Interface Instability of Fe-Stabilized Li₇La₃Zr₂O₁₂ versus Li Metal

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ABSTRACT: The interface stability versus Li represents a major challenge in the development of next-generation all-solid-state batteries (ASSB), which take advantage of the inherently safe ceramic electrolytes. Cubic Li₇La₃Zr₂O₁₂ garnets represent the most promising electrolytes for this technology. The high interfacial impedance versus Li is, however, still a bottleneck toward future devices. Herein, we studied the electrochemical performance of Fe³⁺-stabilized Li₇La₃Zr₂O₁₂ (LLZO:Fe) versus Li metal and found a very high total conductivity of 1.1 mS cm⁻¹ at room temperature but a very high area specific resistance of ~1 kΩ cm². After removing the Li metal electrode we observe a black surface coloration at the interface, which clearly indicates interfacial degradation. Raman- and nanosecond laser-induced breakdown spectroscopy reveals, thereafter, the formation of a 130 μm thick tetragonal LLZO interlayer and a significant deficiency of about 1−2 formula units toward the interface. This shows that cubic LLZO:Fe is not stable versus Li metal by forming a thick tetragonal LLZO interlayer causing high interfacial impedance.

INTRODUCTION

Lithium-oxide garnets based on Li₇La₃Zr₂O₁₂ (LLZO) show very high ionic conductivities coupled with Li⁺ transfer numbers approaching 1. Many studies report good electrochemical stabilities in a wide potential window and, thus, a sufficient chemical stability against Li metal. Such features would make LLZO exceptionally well suited to be used as the electrolyte in “Beyond Li-ion” battery concepts, such as Li/ sulfur, Li/air, and Li-flow batteries using a highly reactive Li-metal anode. In recent years, it has been recognized that interfacial electrochemical stability represents a major drawback hindering long-term operation of, e.g., all solid-state batteries (ASSB). Thus, identifying the origins of the underlying electrochemical limitations occurring at the LLZO/Li interface is of the utmost importance for development of durable systems with inherently safe ceramic electrolytes. Here we chose Fe-stabilized cubic LLZO as a model system to elaborate possible degradation processes at the electrolyte-electrode interface through a multitechnique approach that allowed us to visualize and identify degradation effects. Most importantly, by combining Raman spectroscopy and nanosecond laser-induced breakdown spectroscopy (ns LIBS) we discovered that a Li-deficient tetragonal LLZO interlayer formed at the LLZO/Li interface, which we consider to be responsible for the high interfacial resistance versus Li metal. LLZO occurs in at least three structural modifications: a tetragonal phase (space group (SG) I₄₁/acd), a conventional cubic garnet phase (SG Ia-3d), and the acentric cubic garnet like polymorph (SG I-43d). The Li-ion conductivities of the cubic polymorphs are 2 orders of magnitude higher (σ_total ≈ 10⁻³ to 10⁻⁴ S·cm⁻¹ at room temperature (RT)) compared to that of the tetragonal polymorph (σ_total ≈ 10⁻⁶ S·cm⁻¹ at RT), and the electrochemical properties of the acentric cubic modification seem to be better than the centric one.

The highly conducting polymorphs, however, are not stable at RT and have to be stabilized by replacing, e.g., some of the Li⁺ with low amounts of Al³⁺. Using a more repulsive cation, i.e., using Ga³⁺ instead of Al³⁺, the phase transformation from the centric SG Ia-3d to the acentric SG I-43d can be observed. Very recently, some of us have shown that the acentric cubic phase can also be obtained by substituting some of the Li⁺ with Fe³⁺.

Fortunately, both modifications provide the necessary Li-ion conductivity for a membrane used to manufacture a protected Li electrode (PLE). The total cell resistance is partially a function of the bulk and grain boundary resistance of the dense electrolyte layer as well as the electrode-electrolyte interface resistance. As already mentioned above, the present study is aimed at understanding the interfacial phenomenon taking places at the LLZO/Li interface. For this purpose we studied key electrochemical properties including the Li-ion conductivity...
and the area-specific resistance (ASR) of the promising solid electrolyte Li_{0.4}Fe_{0.2}La_{2}Zr_{2}O_{12} (LLZO:Fe).

## EXPERIMENTAL SECTION

LLZO:Fe was synthesized by high-temperature sintering. The starting materials were Li_{2}CO_{3} (99%, Merck), La_{2}O_{3} (99.99%, Aldrich), ZrO_{2} (99.0%, Aldrich), and Fe_{2}O_{3} (99.945%, Alfa Aesar). Carbonates and oxides were mixed in the necessary proportions, and they were intimately ground together using a hand mortar, a pestle, and isopropanol. This mixture was pressed uniaxially into a pellet and afterward calcined at 850 °C for 4 h with a heating rate of 5 °C/min and then cooled naturally in the furnace to approximately 200 °C. The sample was milled under addition of isopropyl alcohol in a Fritsch Pulverisette 7 ball mill for 2 h (12 times at 800 rpm for 5 min + 5 min break). Finally, the powder was uniaxially pressed (24 kbar) into pellets and sintered at 1230 °C for 6 h, with a heating rate of 20.5 °C/min; then the pellets were allowed to cool to RT.

X-ray powder diffraction (XRPD) measurements were performed using a Bruker AXS D8 diffractometer with Cu Kα radiation. This was done to characterize the synthetic products and to identify all phases present, as well as to determine the symmetry and unit-cell dimension of the garnet. Data were collected from 10° to 140° 2θ. The lattice parameter a_{0} was determined using an internal standard (Si) and by using Rietveld refinement with the program Topas V2.1 (Bruker AXS). The density of the pellets, measured by a pycnometer (Brand GmbH), is about 90% of theoretical.

Raman spectroscopic measurements were obtained using a Thermo DXR Raman microscope (Thermo Fisher Scientific, Madison, USA). The spectra were collected with laser excitation wavelength at 532 nm (2.33 eV) and laser power of 10 mW on the sample. The covered wavenumber range was 50 cm\(^{-1}\) to 1800 cm\(^{-1}\), with a spectral resolution of approximately 2 cm\(^{-1}\) using a 25 μm pinhole like entrance slit to the spectrometer. To provide chemical and structural information over a large area the Raman mapping option using the confocal microscope BX41 (Olympus Corp., Japan) equipped with a 10x microscope objective (NA = 0.25) was used. Altogether we received 1836 single Raman spectra. All measurements were performed with an exposure time of 40 s and 3 accumulations.

Scanning electron microscopy (SEM) analyses were carried out using a ZEISS Ultra Plus device. Small polycrystalline chips, taken from the larger pellets, were embedded in an epoxy holder, and the surface was ground and then polished using diamond paste. For the analysis, special attention was made with regard to extra phases, grain sizes, grain boundaries, and textures using a backscattered electron detector (BSE) and energy-dispersive X-ray spectroscopy (EDS).

Impedance spectra were recorded for a LiILLLZO:FeLi sample at RT in an Ar-filled glovebox. To prepare the sample, metallic lithium was first applied on the surfaces of the pellet, and then the pellet was sandwiched between two lithium foil disks in a Swagelok type cell. The impedance measurements were taken shortly after the LiILLLZO:Li cell was assembled.

Cyclic voltammetry (CV) was measured using the Lil LLLZO:FeAu configuration to assess the electrochemical stability window of the garnet. For this purpose, a Au blocking electrode was sputtered on one side of the garnet pellet, and the reversible Li electrode was applied on the other side. Ni foam was used as the current collector. The measurements were carried out under a protective atmosphere, i.e., inside an Ar-filled glovebox. The cell was scanned at a rate of 2 mV/min covering a potential range from −0.5 to 6 V vs Li/Li\(^{+}\).

Ns LIBS experiments were performed using a commercially available J200 ns LIBS setup (Applied Spectra, Inc, Fremont, CA) equipped with a 266 nm frequency quadrupled Nd:YAG laser and a six-channel Czerny-Turner type spectrometer covering a wavelength range from 185 to 1050 nm. Emission spectra were collected using a laser beam diameter of 40 μm at a laser output energy of 8.4 mJ under Ar atmosphere. The spectrometer was operated at a gate delay of 0.1 μs.

\(^{57}\)Fe Mössbauer spectra were recorded with a multichannel analyzer (1024 channels) operating in conjunction with an electromechanical drive system with symmetric triangular velocity shape. Afterward the two simultaneously obtained spectra (512 channels each) were folded for data processing. During the measurements, the source (\(^{57}\)Co/Rh 50 mCi) and the absorber were kept at RT. Isomer shift values are reported relative to the α-iron at RT.

## RESULTS AND DISCUSSION

The XRPD pattern of LLZO:Fe powder is shown in Figure 1 and exhibits reflections clearly showing cubic symmetry.

![Figure 1. XRPD pattern of Li_{0.4}Fe_{0.2}La_{2}Zr_{2}O_{12} with an internal Si standard (shaded with gray; a = 5.43088).](image)

A reasonable fit could be only achieved by using the cif file of our previous single-crystal diffraction study, confirming the presence of the acentric cubic LLZO modification with space group I-43d (see ref 5). There are no indications of any phases formed other than LLZO. The unit-cell parameter a_{0} was determined by Rietveld refinement using an internal standard (Si (shaded with gray in Figure 1); a = 5.43088). The a_{0} value was determined to be 12.9791(1) Å in agreement with values in the literature.\(^5\)

The RT impedance spectrum of LLZO is shown in Figure 2; it consists primarily of one semicircle. In the high frequency regime the onset of the bulk response can be seen. At lower frequencies the electrode response is present but only as a tiny feature. The latter is typical for Li electrodes but will not be considered further here.\(^8\) A serial combination of a resistance R_{0} and a resistance R_{int} in parallel to a constant phase element R_{int}−CPE_{int} element was used to parametrize the impedance data of LLZO:Fe; see the solid line in Figure 2. Based on our previous work R_{0} characterizes the bulk response and corresponds to σ_{bulk} of 1.1 mS cm\(^{-1}\).\(^9\) The capacitance of the semicircle can be determined via C_{int} = (R_{int}−nCPE_{int})\(^{1/σ}\), where n is a fitting value. The capacitance obtained was in the

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μF range which is a typical value characterizing charge transfer processes at interfaces; the intermediate arc is, therefore, attributed to the interfacial resistance. The corresponding area-specific resistance is given by ASR = R_{int}A/2. The resulting ASR of 1088 Ω cm² is significantly larger than those observed for the Al- and Ga-stabilized counterparts obtained by similar preparation routes.4 A cyclic voltammogram of the Li|LLZO:Fe|Au cell was recorded to check the electrochemical voltage stability window of LLZO:Fe (see Figure 3). We observe small reduction and oxidation peaks at low potentials because of the alloying reaction of Au and Li and the extraction of Li from the alloy. Other than this, there seems to be no redox process occurring below 6 V, indicating a wide stability window for the LLZO:Fe. The latter observation indicates that the Li ions could relatively easily pass through the garnet pellet without significant degradation at higher potentials.

The originally lightly colored pellets, however, turned black at the surface after contact with Li metal as is shown in Figure 4. This was not observed for similar synthesized Al- and Ga-stabilized LLZO. The interfacial impedance measurements were taken shortly after the Li|LLZO|Li cell was assembled.4 During this time, the black coloration region may be dynamically evolving and resulted in a possible mixed conduction black layer. We were not able to separate partial electronic and ionic conduction. The SEM-BSE pictures of cycled LLZO:Fe are shown in Figure 5a. They do not provide any evidence for phases other than LLZO; EDS mapping indicates a homogeneous distribution of all of the heavier elements present (Fe, La, and Zr). By zooming into the surface region (see Figure 5b), we observed a thin layer enriched in oxygen and carbon; interestingly, none of the initially introduced elements were observed. Hence, we conclude that this layer represents Li₂CO₃ formed by the reaction of LLZO or residues of lithium with CO₂ from air.

Since Raman spectroscopy can be used to study the phase composition within a sample we mapped exactly the same area as investigated by SEM. The optical magnification already revealed differences in brightness of the areas near the LLZO:Li surface as shown in Figure 6a. Investigating the optically differing areas by means of Raman spectroscopy clearly revealed that there were different phases present. In particular, the splitting of the first 2 bands at low wavenumbers (<200 cm⁻¹) indicates a decrease in symmetry from cubic (blue) to tetragonal (red) (see Figure 6b,c).10 The adjacent area (green square) seems to be a distorted spectrum of tetragonal LLZO. Most probably, the crystallinity of this area was degraded by a phase separation caused by contact with metallic Li. However, due to the distortion no phases other than tetragonal LLZO can be assigned.

The formation of tetragonal LLZO caused by the contact of cubic LLZO with Li metal was also recently observed by Park et al.11 They suggested that the formation of tetragonal LLZO leads to an increase of the interfacial resistance because of the lower ionic conductivity of tetragonal LLZO, which also serves as an obvious explanation for the high ASR observed here.

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Similar observations were made by Ma et al.; they suggested, however, that a thin tetragonal LLZO interlayer might help prevent interfacial reactions without compromising the Li-ion conductivity of the cell.\textsuperscript{12}

It has to be noted that Ma et al. detected only a very thin tetragonal LLZO interlayer of 6 nm. This is in stark contrast to our study; in the present case we observed the degradation from cubic to tetragonal LLZO over a distance of 130 $\mu$m (see below). A possible explanation might be a partial reduction of Fe$^{3+}$ to Fe$^{2+}$, making the material a mixed conductor producing an electronically conductive pathway so the LLZO can keep reacting to a much deeper depth. A total reduction to Fe$^0$ at the very top of the pellet could explain the observed decoloration by a short heat treatment as illustrated in Figure 4.

Figure 6. (a) Raman mapping of the Li$_{6.4}$Fe$_{0.2}$La$_3$Zr$_2$O$_{12}$; the picture shows a cross section after the solid electrolyte has been in contact with metallic lithium during cyclic voltammetry. (b) Representative spectra of the different areas of the cross section. (c) Magnification of the shaded area in (b) showing cubic and tetragonal LLZO. Color code: Cubic LLZO (blue), tetragonal LLZO (red), (distorted spectrum of) tetragonal LLZO (green), diamond (yellow), epoxy resin (orange).

Figure 7. (a) Area investigated by ns-LiBS. (b) Li mapping of the investigated area shown in (a). (c) Representative line scan of Li, Fe, Zr, and La.
The Raman spectrum of the black surface area only shows a single band (yellow, see Figure 6b) that represents diamond, which is segregated between the epoxy and the electrolyte during the polishing procedure. In summary, neither by SEM-EDS nor with the use of the BSE detector could we discern any inhomogeneities; however, the Raman spectroscopy clearly revealed significant differences in phase homogeneity. To qualitatively evaluate the compositional variation, ns LIBS was used. This is a powerful tool for investigating the spatial distribution of elements in LLZO garnets, as recently demonstrated by Hou et al. The chemical composition within the sample was investigated qualitatively by normalizing the signal intensities in the nondegraded area (orange) to the nominal composition (see Figure 7). The amounts of Fe and Zr remain almost constant, whereas a strong decrease of Li and La of about 30 mol % from the nominal composition within ∼300 μm of the surface was observed (see Figure 7c). This decrease in Li content seems to be accompanied by the formation of the tetragonal LLZO modification as discussed above (see also Figure 6). For tetragonal LLZO, however, a higher Li content (∼7 pfu LLZO) is expected.

We speculated that the formation of tetragonal LLZO is associated with the reduction of Fe3+ to the larger Fe2+ (or even metallic iron). Fe2+ is usually too large for tetrahedral sites in garnets and possibly causes a distortion or even a destabilization of the LLZO lattice. In order to evaluate this assumption, we utilized 57Fe Mössbauer spectroscopy due to its high sensitivity to local structural and electronic changes of Fe. The spectrum and fitting values after cycling are displayed in Figure 8 and Table 1. The Mössbauer spectrum after cycling is very similar to the spectra observed in our previous studies (see refs 5, 15, and 16) and is composed of 2 Mössbauer doublets which can be fitted using doublets with Lorentzian line shapes. On the basis of its isomer shift (δ) and quadrupole splitting (∆EQ), all doublets can be assigned to Fe3+ located in the tetrahedral 12a (blue) and 12b (red) site of the acentric cubic garnet framework (SG: I-43d).

There are no indications for Fe2+ (which would be expressed by a doublet with higher δ and larger quadrupole splitting) or Fe0 (which would be expressed by a sextet instead of a doublet). This could be, however, attributed to the large background possibly hiding small amounts of different iron species. This keeps the question about the cause of the thick tetragonal interlayer observed herein unanswered. Further studies are needed to investigate the tetragonal LLZO interlayer formation and to explain the associated decrease in the Li and La content.

CONCLUSION

Fe-stabilized LLZO was prepared via a solid-state synthesis route and characterized in terms of ion dynamics by impedance spectroscopy using a symmetrical Li cell. For Li6.4Fe0.2La3Zr2O12 we found a very high Li-ion bulk conductivity in the order of 1.1 mS cm−1 at ambient temperature. The area-specific resistance at the Li-electrolyte interface, however, turned out to be as high as 1000 Ω cm−2, which clearly has a negative impact on the application in all-solid-state batteries. Therefore, the origin of this large resistance needs to be clarified. Raman spectra and ns LIBS reveal the formation of a Li-deficient tetragonal LLZO interlayer at the Li electrolyte. The interlayer shows a thickness of 130 μm; the Li deficiency turned out to be 1–2 formula units. The thickness of the interlayer might be caused by an electronically conductive pathway produced by reduction of Fe3+ to Fe2+, making the material a mixed conductor, so the LLZO can keep reacting to a much deeper depth. We attribute the high interfacial impedance to the evolution of this interlayer.

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Notes
The authors declare no competing financial interest.

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