Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information for

High-discharge-voltage Lithium-rich Layered-oxide Cathode Materials Based on Low Oxygen Vacancy

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Experimental

Carbonate precursors ($Mn_{0.54}Ni_{0.13}Co_{0.13}CO_{2.4}$) were prepared by the carbonate co-precipitation method. After carbonate precursors annealing in air at 500 ^oC for 6 hours, MO_x ($Mn_{0.54}Ni_{0.13}Co_{0.13}O_x$) was obtained. Stoichiometric 5.200 g MO_x and 1.504 g $LiOH{\cdot}H_2O$ (molar ratio MO_x : $LiOH{\cdot}H_2O$=1:0.4) were mixed and then the mixture was heated to get spinel $Li_{0.4}Mn_{0.54}Ni_{0.13}Co_{0.13}O_{1.6}$ in air at 850 ^oC for 12 h. Then 2.200 g spinel mixed with 1.000 g $LiOH{\cdot}H_2O$, and the mixture were put in O_2 and heated in 850 ^oC for 12 h to obtain $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ (LSO). And the $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_{2-2x}$ (LSA) were obtained by lithiating the same spinel in Ar by $LiOH{\cdot}H_2O$ at 600 ^oC for 10 h. $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_{2-x}$ (LMO) was prepared by mixing 1.300 g MO_x with demanded 1.136 g $LiOH{\cdot}H_2O$ and heating at 850 ^oC in O_2 for 12 h.

Material Characterization

The structures of the as-prepared samples were characterized by powder X-ray diffraction (XRD, Bruker, D8 advance, CuK_α, scan rate: 10 ^{o}/min). The morphologies of the samples were observed by field-emission scanning electron microscopy (FESEM, Zeiss Supra 55, Carl Zeiss Co.). X-ray photoelectron spectroscopy (XPS) data were collected using an ESCALAB 250 with Al K_α as a source. The C1s peak at 284.6 eV as an internal standard. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES SPECTRO ARCOS EOP) is used to check the elemental stoichiometry ratio of all samples.

Electrochemical Test

The working electrodes were made from a mixture of 80 wt. % of the active materials, 10 wt. % of the conducting agent (Super P), and 10 wt. % of the polyvinylidene difluoride (PVDF) binder. The counter/reference electrode was lithium metal, and the separator was the PE/PP composite membrane. The electrolyte solution was 1 M $LiPF_6$ dissolved in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 in volume) without any additives. Assembly of 2032 coin-type half cells was in an argon-filled dry glove box (UniLab, Mbraun GmbH, Germany; H2O < 1 ppm; O2 < 1 ppm). The cells were cycled at different charge-discharge rates in the voltage range of 2.0-4.8 V on a CT2001A cell test instrument (LAND Electronic Co.)

DFT calculation

DFT calculation was conducted on materials studio v.8.0.0.843 to do density-functional theory (DFT) calculations with the generalized gradient approximation and the Perdew-Burke-Ernzerhof functional. Crystal structure models of LLOs and Li were used by ISCD card named 1529154.cif and 9008542.cif, respectively. In the calculation process, the cutoff energy of three models was set to 457.4 eV, and the κ space was sampled with a κ-point mesh with spacings less than 0.05 $Å^{-1}$.

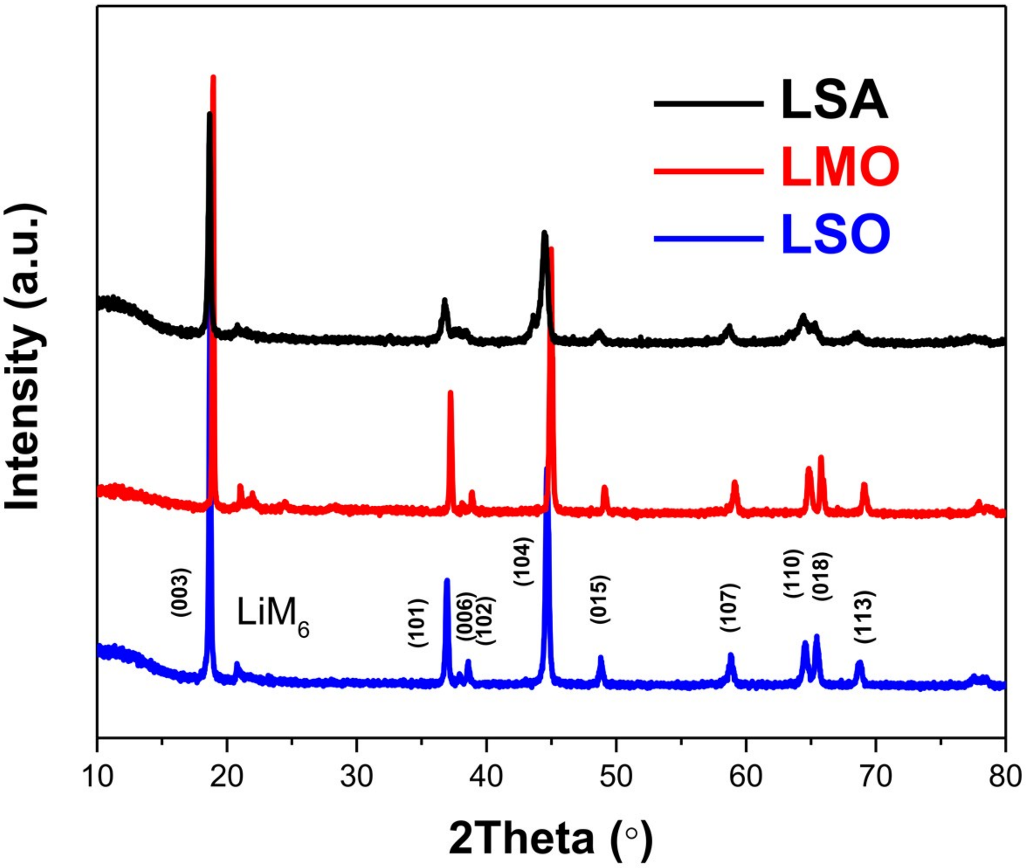

Figure S1 XRD patterns of LSO, LMO, and LSA.

Although the main peaks in three samples are well indexed into α-$NaFeO_2$, there are some new peaks occurring in LSA, which has high oxygen vacancy content, indicating the structure in LLOs with rich oxygen vacancies is unstable.

The slight shift of main diffraction peaks is shown in LSO, LMO, and LSA. We speculate that the slight shift of main diffraction peaks may be caused by the Li/Ni disorder and oxygen vacancy content. Because of the increasing of Li/Ni disorder of LSO (I_{003}/I_{104}=2.00), LSA (I_{003}/I_{104}=1.71) and LMO (I_{003}/I_{104}=1.65), the lattice parameters *a* and *c* of LSO, LSA and LMO decrease in order. Considering the effect of oxygen vacancy content, the lattice parameters *a* and *c* of LSA, LMO and LSO decrease in order. As a result of co-effect, the lattice parameters *a* and *c* of LSA, LSO and LMO decrease in order and the degrees of (003) and (104) peaks of LSA, LSO and LMO increase in order correspondingly.

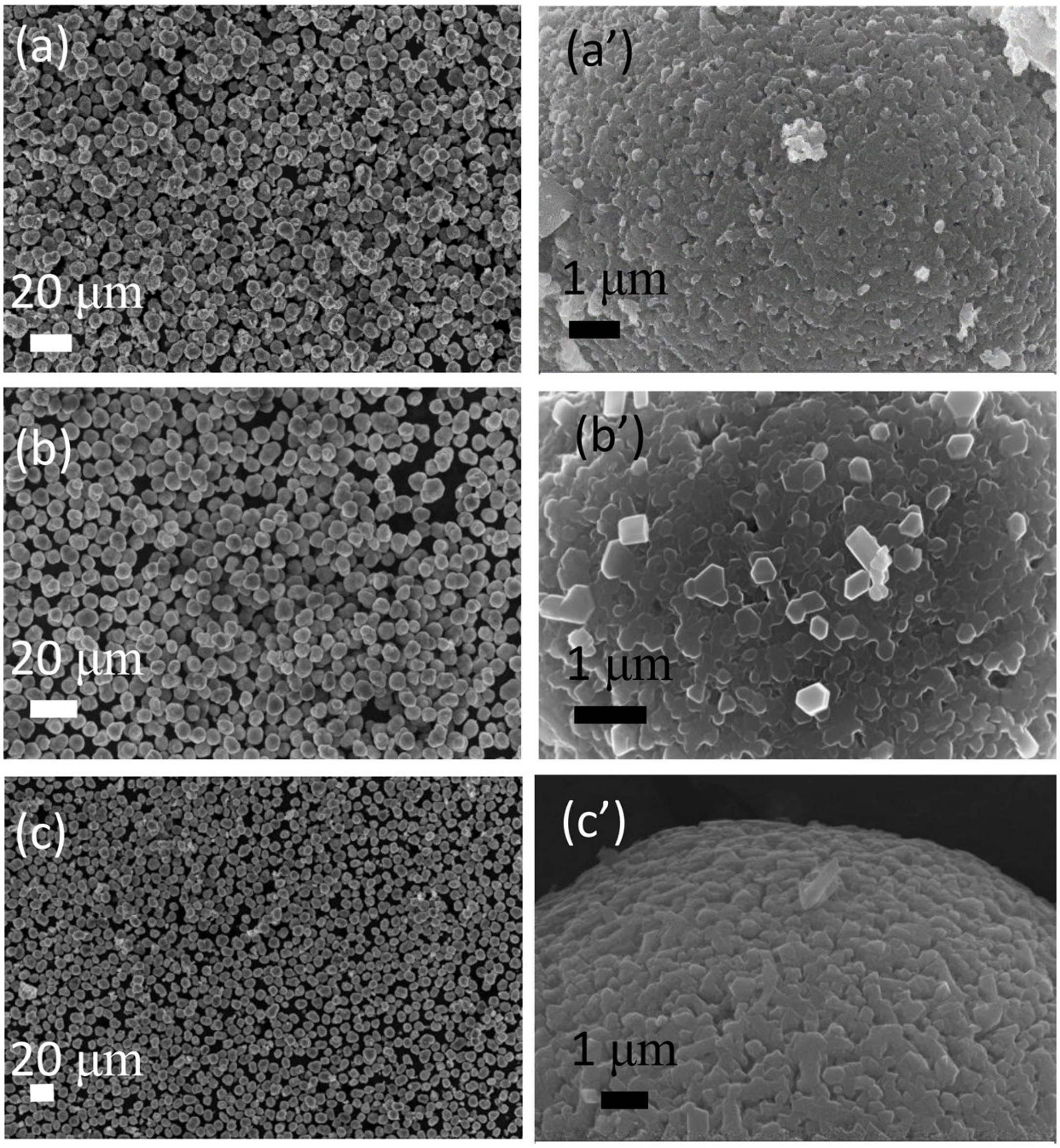

Figure S2 SEM images of (a and a') LSO, (b and b') LMO and (c and c') LSA

Due to the same precursors, as-prepared LSO, LMO, and LSA can keep the same spherical secondary particle size, which is about 15 μm. And their primary particle sizes are basically same as about 300 nm.

Table S1 Different O species relative content from XPS of LSO, LMO, and LSA by the peak-fit process

Samples	Species	Bind energy (eV)[1]	Atom %(Relative content)	Normalizing Atom %(Relative content)
LSO	O^{2-}	529.4	23.03	73.53
	OH^-	530.4	0.94	0.03
	O^-	531.4	6.2	19.80
	Absorbed species	532.8	1.15	0.04
LMO	O^{2-}	529.4	35.79	65.38
	OH^-	530.4	3.12	0.06
	O^-	531.4	13.28	24.26
	Absorbed species	532.8	2.58	0.05
LSA	O^{2-}	529.4	28.68	50.10
	OH^-	530.4	4.45	7.71
	O^-	531.4	20.12	34.84
	Absorbed species	532.8	4.5	7.79

O^{2-} species is lattice O in the bulks; OH^- species are surface M-O-H; O- species include two type mono-valence oxygen ions: limited surface M-O and oxygen vacancy in the bulks; Absorbed species are something like H_2O and CO_2 in air absorbed on the surface of particles.[1]

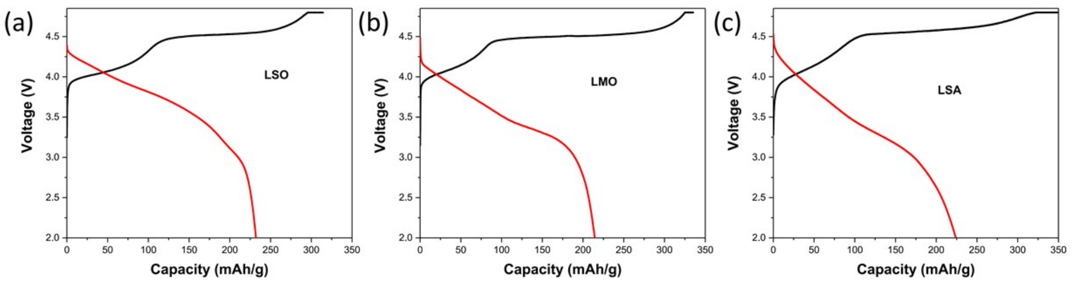

Figure S3 First charge and discharge curves of (a) LSO, (b) LMO and (c) LSA in 2.0-4.8 V voltage window and 0.2 C (50 mA/g) current density, with about 4.0 mg/cm^2 loading materials, respectively

The discharge capacity of LSO, LMO and LSA are 232.1 mAh/g, 214.4 mAh/g and 224.1 mAh/g in the first cycle, respectively. The discharge energy density E can be calculated by the below formula:

$E = C \times V$；

here, C is discharged specific capacity of the above three samples, and V is the average discharge voltage of the samples. The high discharge-energy density increases from 741 Wh/kg (LMO) to 832 Wh/kg (LSO). This result will lift the discharge voltage and energy density of the full cells.

Reference

1. J.-C. Dupin, D. Gonbeau, P. Vinatier and A. Levasseur, *Phys. Chem. Chem. Phys.*, 2000, **2**, 1319-1324.