Ceramic Composite Cathodes for All-Solid-State Lithium Batteries

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Abstract

Oxide-ceramic based all-solid-state lithium batteries (ASSLB) can provide high intrinsic safety, extended operational temperature range, and high energy density. As the first two are intrinsic to the materials system, one prerequisite to obtain high energy densities with such ASSLBs is the manufacturing of composite cathodes. Preferably, cathode active material (CAM) and electrolyte should form an intertwined 3D-network with an intimate extended contact between two phases. The interface between the CAM and the electrolyte should feature high total surface area with a low impedance to enable an efficient charge transfer and transport and minimize the resistance losses in a battery.

Composite solid cathode microstructures can be formed via a co-sintering of solid electrolyte and CAM powders. However, many CAMs such as $Li[Ni_{1-x-y}Co_xMn_y]O_2$ (NMC), $Li[Ni_{1-x-y}Co_xAl_y]O_2$ (NCA) or $Li_2NiMn_3O_8$ (LMO) cannot withstand sintering temperatures required, for oxide class solid electrolytes as $Li_7La_3Zr_2O_{12}$ (LLZ) or $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, to obtain sintered composite cathodes. Furthermore, the thermodynamic stability of CAMs significantly decreases in the presence of solid electrolytes. Still, several groups have demonstrated that thermodynamic limitations can be significantly lessened via a kinetic control of the process such as reduction of reaction times and a careful control of powder morphology during ceramic sintering process.

Following this work, we now demonstrate that FAST/SPS enables fabrication of different solid-state battery components within minutes such as a dense LLZ separator layer with a high ionic conductivity, a dense dual $LiCoCO_2$ (LCO)/LLZ composite cathode without any interfacial reactions, and an integrated cathode half-cell consisting of a composite cathode and a LLZ separator layer at temperatures as low as 675 – 800 °C. Analyzing the structure, morphology, and electrochemical performance of the obtained components, we conclude that the impurities (carbonates) on the surface of LLZ powder play a decisive role in the formation of high-quality interfaces and the minimization of porosity. Furthermore, these impurities decrease the ionic conductivity at low sintering temperature and deteriorate the cycling stability of an ASSLB. High areal capacity of up to 4.0 mA h/cm^2 at 80 °C with a constant current of 50 µA/cm^2 and a good utilization of LCO was achieved for ASSLB with LLZ powders free of surface impurities. FAST/SPS can therefore open new processing windows for ceramic-based ASSLBs to alleviate the problem of interphase formation.