Supporting Information

For

Effects of doping high-valence transition metal (V, Nb and Zr) ions on the structure and electrochemical performance of LIB cathode material $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$

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Table S1 The *U* values of TMs in NCM811

Metal	Ni	Co	Mn	V	Nb	Zr
U value (eV) [a]	6.5	6.0	5.0	3.0	3.0	5.0

[a] *U* values adopted from ref. [1, 2].

Table S2 The lattice parameters for NCMs based on DFT+D3 calculation and experiment, and the average calculated bond lengths of Li-O

Method	NCM	*a* (Å)	*c* (Å)	V (Å^3)	Li-O (Å)
Experiment [a]	Pristine	2.873	14.205	101.552	/
Calculation	Pristine	2.874	14.048	100.434	2.101
	V doped	2.873	14.059	100.486	2.100
	Nb doped	2.874	14.079	100.715	2.101
	Zr doped	2.874	14.090	100.920	2.102

[a] The experimental lattice parameter adopted from ref. [3]

Table S3 The Ionic radii of transition metal ions of NCMs from ref. [4]

Metal ion	Radius (Å)	Metal ion	Radius (Å)
Ni^{2+}	0.69	Mn^{4+}	0.53
Ni^{3+}	0.56	V^{5+}	0.54
Ni^{4+}	0.48	Nb^{5+}	0.74
Co^{3+}	0.55	Zr^{4+}	0.84

Table S4 The oxidation states and electronic configurations of TMs in NCMs

Metal atom	Oxidation state	Electronic configuration
Ni	+2	t_{2g}^6 (|↓↑|↓↑|↓↑|) e_g^2(|↑ |↑ |)
	+3	t_{2g}^6 (|↓↑|↓↑|↓↑|) e_g^1(|↑ | |)
	+4	t_{2g}^6(|↓↑|↓↑|↓↑|) e_g^0(| | |)
Co	+3	t_{2g}^6(|↓↑|↓↑|↓↑|) e_g^0(| | |)

	+4	$t_{2g}^5(\downarrow\uparrow\downarrow\uparrow\downarrow\ )\ e_g^0(\ \ )$
Mn	+4	$t_{2g}^3(\uparrow\ \uparrow\ \uparrow\ )\ e_g^0(\ \ )$
V	+5	$t_{2g}^0(\ \ \ )\ e_g^0(\ \ )$
Nb	+5	$t_{2g}^0(\ \ \ )\ e_g^0(\ \ )$
Zr	+4	$t_{2g}^0(\ \ \ )\ e_g^0(\ \ )$

Table S5 The magnetic moments range and amounts of different Ni ions of the pristine and V-, Nb- and Zr-doped NCMs

NCM	Li content	Ni^{2+}(μB)	Amount	Ni^{3+}(μB)	Amount	Ni^{4+}(μB)	Amount
pristine	1	1.63-1.55	6	1.16-0.94	42	/	0
	0.8	1.35	1	0.75-0.52	39	0.27-0.00	8
	0.6	/	0	0.69-0.33	30	0.22-0.01	18
	0.4	/	0	0.66-0.33	13	0.28-0.01	35
	0.2	/	0	0.36-0.31	2	0.22-0.00	46
	0	/	0	/	0	0.08-0.00	48
V doped	1	1.38-1.26	8	0.92-0.60	39	/	0
	0.8	1.32-1.21	3	0.98-0.45	37	0.25-0.03	7
	0.6	1.25	1	0.95-0.34	25	0.27-0.01	21
	0.4	/	0	0.72-0.30	15	0.28-0.00	32
	0.2	/	0	0.39	1	0.27-0.00	46
	0	/	0	/	0	0.10-0.00	47
Nb doped	1	1.43-1.19	9	0.82-0.45	38	/	0
	0.8	1.31-1.26	3	0.77-0.33	37	0.20-0.04	7
	0.6	1.34	1	0.80-0.36	29	0.29-0.03	17
	0.4	/	0	0.70-0.35	18	0.22-0.00	29
	0.2	/	0	0.61-0.37	4	0.15-0.00	43
	0	/	0	/	0	0.06-0.00	47
Zr doped	1	1.44-1.20	7	0.92-0.59	40	/	0
	0.8	1.27-1.25	2	0.87-0.33	38	0.15-0.01	7
	0.6	1.14	1	0.88-0.32	27	0.24-0.00	19
	0.4	/	0	0.70-0.38	15	0.28-0.00	32
	0.2	/	0	0.56-0.35	2	0.25-0.00	45
	0	/	0	/	0	0.05-0.00	47

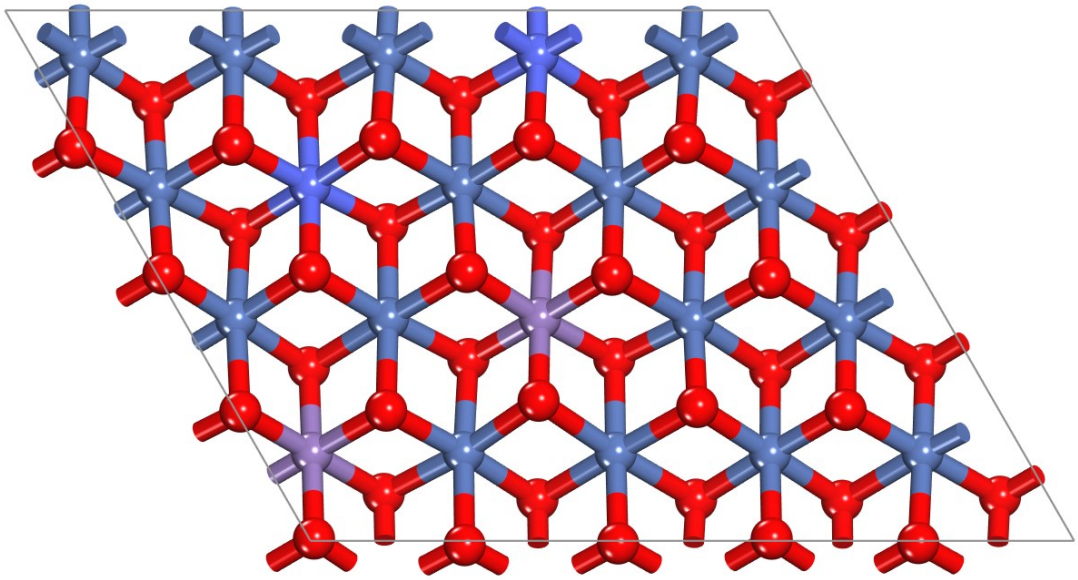

Fig. S1 The TM ordering of the model 1 from Ref. [5].

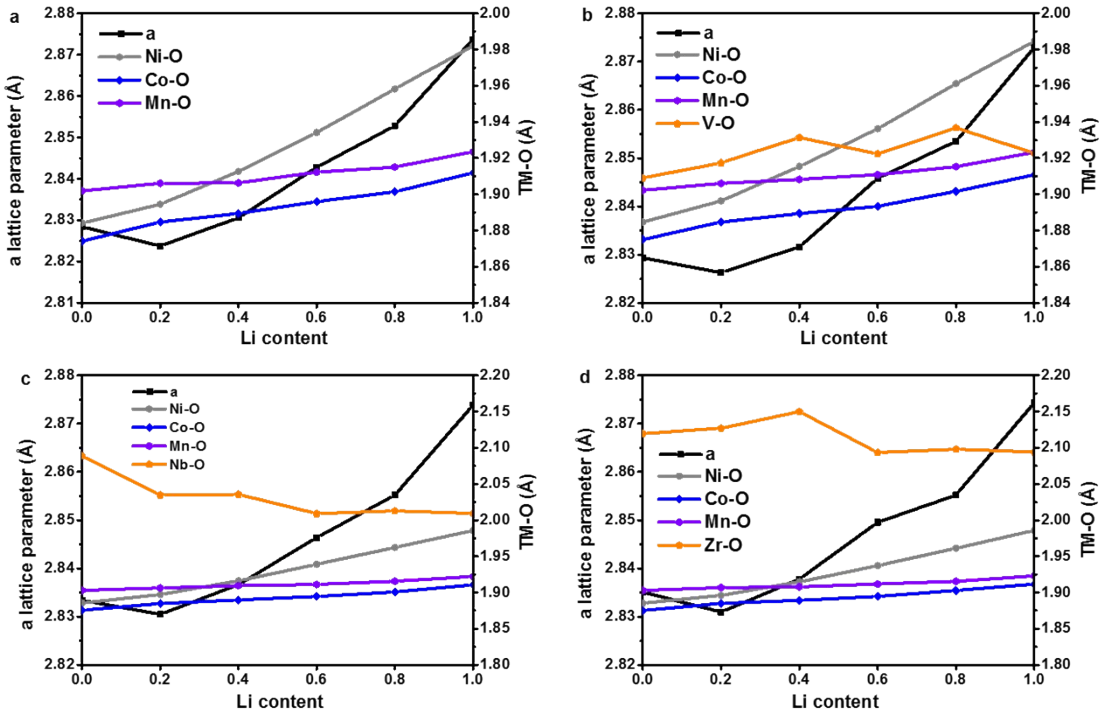

Fig. S2 (a-d) The *a* lattice parameters and TM-O bond lengths of the pristine and V-, Nb- and Zr-doped NCMs, respectively.

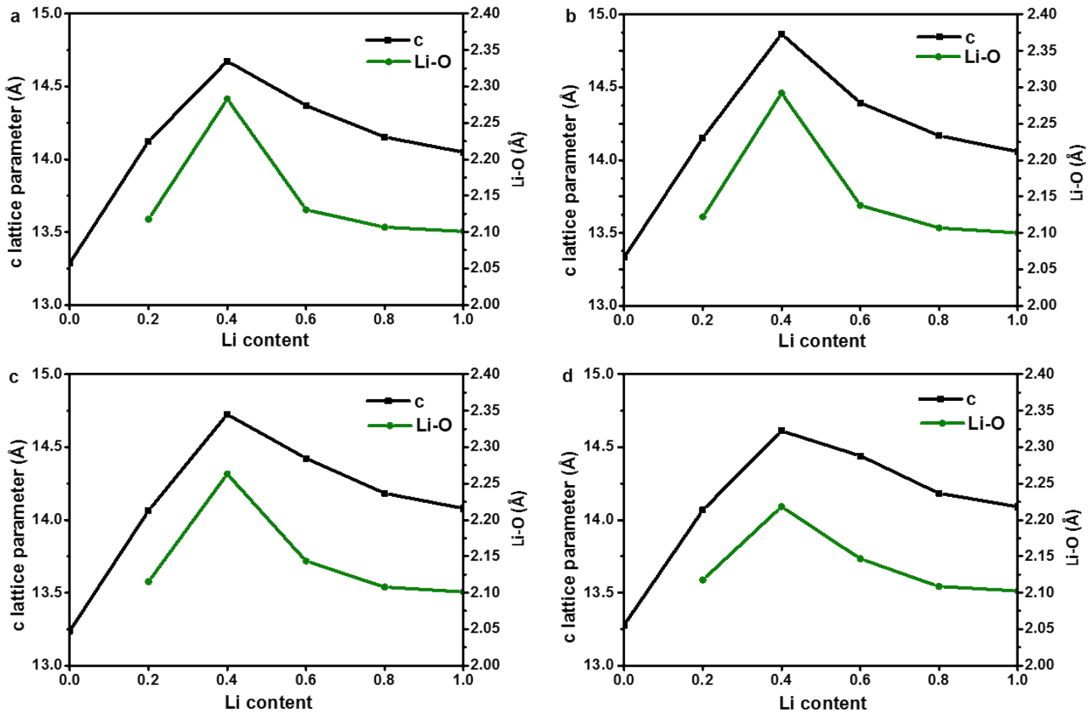

Fig. S3 (a-d) The *c* lattice parameters and Li-O bond lengths of the pristine and V-, Nb- and Zr-doped NCMs, respectively.

References

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