Comparison of layered $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ and LiRhO_2 upon Li-removal: stabilizing effect of Li substitution

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Abstract

Phase transformations upon delithiation in layered oxides with the NaCrS_2 structure type are widely studied for numerous combinations of 3d transition metals because of the application of LiCoO_2 and its derivatives as cathode materials in rechargeable Li-ion batteries. However, complete replacement of 3d by 4d transition metals still yields phenomena never seen in compounds containing 3d metals only. In the present work, structural evolution of Li-rich $\text{O}3\text{-Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, having a mixed occupancy of 20 % Li and 80 % Rh in the metal-oxygen slabs, was studied during electrochemical Li-removal and insertion, and compared with the isostructural stoichiometric LiRhO_2 . The latter compound undergoes a transformation from the layered NaCrS_2 to the tunnel-like rutile-ramsdellite intergrowth structure of the $\gamma\text{-MnO}_2$ type. Partial replacement of Rh by Li, in contrast, completely prevents this transition, resulting in a reversible cell expansion and shrinkage within the layered structure upon (de)lithiation. Moreover, no anomalously short Rh-O and O-O distances were observed in $\text{Li}_{x\approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ with $\text{Rh}^{4.75+}$ intermediate valence state at 4.8 V, in contrast to $\text{Li}_{x\approx 0}\text{RhO}_2$ with Rh^{4+} at 4.2 V, as confirmed by *operando* synchrotron XRD and EXAFS studies. We believe that the difference in Li-O and Rh-O covalency is responsible for the observed structural stabilization. The longer and more ionic Li-O bonds in (Li,Rh) O_2 -layers impede the shortening of oxygen-oxygen distances needed for the transformation to the $\gamma\text{-MnO}_2$ type, because of a higher negative charge on O-anions connected to Li-cations, and the stronger electrostatic repulsion between them.

Keywords: Li-rich layered oxides, topotactical Li-removal, covalent Rh-O bonds, lattice expansion upon delithiation

Introduction

Layered oxides with Li based on the NaCrS_2 structure represent the most promising positive electrode materials for Li-ion batteries.¹ Li-rich materials of the formula Li_2MO_3 , or $\text{Li}(\text{Li}_{0.33}\text{M}_{0.67})\text{O}_2$ with M = 3d and 4d elements, having similar structures, demonstrate anomalously high electrochemical capacities up to 300 mAh/g during charging (Li removal), which is attributed to combined cationic and anionic redox reactions including a partial oxygen oxidation.²⁻⁸ The oxygen redox activity is generally

associated with a strong covalence of the M – O bonding and significant contribution of O2p states to the bands near the Fermi level. This leads to the formation of so-called “peroxo”-like groups with shortened O-O distances of $\sim 2.3 - 2.4$ Å and a cooperative deformation of the oxygen lattice, distorting the MO₆-octahedra into trigonal prisms and changing the rhombohedral 3R sequence to the hexagonal 2H. The layered character of the lattice remains mostly unchanged. In previous work,⁹ the unique behavior of layered LiRhO₂ (space group $R\bar{3}m$), containing Li and RhO₂ layers, upon delithiation is reported. Being charged above 4.0 V in Li-ion batteries, it exhibits a massive and concerted migration of Rh cations towards empty octahedral positions in the Li-layers resulting in the Li_yRh₃O₆ tunnel-like phase of the γ -MnO₂ type, which represents a rutile-ramsdellite intergrowth structure. The Rh migration is accompanied by shortening of O-O distances up to 2.26 Å, and some unusually short Rh-O bond lengths of 1.65 Å, evaluated from synchrotron diffraction experiments. The tunnel-like Li_yRh₃O₆ can accommodate even more Li-ions per formula unit as initial layered LiRhO₂.⁹

The Li,Rh-oxides known from the literature adopt crystal structures related to rock-salt: LiRhO₂ of the layered NaCrS₂ type,¹⁰ spinel-like LiRhO₂,¹¹ or layered, Li-rich compounds of a Li₂MnO₃ type with a honeycomb-like ordering of Li and Rh atoms.^{12,13} Moreover, Li₂RhO₃ undergoes a structural distortion under elevated external pressure resulting in the formation of short Rh-Rh bonds building zigzag chains along the crystallographic *a* direction.¹⁴

To the best of our knowledge, there is no information in the literature regarding compositions between layered LiRhO₂ and Li₂RhO₃, and the role of Li for the phase formation. Since LiRhO₂ of the NaCrS₂ type transforms into the tunnel-like γ -MnO₂ type rutile-ramsdellite intergrowth structure upon delithiation, which has never been seen for other layered transition metal oxides with alkali metals, further studies about parameters influencing this exotic transformation would be beneficial. A Li-excess in the pristine structure in comparison to the LiRhO₂ stoichiometry may also facilitate the transformation, since Li forms a conventional Li₂O₂ peroxide with oxygen-oxygen bonds of about 1.55 Å.¹⁵

In the present work, a layered Li(Li_{0.2}Rh_{0.8})O₂ compound with a partial substitution of Rh- through Li-atoms was synthesized and structurally characterized during Li-removal and following re-insertion, using operando synchrotron XRD and XAS methods. The aim was to analyze the resulting Li-deficient Li_{1-x}(Li_{0.2}Rh_{0.8})O₂ structure and to compare it with Li_{1-x}RhO₂, in order to understand the role of partial substitution of Rh on the delithiation process.

Experimental

Synthesis and phase analysis

Li(Li_{0.2}Rh_{0.8})O₂ samples were prepared by a solid state reaction from Li₂CO₃ (Alfa Aesar, 99.9%) and Rh₂O₃ (Alfa Aesar, 99.95%) placed in Pt crucibles at 950 °C for 24 h in air. The Li/Rh ratio in the initial reaction mixture was 2/1. LiRhO₂ was prepared as described elsewhere.⁹ Phase analysis and

determination of cell parameters of materials after synthesis were carried out at room temperature using X-ray powder diffraction (XPD) with a STOE STADI P diffractometer (Cu-K α_1 -radiation, $\lambda = 1.54059$ Å) in transmission mode. Cation distribution in the compound was evaluated by Rietveld analysis of synchrotron powder diffraction data recorded at the synchrotron facility PETRA III/DESY (Hamburg, Germany) at the beamline P02.1.

Lithium-deficient $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ samples were obtained in electrochemical cells. Diffraction experiments and magnetization measurements on $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ were performed without any contact of the sample to air.

Electrochemical characterization

Electrochemical studies on $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ and LiRhO_2 cathodes were performed with a VMP3 (Biologic, France) multichannel potentiostatic-galvanostatic system in standard Swagelok-type cells with metallic Li as anode material. For the positive electrode, a mixture of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ or LiRhO_2 , Super P Carbon (SPC, TIMCAL), and polyvinylidene difluoride (PVDF, Solef 21216) as polymer binder in an 85:10:5 weight ratio was pressed on Al-meshes with 8 mm diameter and dried in vacuum at 353 K. A 1M solution of LiPF_6 in a mixture of ethylene carbonate and dimethyl carbonate in the volume ratio 1:1 was used as electrolyte (LP30, BASF). The cells were assembled in an Ar-filled glovebox with H_2O and O_2 contents less than 1 ppm.

For galvanostatic intermittent titration (GITT) experiments, a current of 0.05C was applied for 10 minutes, where C corresponds to the current needed for the insertion or extraction of 1 Li per formula unit within one hour. Before the next titration step, a rest period of 12 hours followed to allow the determination of an open circuit voltage (OCV) value near equilibrium conditions.

Chemical diffusion coefficients were calculated according to

$$\tilde{D} = \frac{4}{\pi \tau} \left(\frac{m_B \cdot V_m}{M_B \cdot S} \right)^2 * \left(\frac{\Delta E_s}{\Delta E_\tau} \right)^2$$
 where τ is the time of applied galvanostatic current, m_B and M_B are the mass and the molecular weight of the active material, V_m is the molar volume, S is the electrode surface area, ΔE_s corresponds to the difference in OCV between two titration steps, and ΔE_τ is the total change of the cell voltage during the current pulse, neglecting the IR drop, respectively.¹⁶

Operando investigations of crystal and electronic structure of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ during Li-removal and insertion

a) X-ray diffraction studies

Operando X-ray synchrotron diffraction measurements on $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ were performed at the beamline BL04-MSPD¹⁷ at ALBA (Barcelona, Spain), and at the beamline P02.1 at PETRA III/DESY (Hamburg, Germany), both in transmission mode. The experimental setup containing a coin cell holder

connected to a VMP3 multichannel potentiostat (Biologic, France) is described elsewhere.¹⁸ Data were collected at wavelengths of 0.41289(1) Å at ALBA and 0.20718(1) Å at PETRA III, which were refined from the reflection positions of NIST silicon and LaB₆ reference materials.

In order to characterize the Li(Li_{0.2}Rh_{0.8})O₂ starting material, a pattern was recorded before the electrochemical process (delithiation/lithiation) was started. The cell was then successively charged and discharged in galvanostatic mode at a current corresponding to the intercalation or deintercalation of 1 Li per formula unit during 10 h (0.1C rate). All diffraction patterns were analyzed by Fullprof implemented into the software package FullProf Suite.¹⁹ The Al-foil as current collector on the cathode side served as an internal standard during the measurements, and the refined lattice parameter of Al provided an independent control of the reliability of the obtained model parameters.

Two different phase shifts, one for Li(Li_{0.2}Rh_{0.8})O₂ and the other one for the Al-foil, were considered in the analysis procedure.

b) X-ray absorption studies

Operando X-ray absorption experiments were carried out at the beamline P65 at PETRA III extension (DESY, Hamburg, Germany) in a transmission setup. As described for *operando* XRD measurements, a coin cell holder, coupled with a VMP3 multichannel potentiostat (Biologic, France), was used for electrochemical cycling. For EXAFS data analysis, the measured spectrum below the pre-edge was fitted linearly while the post-edge background contribution was fitted to a quadratic polynomial. This background $\mu_0(E)$ was subtracted from the absorption spectrum $\mu(E)$, and the resulting data were normalized according to $\chi(E) = \{\mu(E) - \mu_0(E)\}/\Delta\mu_0(E)$, where $\Delta\mu_0(E)$ denotes the measured jump in absorption at the edge. The normalized spectrum was converted into k space using $k = [2m(E - E_0)/\hbar^2]^{1/2}$. By weighting $\chi(k)$ with k^3 , contributions of higher k space were amplified. The resulting $k^3\chi(k)$ was Fourier-transformed into the R space, allowing the determination of bond contributions. Least-square fits were performed using the FEFF6 code.²⁰

Magnetization measurements

Magnetization measurements of initial and delithiated Li_{x=0}(Li_{0.2}Rh_{0.8})O₂ were performed using a SQUID magnetometer (MPMS) from Quantum Design. The temperature dependences of the magnetization were measured both in zero-field-cooled (ZFC) and in field-cooled (FC) mode between T= 2 and 330 K at 6 T.

Result and Discussion

1. Synthesis results and electrochemical characterization

Solid state synthesis led to the formation of a Li,Rh-oxide with a layered crystal structure with octahedral oxygen coordination of Li in Li-layers and three formula units in the unit cell (O3 type).

Rietveld analysis of the synchrotron diffraction data confirmed the space group $R\bar{3}m$ and provided the lattice parameters $a = 2.97248(4)$ Å and $c = 14.5578(4)$ Å based on the α -NaFeO₂ structural model.²¹ Comparison with the structural data of LiRhO₂,⁹ having $a = 3.02116(4)$ Å and $c = 14.2499(4)$ Å, evidently confirmed different cation distribution in both materials, since the ionic radius of Li⁺ (0.76 Å) is larger than of Rh³⁺ (0.665 Å) for octahedral oxygen surrounding.²² Refinement of site occupancies for Li and Rh leads to a ratio Li:Rh = 0.174(6):0.828(6) in the “RhO₂”-layers, reflecting the total composition Li(Li_{0.2}Rh_{0.8})O₂. The cation occupancies were refined coupled, meaning the full occupancy of the 3a Wyckoff position by Rh- and Li-atoms. The complete structural models for initial Li(Li_{0.2}Rh_{0.8})O₂ and electrochemically delithiated Li_{x=0}(Li_{0.2}Rh_{0.8})O₂ are presented in the Supporting Information.

Electrochemical tests of Li(Li_{0.2}Rh_{0.8})O₂ as a cathode in Li-cells using a galvanostatic mode showed two pronounced plateaus upon Li-removal (cell charge) and Li-insertion (cell discharge) at about 3.5 and 4.5 V vs. Li⁺/Li. Additionally, a third small plateau was observed below 2.5 V vs. Li⁺/Li, see Fig. 1a. The presence of plateaus may point out two-phase reaction mechanisms including some structural rearrangements. The selected cut-off voltage for Li(Li_{0.2}Rh_{0.8})O₂ and LiRhO₂ during cell charging and discharging corresponds to about 1 Li per formula unit, extracted/inserted from/into the compounds. Similar capacities of about 200 mAhg⁻¹ were reached for both materials, although for LiRhO₂, Li-removal and subsequent re-insertion occurs in a broader potential window, see Fig. 1b.

Kinetics studies of Li⁺ diffusion in Li_x(Li_{0.2}Rh_{0.8})O₂ at 25 °C using the GITT technique revealed chemical diffusion coefficients D_{Li} of 10⁻¹³-10⁻¹⁴ cm²s⁻¹ nearly independent on the composition in a broad potential range between 2.2 and 4.7 V (Fig. 2). Only at high and low cut-off potentials D_{Li} values decrease significantly reflecting inhibited diffusion because of less charge carries at 4.7 V, and full occupancy of Li-positions and an impeded ion mobility at 2.2 V. Therefore, a Li-diffusion mechanism in the material is very similar in the whole potential range, without formation of any superionic phases with highly mobile Li-cations resulting in a high ionic conductivity, at the first or second voltage plateau. In order to clarify the reason for two potential plateaus, structural studies using *operando* synchrotron diffraction were carried out.

Figure 1. Galvanostatic curves of a) $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ and b) LiRhO_2 for comparison, recorded with 0.1C meaning 1 Li / f.u. intercalated/removed during 10h. The upper x-axis points the Li-amount in the compound during the delithiation process for clarity. The different character of electrochemical responses clearly reflects different composition and cation distribution in both materials.

Figure 2. Chemical diffusion coefficients of Li in $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ in dependence on the cell potential.

2. Structural evolution of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ upon Li-removal and insertion

Although the observed plateaus in the galvanostatic curves of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ would suggest significant structural transformations upon Li-removal, *operando* synchrotron powder diffraction experiments (Fig. 3) confirmed the stability of the layered structure in the whole investigated potential range between 2.2 and 4.8 V vs. Li. The cut-off voltage in *operando* experiments was set to 4.8 V, since it corresponds to the removal of one Li per formula unit, which was proven during a plenty of electrochemical *ex situ* measurements. Additionally, the Li-diffusion coefficient decreases drastically at this voltage, thus pointing a very low quantity of mobile Li-ions in the material, and very slow kinetics. However, a continuous development of the voltage curve in *operando* measurements reflects some parasitic side reactions.

Since no new Bragg reflections or splitting of already existing ones was observed, no phase transitions were assumed besides a conventional unit cell shrinkage and possible Rh oxidation due to lithium removal, see for example diffraction patterns of pristine $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ and delithiated $\text{Li}_{x=0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ after cell charge up to 4.8 V in Fig. 4. Obviously, two pronounced plateaus in the electrochemical curve at 3.7 and 4.5 V vs. Li do not arise from a crystal structure transformation, but maybe from electronic effects in the compound, including possible changes in the charge compensation mechanism upon delithiation. A detailed analysis of lattice parameters a and c in dependence on the Li content in $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ revealed a non-linear increase of both upon delithiation, with a stronger rise below $x=0.6$, which corresponds to the first redox plateau at about 3.6 V, see Fig. 5.

Figure 3. Potential-dependent *operando* synchrotron powder diffraction data from an electrochemical cell with $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ cathode on Al current collector, and Li anode, during galvanostatic cycling at 0.1C (a), together with the corresponding voltage profile vs. total Li content in the material, which was determined from the current amount flowing into the cell (b).

In isostructural Li_xRhO_2 , both lattice parameters a and c increase with delithiation as well. This behavior is rather unusual, because in the majority of layered intercalation compounds the a parameter contracts upon Li extraction due to the shrinkage of $M\text{-O}$ bonds in the MO_6 octahedra, since the M cation radius decreases with increasing average oxidation state. On the other hand, the parameter c expands due to the increased repulsion between the two neighboring oxygen layers that come into close contact when the Li ions are removed. The increase of the a parameter can be ascribed to the increased Coulomb repulsion between metal cations, similar to that observed for example in LiNbO_2 .²³

Interatomic distances Rh-O and O-O decrease during Li-removal from $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, showing also a kink at $x=0.6$ (Fig. 5). The cell metrics as well as atomic positions and cation occupancies before and after the first complete cycle fit well together, hence excluding any irreversible cation migration between Li- and (Li,Rh) O_2 -layers. Moreover, detailed structural analysis at all measured states of lithiation during *operando* measurements did not show any mixed Li,Rh-occupancy in the Li-layers, hence excluding any Rh migration from the (Li,Rh) O_2 - to the Li-layers. The O-O distance of 2.71 Å in the highly delithiated (most oxidized) state corresponds to conventional values usually found in oxide structures with the closest oxygen packing.²² This finding rather contradicts the hypothesis of the partial oxygen oxidation in the layered structure.²⁻⁸

Figure 4. Synchrotron powder diffraction patterns of $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ in the initial (top), and charged state at 4.8 V vs. Li^+/Li (bottom), together with the crystal structures. Yellow spheres correspond to Li atoms in Li- and RhO_6 -layers. Bragg position marks from top to bottom correspond to the reflection positions of $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ with the $R\bar{3}m$ space group symmetry, and Al as a current collector in the *operando* cell. Structure refinement was performed using the Rietveld method after background correction by Fullprof software, according to the work.¹⁹ Refined parameters for both compositions are presented in the Supporting Information.

Figure 5. Evolution of the lattice parameters (top) and average interatomic distances (bottom) of rhombohedral $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ in dependence on the Li content during electrochemical Li-extraction and insertion.

3. Local structure and redox mechanism in $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ during Li-removal and insertion

Operando XRD studies showed the stability of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ with the layered NaCrS_2 type structure upon entire Li-extraction from the Li-layers and subsequent Li-insertion. From *operando* XAS studies, more information concerning the local Rh environment and electronic effects can be received. It is known for 3d and 4d transition metal oxides that the position of the absorption edge E_0 correlates with the metal valence state.²⁴ The absorption edge E_0 can either be defined as the energy at the x-ray absorption coefficient $\mu(E) = 0.8$ of normalized post-edge intensities, or as the energy corresponding to the maximum of the energy derivative of $\mu(E)$, which is in coincidence with the inflection point of the absorption edge.²⁴⁻²⁵ While a chemical shift of about 3 eV between absorption edge positions of oxide materials with M^{n+} and $\text{M}^{(n+1)+}$ is usually observed for 3d transition metal oxides with Co,²⁶ for 4d metal oxides the chemical shift of about 1.5-2 V is smaller, as for example it was shown for different Ru-oxides.²⁵

The XAS measurements on the Rh-K edge revealed a shift of about 1.5 eV towards higher energies during delithiation of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ to $\text{Li}_{x \approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, and back during subsequent material lithiation, see Fig.6, thus confirming significant participation of Rh in the redox process. Nearly the same shift of the Rh-K edge was observed during Li-removal from LiRhO_2 (data not shown).

Figure 6. Selected Rh *K*-edge spectra of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, recorded during *operando* measurements. The dotted line at $\mu(E) = 0.8$ of normalized post-edge intensities points the position of the absorption edge E_0 , which correlates with the transition metal oxidation state.

Detailed analysis of EXAFS data of LiRhO_2 and $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ for the local Rh surrounding revealed big similarities between pristine LiRhO_2 and $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ with regard to Rh-O and Rh-Rh interatomic distances, see Table 1. Initial structural models for fitting were taken from analysis results of synchrotron diffraction data; examples of experimental and simulated data are presented in Fig. 7. Oxidation of the compounds *via* Li-removal leads to decrease of the Rh-O distances in both structures. However, while in delithiated layered $\text{Li}_{x\approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ the Rh-O distance of 1.98 Å matches well with the sum of the ionic radii of $\text{Rh}^{4+}/\text{Rh}^{5+}$ and O^{2-} of 1.96 Å,²² Rh-O distances of 1.59 – 1.81 Å in delithiated tunnel-like $\text{Li}_{x\approx 0}\text{Rh}_3\text{O}_6$ are much smaller than the sum of the ionic radii of Rh^{4+} and O^{2-} of 2.00 Å. This finding is in excellent agreement with the structural information from synchrotron powder diffraction reported in the work⁹, and confirms indirectly involving of oxygen in the tunnel-like structure into the redox process. Therefore, both structural methods are sensitive enough to detect structural anomalies like shortened metal-oxygen distances. In both delithiated compounds, the Rh-Rh distance remains much longer than 2.708 Å in metallic Rh,²⁷ thus excluding any direct Rh-Rh interactions. For layered $\text{Li}_{x\approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, the Rh-Rh distance increases slightly with decreasing Li-content, in agreement with the increased parameter *a* calculated from *operando* XRD measurements.

Figure 7. Experimental (black circles) and simulated (red line) Fourier transformations of the k^3 -weighted Rh-K EXAFS data for the layered (left) and tunnel-like rutile-ramsdellite (right) Li,Rh-oxides, both in a delithiated state (x close to 0).

Table 1. Selected fitting results for the Fourier transformed k^3 -weighted Rh *K*-edge EXAFS of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, and LiRhO_2 , for initial and charged states.

Sample	shell	R(Å)	$\sigma^2(\text{\AA}^2)$	$\Delta E(\text{eV})$	R-factor
Pristine $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$	Rh-O	2.038(6)	0.0017(8)	-4(1)	0.0165153
	Rh-Rh	3.03(1)	0.004(1)		

Charged to 4.75 V, layered $\text{Li}_{x \approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$	Rh-O	1.981(9)	0.004(1)	-5(1)	0.0290121
	Rh-Rh	3.04(1)	0.006(1)		
Pristine LiRhO_2	Rh-O	2.027(8)	0.001(1)	-4(1)	0.0160526
	Rh-Rh	3.02(1)	0.004(2)		
Charged to 4.15 V, tunnel- like $\text{Li}_{x \approx 0}\text{Rh}_3\text{O}_6$	Rh1-O1	2.06(8)	0.007(2)	-3(2)	0.0018831
	Rh1-O2	1.59(7)	0.003(2)		
	Rh1-O3	1.90(4)	0.0009(7)		
	Rh2-O1	1.93(2)	0.007(2)		
	Rh2-O2	1.70(4)	0.003(2)		
	Rh2-O3	1.81(1)	0.0009(7)		
	Rh1-Rh1	3.0(1)	0.006(2)		
	Rh1-Rh2	3.51(7)	0.009(3)		

A small hysteresis in Rh-O bond lengths was observed between battery charging and discharging for $0.8 \leq x(\text{Li}) \leq 0.4$ in $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, corresponding to the first plateau in the electrochemical curve (Fig. 8). Comparison of shorter Rh-O distances from *operando* EXAFS and longer average $(\text{Li}_{0.2}\text{Rh}_{0.8})\text{-O}$ distances from *operando* XRD measurements in the delithiated layered $\text{Li}_{x \approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ argues for an expansion role of Li in $(\text{Rh},\text{Li})\text{O}_2$ -layers for the total crystal structure, at least along the c-direction.

Figure 8. Interatomic Rh-O distances vs. Li-content in $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ evaluated from *operando* XAS measurements, for two delithiation and one lithiation processes. A small hysteresis in Rh-O between Li-content of 0.8 and 0.4 corresponds to the first plateau in the electrochemical curve.

4. Magnetization measurements

Calculation of a paramagnetic moment can provide additional information about the oxidation state of a transition metal in the compound. However, temperature dependence of magnetization in zero-field-cooling (ZFC) and field-cooling (FC) measurements for initial $\text{Li}_{x=1}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ (Fig. 9), does not obey the Curie-Weiss behavior between 2 and 330 K. Applying of the Curie-Weiss equation for the delithiated $\text{Li}_{x\approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ sample after correction of the diamagnetic contribution from the gelatin capsule, in which the materials were measured, provides a paramagnetic moment of $0.65(1) \mu_B$. This value is only slightly smaller than the theoretical spin-only paramagnetic moment of $0.77 \mu_B$ calculated on the assumption of an average valence state $\text{Rh}^{4.75+}$, which is composed of LS- Rh^{5+} ($S=0$, d^4) and LS- Rh^{4+} ($S=1/2$, d^5). Therefore, a simplified ionic model with the charges, localized on Rh-cations and O^{2-} anions, provides a satisfactory explanation of experimental magnetization data for this highly-oxidized Rh-oxide.

Figure 9. Temperature dependence of magnetization for $\text{Li}_{x=1}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ and $\text{Li}_{x=0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ at 6T, during zero-field-cooling (ZFC) and field-cooling (FC) measurements.

Discussion

The most common phase transformations in layered oxides with the NaCrS_2 type structure during delithiation result in the formation of either a spinel-type structure or spinel-like domains, as it was reported for LiMnO_2 and LiCoO_2 , or phases with Li-ion ordering like Li_xNiO_2 .¹ The case of LiRhO_2 with the phase transformation into the rutile-ramsdellite intergrowth structure of the $\gamma\text{-MnO}_2$ type is therefore unique.⁹ It occurs *via* a cooperative movement of RhO_6 -octahedra within the RhO_2 -layers in the half-delithiated $\text{Li}_{0.5}\text{RhO}_2$ of the NaCrS_2 type. A replacement of 20 %Rh by Li in the RhO_2 -layers does

not significantly influence the initial crystal structure besides the increase of the lattice parameters of the rhombohedral lattice due to the larger Li^+ cations, but completely suppresses the phase transformation into the $\gamma\text{-MnO}_2$ type even after entire extraction of Li-cations from the Li-layers. Suppression of phase transformations in layered Li-oxides during delithiation *via* a partial substitution of cations is a well-known phenomenon.¹ The best example for that is the layered LiMnO_2 , transforming into a spinel structure. It occurs because of the intrinsic electronic instability of Jahn-Teller Mn^{3+} cations ($S=2$, d^4) in the layered structure, and their disproportion into Mn^{2+} and Mn^{4+} , followed by migration of Mn^{2+} to tetrahedral sites.¹ This process can be eliminated by replacement of some amount of Mn through for example other transition metals like Co, Ni¹ or Cr.²⁸ As reported for the Cr-substitution, Mn cations are probably stabilized in Mn-O layers through the shortening of Mn-O bond distances.²⁸

The stabilizing mechanism in Li-rich $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ must be different. Obviously, the longer and more ionic Li-O bonds in (Li,Rh) O_2 -layers impede formation of short metal-oxygen and oxygen-oxygen bonds, most probably because of the higher negative charge of O-anions connected to Li-cations, and the stronger electrostatic repulsion between these anions. Note the isostructural O3-NaRhO_2 compound maintains its crystal structure after removal of a half the Na content, but a zig-zag Na-ordering in Na-layers leads to a monoclinic lattice distortion.²⁹ Moreover, a semiconductor-to-metal transition was observed while Na-atoms were removed from NaRhO_2 .²⁹⁻³⁰

The delithiation process in LiRhO_2 and $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ starts at about 3.5 V vs. Li, although the initial valence states of Rh in both compounds are different, namely Rh^{3+} in LiRhO_2 and $\text{Rh}^{3.5+}$ in $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$. Removal of 1 Li per formula unit is completed at about 4.2 V for LiRhO_2 , and at 4.8 V for $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$. After delithiation, Rh^{4+} and $\text{Rh}^{4.75+}$ are formally present in $\text{Li}_{x\approx 0}\text{RhO}_2$ and $\text{Li}_{x\approx 0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, respectively. A simplified ionic model with highly charged rhodium cations and oxygen anions can quantitatively explain two plateaus in the galvanostatic charging curve observed for $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$: the first plateau reflects the coexistence of $\text{Rh}^{3+}/\text{Rh}^{4+}$ in $\text{Li}_x(\text{Rh}_{0.8}\text{Li}_{0.2})\text{O}_2$, while the second plateau $\text{Rh}^{4+}/\text{Rh}^{5+}$ coexistence. The higher charge cut-off potential of $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ matches well with the presence of Rh^{5+} in the material. Although a single-phase delithiation mechanism was concluded for $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ from *operando* synchrotron diffraction studies, an almost flat voltage profile of the first plateau as well as a hysteresis in the Rh-O distances from *operando* EXAFS studies argues rather for a more complicated process. Some electronic effects similar to detected in desodiated $\text{Na}_{1-x}\text{RhO}_2$, could be a reason for the observed phenomena. Further experiments, performed on $\text{Li}_{1-x}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ single crystals, are necessary to clarify this point.

The question about involvement of oxygen in the redox process in $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ can be answered rather negatively in comparison to LiRhO_2 , based on the structural studies. Two different methods for

analysis of the local and global crystal structures, synchrotron XRD and EXAFS, provide similar structural characteristics for each material. The EXAFS studies showed conventional Rh-O distances of about 1.9-2.0 Å in layered delithiated $\text{Li}_{x=0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, while very short bond lengths of 1.59-1.8 Å in delithiated tunnel-like $\text{Li}_{x=0}\text{RhO}_2$. These data are well in line with the synchrotron diffraction data. The O-O-distance even for the most delithiated (oxidized) $\text{Li}_{x=0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ compound agrees with values of 2.7-2.9 usually observed in oxides as a sum of ionic radii of two O^{2-} anions. It is in contrast to delithiated LiRhO_2 with much shorter O-O distances of 2.26 Å in the $\gamma\text{-MnO}_2$ type structure.⁹

Conclusions

A partial replacement of Rh-cations by Li in the layered rhombohedral LiRhO_2 structure, resulting in the composition $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$, completely changes the structural behavior during electrochemical Li-removal and insertion: it prevents the layered-to-tunnel phase transformation observed in the stoichiometric LiRhO_2 . One Li per formula unit can be removed from the Li-layers with preserving of the initial rhombohedral structure, and inserted back, which corresponds to a charge/discharge capacity of about 200 mAh g⁻¹. Structural analysis during delithiation revealed conventional Rh-O and O-O distances in $\text{Li}_x(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ which are usually observed in oxides. Therefore, most probably, oxygen atoms do not participate in the redox process. This finding stands in contrast to LiRhO_2 with significantly shorter Rh-O and O-O interatomic distances. The $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ compound has a Li chemical diffusion coefficient of about $5 \cdot 10^{-13} \text{ cm}^2 \cdot \text{s}^{-1}$ weakly dependent on the Li-content. Magnetization measurements showed a Curie-Weiss behavior for delithiated $\text{Li}_{x=0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$.

Supporting Information

The Supporting Information is available free of charge. It contains crystallographic data for the initial $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ and delithiated $\text{Li}_{x=0}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ materials, revealed from Rietveld analysis of X-ray synchrotron diffraction data.

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Notes

The authors declare no competing financial interest.

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The stabilizing effect of a partial Rh-substitution by Li-atoms in LiRhO_2 for the crystal structure during delithiation was revealed. Upon electrochemical Li-removal and re-insertion, $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ retains its structure, in contrast to the isostructural LiRhO_2 , showing a transformation from the layered NaCrS_2 type into the tunnel-like rutile-ramsdellite intergrowth $\gamma\text{-MnO}_2$ type. Moreover, any involvement of oxygen into the redox process in $\text{Li}(\text{Li}_{0.2}\text{Rh}_{0.8})\text{O}_2$ during delithiation can be excluded as elucidated from operando synchrotron XRD and EXAFS studies.