

# SUPPORTING INFORMATION

## Structural Evolution of Layered Manganese Oxysulfides during Reversible Electrochemical Lithium Insertion and Copper Extrusion

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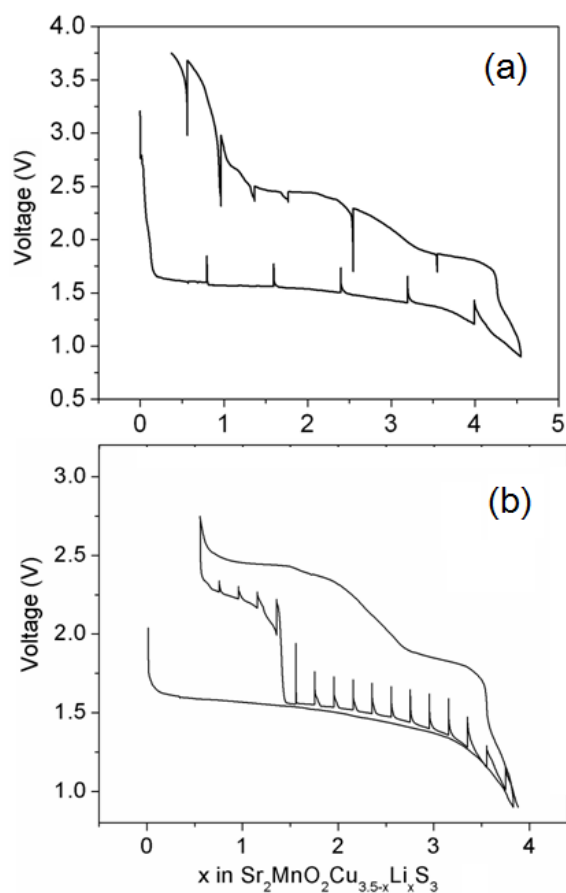
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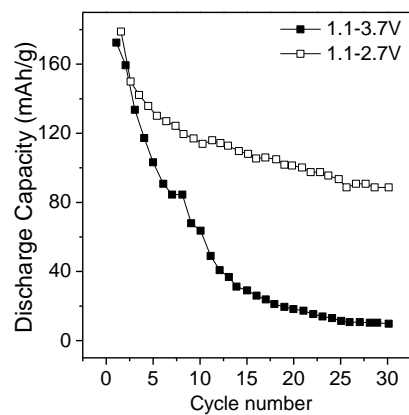
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**Table S1. Summary of the sample descriptions during each process.**

	Sample label & name	Descriptions
The 1 <sup>st</sup> discharge	a: Li1.0	Partially lithiated sample obtained following insertion of 1.0 mol of Li per formula unit.
	b: Li2.0	Partially lithiated sample obtained following insertion of 2.0 mol of Li per formula unit.
	c: Li3.0	Partially lithiated sample obtained following insertion of 3.0 mol of Li per formula unit.
	d: Li4.0	Sample discharged to 1.1 V. The lithium content for this fully lithiated sample should be around 4.0 mol but may vary slightly from different batteries. It is denoted as “Li4.0” for consistency with other discharged samples during the 1 <sup>st</sup> discharge.
The 1 <sup>st</sup> charge (after the 1 <sup>st</sup> discharge to 1.1 V)	e: Ch1.8V	Sample charged back to 1.8 V after being discharged to 1.1 V during the 1 <sup>st</sup> discharge. It is after the 1 <sup>st</sup> process at ~ 1.8 V of the charge.
	f: Ch2.5V	Sample charged back to 2.5 V after being discharged to 1.1 V during the 1 <sup>st</sup> discharge. It is the onset of the 2 <sup>nd</sup> process at ~ 2.5 V of the charge.
	g: Ch2.75V	Sample charged back to 2.75 V after being discharged to 1.1 V during the 1 <sup>st</sup> discharge. It is after the 2 <sup>nd</sup> process at ~ 2.5 V of the charge.
	h: Ch3.3V	Sample charged back to 3.3 V after being discharged to 1.1 V during the 1 <sup>st</sup> discharge. It is during the 3 <sup>rd</sup> process at ~ 3.3 V of the charge.
	i: Ch3.75V	Sample charged back to 3.75 V after being discharged to 1.1 V during the 1 <sup>st</sup> discharge. It is after the 3 <sup>rd</sup> process at ~ 3.3 V of the charge.
The 2 <sup>nd</sup> discharge (after the 1 <sup>st</sup> charge to 3.75 V)	j: (H)2ndDis_1.5V	Sample at an early stage of the 2 <sup>nd</sup> discharge after the 1 <sup>st</sup> charge to 3.75 V. The Li content in this sample is comparable with that in sample a: Li1.0 during the 1 <sup>st</sup> discharge.
	k: (H)2ndDis_1.1V	Sample at the end of the 2 <sup>nd</sup> discharge (discharged to 1.1 V) after the 1 <sup>st</sup> charge to 3.75 V. This sample resembles to the fully discharged sample d: Li4.0 during the 1 <sup>st</sup> discharge.
The 2 <sup>nd</sup> discharge (after the 1 <sup>st</sup> charge to 2.75 V)	l: (L)2ndDis_1.7V	Sample at a middle stage of the 2 <sup>nd</sup> discharge after the 1 <sup>st</sup> charge to 2.75 V. It is after the 1 <sup>st</sup> process at ~2.2 V during the 2 <sup>nd</sup> discharge.
	m: (L)2ndDis_1.1V	Sample at the end of the 2 <sup>nd</sup> discharge (discharged to 1.1 V) after the 1 <sup>st</sup> charge to 2.75 V.



**Figure S1.** Open circuit voltage curve of MnCu(II)|Li batteries during (a) the 1<sup>st</sup> cycle, and (b) the 2<sup>nd</sup> discharge after being charged to 2.75 V, obtained by the galvanostatic intermittent titration technique (GITT). The batteries were both operated at a C/20 rate. For each step, the battery shown in (a) was (dis)charged for 4 h and then allowed to rest for 8 h, and the one shown in (b) was discharged for 1 h and then allowed to rest for 8 h.



**Figure S2.** Cycle performance of MnCu(II) using the 1.1 to 3.75 V and 1.1 to 2.7 V windows. The applied current rate is C/20.

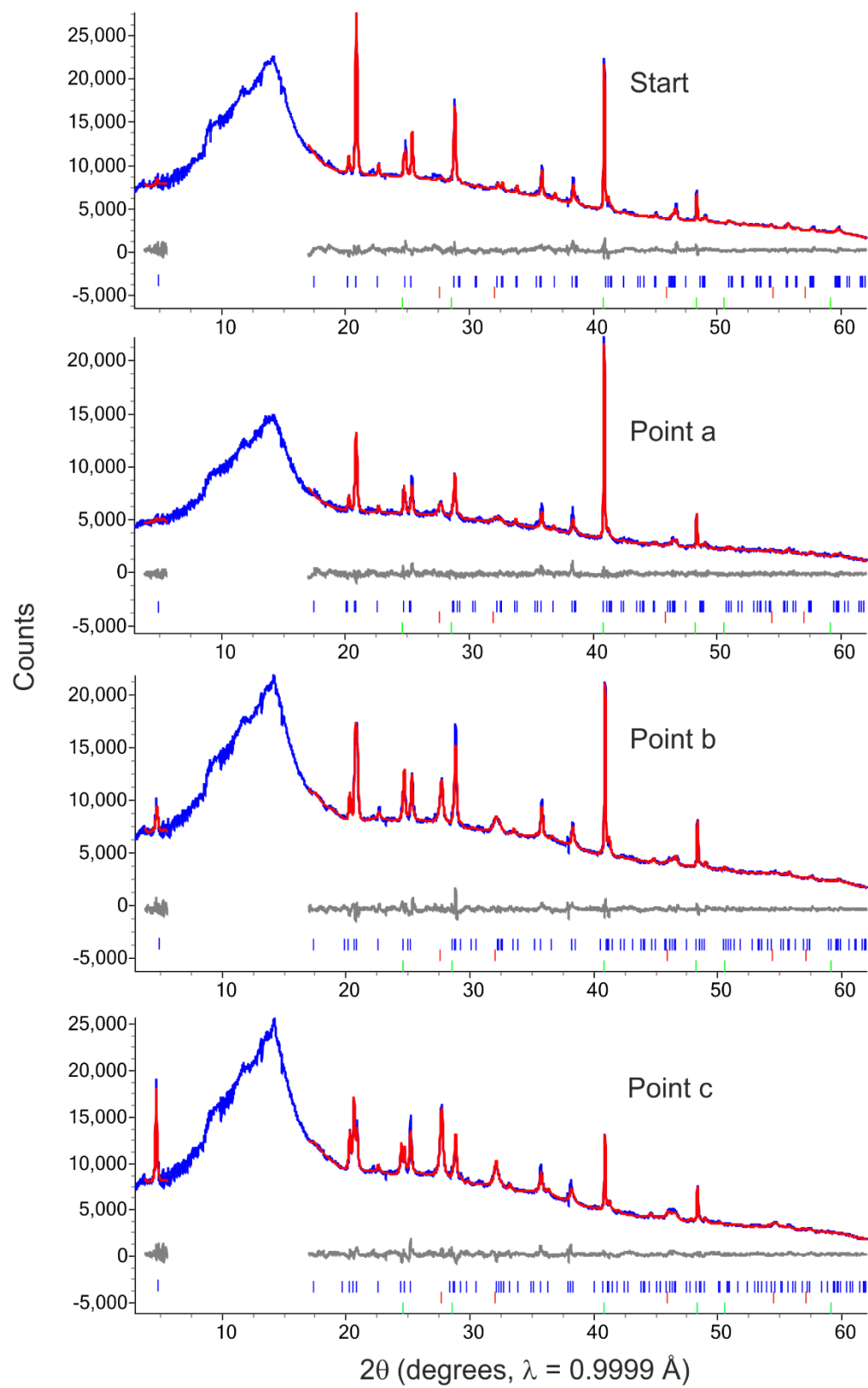
**Table S2. Refinement results from the *in situ* PXRD measurements for OS-I before and after the 1<sup>st</sup> discharge and for the OS-II phase after charging to 2.75 V.**

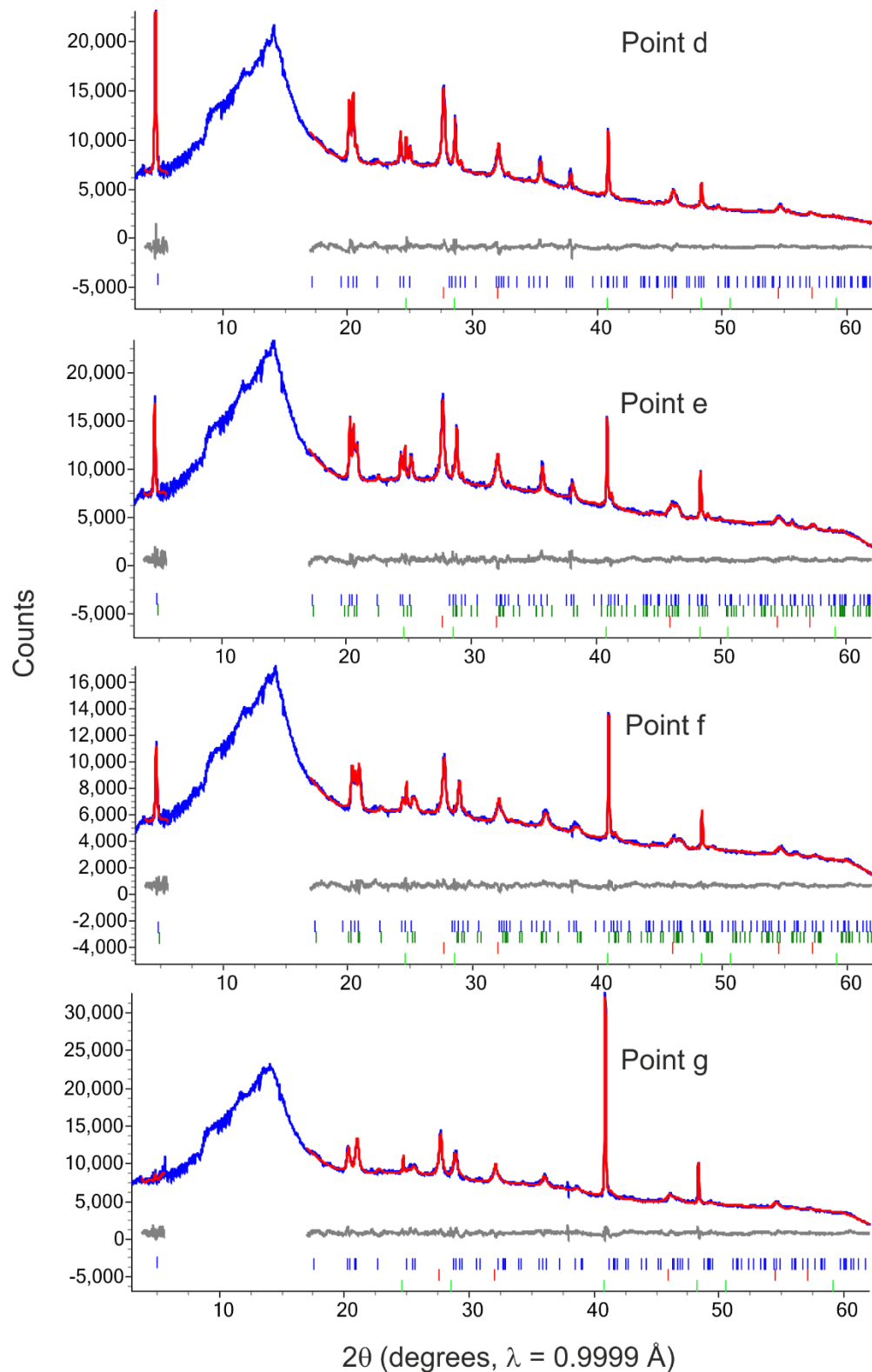
Compound	Sr <sub>2</sub> MnO <sub>2</sub> Cu <sub>3.5</sub> Se <sub>3</sub> OS-I pre-1 <sup>st</sup> discharge. (“Start” in Figure S3)	Sr <sub>2</sub> MnO <sub>2</sub> Li <sub>4</sub> S <sub>3</sub> OS-I end of 1 <sup>st</sup> discharge to 1.1 V vs Li <sup>+</sup> /Li (point d in Figure S3)	Sr <sub>2</sub> MnO <sub>2</sub> Cu <sub>4</sub> Li <sub>3</sub> Se <sub>3</sub> OS-II after 1 <sup>st</sup> charge to 2.75 V vs Li <sup>+</sup> /Li (point g in Figure S3)
Radiation	PXRD P4/mmm		
Space group			
<i>a</i> (Å)	4.0193(4)	4.0465(6)	4.0153(8)
<i>c</i> (Å)	11.402(2)	11.777(1)	11.260(6)
<i>c/a</i>	2.8368(6)	2.9104(6)	2.804(2)
Volume (Å <sup>3</sup> )	184.20(5)	192.84(6)	181.5(1)
<i>z</i> (Sr)	0.1511(7)	0.1430(9)	0.160(2)
<i>z</i> (S1)	0.261(1)	0.253(2)	0.279(3)
<i>z</i> (Cu/Li(1))	0.358(5)	0.383 <sup>a</sup>	0.31(1)
<i>x</i> (Cu(2))	0.391(4)	0.360 <sup>a</sup>	0.32(1)
<i>z</i> (Cu(2))	0.410(2)	0.40 <sup>a</sup>	0.41(1)
occ Cu/Li(1)	0.24(2) Cu	1.00(2) Li	0.18(2) Cu
occ Cu(2)	0.30(1) Cu	0.00(1) Cu	0.16(1) Cu
Cu / Li per Mn	3.4(1) Cu	4.0(1) Li	2.1(1) Cu <sup>b</sup>
wRp	0.032	0.031	0.030

Coordinates: Sr 2*h* (0.5, 0.5, *z*Sr); Mn 1*a* (0,0,0); O 2*f* (0, 0.5, 0); S(1) 2*g* (0, 0, *z*(S1)); S(2) 1*d* (0.5, 0.5, 0.5); Cu/Li(1) 4*i* (0, 0.5, *z*(Cu/Li(1))); Cu(2) 8*s* (*x*(Cu(2)), 0, *z*(Cu(2)))

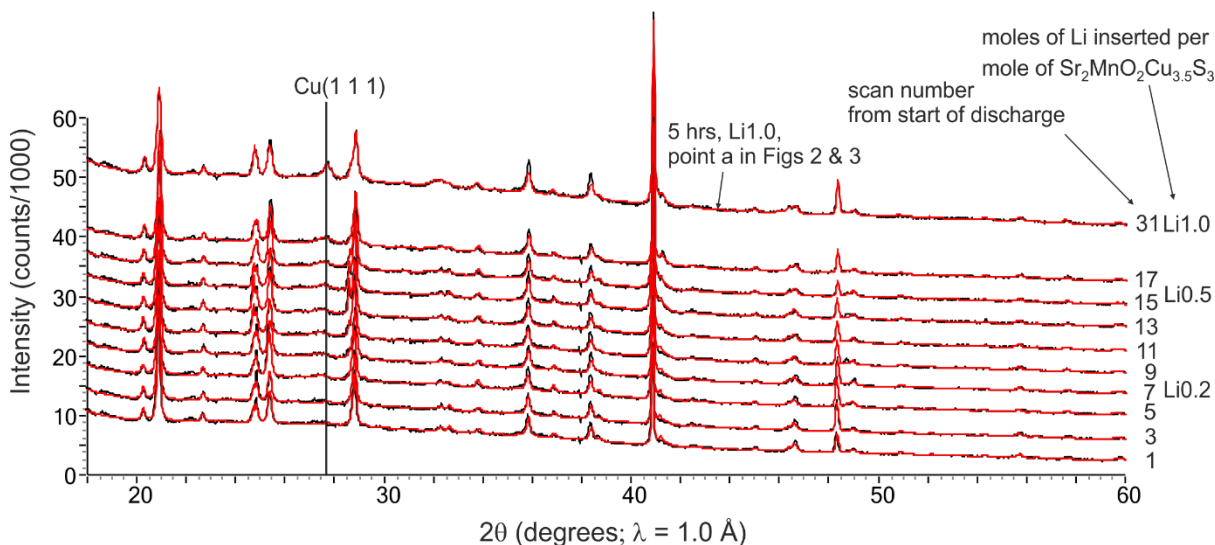
<sup>a</sup>not refined.

<sup>b</sup>scattering in the sulfide layer of the OS-II phase modelled as exclusively Cu, but the phase contains some residual Li and vacant sites in the sulfide layer.

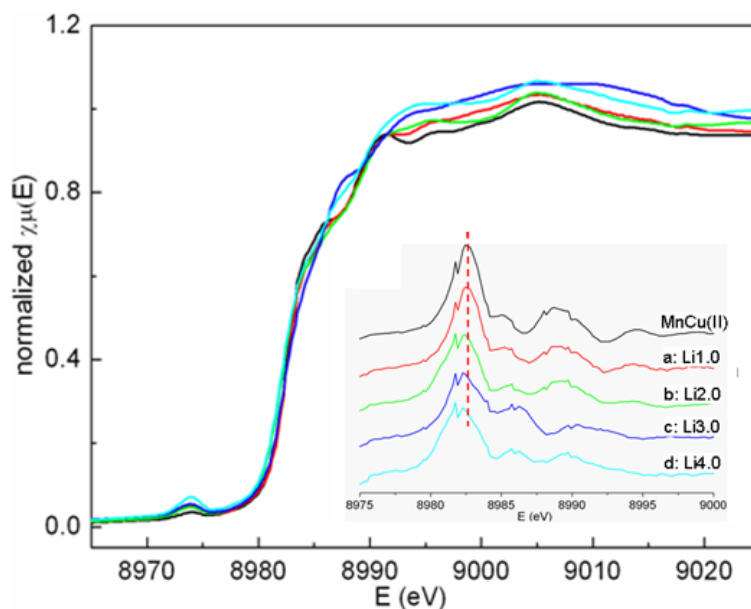




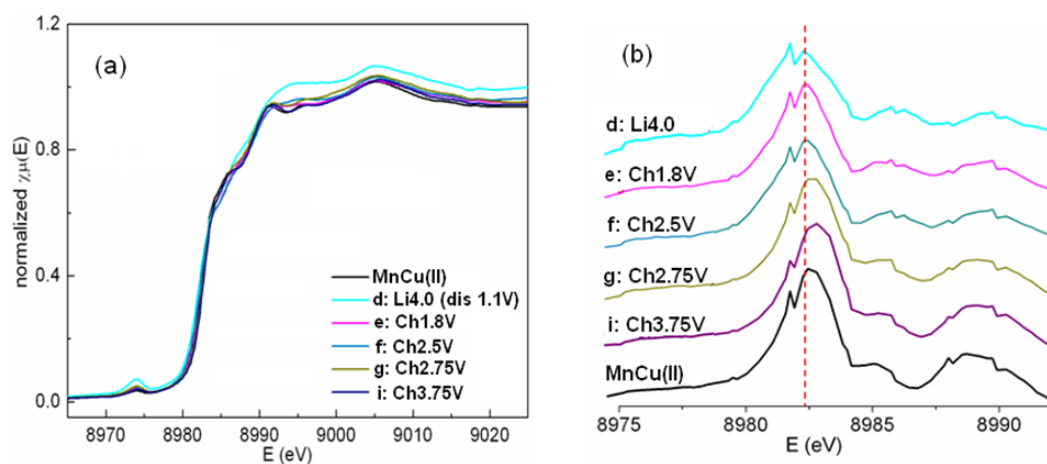
**Figure S3.** Rietveld refinements against *in situ* X-ray diffraction data. The data at start of the discharge and the points corresponding to the letters in the discharge/charge voltage profiles in the main paper (Figure 2b) are shown from top to bottom. The output parameters from the refinements are shown in Figure 4. The data (blue) calculated (red) and difference (grey) profiles are shown. Tick marks are from bottom: the Al parts of the sample holder (light green), the elemental Cu in the main phase (red) and the two oxysulfide phases (in the two-phase region the tick marks for the OS-I phase are above those of the OS-II phase).



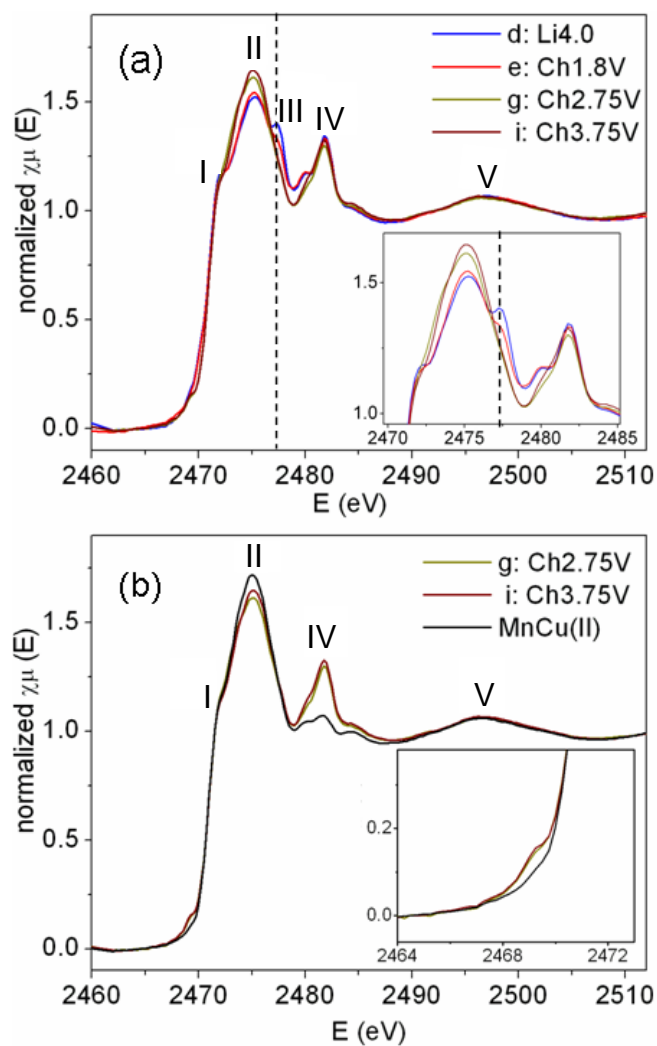
**Figure S4.** Rietveld refinements against the *in situ* PXRD data collected at the start of the first discharge showing the development of the Cu (111) reflection. The peak is clearly discernable, above the background level of the first scan, in the early scans which correspond to numbers of moles of inserted Li which are much smaller than the number of moles of tetrahedral site vacancies (0.5) per mole of  $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ . This shows that the initial stage does not just involve the insertion of 0.5 moles of Li to fill these vacancies, but also involves extrusion of Cu, at least from the point where 0.2 moles of Li have been delivered per mole of  $\text{Sr}_2\text{MnO}_2\text{Cu}_{3.5}\text{S}_3$ . Note that measurements were of poor signal-to-noise ratio between scans 17 and 31 due to experimental problems on the beamline.



**Figure S5.** Normalized Cu K-edge XANES spectra of pristine and lithiated  $\text{MnCu(II)}$  phases during the 1<sup>st</sup> discharge, and inset stacked plot of the corresponding first derivative curves. The dashed line in (b) indicates the energy position observed for the pristine sample  $\text{MnCu(II)}$ .

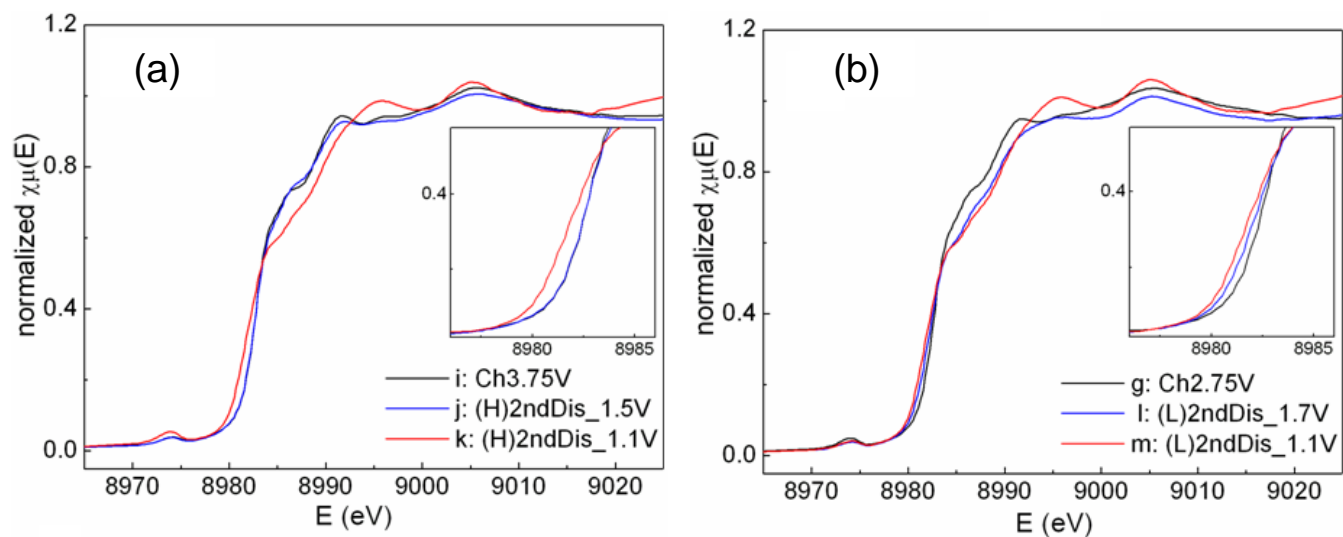


**Figure S6.** (a) Normalized Cu K-edge XANES spectra of MnCu(II) phases during the 1<sup>st</sup> charge, and (b) a stacked plot of the corresponding first derivative curves. The spectra of pristine MnCu(II) and the fully lithiated form (d: Li4.0) are also included for comparison. The dashed line in (b) indicates the energy position observed for the fully lithiated phase (d: Li4.0)

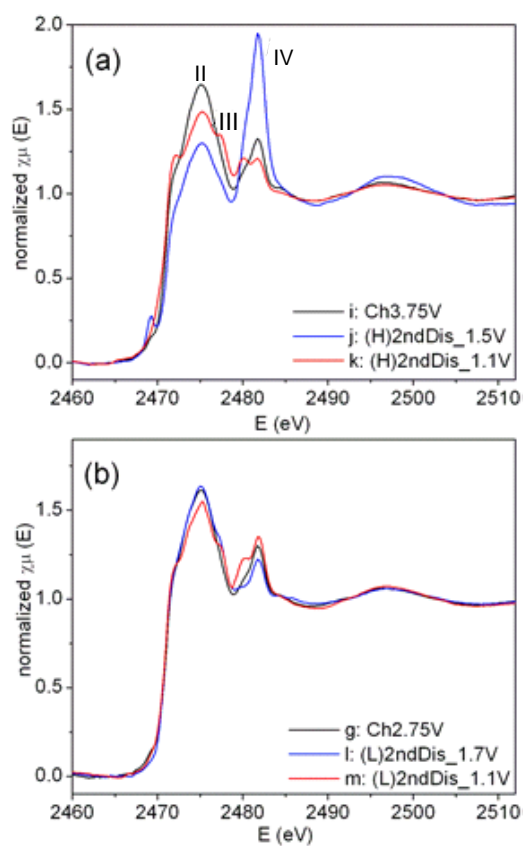


**Figure S7.** Normalized S K-edge XANES spectra of (a) MnCu(II) phases during the 1<sup>st</sup> charge and (b) the pristine MnCu(II) and two samples charged to 2.75 and 3.75 V, respectively. The insets show zoomed views of the spectra: (a) between 2470 to 2485 eV, and (b) between 2464 to 2473 eV. The absorption features are labeled with numbers I to V (see text).





**Figure S8.** Normalized Cu K-edge XANES spectra of MnCu(II) phases during the two 2<sup>nd</sup> discharge processes after the 1<sup>st</sup> charge. The cut off voltage of the 1<sup>st</sup> charge is (a) 3.75 V, and (b) 2.75 V. The insets in (a) and (b) are zooms of the absorption edge regions.



**Figure S9.** Normalized S K-edge XANES spectra of MnCu(II) phases during the two 2<sup>nd</sup> discharge processes after the 1<sup>st</sup> charge. The cut off voltage of the 1<sup>st</sup> charge is (a) 3.75 V, and (b) 2.75 V, respectively.