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Oxygen deficiency in lithium ion materials

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Little attention has so far been paid to the oxygen stoichiometry of lithium ion battery materials. In most cases presented in the literature, materials were assumed to be fully oxidised. In the light of recent studies, we showed that this assumption must clearly not be done and that performance may be improved by using careful heat treatments. In the spinel material $LiCoMnO_{4-\delta}$, a full oxidisation of the material allowed to eliminate the undesirable 4V plateau.[1] In the theoretically-inactive cathode material Li_2MnO_{3-d}, oxygen deficiency was clearly shown to be a factor for the electrochemical activity of the material.[2] In the layered rock-salt material $Li_{1.93}Mn_{0.97}Ni_{0.10}O_{3-\delta}$, a large increase in capacity was observed in materials prepared using an appropriate quenching technique.[3]
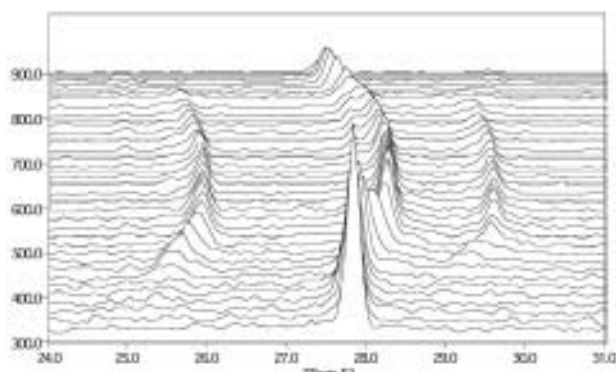

Fig. 1: X-ray peak positions vary with temperature and oxygen content of $LiCoMnO_{4-\delta}$

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Lithium Ion Conducting $Li_{0.3}La_{0.567}TiO_3$ Perovskite: Neutron Diffraction Study of the Quenched Form

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The perovskite structure, though very simple in its basic cubic configuration, is well known to be associated to an amazing variety of compositions, properties, and crystallographic variations. We are interested here in the family of defective lithium perovskites named LLTO, with general formula $Li_xLa_{2/3-x/3}TiO_3$, which exhibits the highest lithium electrical conductivity at room temperature (about 10^{-3} S/cm for $x = 0.3$) [1-3]. A liquid-N_2-quenched form of $Li_{0.3}La_{0.567}TiO_3$ was synthesized and studied by time-of-flight powder neutron diffraction at high resolution (HRPD instrument, ISIS facility, R.A.L., U.K.). The data were Rietveld refined by the FullProf2K computer package [4]. At room temperature a tetragonal perovskite superstructure was found, whose superlattice Bragg peaks were completely invisible in the X-ray powder diffraction profile. The body-centred unit-cell ($a=5.4803$ Å, $c=7.7559$ Å, $Z=4$) is of type $\varsigma 2a_p \times \varsigma 2a_p \times 2a_p$, with respect to the ideal cubic cell edge $a_p=3.875$ Å. Superlattice hkl reflections with odd l were systematically weaker and broader, so that two different peak profile functions had to be used for the even and odd l cases, respectively, in the Rietveld refinement. The crystal structure, solved in the $I4/mcm$ space group, is characterized by an $a^0a^0c^-$ tilt system of the TiO_6 octahedra [5] and by a single independent La site. To our knowledge, this body-centred structural configuration had never been observed before within the LLTO family. The lithium atoms were located by Fourier difference maps in disordered positions within the cages surrounding lanthanum vacant sites. The full Rietveld refinement converged to $R_p=6.56\%$, R_{Bragg}(even l)$=3.26\%$, R_{Bragg}(odd l)$=11.6\%$. A structural pathway for lithium ion mobility within the structure was devised, on the basis of the disordered configuration found. Above 600 C a reversible group/subgroup phase transition was detected, involving the disappearance of superlattice reflections. At 650 C a pseudo-cubic tetragonal $P4/mmm$ perovskite structure was refined (a=3.8964, c=3.8975 Å, $Z=1$; $R_p=6.10\%$, $R_{Bragg}=4.86\%$), where part of the oxygen atoms are disordered, and Li atoms are located on the layer of Ti atoms, rather than on that of La as in the room-temperature phase.

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