All-solid-state Li batteries with NCM-LLZO based composite cathodes

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Garnet-based all-solid-state lithium batteries (ASBs) featuring a thick composite cathode, composed of a solid-state electrolyte (SSE) and a high-capacity active material (CAM), are promising candidates for the next generation energy storage systems. They address several challenges of conventional lithium-ion batteries (LIBs) by promising higher energy densities and intrinsic safety. However, the fabrication of such ceramic batteries is challenging due to the necessary high temperature processing leading to material compatibility issues. High capacity CAMs, like $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM), show insufficient material compatibility towards the solid electrolyte $Li_{6.45}Al_{0.05}La_3Zr_{1.6}Ta_{0.4}O_{12}$ (LLZO:Ta) during co-sintering, leading to the formation of detrimental interphases. Thus, the thermodynamic stability of NCM towards LLZO:Ta, at elevated temperatures, needs to be increased. Here, we investigated two NCM compositions (NCM111 and Ni-rich NCM811), to assess the impact of the transition metal composition on the compatibility with LLZO:Ta. Additionally, we investigated B-doping of the NCM host structure, since Li_3BO_3 (LBO) is often used as a sintering additive in garnet based composite cathodes and can eventually diffuse in the NCM structure. Surprisingly, the Ni-rich NCM811 was found to be the most promising CAM for the combination with garnet type LLZO:Ta in composite cathodes of ceramic ASBs. During Co-sintering up to 1000 °C, NCM811/LLZO:Ta mixtures form only small amounts of secondary phases and B-doping does not negatively affect the thermodynamic stability. Therefore, a fully inorganic ASB based on a Li-metal anode, a LLZO:Ta separator and a composite cathode, consisting of Ni-rich NCM811, LBO and LLZO:Ta, could be successfully manufactured by conventional sintering. This ceramic ASB, exhibits one of the highest active material loading (5.7 mg cm^{-2}) reported so far and delivers significant higher specific areal capacities (0.7 mAh cm^{-2}) than comparable ceramic ASBs based on LLZO:Ta and NCM811.