Supporting Information

Effect of Ru Substitution on the First Charge-Discharge Cycle of Lithium-rich Layered Oxides

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As the Ru content increases in the samples of this series, the compositions become closer to Li_2RuO_3. Li_2RuO_3 has been described as having either a *C2/c* or a *P12/m* structure. These structures are similar, but the main difference is that the *P12/m* structure contains Ru-Ru dimers. In order to see which form of Li_2RuO_3 the samples in this study more closely resembled, Rietveld refinement was carried out on the $x = 0.6$ sample, which has a composition of $Li_{1.2}Ru_{0.6}Ni_{0.2}O_2$. Li-rich layered oxides are most often modeled using an $R\bar{3}m$ phase and a monoclinic phase. For this sample, Rietveld refinement was attempted using the $R\bar{3}m$ phase and one of the *C2/c* or *P12/m* monoclinic structures.

The refined pattern using the $R\bar{3}m$ phase and the *P12/m* phase is included as Figure 4 in the manuscript as it provided the best model for the sample. The R_p value was 8.8%. On the other hand, Figure S1 displays the best fit refined pattern of the $x = 0.6$ sample using a model of the $R\bar{3}m$ and *C2/c* phases. The R_p value of this model was 25.4%. Both figures include a zoomed-in portion to show the fit of the superstructure peaks and some additional peaks. It is clear that the model including the *P12/m* phase produces a much better fit in this region and the pattern as a whole, as the *C2/c* containing model cannot accurately capture the 1st and 3rd superstructure peaks, as well as the peak at ~ 37°. The same parameters were refined, and the same refinement process was carried out on each sample, so it is clear that the *P12/m* structure more accurately describes this material. Significant effort was used in refining the model

utilizing the *C2/c* phase, but no better fit could be produced. In fact, the best fit actually did not include any of the $R\bar{3}m$ phase at all. The fact that the *P12/m* containing model best describes this sample also provides preliminary experimental evidence of Ru-Ru dimer formation, which may explain some of the electrochemical properties seen in this series of materials. Table S1 lists the refined parameters from both models.

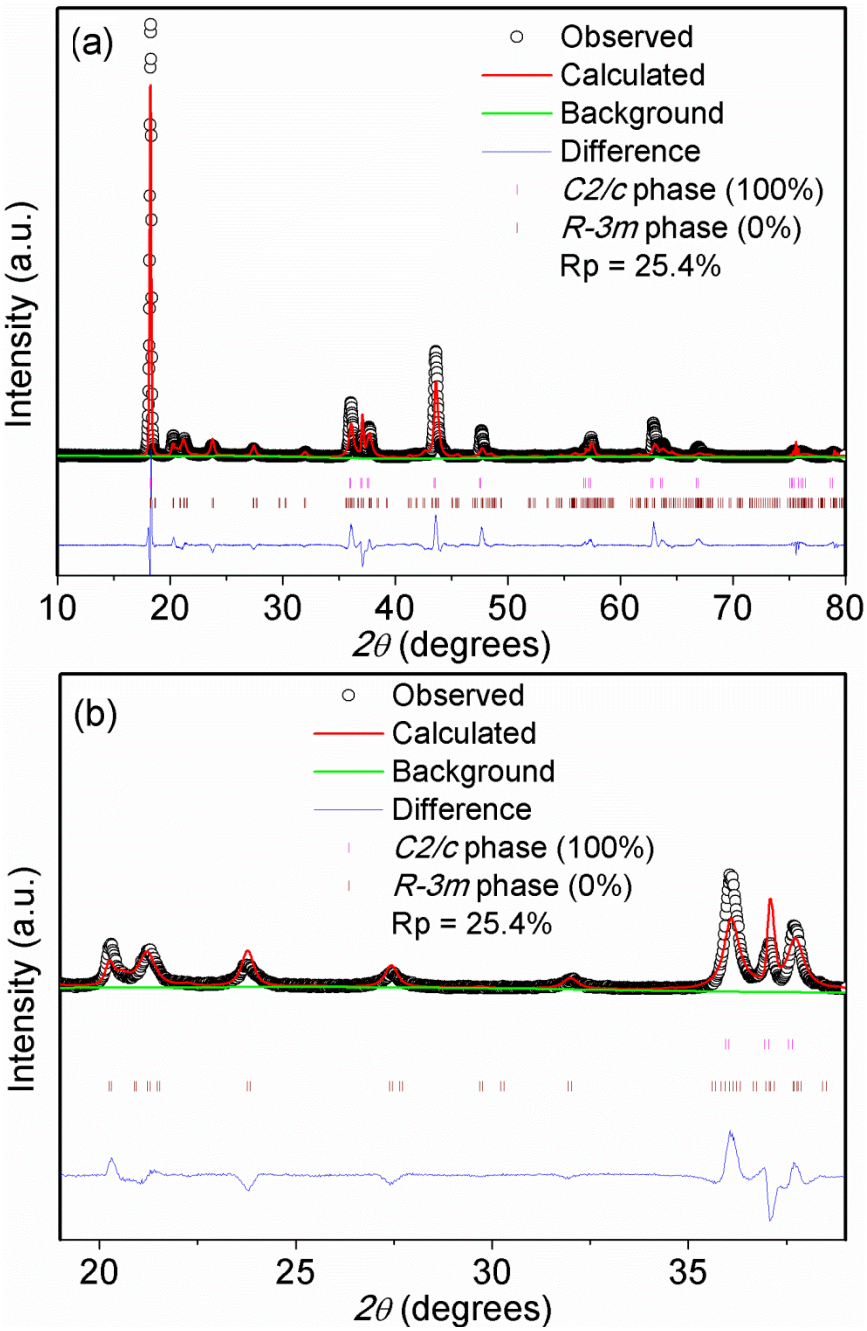

Figure S1. Refined XRD patterns of the $x = 0.6$ sample using a model of $R\bar{3}m$ and *C2/c* phases: (a) full pattern and (b) zoomed-in portion to better show the fit of superstructure peaks.

Table S1: Rietveld refinement parameters from the two different models employed to fit the x = 0.6 sample

C2/c and $R\bar{3}m$ Model			R_p: 25.4%				
Atom	*x/a*	*y/b*	*z/c*	Occupancy	U_{iso}(Å^2)	Lattice Parameters (Å)	
O (3)	0.163507	0.178434	0.553468	1	0.0001	a	5.026675
O (1)	0.145791	0.259051	0.118412	1	0.0001	b	8.74081
Ru	0.268983	0.082827	0.007005	0.9	0.02405	c	9.82327
O (2)	0.391933	0.078152	0.383536	1	0.0001	β	99.9576
Li (2)	0	0.083	0.25	0.9	0.0001		
Li (3)	0	0.416	0.25	0.9	0.0001		
Li (4)	0	0.75	0.25	0.9	0.0001		
Li (1)	0.25	0.25	0.5	0.9	0.0001		
Ni (1)	0.25	0.25	0.5	0.1	0.0001		
Ni (2)	0	0.083	0.25	0.1	0.0001		

P12/m and $R\bar{3}m$ Model			R_p: 8.8%				
P12/m Phase							
Atom	*x/a*	*y/b*	*z/c*	Occupancy	U_{iso}(Å^2)	Lattice Parameters (Å)	
O (2)	0.029707	0.107823	0.239273	1	0.0001	a	5.030993
Li (2)	0.266647	0.57266	0.412157	0.9	0.0001	b	8.763909
Ru	0.26535	0.084908	0.005513	0.9	0.04533	c	5.136355
O (1)	0.454334	0.542645	0.224496	1	0.0001	β	108.9129
O (3)	0.073444	0.25	0.808246	1	0.0001		
Li (3)	0.396504	0.25	0.232546	0.9	0.0001		
O (4)	0.935578	0.25	0.00899	1	0.0001		
Li (1)	0.625378	0.25	0.003623	0.9	0.0001		
Ni (1)	0.26535	0.084908	0.005513	0.1	0.04533		
Ni (3)	0.266647	0.57266	0.412157	0.1	0.0001		
Ni (4)	0.396504	0.25	0.232546	0.1	0.0001		
Ni (2)	0.625378	0.25	0.003623	0.1	0.0001		
$R\bar{3}m$ Phase							
Atom	*x/a*	*y/b*	*z/c*	Occupancy	U_{iso}(Å^2)	Lattice Parameters (Å)	
O	0	0	0.243656	1	0.0001	a	2.925558
Ru	0	0	0.5	0.6	0.0001	b	2.925558
Li	0	0	0	1	0.0001	c	14.586965
Ni	0	0	0.5	0.2	0.0001		
Li	0	0	0.5	0.2	0.0001		