

A new perspective on the anti-perovskite $\text{Li}_{2.99}\text{Ba}_{0.005}\text{OCl}$

Constantin Pompe^c, Daniel Schröder^a, Wolfgang Zeier^a, Jürgen Janek^a

^a *Justus-Liebig-Universität, Heinrich-Buff-Ring 17, D-35392 Giessen*

E-mail: constantin.pompe@phys.chemie.uni-giessen.de

Recently Braga et al. presented a cell concept with an extraordinary performance, which was much noticed in the community. The discussed cell consisted of a lithium anode and a sulfur-carbon composite cathode, which were separated by a glassy solid electrolyte (SE). The cell showed low cell resistance, high cycle stability and an unusual overcapacity.^[1] This overcapacity was a gladly argued subject in the past and was not reproduced so far. Steingart and Viswanathan commented, that this effect simply violates the first law of thermodynamics. According to that, the electrochemical processes described by Braga et al. are no explanation for gaining energy.^[2]

Furthermore, the used SEs, such as $\text{Li}_{2.99}\text{Ba}_{0.005}\text{OCl}$ (LOC:Ba), feature very high ionic conductivity of approximately 25 mS/cm and activation energies of around 0.06 eV.^[3]

Herein we present an overview on the reported compounds, which crystallize in the anti-perovskite structure, and their Goldschmidt tolerance factor.^[4] We reveal that LOC:Ba can only be stabilized by the substitution of Li with protons – in fact, there is no literature reported where pure Li_3OCl was synthesized by the use of proton-free reactants. Further on we revisit the synthesis of LOC:Ba by optimizing the synthesis parameters, and show via in-situ XRD that fast and complete decomposition of LOC:Ba occurs in air, which results in the formation of hydroxides. Contrary to the report of Braga et al., grinding the powder in ethanol does not prevent that process.

Temperature dependent electrochemical impedance spectroscopy (EIS) unveils a significant lower conductivity of LOC:Ba than reported by Braga et al.. In extreme cases, samples with an initially high content of protons show a positive slope in the Arrhenius plot above 100°C. This is caused by the loss of protons, when the samples begin to dry so that the number of charge carriers, and thus also the ionic conductivity, decreases. For samples prepared as reported by Braga et al., we surprisingly achieved a slope of -0.04 eV in the Arrhenius plot.

We conclude, that slopes in the Arrhenius plots loose their physical meaning, if samples change their composition or especially the content of charge carriers during the EIS measurements. All in all, our analysis sheds light on the anti-perovskite structures and their physico-chemical properties, which helps to thoroughly judge their applicability as novel material for SEs.

References:

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