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Electronic Supplementary Information

CeO_2 modified Li-rich layered oxide cathode with tunable interfacial oxygen for durable Li-ion batteries

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1. Experimental Section

1.1 Materials synthesis

Preparation of pristine $Li_{1.20}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$. The $Mn_{0.54}Ni_{0.13}Co_{0.13}CO_3$ precursor was fabricated via a co-precipitation method. In brief, 2.0 M mixed solution of $NiSO_4{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$ and $MnSO_4{\cdot}H_2O$ (Mn: Ni: Co= 0.54:0.13:0.13, molar ratio), 2.0 M Na_2CO_3 and 1.5 M NH_4OH were separately pumped into the reactor and keep stirring for 25 h under Ar protection, while the temperature of the reacting mixture was maintained 50 °C. The $Mn_{0.54}Ni_{0.13}Co_{0.13}CO_3$ precursor was obtained by filtering, washing with distilled water several times and then drying at 120 °C for 24 h. The pristine $Li_{1.20}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ cathode material (denoted as pristine LLO) was prepared by heating stoichiometrically mixed carbonate precursor and Li_2CO_3 (molar ratio of lithium to transition metals = 1.05) at 450 °C for 5 h and 900 °C for 10 h with the heating rate of 10 °C min^{-1}.

Preparation of $Li_{1.20}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$@$CeO_2$. The preparation processes of $Li_{1.20}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$@$CeO_2$ (denoted as LLO@CeO_2) is similar to Pristine LLO. The only difference is that after the reaction of transition metals salt, Na_2CO_3 and NH_4OH for 1 h in the co-precipitation process, the solution of $Ce(NO_3)_3$ was slowly pumped into the reactor (molar ratio of Ce to transition metals = 0.05) and the mixed solution were then kept stirring for 24 h to obtain $Mn_{0.54}Ni_{0.13}Co_{0.13}CO_3$@$Ce_2(CO_3)_3$ precursor. The subsequent calcination process was the same with LLO and finally the product $Li_{1.20}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$@$CeO_2$ was prepared.

1.2 Characterization

The morphology and microstructure of products were characterized by scanning electron microscope (SEM, S-4800) and field high resolution transmission electron microscopy (HRTEM; FEI Talos F200X) with accessory of energy disperse X-ray spectroscopy (EDS). The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray powder diffractometer with Cu Kα radiation (λ = 0.154 nm). The X-ray photoelectron spectra (XPS, Al Kα) was employed to study the surface chemistry of the cathodes, and the acquired data were calibrated by means of the C 1 s peak (284.8

eV). The soft XANES measurements with both TEY and FLY modes at the Mn $L_{3,2}$-edges and O K-edge were collected at the BL20A1 beamline in the National Synchrotron Radiation Research Center (NSRRC) and the BL08U beamline in Shanghai Synchrotron Radiation Facility (SSRF).

1.3 Electrochemical measurements

Electrochemical measurements were performed on the basis of coin-type 2016 cells. The working electrode consists of the as-prepared active materials (LLO and LLO@CeO_2), carbon black, and poly (vinyl difluoride) (PVDF) at a weight ratio of 8:1:1, the a few drops of N-Methyl-2-pyrrolidone (NMP) were added and the mixture was kept stirring for 12 h. The obtained slurry was then pasted on pure Al foil with the coating thickness of 100 μm. The electrode was finally got after drying in a vacuum oven at 120 °C for 24 h and the loading amount of the active materials is ~ 2 mg cm^{-2}. The cells were assembled in an argon-filled glove box with pure lithium foil was used as the counter electrode, and the separator was a polypropylene membrane (Celgard 2400). The electrolyte consists of a solution of 1.0 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume). The charge and discharge measurements were carried out on a LAND-CT2001C test system at different current densities. Cyclic voltammogram experiments were performed on an Autolab PGSTAT302N electrochemical workstation at a voltage range from 2.0 - 4.8 V.

2. Figures

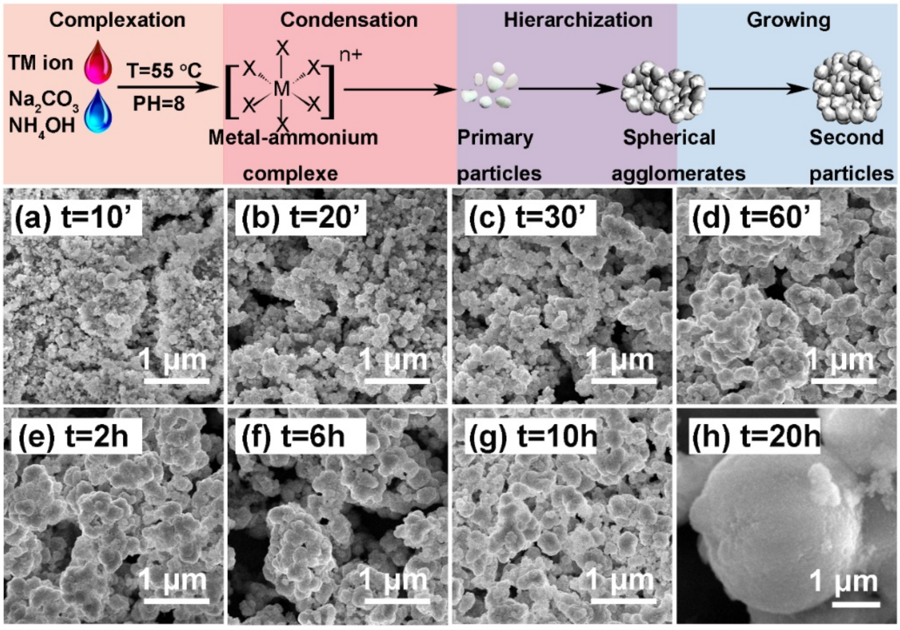

Fig. S1. In-situ co-precipitation process of the spherical carbonate microparticals of LLO precursor.

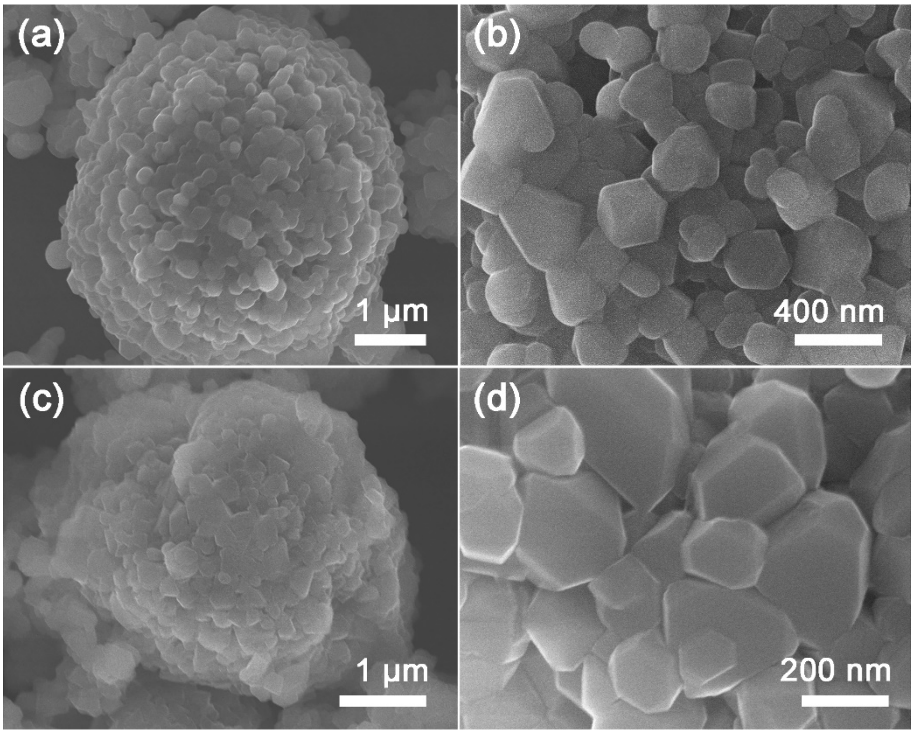

Fig. S2 SEM images of (a-b) LLO@CeO_2 and (c-d) pristine LLO.

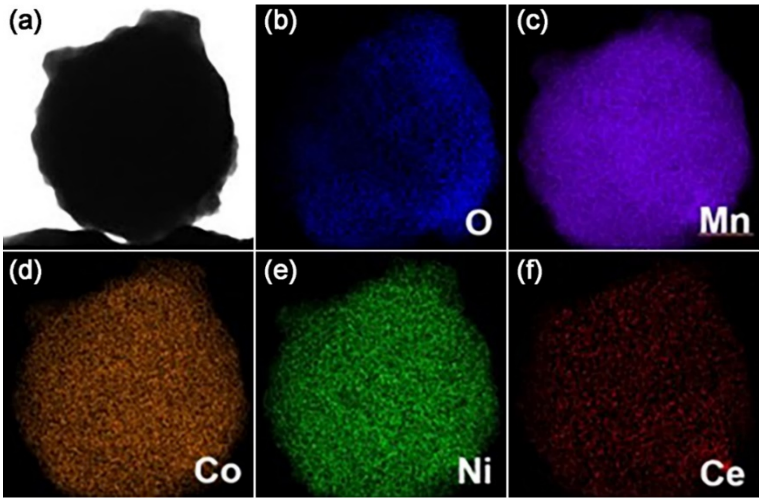

Fig. S3 (a) TEM image of LLO@CeO_2 and its corresponding element distribution of (b) O, (c) Mn, (d) Co, (e) Ni and (f) Ce.

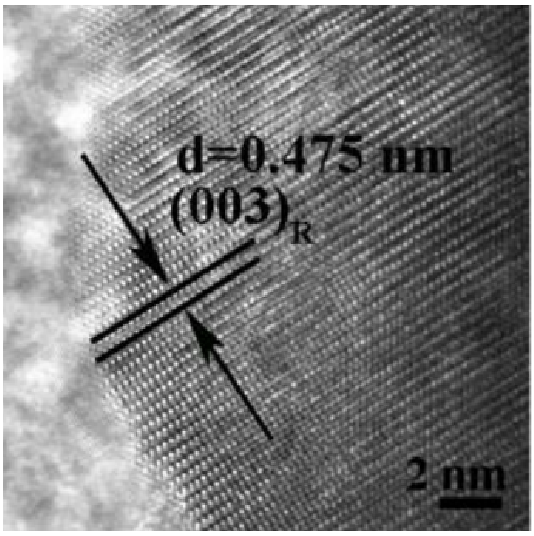

Fig. S4 HRTEM image of pristine LLO

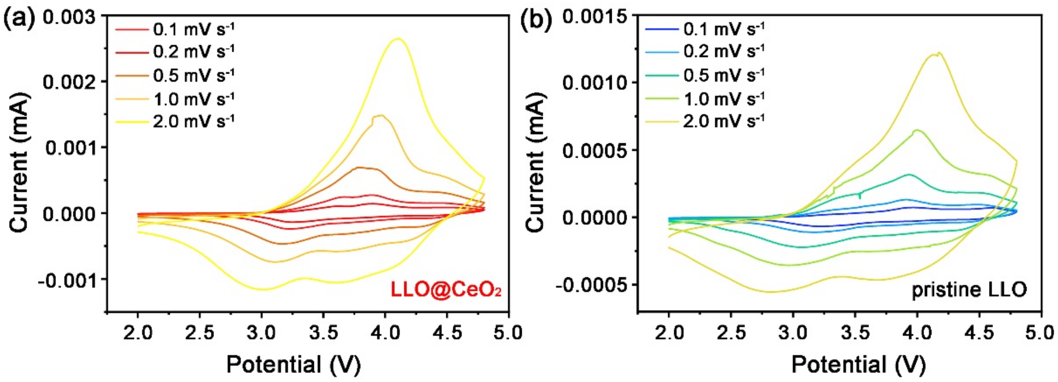

Fig. S5 CV plots of at various scan rates for (a) LLO@CeO_2 and (b) pristine LLO.

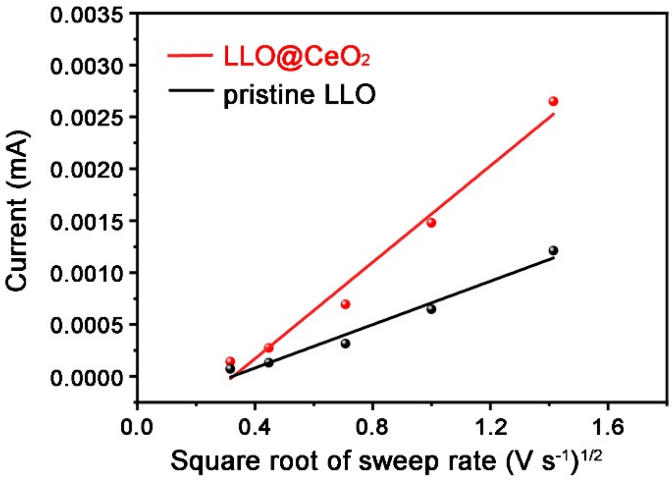

Fig. S6 Plots of the peak current density versus the square root of sweep rate.

3. Tables

Table S1 Proportion of lattice oxygen, oxygen vacancies and surface adsorbed oxygen obtained by means of XPS-peak-differentation-imitating analysis

Sample	**Surface adsorbed oxygen (532.6 eV)**	**Oxygen vacancies (531.1 eV)**	**Lattice oxygen (529.2 eV)**
pristine LLO	63.3%	32.9%	3.8%
LLO@CeO_2	68.0%	18.9%	13.1%

Table S2 The detailed rate capacity values of the pristine LLO and LLO@CeO_2

Sample	**pristine LLO (mAh g^{-1})**	**LLO@CeO_2 (mAh g^{-1})**
0.1 C	272.2	282.2
0.2 C	238.3	248.6
0.5 C	206.1	231.1
1.0 C	182.0	207.9
2.0 C	138.2	181.1
5.0 C	24.9	124.9

Table S3 Comparisons of electrochemical properties for as-prepared LLO@CeO_2 with other LLO cathodes.

Samples	**Current density**	**Capacity (mAh g^{-1})**	**Ref.**
15%HEPES-LLO-H2	0.1 C	273.2	1
	1.0 C	218.4	
W@LLMO	0.1 C	249.8	2
	1.0 C	~ 175	
LTO@LRMO	0.1 C	276.5	3
	1.0 C	~ 224	
W2-LLO	0.1 C	259	4
	1.0 C	174	
ZT-LLO	0.1C	245.2	5
LRM	0.1 C	250.8	6
3%G@LMNCO	0.2 C	270.3	7
	5.0 C	119.1	
s-LNCM	0.1 C	209.7	8
	1.0 C	157.1	
LLO@CeO_2	0.1 C	282.2	***This work***
	1.0 C	207.9	

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