

Modified Cathode Materials for Garnet based All-Solid-State Lithium Batteries

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All solid-state batteries (ASB) are an emerging energy storage technology, which is expected to improve the safety on the cell level and to increase the battery energy density. One of important issues in the development of bulk-type ASBs with a high energy density is a possibility of processing thick composites cathodes with percolating pathways for ion and electron transport. For the ceramic electrolytes such as garnet-type Ta-substituted LLZ ($\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$; LLZ:Ta) the practical realization of composite cathodes is however challenging due to the necessity of high temperature processing, raising the issues of material compatibility and the formation of reaction interphases influencing the total cell resistance. So far, the thick garnet-based composite cathodes could be made only with LiCoO_2 (LCO) as an active material. For this kind of ASB, high areal capacities of up to 1.63 mAh/cm^2 were obtained. However, the utilization of high capacity cathode materials like $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ (NCM) was so far not possible due to the lower thermal stability of NCM as compared to LCO and the resulting enhanced reactivity between LLZ:Ta and NCM.

Usually NCM materials were only optimized for liquid electrolyte based batteries. Therefore, an optimization of these active materials with respect to their integration into ASBs is intended in this work. Possible strategies for this optimization are doping or substitution, surface coatings or core-shell structures.

We present the synthesis of optimized cathode materials for bulk-type, fully inorganic ASBs based on ceramic materials. A detailed material screening of NCM materials with different compositions and modifications is performed by evaluating the compatibility with cubic LLZ:Ta during co-sintering at elevated temperatures. The compatibility is tested by *in situ* high temperature X-ray diffraction (HT-XRD), differential thermal analysis/thermogravimetry (DTA/TG), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The experimental work is supported by simulation studies using ab-initio-based approaches such as density functional theory (DFT), ab initio molecular dynamics (AIMD) as well as ab initio atomistic thermodynamics and kinetics approaches. These simulation based methods enable the prediction of lattice parameter of NCM at different stages of charge. Additionally, the calculation of interchange energies needed for the cation interchange between NCM and cubic LLZ:Ta during co-sintering is possible.

Boron doping of NCM was investigated as a possible strategy to improve its compatibility with LLZ:Ta, as this strategy was demonstrated to be very efficient for liquid electrolytes. The theoretical and experimental results on B-doped NCM with different compositions are already available. However, the

formation of secondary phases after co-sintering that was predicted by us theoretically and confirmed experimentally using Rietveld refinement discard boron doping as a way to enhance thermal stability of NCM during the co-sintering with cubic LLZ:Ta. Introduction of other dopants and surface coatings is currently investigated to improve the compatibility of NCM with cubic LLZ:Ta during co-sintering. The combined experimental and theoretical approach is expected to result in an optimized cathode material for ASBs with enhanced performance.