Suppressing Chromium Disproportion Reaction in O3-type Layered Cathode Material for High Capacity Sodium-ion Batteries

Ming-Hui Cao,[a] Yong Wang,[c] Zulipiya Shadike,[a] Ji-Li Yue,[a] Enyuan Hu,[d] Seong-Min Bak,[d] Yong-Ning Zhou*[b] and Xiao-Qing Yang*[d] and Zheng-Wen Fu*[a]

[a]*Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Department of Chemistry & Laser Chemistry Institute, Fudan University, Shanghai, 200433, P.R. China *E-mail: zwfu@fudan.edu.cn*
[b]*Department of Materials Science, Fudan University, Shanghai, 200433, P.R. China *E-mail: zhouyongning@gmail.com*
[c]*Shanghai Institute of Space Power-Sources, Shanghai, 200245, P.R. China.*
[d]*Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, USA *E-mail: xyang@bnl.gov*

Electronic Supplementary Information (ESI)

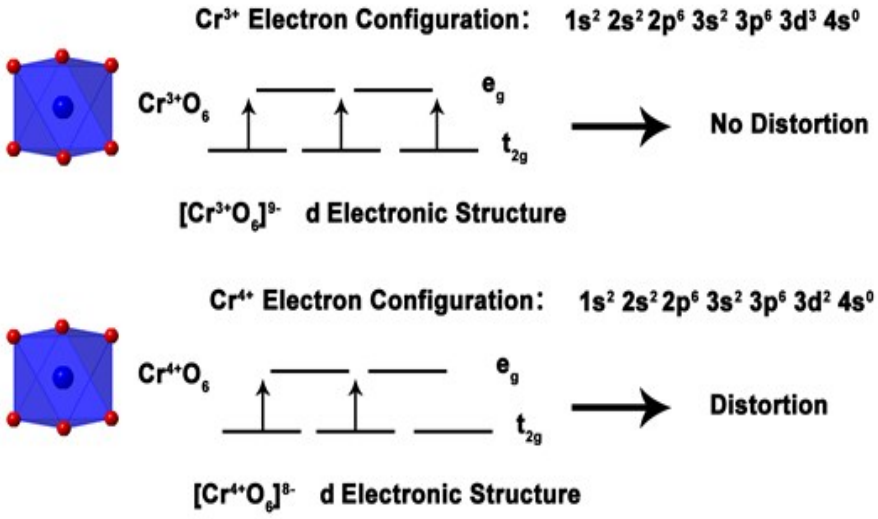

Figure S1. Electron configuration and distortion schematics of Cr^{3+} and Cr^{4+} in CrO_6 octahedral coordination. [S1]

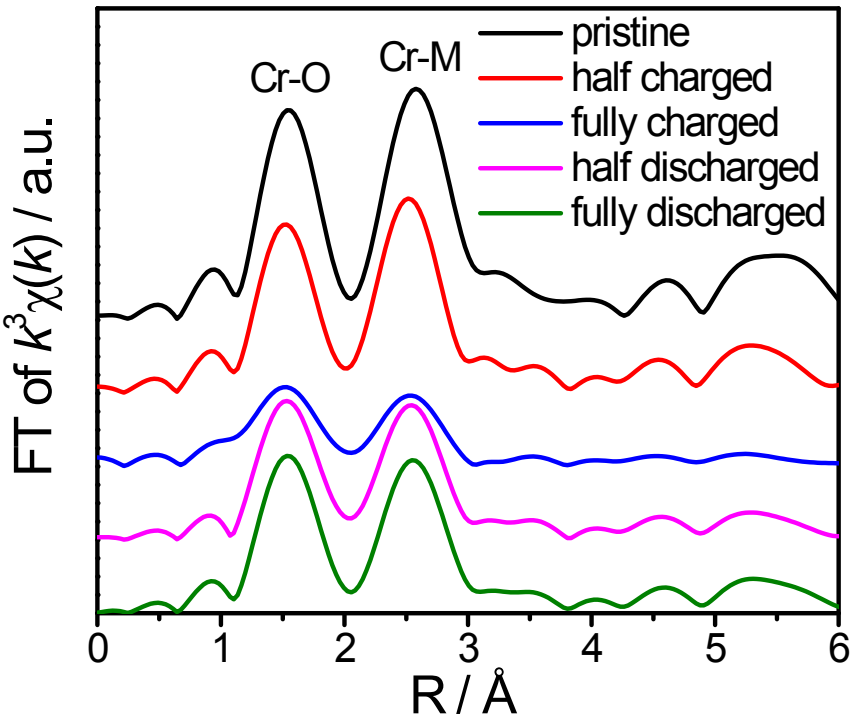

Figure S2. Fourier transform X-ray absorption near-edge structure (XANES) spectra at Cr K-edges of NCFM electrodes during the initial cycle.

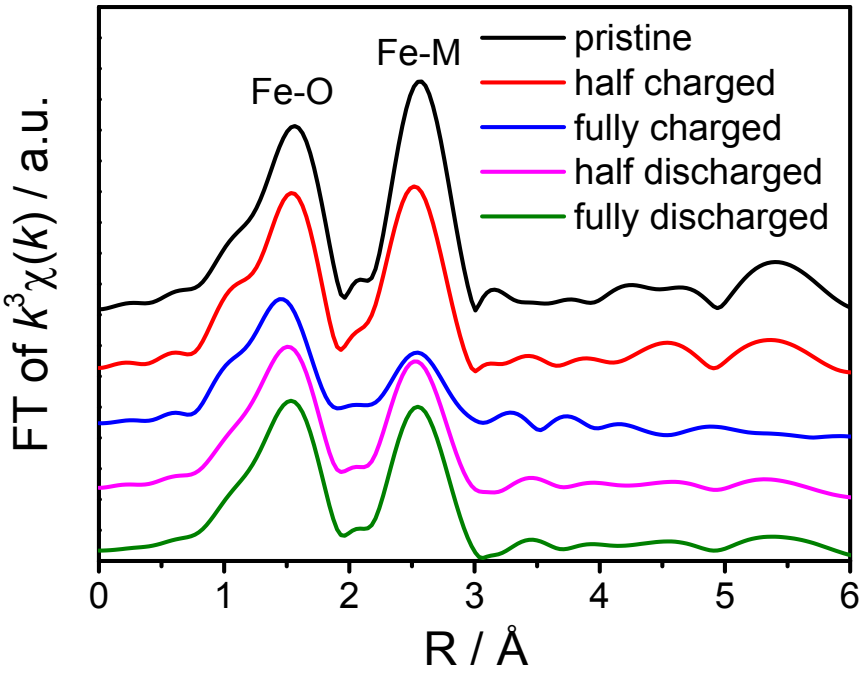

Figure S3. Fourier transform X-ray absorption near-edge structure (XANES) spectra at Fe K-edges of NCFM electrodes during the initial cycle.

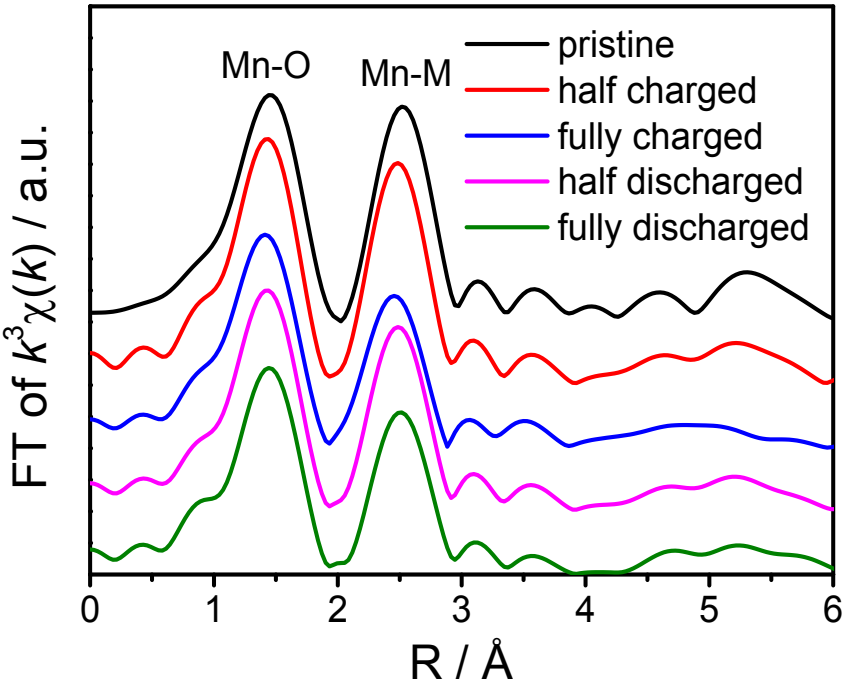

Figure S4. Fourier transform X-ray absorption near-edge structure (XANES) spectra at Mn K-edges of NCFM electrodes during the initial cycle.

Table S1. Structural parameters and atomic positions of as-prepared O3-type $NaCr_{1/3}Fe_{1/3}Mn_{1/3}O_2$ deducted from Rietveld Refinement.

Atom	***Wyckoff***	***Occupancy***	***x/a***	***y/b***	***z/c***
Na	3b	1	0	0	0.0
Cr	3a	1/3	0	0	0.5
Fe	3a	1/3	0	0	0.5
Mn	3a	1/3	0	0	0.5
O	6c	1	0	0	0.230065
R-3m:	***a*** **= *b* = 2.9639(4) Å**			***c*** **= 16.1693(5) Å**	
	R_p **= 1.91%**		R_{wp} **= 2.9%**	$GOF(\chi^2)$ **= 1.102**	

Table S2. Comparison of the electrochemical properties of O3-layered cathode materials for sodium ion batteries.

	Electrode materials	**Voltage Range (V)**	**Initial Capacity (mAh/g)**	**Reference**
unary	$NaNiO_2$	1.25-3.75	125(0.1C)	S2
	$NaFeO_2$	1.5-3.6	82(0.1C)	S3
	$NaTiO_2$	0.6-1.6	152(0.1C)	S4
	$NaCoO_2$	2.0-3.8	116(0.1C)	S5
	α-$NaMnO_2$	2.0-3.8	187(0.1C)	S6
	β-$NaMnO_2$	2.0-4.2	No Info.	S7
	$NaCrO_2$	2.0-3.6	112(0.1C)	S8
	$NaCrO_2$/C	2.0-3.6	121(0.1C)	S8
Binary	$NaNi_{0.5}Mn_{0.5}O_2$	2.2-3.8	125(0.033C）	S9
	$NaFe_{0.5}Co_{0.5}O_2$	2.5-4.0	160(0.1C)	S10
	$NaNi_{0.5}Ti_{0.5}O_2$	2.0-4.0	102(0.1C)	S11
	$NaMn_{0.5}Fe_{0.5}O_2$	1.5-4.2	135(0.01C)	S12
	$NaFe_{0.5}Mn_{0.5}O_2$	1.5-4.2	125(0.05C)	S13
Ternary	$NaNi_{0.25}Fe_{0.5}Mn_{0.25}O_2$	2.1-3.9	140(0.1C)	S14
	$NaNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	2.0-3.75	120(0.1C)	S15
	$NaNi_{0.33}Fe_{0.33}Mn_{0.33}O_2$	2.0-4.0	125(0.1C)	S16
	$NaNi_{0.4}$ $Fe_{0.2}Mn_{0.4}O_2$	2.0-4.0	131(0.1C)	S17
	$NaNi_{0.33}Co_{0.33}Fe_{0.33}O_2$	2.0-4.2	165(0.1C)	S18
	$NaFe_{0.2}Ni_{0.4}Ti_{0.4}O_2$	2.6-3.75	120(0.1C)	S19
	$NaFe_{0.2}(Ni_{1/2}Ti_{1/2})_{0.6}O_2$	2.0-3.8	130(0.05C)	S20
	$NaFe_{0.33}Cr_{0.33}Mn_{0.33}O_2$	**1.5-4.2**	**186(0.05C)**	**This work**
Quaternary	$NaNi_{0.25}Fe_{0.25}Co_{0.25}Mn_{0.25}O_2$	1.9-4.3	183(0.1C)	S21
	$NaNi_{0.4}Fe_{0.2}Mn_{0.25}Ti_{0.2}O_2$	2.0-4.2	145(0.1C)	S22
Quinary	$NaNi_{0.25}Fe_{0.25}Co_{0.25}Mn_{0.125}Ti_{0.125}O_2$	2.0-4.1	128(0.1C)	S23

Tables S3. Structure parameters from nonlinear least-squares fits to the first two peaks of the Fourier transform at the Cr K-edge EXAFS of NCFM electrode at different states.

Samples	Path	*r*/Å	σ^2 /10^{-3}Å^2	*ΔE*/eV	*R*
pristine	Cr-O	1.99(1)±0.013	0.10 ± 2.10	0.95 ± 1.78	0.011
	Cr-TM	2.95(9)±0.014	1.10 ± 1.77		
half charged	Cr-O	1.95(6) ± 0.017	2.20 ± 2.84	-1.36 ± 2.32	0.018
	Cr-TM	2.92(7) ± 0.018	2.84 ± 2.33		
fully charged	Cr-O	1.97(3) ± 0.029	3.13 ± 1.86	-2.67 ± 2.18	0.005
	Cr-TM	2.93(3) ± 0.037	4.26 ± 1.47		
half discharged	Cr-O	1.97(8) ± 0.016	0.14 ± 2.66	-1.19 ± 2.41	0.019
	Cr-TM	2.94(6) ± 0.019	2.33 ± 2.44		
fully discharged	Cr-O	1.98(3) ± 0.016	0.37 ± 2.41	0.55 ± 2.30	0.002
	Cr-TM	2.95(9) ± 0.018	2.64 ± 2.36		

r: bond length; σ^2: Debye-Waller factor (disorder); *ΔE*:inner shell potential shift;*R*: R-factor.

Table S4. Structure parameters from nonlinear least-squares fits to the first two peaks of the Fourier transform at the Fe K-edge EXAFS of NCFM electrode at different states.

Samples	Path	*r*/Å	σ^2 /10^{-3}Å^2	*ΔE*/eV	*R*
pristine	Mn-O	1.90(8)±0.008	2.55±1.25	-4.38±1.20	0.006
	Mn-TM	2.94(9)±0.009	3.90 ±1.05		
half charged	Mn-O	1.90(2) ± 0.010	2.78±1.59	-4.74±1.51	0.010
	Mn-TM	2.93(2) ± 0.011	4.10±1.34		
fully charged	Mn-O	1.89(4) ± 0.014	7.79 ± 1.84	-5.09 ± 1.80	0.013
	Mn-TM	2.91(9) ± 0.011	3.75 ± 2.55		
half discharged	Mn-O	1.90(2) ± 0.009	2.88 ± 1.48	-4.82 ± 1.44	0.009
	Mn-TM	2.93(8) ± 0.011	5.07 ± 1.32		
fully discharged	Mn-O	1.91(2) ± 0.009	2.25 ± 1.53	-3.57 ± 1.52	0.010
	Mn-TM	2.95(7) ± 0.012	4.92 ± 1.41		

r: bond length; σ^2: Debye-Waller factor (disorder); *ΔE*:inner shell potential shift;*R*: R-factor.

Table S5. Structure parameters from nonlinear least-squares fits to the first two peaks of the Fourier transform at the Mn K-edge EXAFS of NCFM electrode at different states.

Samples	Path	*r*/Å	σ^2 /10^{-3}Å^2	*ΔE*/eV	*R*
pristine	Fe-O	2.03(1)±0.006	4.72±0.90	-0.83±0.61	0.002
	Fe-TM	2.98(2)±0.005	4.21 ±0.65		
half charged	Fe-O	2.01(4) ± 0.005	6.58±0.85	-1.23±0.55	0.002
	Fe-TM	2.96(8) ± 0.005	6.62±0.64		
fully charged	Fe-O	1.96(6) ± 0.014	8.43±2.40	-1.40±1.73	0.013
	Fe-TM	2.98(0) ± 0.020	14.01±2.55		
half discharged	Fe-O	2.00(0) ± 0.007	7.20±1.19	-1.34±0.79	0.003
	Fe-TM	2.98(4) ± 0.008	8.54 ±0.97		
fully discharged	Fe-O	2.01(5) ± 0.006	6.32±1.09	-0.95±0.73	0.003
	Fe-TM	2.99(5) ± 0.007	7.08±0.86		

r: bond length; σ^2: Debye-Waller factor (disorder); *ΔE*:inner shell potential shift;*R*: R-factor.

Tables S6. Electronegativity parameters of ions in NCFM. [S24]

ions	Z^*	r/Å	X_i
Fe^{3+}	4.95	1.24	1.9
Cr^{4+}	5.5	1.85	3.917
Mn^{4+}	5.65	1.79	4.09
Z^*:effective nuclear number	r:atomic radium;	X_i:electronegativity	

$$x_{Fe}{}^{3+} < x_{Cr}{}^{4+} < x_{Mn}{}^{4+}$$

Electronic Configuration of Ions: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^y 4s^0$

Correlation Formula:

$$Z^* = Z - [0 \times 0.35 + (8+y) \times 0.85 + 10 \times 1.0]$$

$$X_i = \frac{3.59 \times 103 \times Z^*(\text{pm})2}{r2} + 0.744$$

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