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 Li₂RuO₃. Li₂RuO₃ 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 Li₂RuO₃ 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}O₂. Li-rich layered oxides are most often modeled using an $R^{3}m$ phase and a monoclinic phase. For this sample, Rietveld refinement was attempted using the $R^{3}m$ phase and one of the *C2/c* or *P12/m* monoclinic structures.

The refined pattern using the R^{3m} 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^{3m} 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 $R^{3}m$ 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 $R^{3}m$ and C2/c phases: (a) full pattern and (b) zoomed-in portion to better show the fit of superstructure peaks.

Atomx/ay/bz/cOccupancy $U_{lisc}(\dot{h}^2)$ Lattice Parameters (\dot{h})O (3)0.1635070.1784340.55346810.0001a5.026675O (1)0.1457910.2590510.11841210.0001b8.74081Ru0.2689830.0828270.0070050.90.02405c9.82327O (2)0.3919330.0781520.38353610.0001β99.9576Li (2)00.0830.250.90.000111Li (4)00.750.250.90.000111Ni (1)0.250.250.50.10.000111Ni (1)0.250.250.50.10.000111P12/m and R ³ m ModelR _p : 8.8%P12/m PhaseAtomx/ay/bz/cOccupancy $U_{lisc}(\dot{h}^2)$ Lattice Parameters (\dot{h})O (2)0.0297070.1078230.23927310.0001a5.030993Li (2)0.2666470.572660.4121570.90.0001b8.763909Ru0.265350.0849080.055130.90.0001β108.9129O (1)0.4543340.5426450.22449610.0001LLLi (3)0.3965040.250.232560.10.0001LLNi (1)0.6253780.250.03623 <th>C2/c and R</th> <th>$\overline{3}m$ Model</th> <th></th> <th><i>R</i>_p: 25.4%</th> <th></th> <th></th> <th></th> <th></th>	C2/c and R	$\overline{3}m$ Model		<i>R</i> _p : 25.4%					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Atom	x/a	y/b	z/c	Occupancy	U _{iso} (Ų)	Lattice Parameters (Å)		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	O (3)	0.163507	0.178434	0.553468	1	0.0001	а	5.026675	
Ru0.2689830.0828270.0070050.90.02405c9.82327O (2)0.3919330.0781520.38353610.0001β99.9576Li (2)00.0830.250.90.00011Li (3)00.4160.250.90.00011Li (4)00.750.250.90.00011Li (1)0.250.250.50.90.00011Ni (1)0.250.250.50.10.00011Ni (2)00.0830.250.10.00011P12/m and R ³ m ModelR _p : 8.8%P12/m PhaseAtomx/ay/bz/cO (2)0.0297070.1078230.23927310.0001a5.030993Li (2)0.2666470.572660.4121570.90.0001b8.763909Ru0.265350.849080.025130.90.04533c5.136355O (1)0.4543340.5426450.22449610.0001IIO (3)0.0734440.250.2325460.90.0001IIO (4)0.3355780.250.0036230.10.0001IINi (3)0.2666470.572660.4121570.10.0001IINi (3)0.2666470.572660.4121570.10.0001II<	O (1)	0.145791	0.259051	0.118412	1	0.0001	b	8.74081	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Ru	0.268983	0.082827	0.007005	0.9	0.02405	С	9.82327	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O (2)	0.391933	0.078152	0.383536	1	0.0001	β	99.9576	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Li (2)	0	0.083	0.25	0.9	0.0001			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Li (3)	0	0.416	0.25	0.9	0.0001			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Li (4)	0	0.75	0.25	0.9	0.0001			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Li (1)	0.25	0.25	0.5	0.9	0.0001			
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Ni (1)	0.25	0.25	0.5	0.1	0.0001			
P12/m and R^3m Model R_p : 8.8%P12/m PhaseAtomx/ay/bz/cOccupancyU _{iso} (Ų)Lattice Parameters (Å)O (2)0.0297070.1078230.23927310.0001a5.030993Li (2)0.2666470.572660.4121570.90.0001b8.763909Ru0.265350.0849080.0055130.90.04533c5.136355O (1)0.4543340.5426450.22449610.0001 β 108.9129O (3)0.0734440.250.80824610.0001 β 108.9129O (3)0.3965040.250.2325460.90.0001 β 108.9129O (4)0.9355780.250.0089910.0001 β 108.9129O (4)0.9355780.250.0036230.90.0001 γ γ Li (1)0.6253780.250.0036230.90.0001 γ γ Ni (3)0.2666470.572660.4121570.10.0001 γ γ Ni (4)0.3965040.250.2325460.10.0001 γ γ Ni (2)0.6253780.250.036230.10.0001 γ Ni (2)0.6253780.250.036230.10.0001 γ Ni (2)0.6253780.250.036230.10.0001 γ Ni (2)0.6253780.250.036230.10.0001 </td <td>Ni (2)</td> <td>0</td> <td>0.083</td> <td>0.25</td> <td>0.1</td> <td>0.0001</td> <td></td> <td></td>	Ni (2)	0	0.083	0.25	0.1	0.0001			
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Atomx/ay/bz/cOccupancy $U_{lso}(Å^2)$ Lattice Parameters (Å)O (2)0.0297070.1078230.23927310.0001a5.030993Li (2)0.2666470.572660.4121570.90.0001b8.763909Ru0.265350.0849080.0055130.90.04533c5.136355O (1)0.4543340.5426450.22449610.0001β108.9129O (3)0.0734440.250.80824610.000111Li (3)0.3965040.250.2325460.90.000111O (4)0.9355780.250.0089910.000111Li (1)0.6253780.250.0036230.90.000111Ni (1)0.2666470.572660.4121570.10.000111Ni (2)0.6253780.250.036230.10.000111Ni (2)0.6253780.250.036230.10.000111Ni (2)0.6253780.250.036230.10.000112.92558RuQQ00.50.60.0001a2.92558LiQ00.50.20.0001c14.586965NiQ00.50.20.0001114.586965	P12/m Phase								
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Atom	x/a	y/b	z/c	Occupancy	U _{iso} (Ų)	Lattice Parameters (Å)		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O (2)	0.029707	0.107823	0.239273	1	0.0001	а	5.030993	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Li (2)	0.266647	0.57266	0.412157	0.9	0.0001	b	8.763909	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru	0.26535	0.084908	0.005513	0.9	0.04533	С	5.136355	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O (1)	0.454334	0.542645	0.224496	1	0.0001	β	108.9129	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O (3)	0.073444	0.25	0.808246	1	0.0001			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Li (3)	0.396504	0.25	0.232546	0.9	0.0001			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O (4)	0.935578	0.25	0.00899	1	0.0001			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Li (1)	0.625378	0.25	0.003623	0.9	0.0001			
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 $R\overline{3}m$ Phase $R\overline{3}m$ Phase $R\overline{3}m$ Phase $V_{iso}(Å^2)$ Lattice Parameters (Å)O00 0.243656 1 0.0001 a 2.925558 Ru000.5 0.6 0.0001 b 2.925558 Li00 0.55 0.2 0.0001 c 14.586965 Ni00 0.55 0.2 0.0001 LLLi00 0.55 0.2 0.0001 LL	Ni (1)	0.26535	0.084908	0.005513	0.1	0.04533			
Ni (4) 0.396504 0.25 0.232546 0.1 0.0001 Ni (2) 0.625378 0.25 0.003623 0.1 0.0001 $R3m$ phaseAtom x/a y/b z/c Occupancy $U_{iso}(Å^2)$ Lattice Parameters (Å)O00 0.243656 1 0.0001 a 2.925558 Ru00 0.5 0.6 0.0001 b 2.925558 Li0001 0.0001 c 14.586965 Ni00 0.5 0.2 0.0001 c 14.586965 Li00 0.5 0.2 0.0001 c 14.586965	Ni (3)	0.266647	0.57266	0.412157	0.1	0.0001			
Ni (2)0.6253780.250.0036230.10.0001 $R3m_{Phase}$ Atomx/ay/bz/cOccupancy $U_{iso}(Å^2)$ Lattice Parameters (Å)O000.24365610.0001a2.925558Ru000.50.60.0001b2.925558Li00010.0001c14.586965Ni000.50.20.0001LetterLi000.50.20.0001Letter	Ni (4)	0.396504	0.25	0.232546	0.1	0.0001			
$R\bar{3}m$ PhaseAtomx/ay/bz/cOccupancy $U_{iso}(Å^2)$ Lattice Parameters (Å)O000.24365610.0001a2.925558Ru000.50.60.0001b2.925558Li00010.0001c14.586965Ni000.50.20.0001LLi000.50.20.0001L	Ni (2)	0.625378	0.25	0.003623	0.1	0.0001			
Atom x/a y/b z/c Occupancy U _{iso} (Ų) 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 0.5 0.6 0.0001 c 14.586965 Ni 0 0 0.5 0.2 0.0001 c 14.586965 Li 0 0 0.5 0.2 0.0001 c 14.586965 Li 0 0 0.5 0.2 0.0001 c 14.586965	R3m Phase								
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Ru000.50.60.0001b2.925558Li00010.0001c14.586965Ni000.50.20.0001-Li000.50.20.0001-	0	0	0	0.243656	1	0.0001	а	2.925558	
Li 0 0 0 1 0.0001 c 14.586965 Ni 0 0 0.5 0.2 0.0001 - <td>Ru</td> <td>0</td> <td>0</td> <td>0.5</td> <td>0.6</td> <td>0.0001</td> <td>b</td> <td>2.925558</td>	Ru	0	0	0.5	0.6	0.0001	b	2.925558	
Ni 0 0.5 0.2 0.0001 Li 0 0 0.5 0.2 0.0001	Li	0	0	0	1	0.0001	С	14.586965	
Li 0 0 0.5 0.2 0.0001	Ni	0	0	0.5	0.2	0.0001			
	Li	0	0	0.5	0.2	0.0001			

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