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Quantifying Lithium in Lithium-ion battery solid electrolyte by atom probe tomography correlated with high-resolution scanning electron microscopy

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Lithium is the least dense metal and the least dense solid element available in nature. Yet, these facts have not prohibited Lithium from being a key element in solid-state battery devices. To be precise, Lithium ions are small enough (third only to hydrogen and helium) to diffuse very fast through the solid electrolyte[1], found between the cathode and anode, allowing battery devices to reach a very high voltage and charge storage capacity per unit mass and unit volume.

However, Lithium is impossible to be detected by standard analytical techniques such as energy dispersive X-ray spectroscopy (EDXS) in combination with (scanning) transmission electron microscopy ((S)TEM) because of the insufficient energy resolution of standard EDXS detectors for Li detection (Li-K line at only 55 eV). Moreover, Li detection by electron energy loss spectroscopy (EELS) in combination with STEM is a substantial challenge because the acquisition of EELS spectra requires a sufficient electron dose that may change the original Li distribution in LLZO. Furthermore, Li is a weakly scattering element that is difficult to image by (S)TEM and requires special imaging conditions for atomic-resolution imaging[2].

Therefore, in the present work we prove the big promise of atom probe tomography (APT) to probe and quantify Lithium redistribution in the very highly resistive $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte. It is not known to date if a Lithium enrichment takes place at grain boundaries of LLZO and what are the implications in terms of ionic conductivity.

Yet, there are challenges in accurately probe and quantify Lithium in these highly resistive solid electrolytes explaining why only very few works exist until now[3, 4]. One of these challenges is to impede Lithium ions to experience any displacements during APT experiments given the high mobility of Lithium ions in LLZO as explained above. During an APT experiment, the needle shaped specimen is subjected to temperature-sensitive conditions such as cryo-cooling and ultra-fast laser illumination. If not treated cautiously, Lithium ion transport can happen especially during highly energetic ultra-fast laser pulsing. Therefore, in the present work we have studied not only the impact of the base temperature (for cryo-cooling) and laser energy (for laser illumination) on the Lithium composition, but also on the three-dimensional Lithium redistribution. Six different 3D reconstruction maps exhibiting the Lithium redistribution for three different base temperatures (40K, 50 K and 60 K) as well as for two different laser pulse energies (10 pJ and 20 pJ) are shown in Figure 2a,b,c. Interestingly, we found that Lithium artificially accumulates and form Lithium-rich lamellas for specific conditions (highlighted in Figure 1a,b,c by the Lithium iso-composition surfaces) which are representative for a temperature increase of the APT needle (such as base temperature >50K and laser pulse energies >10 pJ). Yet, such Lithium-rich lamellas completely disappeared for low-temperature conditions such as base temperature of 40 to 50K and low laser pulse energy of 10 pJ (see Figure 1b,c).

But what is the mechanism responsible for the formation of these Lithium-rich lamellas under high laser energies during APT experiments? The Lithium ionic conductivity in the LLZO bulk is very high (ionic conductivity of 0.25 mS/cm in this work; close to the existing literature of ~1 mS/cm[5]) which supports the idea that the Lithium ionic conductivity and, hence, mobility at the surface of the APT needle is more enhanced than the Lithium mobility in the bulk due to the missing bonds on one side of the surface atoms. As schematized in Figure 1d, the Lithium atoms coming from the sides of the APT tip (surface of the dark-grey areas in Figure 2d; areas found outside the field-of-view in APT) might diffuse towards the apex of the APT needle when the temperature is high enough. The accumulation of Lithium at the apex leads to a Lithium-rich phase characterized by a lower evaporation than the LLZO bulk. This lower evaporation field F is validated by the systematic 20 to 30 % decrease in voltage V ($F = \frac{V}{kR}$, where k is the field factor and R is the radius of the APT needle[6]) observed when such Lithium-rich nanostructures are measured.

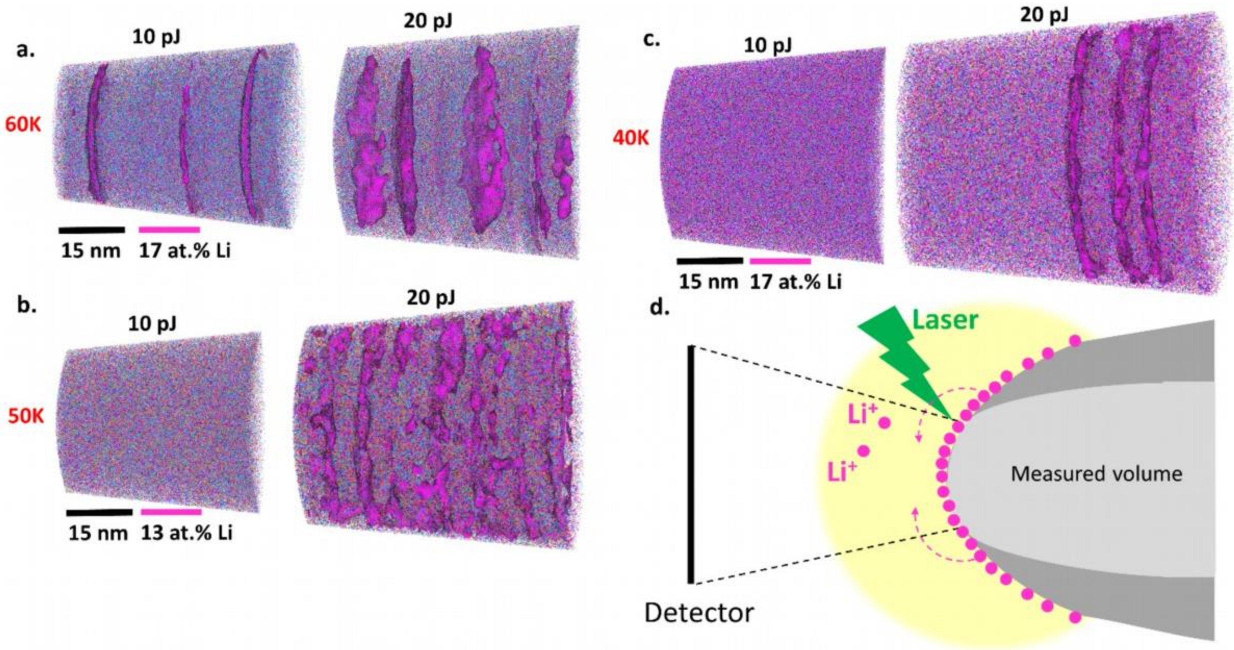

Figure 1. Possible artefacts taking place during APT analyses of LLZO solid electrolyte. a,b,c. Three dimensional APT reconstructions showing the distribution of Li (pink), La (orange), Zr (violet), O (light blue) and Ta (dark) for three base temperatures of 40 K, 50 K and 60 K and two laser pulse energy of 10 pJ and 20 pJ. **d.** Schematization of the mechanism responsible for the artificially-formed Li-rich lamellas.

Finally, in this work we prove that Li strongly accumulates at grain boundaries beyond the classical segregation phenomenon, i.e. beyond 1-2 monolayers expected typically for a grain boundary[7] as shown in Figure 2. We assign this to the formation of 3D thermodynamically stable interfacial phases such as Li_xO_y called “complexions”[8] exhibiting thicknesses above 5 nm. Similar Li-rich complexions have been recently discovered for the $Li_{(1+x)}Al_{(x)}Ti_{(2-x)}(PO_4)_3$ solid-state electrolyte[3], but with considerably lower Li accumulation. Li-composition data is correlated in our study with Li-ionic conductivities within the grain interior and across GBs obtained by impedance spectroscopy on the same material that was studied by APT. We suggest that the presence of Li-rich complexions at LLZO GBs is the reason for the lower Li conductivity observed for GBs in LLZO when comparing with the Li conductivity for the grain interior.

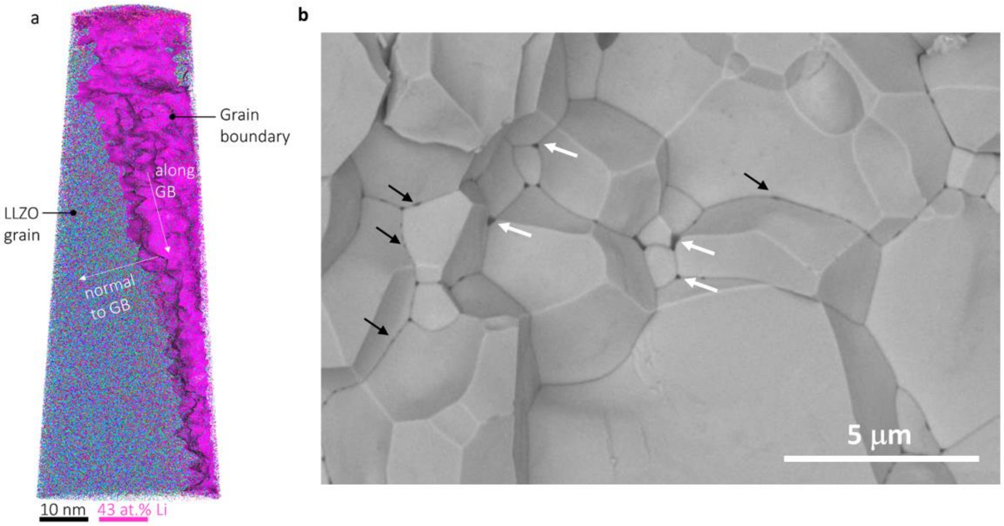

Figure 2. APT investigations of a grain boundary in LLZO oriented almost parallel to the tip axis. a. 3D APT map exhibiting the Li (pink) strong accumulation at the grain boundary position. This Li accumulation is highlighted by using an iso-composition surface (pink) built with 43 at.% Li. **b.** Backscattered-electron (BSE-)SEM imaging studies on freshly fractured LLZO solid electrolyte using a 5keV BSE-SEM image. The presence of low atomic-number phases (dark contrast) is clearly visible in b at some triple junctions and grain boundaries.

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