Electronic Supplementary Information (ESI)

Path ^a	N _{degen} ^b	$\mathbf{R}_{theory}{}^{c}(\mathrm{\AA})$	$lpha_{fit}$	$\Delta \mathbf{R}^{d}(\mathbf{A})$	$\mathbf{R}_{fit}^{e}(\mathbf{A})$	σ_{fit}^2 (Å ²)	
	2	1.904		-0.006(6)	1.898(6)		
Mn- O_{n-n}	2	1.912	-0.003(3)	-0.006(6)	1.906(6)	0.0023 (7	
	2	1.919		-0.006(6)	1.913(6)		
Mp TM	2	2.845	0.000(2)	0.000(6)	2.845(6)	0.0010.(6	
10111-1101	1	2.851	0.000(2)	0.000(6)	2.851(6)	0.0010(6)	
	2	3.513		-0.074 (30)	3.439 (30)		
Mn-O	2	3.515	-0.021 (8)	-0.074 (30)	3.441 (30)	0.005(3)	
	2	3.516		-0.074 (30)	3.442 (30)		
	2	3.686		-0.077 (30)	3.609 (30)		
	2	4.388		0.105 (28)	4.493 (28)		
	2	4.390		0.105 (28)	4.495 (28)		
	2	4.395		0.105 (28)	4.500(28)		
	2	4.578		0.110(28)	4.688 (28)		
	2	4.579		0.110(28)	4.689 (28)		
Mn-O	2	4.587	0.024(6)	0.110(28)	4.697 (28)	0.002(2)	
iiiii O	2	4.594	0.021(0)	0.110(28)	4.704 (28)	0.002(2	
	2	4.599		0.110(28)	4.709 (28)		
	2	4.638		0.111 (28)	4.749 (28)		
	2	4.672		0.112 (28)	4.784 (28)		
	2	4.693		0.113 (28)	4.806 (28)		
	2	4.721		0.113 (28)	4.834 (28)		
	4	4.929		0.020(15)	4.949(15)		
Mn-TM	2	4.937	0.004(3)	0.020(15)	4.957 (15)	0.002(1	
	2	5.012	0.001(0)	0.020(15)	5.032(15)	0.002(1)	
	2	5.030		0.020(15)	5.050(15)		

Table S1 EXAFS fit parameters at the Mn K-edge of 0.5Li2MnO3 · 0.5LiCoO2 in the pristine state. The values in parentheses indicate uncertainties to the least significant digit(s). The parameters without uncertainties were constrained in the fit.

^a Scattering paths from the theoretical model

^b N_{degen} = Degeneracy of scattering paths from the theoretical model ^c R_{theory} = Interatomic distances from the theoretical model

$$^{d}\Delta \mathbf{R} = \alpha_{fit} \times \mathbf{R}_{theor}$$

 $e R_{fit} = R_{theory} + \Delta R$

$S_0^2 = 0.68$ $\Delta E_0 = 5.1 (9)$								
Path	N _{degen}	$R_{theory}(\text{\AA})$	$lpha_{fit}$	$\Delta R(\text{\AA})$	$\mathbf{R}_{fit}\left(\mathrm{\AA}\right)$	$\sigma_{fit}^2({\rm \AA}^2)$		
Mn- O_{n-n}	6.7(6)	1.921	-0.014(2)	-0.027(4)	1.894(4)	0.0066(9)		
Mn-TM	6	2.816	0.016(2)	0.045(6)	2.861 (6)	0.0069(3)		
Mn-O	6 2	3.409 3.661	0.016(7)	0.055 (26) 0.059 (26)	3.419 (26) 3.672 (26)	0.009(3)		
Mn-O	12 12	4.422 4.619	-0.020(7)	-0.088 (32) -0.092 (32)	4.334 (32) 4.527 (32)	0.009(5)		
Mn-TM	6 6	4.878 4.959	0.003 (4)	0.015 (20) 0.015 (20)	4.893 (20) 4.974 (20)	0.012(2)		

 $\textbf{Table S2} \text{ EXAFS fit parameters at the Mn K-edge of } 0.5 \text{Li}_2 \text{MnO}_3 \cdot 0.5 \text{LiCoO}_2 \text{ when charged to } 4.8 \text{ V}.$

 $\textbf{Table S3} \text{ EXAFS fit parameters at the Mn K-edge of } 0.5 \text{Li}_2 \text{MnO}_3 \cdot 0.5 \text{LiCoO}_2 \text{ when discharged to } 2.5 \text{ V.}$

$S_0^2 = 0.68$							
$\Delta E_0 = 3.0$	(1.4)						
Path	N _{degen}	$R_{theory}(\text{\AA})$	α_{fit}	$\Delta R(\text{\AA})$	$\mathbf{R}_{fit}\left(\mathrm{\AA}\right)$	$\sigma_{fit}^2({ m \AA}^2)$	
Mn- O_{n-n}	4.9(6)	1.904	-0.003(3)	-0.006(6)	1.898(6)	0.003(1)	
Mn-TM	2	2.845	0.001(2)	0.003(6)	2.848(6)	0.0019(4)	
	1	2.851	0.001(2)	0.003(6)	2.854(6)	0.0019(4)	
	2	3.513		-0.127 (48)	3.386(48)		
Mn O	2	3.515	-0.036(13)	-0.127 (48)	3.388 (48)	0.011(7)	
Mn-O	2	3.516		-0.127 (48)	3.389 (48)	0.011(7)	
	2	3.686		-0.133 (48)	3.553 (48)		
	2	4.388		0.053 (24)	4.441 (24)		
	2	4.390		0.053 (24)	4.443 (24)		
	2	4.395		0.053 (24)	4.448 (24)		
	2	4.578		0.055 (24)	4.633 (24)		
	2	4.579		0.055 (24)	4.634 (24)		
	2	4.587	0.012(5)	0.055 (24)	4.642 (24)	0.002(2)	
Mn-O	2	4.594	0.012(5)	0.055 (24)	4.649 (24)	0.003(2)	
	2	4.599		0.055 (24)	4.654 (24)		
	2	4.638		0.056(24)	4.694 (24)		
	2	4.672		0.056(24)	4.728 (24)		
	2	4.693		0.056(24)	4.749 (24)		
	2	4.721		0.057 (24)	4.778 (24)		
	4	4.929		-0.005 (20)	4.924 (20)		
$M_{\rm m} = TM$	2	4.937	0.001(4)	-0.005 (20)	4.932 (20)	0.007(2)	
IVIN- I IVI	2	5.012	-0.001 (4)	-0.005 (20)	5.007 (20)	0.007(2)	
	2	5.030		-0.005 (20)	5.025 (20)		

$S_0^2 = 0.82(5)$ $\Delta E_0 = 2.5(7)$								
Path	N _{degen}	$R_{theory}(\text{\AA})$	$lpha_{fit}$	$\Delta R(Å)$	$\mathbf{R}_{fit}\left(\mathbf{\mathring{A}}\right)$	$\sigma_{fit}^2({\rm \AA}^2)$		
Co-O	6	1.921	-0.001 (2)	-0.002(4)	1.919(4)	0.0037(6)		
Co-TM	6	2.816	0.004(1)	0.011(3)	2.827(3)	0.0040(4)		
Co-O	6 2	3.409 3.661	-0.002(4)	-0.007 (15) -0.007 (15)	3.402 (15) 3.654 (15)	0.005(2)		
Co-O	12 12	4.422 4.619	0.000(6)	0.000 (28) 0.000 (28)	4.422 (28) 4.619 (28)	0.005(3)		
Co-TM	6 6	4.878 4.959	0.005(3)	0.024 (15) 0.025 (15)	4.902 (15) 4.984 (15)	0.008(2)		

Table S4 EXAFS fit parameters at the Co K-edge of $0.5Li_2MnO_3 \cdot 0.5LiCoO_2$ in the pristine state.

Table S5 EXAFS fit parameters at the Co K-edge of $0.5Li_2MnO_3 \cdot 0.5LiCoO_2$ when charged to 4.8 V.

$S_0^2 = 0.78 (6)$ $\Delta E_0 = 1.5 (8)$								
Path	N _{degen}	$R_{theory}(\text{\AA})$	α_{fit}	$\Delta R(\text{\AA})$	$R_{fit}(Å)$	σ_{fit}^2 (Å ²)		
Co-O	6	1.921	-0.013(2)	-0.025(4)	1.896(4)	0.0048(7)		
Co-TM	6	2.816	0.007(2)	0.020(6)	2.836(6)	0.0063(5)		
Co-O	6 2	3.409 3.661	-0.008(5)	-0.027 (18) -0.029 (18)	3.382 (18) 3.632 (18)	0.006(2)		
Co-O	12 12	4.422 4.619	-0.002(8)	-0.009 (37) -0.009 (37)	4.413 (37) 4.610 (37)	0.007(4)		
Co-TM	6 6	4.878 4.959	0.002(4)	0.010 (20) 0.010 (20)	4.888 (20) 4.969 (20)	0.011 (2)		

$S_0^2 = 0.78 (4)$ $\Delta E_0 = 1.7 (6)$								
Path	N _{degen}	$R_{theory}(\text{\AA})$	α_{fit}	$\Delta R(\text{\AA})$	$\mathbf{R}_{fit}\left(\mathbf{\mathring{A}}\right)$	$\sigma_{fit}^2({\rm \AA}^2)$		
Co-O	6	1.921	-0.003(2)	-0.006(4)	1.915(4)	0.0042(5)		
Co-TM	6	2.816	0.006(1)	0.017(3)	2.833 (3)	0.0050(4)		
Co-O	6 2	3.409 3.661	-0.001 (4)	-0.003 (15) -0.003 (15)	3.406 (15) 3.657 (15)	0.005(1)		
Co-O	12 12	4.422 4.619	0.002(6)	0.009 (28) 0.009 (28)	4.431 (28) 4.628 (28)	0.006(3)		
Co-TM	6 6	4.878 4.959	0.009(3)	0.043 (15) 0.045 (15)	4.921 (15) 5.004 (15)	0.010(2)		

Table S6 EXAFS fit parameters at the Co K-edge of $0.5Li_2MnO_3 \cdot 0.5LiCoO_2$ when discharged to 2.5 V.

Table S7 Statistical EXAFS fit parameters at the Mn and Co K-edges of $0.5Li_2MnO_3 \cdot 0.5LiCoO_2$ in the pristine, charged and discharged states.

K-edge	State of cathode	$\Delta k ({ m \AA}^{-1})$	ΔR (Å)	N _{idp}	N _{vary}	v	χ^2	χ^2_v	R
	Pristine	3.8 - 12.5	1.0 - 5.1	23	12	11	237	22	0.016
Mn	4.8 V	3.8 - 11.7	1.1 - 5.0	19	12	7	68	10	0.005
	2.5 V	3.8 - 12.3	1.2 - 5.0	20	12	8	83	10	0.014
	Pristine	3.8 - 12.4	1.2 - 4.9	20	12	8	11	2	0.005
Co	4.8V	3.7 - 12.2	1.2 - 4.9	20	12	8	42	5	0.007
	2.5V	3.7 - 12.3	1.2 - 4.9	20	12	8	43	6	0.004



Fig. S1 EXAFS fits to the data of (a) CoO and (b) LiCoO₂ reference compounds.

Table S8 EXAFS fit parameters for the 1st shell of O atoms around Co absorbers in CoO and LiCoO₂ reference compounds.

Sample	Degeneracy of O atoms	R _{theory} (Å)	ΔR (Å)	\mathbf{R}_{fit} (Å)	σ_{fit}^2 (Å ²)
CoO	6	2.133	-0.013 (11)	2.120(11)	0.0085 (1)
LiCoO ₂	6	1.921	-0.006 (4)	1.915(4)	0.0039 (6)