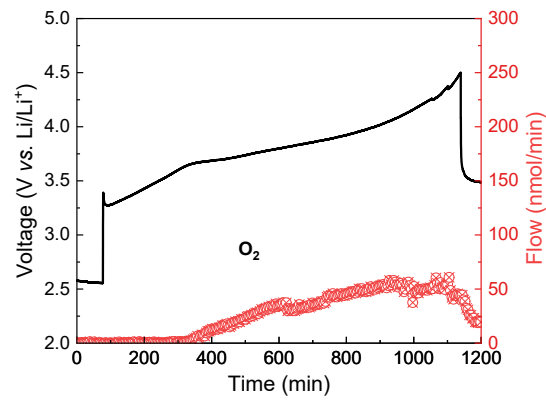
In theory, the amount of LFO required to compensate for the Li loss of SiC950 is calculated about 9.7% ( $1.77 / 18.27 = 9.7\%$ ) of the weight of NCM85E, which can achieve close to full utilization of lithium from the NCM85E cathode. In the manuscript, we added 10% LFO, and the addition of a little excess LFO is just to provide a little extra lithium inventory, which may improve capacity retention.



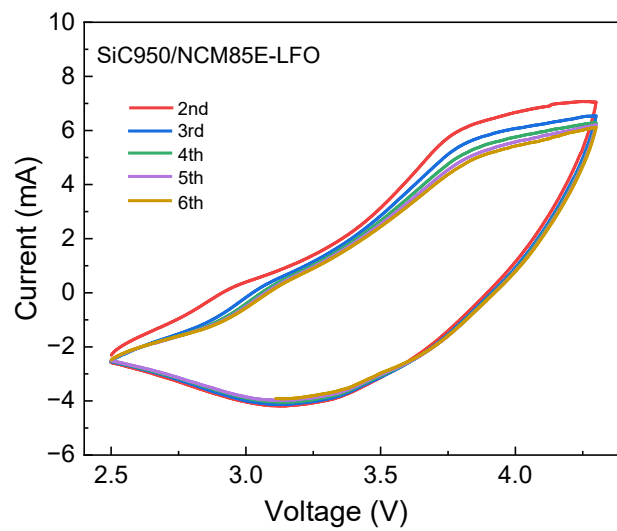
**Fig. S1** (a, b) SEM images of the LFO powder and the EDS mapping of Fe signal (c) and O signal (d) corresponding to (b).



**Fig. S2** (a, b) SEM images of the NCM85E-LFO electrode and the EDS mapping of Fe signal (c) and O signal (d) corresponding to (b).

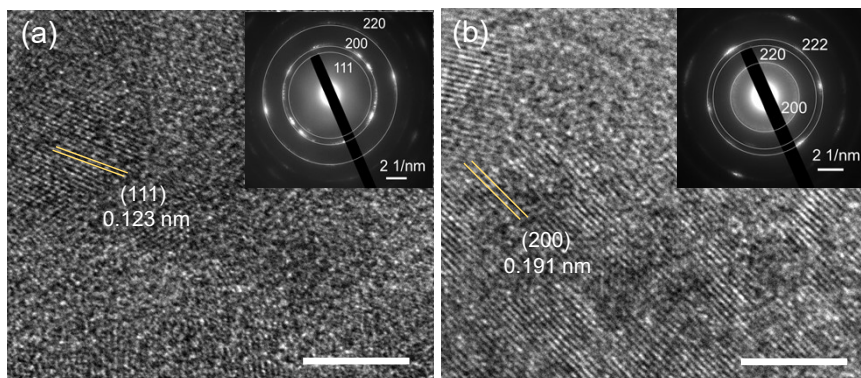


**Fig. S3** DEMS data for O<sub>2</sub> released in the Li/LFO half cell in the first charge to 4.5 V.



**Fig. S4** CV curves of SiC950/NCM85E-LFO full cell for 2-6 cycles.





**Fig. S5** HR-TEM image of the LFO during the initial charge to 3.7 V (a) and 4.1 V (b). Scale bars, 2 nm. Inset: the corresponding SAED pattern.

**Table S1** Summary of first cycle of different half cells.

<b>Half cell</b>	<b>First cycle charge specific capacity (mAh/g)</b>	<b>First cycle discharge specific capacity (mAh/g)</b>	<b>Coulombic efficiency (%)</b>
Li/SiC950	777.9	977.4	79.6
Li/NCM85E	221.3	199.1	90.0
Li/LFO	620.7	-	-
Li/NCM85E-LFO	290.5	199.8	68.8

**Table S2** Summary of first cycle of SiC950/NCM85E and SiC950/NCM85E-LFO full cells.

<b>Full cell</b>	<b>First cycle charge specific capacity (mAh/g)</b>	<b>First cycle discharge specific capacity (mAh/g)</b>	<b>Reversible specific capacity for 100 cycles (mAh/g)</b>	<b>Reversible specific capacity for 200 cycles (mAh/g)</b>
SiC950/NCM85E	214.0	151.0	113.8	103.1
SiC950/NCM85E-	273.4	193.4	147.3	129.0