Electrochemical and chemical analysis of dendrites formation in Al- and Ga- doped $Li_7La_3Zr_2O_{12}$

Federico M Pesci [a], Rowena H. Brugge,[a] A. K. Ola Hekselman,[a] Andrea Cavallaro,[a] Richard J. Chater[a] and Ainara Aguadero[a]
[a] *Department of Materials, Imperial College London, Exhibition Road, SW7 2AZ, London, UK*

E-mail: f.pesci@imperial.ac.uk

The development of solid state lithium-ion batteries is a key requirement to enable the use of energy storage systems with high energy and power densities in the automotive sector. Particular interest has been given to solid electrolytes with relatively high ionic conductivity at room temperature (10^{-3}S cm^{-1}) such as garnets due to their high thermodynamic and electrochemical stability and the possibility to use of lithium metal as anode.[1] Despite these advantages, the use of garnet is limited because of their short life-time due to the formation of lithium dendrites.[2] A better understanding of the mechanism of formation of dendrites and their chemical nature is therefore urgently required in order to engineer and develop solid electrolytes to be employed in commercial systems.

In this work, we employed cubic Al- and Ga- doped $Li_7La_3Zr_2O_{12}$ (LLZO) as solid electrolyte in symmetrical cells and we investigated the formation of dendrites as a result of electrochemical cycling. We used surface analysis techniques such as FIB-SIMS, ToF-SIMS and LEIS in order to clarify the chemical composition of dendrites. Al-LLZO displays a critical current density (CCD) of 0.10 mA/cm^2, sensibly lower than the CCD of Ga-LLZO (0.16 mA/cm^2) suggesting that the type of dopant used to stabilise the cubic phase of LLZO also plays a fundamental role on dendrites formation. Chemical analysis revealed that in Al-LLZO the dendritic features are composed of a mixture of Al and Li, whereas in Ga-LLZO are uniquely composed of Li. FIB-SIMS and ToF-SIMS highlighted that Al preferentially segregates at the grain boundaries, whereas Ga is uniformly distributed on the grains. This suggests that the presence of local chemical inhomogeneities promoted by the type of dopants or impurities might greatly affect the CCD for the dendrite formation and propagation. This can have tremendous implications in the further development of solid state battereis.[3]

References:

[1] T. Thompson et al. ACS Energy Lett. 2 (2017) 462–468
[2] A. Sharafi et al., J. Power Sources 302 (2016) 135–139
[3] F. M. Pesci et al., Manuscript in preparation