

Effect of composite electrode thickness on the electrochemical performances of all-solid-state Li-ion batteries

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All-solid-state batteries with inorganic solid electrolytes are expected to exhibit high safety, reliability and energy density. In microelectronics field, considerable effort has been devoted to the development of micro-batteries that consist of a stack of three thin dense components; namely a positive electrode, a solid electrolyte and a negative electrode. The surface capacities of these batteries lie between 5 and 100 μAhcm^{-2} , depending on the thickness of the electrodes, which is typically around 1 μm . The main challenge facing all-inorganic Li-ion batteries is to increase the surface capacity (i.e. the thickness of the electrode). However, many attempts to increase the thickness has failed so far because of the formation of micro-cracks between the components, due to stress generated at the solid/solid interfaces, caused by volume change of the active material during cycling. Furthermore, strong kinetic limitations have been observed when an upscale in the third dimension is done, due to the low mobilities of the ions/electrons in solid-state active materials¹. A possible answer to this issue is to build in place of a dense phase pure electrode, a composite electrode which is a multifunctional material. This composite electrode should contain a lot of electrochemically active material, the reservoir of energy; together with electronic and ionic conductor additives, to ensure efficient and homogeneous transfer of electrons and ions in the electrode volume. The good way forward would be to use the same electrolyte material through the whole battery to provide a continuous Li^+ conduction pathway between the anode and the cathode as well as a strong mechanically framework for the battery. Recently, some investigations have been carried out on the development of such an all-solid-state battery. It has been shown that composite electrodes and the electrolyte can be assembled together in few minutes in one step by using the spark plasma sintering (SPS) technique². The NASICON-type structured $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ ceramic (later called LAG) was chosen as solid electrolyte as it offers a high ionic conductivity ($3 \times 10^{-4} \text{ S.cm}^{-1}$ at 25°C ³). LiFePO_4 active material is employed in this study as a model material that offers an average flat potential of 3.4 V vs. Li/Li. The choice of these materials was also driven by their respective stability upon heat treatment by SPS when they are mixed together (AM/electrolyte/carbon). The composite formulation (25wt%AM/60wt%electrolyte/15wt%carbon) as well as the sintering parameters has been determined using the electrical and electrochemical properties of the materials⁴. In such system, composite electrodes can reach several hundred of micrometers enabling surface capacity in between 2 to 6mAhcm^{-2} . However, in classical Li-Ion technology, composite electrode thickness generally does not reach value above $90\mu\text{m}$ due to strong limitation in power because of Lithium-ion concentration gradient formation into the electrode volume. The difference comes from the fact that in inorganic battery the cationic transport number of the electrolyte is 1 which prevents the formation of such gradient of concentration. In order to analyze this point more deeply, this paper presents a study of the impact of composite electrode thickness on electrochemical performances. Several half cells with different electrode composite thickness but presenting the same formulation were assembled by SPS in order to conduct comparable investigations of the kinetic limitations.

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