The Battery's New Clothes: Structure and Li-ion dynamics of the Crystalline Lithium-Rich Anti-Perovskites Li_3OCl and $Li_2(OH)Cl$

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Lithium-rich anti-perovskites (LiRAPs) might belong to the next-generation of promising solid electrolytes for all-solid-state batteries. Their 3D Li^+ migration channels are supposed to be beneficial for rapid Li ion dynamics [1, 2]. Their reliable preparation is, however, fraught with difficulties, especially when glassy samples have to be prepared [3]. Thermodynamic instabilities, sensitivity to moisture, and impurity phases often hinder the systematic study of ion transport properties in this class of materials.

Here, we prepared phase pure LiRAPs by hydrothermal synthesis with and without subsequent annealing steps. We investigated both structure and ionic conductivity and diffusivity of Li_3OCl and compared the results to those of $Li_2(OH)Cl$. Li_3OCl transforms into $Li_2(OH)Cl$ if proton sources are present. We applied a variety of methods, such as X-ray diffraction (XRD), neutron diffraction, conductivity spectroscopy, ^7Li NMR line shape measurements and NMR relaxometry experiments, to study the crystal chemistry as well as short-range ion dynamics and long-range ion transport. As revealed by XRD, $Li_2(OH)Cl$ undergoes a reversible phase transition at 313 K. This transition is associated with a jump in ionic conductivity by three orders of magnitude yielding $\sigma(313\ K) = 5.1 \times 10^{-6}\ S\ cm^{-1}$. Such behaviour was, however, not seen for phase pure H-free Li_3OCl, which is characterized by the following parameters ($\sigma_{bulk}(293\ K) = 0.84 \times 10^{-6}\ S\ cm^{-1}$, 0.63(1) eV; $\sigma_{grain\ boundary}(293\ K) = 0.28 \times 10^{-6}\ S\ cm^{-1}$, $E_a = 0.62(2)$ eV). The steep increase in ion conductivity of $Li_2(OH)Cl$ is also corroborated by ^7Li NMR line widths (Δ_{NMR}) measurements. Significantly narrowed NMR lines show up above 313 K ($\Delta_{NMR} = 1100$ Hz) due to rapid Li^+ jump processes in LiRAPs that successfully average dipolar interactions giving rise to broadened lines at much lower temperature ($\Delta_{NMR}(273\ K) = 8700$ Hz). Our measurements suggest that besides Li^+ also other charge carriers contribute to the overall conductivity of $Li_2(OH)Cl$. While long-range Li^+ transport in $Li_2(OH)Cl$ is governed by 0.57(1) eV, ^7Li NMR relaxometry senses local ion jumps with an activation energy of 0.36(1) eV. The latter value includes the effect of correlated motion on NMR activation energies measured in the low-temperature regime of the corresponding NMR spin-lattice relaxation rate peak, see Ref. [4]. Variable-temperature measurements of the real part of the complex resistivity ($\rho' = M''/\omega$), see Ref. [5] for another example, revealed an asymmetric peak with activation energies of 0.38(2) eV and 0.55(2) eV. These results clearly show complex dynamics in Li_3OCl presumably including both translational and (interrelated) rotational motions.

References:
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