Supplementary Information

Constructing LiF-rich Cathode Electrolyte Interphase to Enhance the Cyclic Stability of Lithium-rich Manganese-based Oxide Cathode

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1. Experimental

1.1 Sample Preparation

$Ni_{0.12}Co_{0.12}Mn_{0.76}CO_3$ (Zhongwei New Materials Co., Ltd) and Li_2CO_3 (Innochem Co., Ltd) were mixed at a weight ratio of 1:1.4 and reacted at 500 ℃ for 5 h under an oxygen atmosphere, and then preserved at 850 ℃ for 12 h to obtain the bare $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ (LR-bare).

According to the mass ratio of 1:0.01, 1:0.03, and 1:0.05, LR-bare and fluorinated carbon (CF) were mixed to a total of 2 g, and then spherical ground for 2 h at 200 r min^{-1} in a ball mill tank to obtain the composites LR@CF, named LRCF1, LRCF3 and LRCF5 respectively.

Si and C composite material was purchased from Tianmulake Excellent Anode Materials Co., Ltd.

1.2 Coin-cell assembling

The cathode electrode was prepared by coating the slurry on Al foil by a ratio of active material: Super P: poly-vinylidene fluoride (PVDF) = 8:1:1, and then cast into Φ12 mm tablets. The as-prepared tablets were dried at 120 ℃ for 24 h in a vacuum oven before assembly. CR2032-type coin-cells were assembled with the tablets as cathode and Li foil as anode in a glovebox filled with argon (H_2O and O_2< 0.1 ppm). The electrolyte was 1M $LiPF_6$ in ethylene (EC) and dimethyl carbonate (DMC) (3:7 in volume) and the separator was $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) coated polypropylene (PP)/polyethylene (PE) film.

1.3 Full pouch-cells assembling

The anode electrode was prepared by coating the slurry on Cu foil by a ratio of active material: Super P: carboxymethyl cellulose sodium (CMC): styrene-butadiene rubber (SBR)= 96:2:1:1. The prepared cathode and anode electrodes were punched into 73 × 60 mm and 75 × 62 mm rectangular pieces, respectively. All electrodes were dried in a vacuum oven for 24 h (120 ℃ for cathode and 80 ℃ for anode) before assembly. Pouch cells were produced in a dry room (dewpoint -60 ℃) with a N/P of 1.1.

1.4 Characterization

The electrochemical performance of coin-cells was carried out with a Land CT2001A battery test system (Wuhan, PR China) in a voltage range of 2.0-4.8 V under different current rates (1C=250 mAh g^{-1}) at room temperature under different current rates (1C=250 mAh g^{-1}) at room temperature. And full pouch-cells were tested within a voltage range of 2.05 - 4.75 V during the first charge and discharge at 0.1C. Subsequently, a cycle test was conducted at 0.5C within a voltage range of 2.1 - 4.7 V

(the design capacity is 1.0Ah).

Electrochemical impedance spectroscopy (EIS) was measured by Autolab (Metrohm), with a 5 mV amplitude of AC in the frequency range of 0.01 Hz-100 kHz. The surface morphology and element distribution were observed by Scanning Electron Microscopy (SEM, Hitachi S-840) with Energy Dispersive Spectrometer (EDS). Transmission electron microscope (TEM, JEOL JEM-F200) was used to observe the coating layer structure on the surface of the samples. The structure of materials was measured by an X-ray diffractometer (XRD, Bruker D8) with Cu-Kα radiation (λ = 1.5405 Å) in the 2θ scan range of 10-80^{o}. X-ray photoelectron spectroscopy (XPS) was recorded by an ESCALAB 250 Xi system (Thermo Scientific).

2. Supplementary Figures

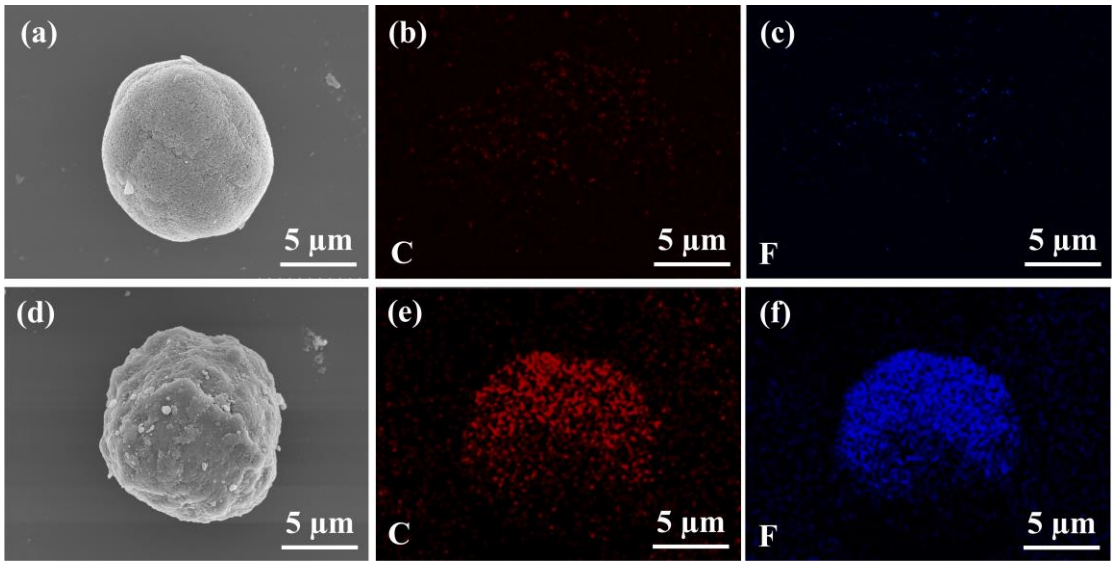

Fig S1. SEM-EDS mapping images of (a-c) LR-bare and (d-f) LR@CF3 samples.

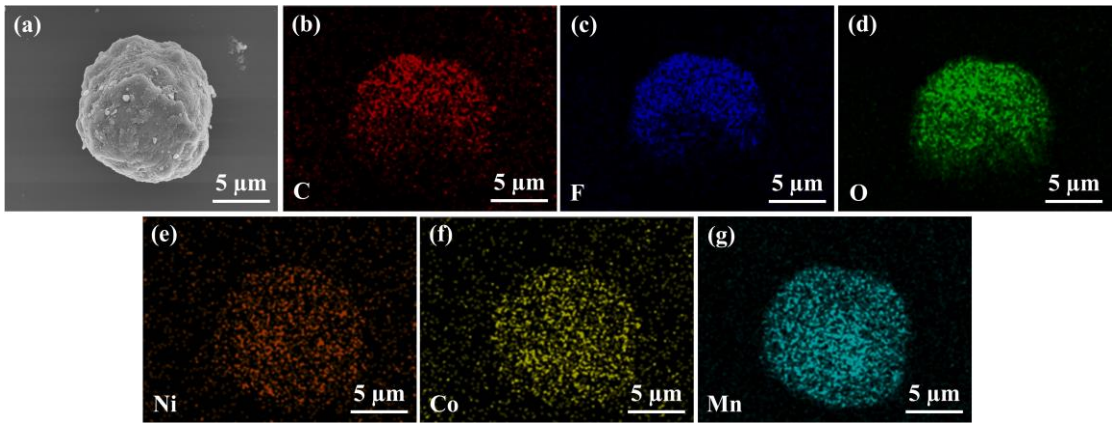

Fig S2. The EDS mapping spectrum of different elements on the surface of LR@CF,

(a) LR@CF, (b) C, (c) F, (d) O, (e) Ni, (f) Co, (g) Mn.

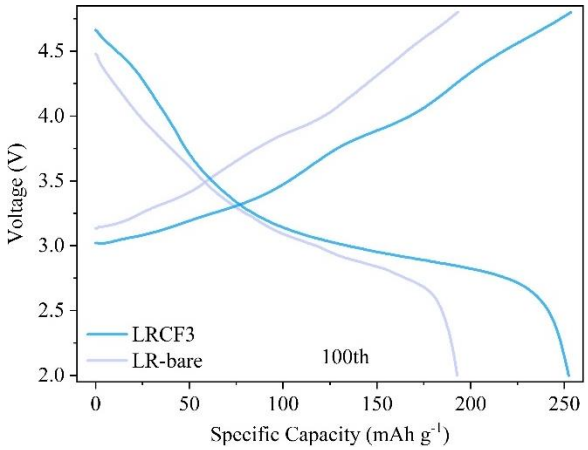

Fig S3. Charge and discharge curves of LR-bare and LRCF3 after 100 cycles.

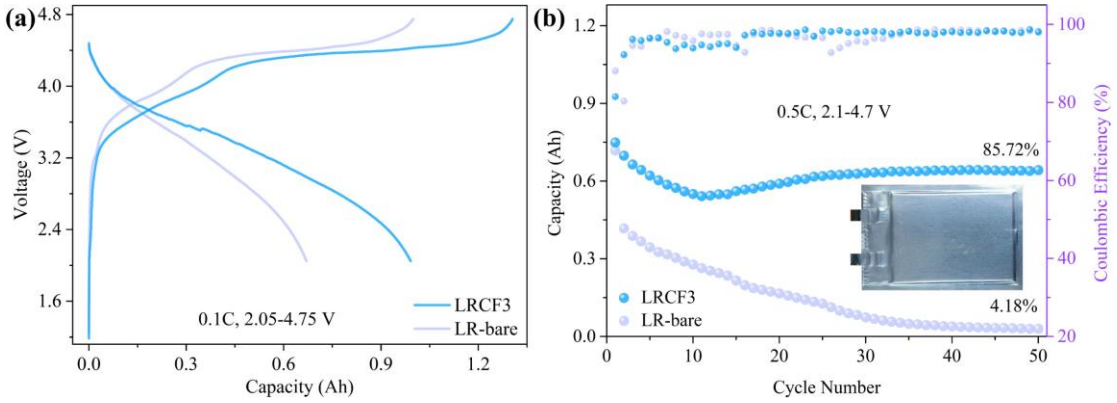

Fig S4. The electrochemical performance of full pouch-cells with SiC as anode and LR-bare and LRCF3 as cathode respectively, (a) the initial charge and discharge curves, (b)cycle performance.

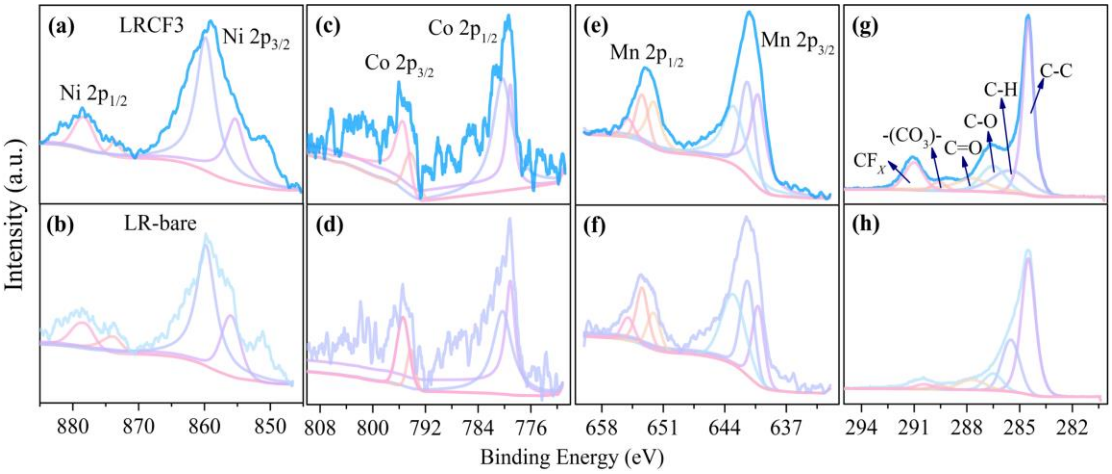

Fig S5. XPS spectra of LR-bare and LRCF3 after the initial discharge, (a-b) Ni 2p, (c-d) Co 2p, (e-f) Mn 2p, (g-h) C 1s.

Table S1. Statistical table for performance comparison between this work and previous studies.

Materials	Maximal capacity@RT (mAh g^{-1})	ICE (%)	Rate capabilities (mAh g^{-1})	Voltage (V)	Capacity retention (%/cycle/rate)	Re
$Li_{1.13}Mn_{0.517}Ni_{0.256}Co_{0.097}O_2$	261.5(0.1C)	88.1	0.5C/210	2.0-4.8	85.3/300/0.5C	1
$Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$	277.1(0.2C)	71.2	5C/133	2.0-4.8	81.9/100/1C	2
$Li_{1.14}Ni_{0.133}Co_{0.133}Mn_{0.544}O_2$	390(0.1C)	99.5	5C/131	2.0-4.8	~78/100/1C	3
$Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$	289.5(0.1C)	82.4	5C/182.9	2.0-4.8	94.6/100/0.5C	4
$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$	288(0.1C)	95.9	5C/~90	2.0-4.8	91/100/0.2C	5
$Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$	305.5(0.1C)	94.15	5C/213.1	2.0-4.8	94.07/100/1C	This work

Table S2. The equivalent circuit fitting results corresponding to the EIS of LR-bare and LRCF3.

Samples	R_s (Ω)	R_{sf} (Ω)	R_{ct} (Ω)
LR-bare	3.13	115.90	172.70
LRCF3	2.57	109.10	85.96

References：

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