



## Reactions of garnet-based solid-state lithium electrolytes with water — A depth-resolved study

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### ABSTRACT

Garnet  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$  thin films prepared by magnetron sputtering were analysed by secondary ion mass spectrometry, nuclear reaction analysis and Rutherford backscattering to identify, localize and quantify the reactions associated with the presence of low amounts of water and carbon dioxide. Samples in a pristine state and after storage in an Argon-filled glove box for months were compared. Both, lithium hydroxide and lithium carbonate were detected, with carbon-containing species and hydrogen-containing having surprisingly different depth profiles.

### 1. Introduction

Garnet-based solid-state lithium ion conductors have recently attracted a lot of attention due to their outstanding properties like high ionic conductivity, high stability versus lithium (Li) metal, even in the molten state, and high stability against rather high positive potentials [1,2] which might allow battery cells with open circuit voltages significantly higher than about 4.5 V. However, this class of materials also exhibits drawbacks like significant chemical reaction with so-called high-voltage cathode active materials during common processing [3], and the sensitivity to moisture. The latter fact has a negative impact on the battery processing and can significantly deteriorate the battery performance.

The reaction of some garnet materials with water and air (incl. moisture and partly also carbon dioxide) is under lively discussion, and there seems to be evidence that the stability crucially depends on details of the composition of the garnet [1,4–6]. Many experiments with regard to the reaction of garnets with water have been done under heavy exposure to water ( $\text{H}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ), respectively. Y. Li et al. [7] immersed milled powder in de-ionized water (with pH 7) and found about 21% of  $\text{Li}^+/\text{H}^+$  exchange after 48 h. C. Ma et al. [5] observed a  $\text{Li}^+/\text{H}^+$  exchange reaction on a time scale of seconds by monitoring the pH value of an aqueous suspension of garnet  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ , and found a  $\text{Li}^+/\text{H}^+$  exchange as high as ~64% in de-ionized water. W. Xia et al. [8] reported that a certain level of humidity appeared to be required for the reaction of lithium hydroxide (LiOH)

and  $\text{CO}_2$  to lithium carbonate ( $\text{Li}_2\text{CO}_3$ ). Dense pellets were exposed to rather dry (5% relative humidity) as well as to humid (80% relative humidity) air for six weeks. The specimens in humid air showed a reaction layer of 100  $\mu\text{m}$  while the samples in dry conditions exhibited almost no change. A. Sharafi et al. [9] also stressed the importance of the level of humidity. The group exposed  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  in air with 0.5 and 50% relative humidity, respectively, for durations of 0 to 240 h of exposure time. The reaction was much more pronounced with higher humidity. However, they also found by Raman spectroscopy indications for a reaction with low water partial pressure after long exposure time. W. Xia et al. [6] stored dense pellets in air for three months. Samples prepared in an alumina crucible had slightly increased lattice parameters during storage while samples prepared in a platinum crucible did not. Some reports describe preferred reaction close to grain boundaries [6,8], while reaction layers finally seem to extend over the entire surface [6,9].

The approach by means of extreme conditions is useful to identify general reactions of garnets. In contrast to the publications dealing with the reactions with excessive water, this paper focusses more on sample exposition conditions that are closer to a potential handling during processing or operation of solid-state battery cells, like preparing batteries under protective gas or in dry rooms, and operating as pouch cells where the housings may have very high but not perfect gas tightness. Therefore the specimens were stored in inert technical atmospheres with low content of oxygen and water, respectively, i.e. in argon-filled glove boxes with oxygen and water extraction units. Clear indications

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were found that conditions with water/air constituent concentrations in the order of magnitude of parts per million may suffice for a proton – lithium ion exchange in garnet  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$  (nominal composition). The analysis presented in this work is based on depth-resolved methods: nuclear reaction analysis, along with Rutherford backscattering, secondary ion mass spectrometry, and Raman microscopy. These techniques are particularly useful for analysis of lithium-containing compounds compared to methods using X-rays: energy/wavelength dispersive X-ray spectroscopy has a very low sensitivity to lithium due to the low atomic number of lithium which directly correlates with low signals. X-ray Photoelectron Spectroscopy (XPS) is limited with regard to the maximum beam penetration/information depth. A depth-resolved analysis can be performed by sputtering off a few nanometers near the surface after each XPS measurement; however different sputter yields in multi-component systems may make the interpretation more complicated. Secondary ion mass spectrometry has excellently low detection limits for lithium (and also many other elements) and outstanding resolution, however the measured intensities are rather difficult to convert into actual concentrations, and there are also artifacts possible, like so-called “matrix effects”, for example certain ions may be removed more easily by the analysis beam in one compound (“matrix”) while the same ions are less easily sputtered by the same beam out of a different compound where the ion is bound in a stronger manner. Therefore, as a complementary technique, nuclear reaction analysis was used to quantify the elements in the specimens. In nuclear reaction analysis, a particle beam (for example protons) hits the sample and causes scattering as well as nuclear reactions with the elements. As an example for  ${}^7\text{Li}$ , protons can be absorbed by the lithium core, which is then instable and quickly decays into  $\alpha$  particles of well-defined energy which can be easily detected. A significant advantage is that the energy ranges for reactions with different elements are well separated which allows an unambiguous assignment of the detected charges (equivalent to numbers of particles) and energies to distinct reactions and thus elements. The energy loss of the involved particles caused by different interaction processes with the surrounding solid in combination with the cross section of the investigated nuclear reaction also gives an information about the depth resolved elemental concentration.

Raman microscopy is based on photon-phonon interaction and thus provides information about (local) crystal structure. It is sensitive to changes in the chemical bondings and for instance allows measuring the distribution of tetragonal and cubic structures with a spatial resolution in the micrometer range.

## 2. Materials and methods

The nuclear reaction  ${}^7\text{Li}(p,\alpha){}^4\text{He}$  was used for  ${}^7\text{Li}$  detection. The penetration depth in matter is limited to a few micrometers: the protons have to go into the material and experience a continuous energy loss, react with lithium, and the  $\alpha$  particles of the decay process need to get out of the layer without losing all their kinetic energy by scattering processes inside of the specimen. This requires layer thicknesses in the order of micrometers. Coincidentally, the storage conditions in a glove box applied in this work lead to thicknesses of additional surface layers of less than 1  $\mu\text{m}$  thus allowing a detection of species from the surface layers as well as from the garnet layer underneath.

Secondary ion mass spectrometry (SIMS) has a typical material erosion rate in the order of magnitude of 1  $\mu\text{m}$  per hour, i.e., SIMS also takes advantage of multilayer set-ups in the range of a few micrometers.

Both techniques benefit from planar, smooth geometries with well-defined planar interfaces. Graded interfacial areas complicate the detection of additional interdiffusion due to signal mixing and artifacts caused by matrix effects in SIMS measurements. Nuclear reaction analysis has less spatial resolution, and planar, sharp interfaces help to distinguish between adjacent layers. Hence thin films of garnet were prepared by physical vapor deposition on planar substrates. The

technical details of the techniques are listed below.

### 2.1. Thin-film preparation of $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$

Thin-film coatings of nominally  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$  (LLZ) were made with a commercial high-vacuum physical vapor deposition (PVD) cluster system CS 800 ES (manufacturer: Von Ardenne Anlagentechnik, Dresden, Germany). Radio frequency (RF) magnetron sputtering was used for the preparation of the thin films. FeCrAlY metal alloy sheets (Aluchrom YHf®, material code EN 1.4767) were used as substrates. Details of the target preparation, deposition conditions and subsequent basic analysis of the films by X-ray diffraction for phase content and by inductively-coupled plasma optical emission spectrometry can be found in [10].

### 2.2. Sample storing conditions

The samples were stored in an argon-filled glove box MB 200 B (manufacturer MBraun, Germany), equipped with water and oxygen sensors and a gas purification system for the removal of oxygen and water. The leakage class was ISO 10648-2, class 1. Argon was taken from a liquid argon gas tank with a rated purity of 99.9999%. The glove box atmosphere contained in the order of magnitude of 1–10 ppm of oxygen and 0.1–1 ppm of water, according to the gas sensors. The pressure inside the glove box was set to 1–1.5 mbar above ambient pressure. The temperature was 20 °C (laboratory with air condition). The samples were in direct contact to this atmosphere, i.e. they were not specially sealed.

### 2.3. Secondary ion mass spectrometry (SIMS)

Time-of-flight (ToF) SIMS analyses were performed with a dual beam setting in non-interlaced mode in a TOF-SIMS IV system (ION-TOF GmbH, Münster, Germany). For the material erosion, a  $\text{Cs}^+$  ion beam was rasterized to produce a sputter crater of  $300 \times 300 \mu\text{m}^2$ . A focused 25 keV  $\text{Bi}_3^+$  ion beam was used for the generation of secondary ions for analysis. The analysed area was  $82 \times 82 \mu\text{m}^2$ . The data analysis was done with the Software package SurfaceLab 6.4 (ION-TOF GmbH, Münster, Germany). More experimental details were already published [11]. SIMS is a semi-quantitative analysis tool and allows a comparison between samples with similar matrices (i.e. composition) with high resolution. SIMS data of specimens with different matrices are rather difficult to compare since the quantitative extraction of secondary ions significantly depends on the properties of the specimens. Therefore, Nuclear reaction analysis was used as complementary technique which allows a quantitative assessment of the composition without the need of specific reference measurements for each chemical element.

### 2.4. Nuclear reaction analysis (NRA)

A 3 MeV proton beam with 3 mm in its diameter was generated by a tandetron accelerator. A 50 mm<sup>2</sup> passivated implanted planar silicon detector with 100  $\mu\text{m}$  sensitive thickness and 25 keV FWHM resolution was installed in backscattering geometry at 165° and at a distance of 100 mm. The proton current was set to ~20 nA. The collected charge was about 1 to 80  $\mu\text{C}$  for each measurement. Cross-section data from [12] were used for the  ${}^7\text{Li}(p,\alpha){}^4\text{He}$  reaction, sigmacalc [https://doi.org/10.1016/j.nimb.2015.09.035] for backscattering from 16O, 12C and Rutherford cross-sections for the remaining elements. The results were fitted using the SIMNRA 6.06 software [13]. During the measurement a vacuum pressure of  $10^{-7}$  mbar was maintained.

### 2.5. Raman spectroscopy

The measurements were carried out with a Renishaw inVia Qontor Raman microscope using a solid state 532 nm excitation Laser and an

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