Mitigation of grain boundary resistance in $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ perovskite as an electrolyte for solid-state Li-ion batteries

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ABSTRACT

In this work, we report that modification of the chemical composition of grain boundaries of $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ double perovskite, one of the most promising Li-ion conducting solid electrolytes, can be a convenient and versatile way of controlling the space charge potential, leading to a mitigated electrical resistance of the grain boundaries. Two groups of additives are investigated: lithium-enriching agents (Li_3BO_3 , LiF) and 3d metal ions (Co^{2+} , Cu^{2+}), both expected to reduce the Schottky barrier. It is observed that Li-containing additives work effectively at a higher sintering temperature of 1250 °C. Regarding copper, it shows a much stronger positive impact at lower temperature, 1150 °C, while the addition of cobalt is always detrimental. Despite overall complex behavior, it is documented that the decreased space charge potential plays a more important role in the improvement of lithium conduction than the thickness of the grain boundaries. Among the proposed additives, modification of $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ by 2 mol.% Cu^{2+} results in the space charge potential reduction by 32 mV in relation to the reference sample, and the grain boundary specific conductivity increase by 80%, as measured at 30 °C. Introduced additive allows to obtain a similar effect on the conductivity as elevating the sintering temperature, which can facilitate manufacturing procedure.

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GRAPHIC ABSTRACT

Introduction

Due to a rapidly increasing number of electric vehicles and a growing share of renewable energy sources in the power generation mix, the development of effective and reliable electrochemical energy storage systems has become very urgent. Among commercial reversible batteries, the highest performance is achieved for lithium-ion cells; however, it is believed that regrettably the Li-ion technology is close to the physical limits, and increasing safety requirements are not fully met. Solid-state lithium batteries, i.e., with the solid-state electrolyte, are considered to be a promising alternative for the state-of-the-art Li-ion batteries, as they would mitigate issues related to the presence of liquid organic electrolytes: flammability, chemical instability and risk of leakage, as well as possible dendritic growth of lithium during charging. In recent years, various organic materials, as well as inorganic materials, have been studied as solid electrolytes for reversible lithium cells [1–4]. Among them, $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ (LLTO) exhibits one of the highest bulk lithium ion conductivity, exceeding $1 \cdot 10^{-3} \text{ S cm}^{-1}$ at room temperature (RT) [5–11]. Taking into account its low electronic conductivity [6, 12], simple synthesis and good sinterability

[5, 9, 13–15], as well as decent stability in air and at high redox potentials [13, 16], LLTO can be considered as a promising solid electrolyte material for solid-state lithium batteries.

LLTO is an A-site layered double perovskite with La-rich layers arranged alternately with Li-rich ones [12, 17]. As a consequence, such ordering results in a highly anisotropic, two-dimensional ionic transport [18]. Close investigations of the microstructure of polycrystalline sinters of LLTO revealed that besides grain boundaries, also high-angle domain boundaries present within crystallites exhibit reduced concentration of lithium [19–22]. Both features, 2D ionic transport and complex microstructure contribute to particularly low apparent grain boundary ionic conductivity ($\sigma_{\text{gb,ap}}$), about 10^{-7} – $10^{-6} \text{ S cm}^{-1}$ [23–26] at RT, which is several orders of magnitude lower than the bulk ionic conductivity. It should be noticed, however, that there is a fundamental difference between the apparent and the specific conductivity of the grain boundaries (σ_{gb}). While the former is calculated using outer dimensions of the sample, the latter requires the determination of the microscopic size of the grain boundary, which is usually difficult to define. In this work, we apply the Brick Layer Model (BLM) [27] to calculate true specific grain boundary conductivity based on the ratio of bulk and

grain boundary electrical capacitances measured using impedance spectroscopy technique (for details, see Supporting Information).

A few ways of enhancement of ionic conductivity in polycrystalline LLTO have been proposed. One of them is the coarsening of grains as a consequence of annealing, leading to a reduced fraction of boundaries in the sinter [15, 22]. It was reported that annealing of sinters of LLTO at temperatures between 1300 °C and 1400 °C caused a significant increase of the average size of domains and grains, resulting in enhanced apparent grain boundary conductivity, up to $3.55 \cdot 10^{-4} \text{ S cm}^{-1}$ at RT [5, 12, 15, 28–31]. Although this type of processing seems to give encouraging results, rising sintering temperature hampers technological applicability due to the increased costs and intensified lithium evaporation [5, 15], leading to difficulties in control of stoichiometry and lack of reproducibility.

Another proposed way to improve grain boundary conductivity is the alternation of its chemical composition. For example, Chen et al. [32] reported that introducing $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ precursor sol into LLTO powder, and subsequent sintering at 1350 °C, changed grain boundary composition in such a way that $\sigma_{\text{gb,ap}}$ raised from $0.63 \cdot 10^{-4} \text{ S cm}^{-1}$ to $1.5 \cdot 10^{-4} \text{ S cm}^{-1}$ at room temperature. Similarly as for high-temperature annealing, also here high-temperature heat treatment was required, which keeps technological limitations unresolved.

In fact, the issue of high resistance of grain boundaries is one of the major and ubiquitous concerns in the development of various solid electrolytes, e.g., $\text{Zr}_{1-x}\text{Y}_x\text{O}_2$ [33], $\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$ [33], $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_3$ [34], β -alumina [35, 36], NaSICONs [37–39], $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [40–42], which are important for numerous applications, such as fuel cells, batteries and electrolyzers.

According to a model developed by Guo and Maier for various ion-conducting oxides [27, 43], an electrostatic potential difference ($\Delta\phi$), so-called the Schottky barrier or the space charge potential, is formed between a grain interior and a boundary core. Such potential difference affects the distribution of ionic and electronic charge carriers across the grain boundaries, and therefore, disturbs electrical conductivity at the grain boundary area. Wu and Guo applied this model for the LLTO electrolyte [22, 44], and confirmed quantitatively that the lithium-ion depletion zone at the grain boundary region was the

actual reason of the high grain boundary resistance for Li^+ transport. They also reported that an increase of the specific grain boundary conductivity can be achieved by chemical substitution of Ti with higher valence Nb in the $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ crystal. The formed bulk Nb_{Ti} point defects, carrying a positive effective charge, allowed to decrease the Schottky barrier [44]. This can be interpreted as that more lithium is located at the grain boundaries. On the other hand, a similar effect can be obtained by the creation of point defects, e.g., M_{Ti}'' , having a negative effective charge and being located at the grain boundary zone (Fig. 1). Through Coulombic interactions, such defects are expected to draw more lithium to the grain boundary zone. Alternatively, this can be also achieved by a simple, chemical enrichment of the boundaries with lithium excessive layer.

Consequently, in this work, we propose that modification of the chemical composition of grain boundaries, without changing the composition of the grain bulk, can be a convenient and versatile way of controlling the space charge potential, leading to mitigated resistance of the grain boundaries. Two groups of additives for $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ were selected: one comprises lithium-enriching agents (Li_3BO_3 , LiF), aiming at a direct increase of concentration of lithium ions at the grain boundary region. The other one includes 3d metal ions (Co^{2+} , Cu^{2+}), affecting the Schottky barrier by the introduction of the charge lower than Ti^{4+} , which is expected to indirectly, through electrostatic interactions, to rise the Li^+ amount at the grain boundaries. Consequently, through such a modification, space charge potential is expected to be lowered. Besides this, the effect of the additives on sinterability and densification of the studied materials was investigated. It was documented that smaller space charge potential plays a more important role than the thickness of the grain

Figure 1 Schematic representation of the coulombic interaction of negative point defects at the grain boundary zone with lithium ion charge carriers from LLTO.

boundaries. To the best of our knowledge, such studies are original and novel and the reported findings have not been published before. The results can be also regarded as having a broader impact, and be utilized in various solid electrolyte systems.

Materials and methods

$\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ perovskite was synthesized in a solid-state reaction between La_2O_3 (99.9%, Sigma Aldrich), TiO_2 (anatase, 99.9%, Alfa Aesar), Li_2CO_3 (99%, Acros Organics). La_2O_3 before weighting was dried at 1000 °C for 12 h in a flow of dry synthetic air. All reactants were weighted in stoichiometric ratio and homogenized in a SPEX Sample Prep 8000 M high energy ball mill for 30 min in the 2-propanol medium. Homogenized reactants were pelletized to form 13 mm disk-shaped pellets and calcined at 1000 °C in dry synthetic air for 12 h. Then, calcined powders were ball-milled and uniaxially pressed under 150 MPa. Final synthesis and sintering were carried out at 1150 °C in dry synthetic air for 12 h. After sintering, LLTO disks were milled again to obtain fine LLTO powder. The distribution of particle size in the powder was measured with a Malvern Master-sizer 3000 particle size analyzer.

Such obtained LLTO powder was mixed with Li_3BO_3 , LiF , $\text{Co}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ additives in the amount of 2 mol.% in an agate mortar in methanol medium to form a homogenous paste. It is assumed that during heat treatment in the air in the subsequent steps the introduced nitrates decompose into corresponding oxides. Li_3BO_3 was synthesized in a solid-state reaction between Li_2CO_3 and B_2O_3 (anhydrous, 99.9%, Sigma Aldrich) at 600 °C for 10 h in synthetic airflow, according to the procedure described by Ohta et al. [40], while other additives were applied as purchased: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Sigma Aldrich), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%, Sigma Aldrich), LiF

(99%, Sigma Aldrich). After drying the paste at 70 °C, the obtained powder was formed into pellets, with the addition of 1 wt% of polyvinyl alcohol (Sigma Aldrich) to improve their strength. Then, the pellets were finally sintered at 1150 °C or 1250 °C for 12 h. The investigated samples were named according to Table 1.

Surface and cross-section microstructure was investigated using a scanning electron microscope FEI Nova Nano SEM 200 equipped with EDAX EDX elemental analyzer. Samples for surface analysis were polished on a fine sandpaper and thermally etched (1100 °C for 3 h in synthetic air), while pellets for cross-section investigations were immersed in epoxy resin, rubbed down with sandpaper, and polished using a diamond suspension.

Shrinkage curves during sintering were measured using Linseis L75HS 1600 horizontal dilatometer with a constant 5 °C/min heating/cooling rate. The phase composition and unit cell parameters were examined by X-ray diffraction (XRD) method using CuK_α radiation and a Panalytical Empyrean diffractometer equipped with a Pixcell 3D detector. Phase analysis of the XRD patterns was performed according to PDF-4 2018 database, and crystal lattice parameters were determined using the Rietveld refinement method as implemented in the GSAS/EXPGUI software.

Apparent density of the sintered pellets was measured using the hydrostatic method in a propanol environment according to PN/EN 1936:2001. The ionic conductivity of the sinters was investigated using the impedance spectroscopy technique. Prior to measurement, opposite surfaces of disk samples were covered with Au paste (ESL type 8844-G) and heated at 800 °C for 15 min to form well-defined continuous electrodes. Temperature dependence of the electrical conductivity of the samples was measured using a Solartron 1260 frequency response analyzer and a Probostat sample holder. Impedance spectra were

Table 1 $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples investigated in this work

Composition	Name of the sample	
	Sintering: 1150 °C	Sintering: 1200 °C
$\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$	Ref_L	Ref_H
$\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 + 2 \text{ mol.}\% \text{ Li}_3\text{BO}_3$	LBO_L	LBO_H
$\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 + 2 \text{ mol.}\% \text{ LiF}$	LF_L	LF_H
$\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 + 2 \text{ mol.}\% \text{ Co}(\text{NO}_3)_2$	Co_L	Co_H
$\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 + 2 \text{ mol.}\% \text{ Cu}(\text{NO}_3)_2$	Cu_L	Cu_H

recorded in a 1 MHz—1 Hz frequency range with sinusoidal excitation voltage of 0.1 V amplitude (r.m.s.), every 10 °C in 30–100 °C temperature range, in a dry air atmosphere. The frequency response was modeled using leastsquares fitting protocol as implemented in ZView2 software from Scribner Associates.

Analysis

Apparent macroscopic electrical conductivity of bulk- or grain boundaries in a polycrystalline sample is defined in Eq. 1:

$$\sigma_{\text{ap}} = \frac{1}{R} \cdot \frac{L}{A} \quad (1)$$

where R is the electrical resistance for bulk or grain boundary, L is the distance between electrodes and A is their surface area.

Application of the BLM model [27] allows to determine the true specific grain boundary conductivity σ_{gb} , assuming that the effective thickness of a grain boundary δ_{gb} is related to its electrical capacitance according to Eq. 2.

$$\delta_{\text{gb}} = \frac{C_{\text{bulk}}}{C_{\text{gb}}} d \quad (2)$$

where C_{bulk} and C_{gb} represent capacitance of grains and grain boundaries and d stands for average grain size, e.g., determined from electron microscopy images. As a constant phase element (CPE, impedance defined in Eq. 3) was used in the equivalent circuit applied to model impedance spectra the electrical capacitance, C , is estimated according to Eq. 4.

$$Z_{\text{CPE}} = \frac{1}{Q(i\omega)^n} \quad (3)$$

where: Z_{CPE} —impedance of a Constant Phase Element, Q , n —parameters of the CPE, i —imaginary unit, ω —angular frequency of the AC signal.

$$C = (R^{1-n}Q)^{1/n} \quad (4)$$

Consequently, true specific grain boundary conductivity was calculated according to Eq. 5.

$$\sigma_{\text{gb}} = \sigma_{\text{gb,ap}} \frac{\delta_{\text{gb}}}{d} \quad (5)$$

where

$$\sigma_{\text{gb,ap}} = \frac{1}{R_{\text{gb}}} \cdot \frac{L}{A} \quad (6)$$

Once true specific conductivity for bulk and grain boundaries are known space charge potential (Schottky barrier) $\Delta\phi$ can be calculated from Eq. 7 [43].

$$\frac{\sigma_{\text{bulk}}}{\sigma_{\text{gb}}} = \frac{e^{\frac{z \cdot e \cdot \Delta\phi}{T \cdot k_B}}}{\frac{2 \cdot z \cdot e \cdot \Delta\phi}{T \cdot k_B}} \quad (7)$$

where e , k_B , z and T are the elementary electrical charge, Boltzmann constant, effective charge of the charge carriers and temperature in Kelvin scale.

Results

X-ray diffraction patterns (Fig. 2) revealed predominant tetragonal perovskite (P4/mmm) phase for all of the synthesized samples sintered both at 1150 °C and 1250 °C. For the reference LLTO samples sintered without additives all the diffraction peaks could be indexed with the perovskite crystal structure suggesting a single phase composition. On the other hand, for samples containing additives, new low-intensity peaks appeared, which were ascribed to secondary crystalline phases precipitated from the host material. Identified compounds, as well as their weight and molar fractions taken from Rietveld refinement, were gathered in Table 2.

To corroborate or refute the formation of solid solutions, unit cell parameters for the LLTO phase were calculated using Rietveld refinement of the XRD patterns for sample sintered with additives and compared with the unmodified reference samples. The obtained values were gathered in Table 3. The reference sample sintered at 1150 °C exhibited $a = 3.8729 \text{ \AA}$ and $c = 7.7504 \text{ \AA}$. These values remain in good agreement with previously reported data for $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ perovskite with x equal to 0.11 [11], confirming the formation of the intended compound and indicating low lithium loss during sintering [45]. With sintering temperature increased to 1250 °C unit cell volume moderately expanded (+ 0.09%), suggesting slightly higher lithium evaporation.

Along with the effect that additives may have on transport properties of grain boundaries, also their effect on sintering should be considered. One of the key concerns, over the fabrication of LLTO

Figure 2 X-ray diffraction patterns of $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with 2 mol.% additives sintered at 1150 and 1250 °C.

Table 2 Phase composition of $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with 2 mol.% additives sintered at 1150 °C and 1250 °C. Numbers in brackets denote uncertainty expressed in terms of the least significant digit

Sample name	Composition of precipitate	Amount of precipitates (wt%)	Amount of precipitates (mol.%)	R_p (%)	R_{wp} (%)
Sintering temperature 1150 °C					
Ref_L	—	—	—	4.4	6.4
LBO_L	—	—	—	4.2	6.2
LF_L	$\text{La}_2\text{Li}_2\text{Ti}_3\text{O}_{10}$	1.4(5)	0.4(2)	3.9	5.8
Co_L	$\text{LiCo}_{0.5}\text{Ti}_{1.5}\text{O}_4$	1.9(5)	1.9(5)	4.0	5.7
Cu_L	$\text{La}_2\text{Ti}_2\text{O}_7$	2.2(5)	0.8(2)	4.3	6.6
Sintering temperature 1250 °C					
Ref_H	—	—	—	4.3	5.3
LBO_H	—	—	—	4.4	6.4
LF_H	—	—	—	4.1	6.2
Co_H	$\text{LiCo}_{0.5}\text{Ti}_{1.5}\text{O}_4$	2.4(5)	2.4(5)	4.0	5.8
Cu_H	$\text{La}_2\text{Ti}_2\text{O}_7$	0.9(5)	0.3(2)	4.1	5.7

Table 3 Unit cell parameters for the main tetragonal phase of $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples sintered at 1150 °C and 1250 °C with 2 mol.% additives. Numbers in brackets denote uncertainty expressed in terms of the least significant digit

Sample name	a (Å)	c/2 (Å)	V (Å ³)
Sintering temperature 1150 °C			
Ref_L	3.8729(2)	3.8752(4)	116.248(2)
LBO_L	3.8747(1)	3.8731(2)	116.292(1)
	+ 0.05%	− 0.05%	+ 0.04%
LF_L	3.872(2)	3.8752(4)	116.194(2)
	− 0.02%	0%	− 0.05%
Co_L	3.8754(2)	3.8784(4)	116.469(2)
	+ 0.06%	+ 0.08%	+ 0.19%
Cu_L	3.8775(1)	3.8756(1)	116.541(1)
	+ 0.12%	+ 0.01%	+ 0.25%
Sintering temperature 1250 °C			
Ref_H	3.8753(3)	3.8738(6)	116.349(2)
LBO_H	3.8727(1)	3.8758(2)	116.256(1)
	− 0.07%	+ 0.05%	− 0.08%
LF_H	3.8723(1)	3.8755(2)	116.286(1)
	− 0.08%	+ 0.04%	− 0.05%
Co_H	3.8735(4)	3.8822(3)	116.5(3)
	− 0.05%	+ 0.22%	+ 0.13%
Cu_H	3.8759(1)	3.8796(1)	116.565(1)
	+ 0.02%	+ 0.15%	+ 0.18%

Figure 3 **a** Shrinkage and **b** shrinkage rate as a function of temperature for sintering of $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with and without additives.

electrolytes is lowering the sintering temperature. It was previously reported that high relative density and low porosity LLTO sinters can be fabricated via a sintering above 1300 °C [7, 8, 10, 12, 32]. In this work, however, we demonstrate that certain modifications of chemical composition can improve sinterability even at lower temperatures. In order to evaluate the effect of introduced additives on the sintering of LLTO powder, a dilatometric technique was applied. Relative shrinkage and shrinkage rate for the investigated samples as a function of temperature are presented in Fig. 3a, b. For the reference sample, a sintering curve with a single main shrinkage step was observed with an onset point at ca. 1165 °C and maximum sintering rate of $1.17\% \text{ min}^{-1}$ at 1230 °C. On the other hand, when LLTO powder was blended with the additives, the process of sintering can be markedly affected, and sintering temperature can be lowered. All temperatures for sintering onset and of maximum sintering rate were shown as an inset in Fig. 3. Above all, for the LBO sample, sintering onset was considerably reduced to 935 °C, while for other additives, sintering onset was between 1100 °C and 1140 °C. This can be connected with a low melting point of the additive (ca. 700 °C) and its glass forming ability. The addition of LiF, also having a low melting temperature of 850 °C, allows to decrease the onset temperature of sintering only by 50 °C, as compared with the reference sample. These observations were not investigated further as they were outside the main scope of this article; however, a tentative explanation of the observed difference between both liquid-phase forming additives can be related to the fact that they demonstrate different wettability of the LLTO grains. Similarly, relatively small effect on sintering of LLTO as for LiF was observed for Co^{2+}

and Cu^{2+} containing additives. It is worth noting that with decreased sintering onset temperature sintering rate also decreased, probably due to a lower rate of mass transfer. Therefore, sintering with additives probably would require longer sintering times.

Figure 4 gathers scanning electron microscopy images presenting cross-sections of LLTO samples sintered with and without additives for 12 h at 1150 °C and 1250 °C. Exemplary images of surface microstructure of the reference, as well as the Cu_H sample, were presented in Fig. S1. Numerical average grain diameter along with the relative density of the sinters is gathered in Table 4.

The reference sample sintered at 1150 °C possessed well-developed grains with an average diameter close to 2.7 μm. In this case, a relatively large amount of porosity could be observed, which is consistent with a moderate relative density of about 83%. When sintering temperature was increased to 1250 °C, grains became larger (3.3 μm) and relative density reached 94%. Such high relative density led to negligible open porosity, as visible in SEM images. Among examined additives, Li_3BO_3 , Co and Cu turned out to provide improved density after sintering at 1150 °C. The biggest improvement was observed for Co, where relative density was raised to 87% with unchanged sintering time. On the contrary, the introduction of LiF to LLTO electrolyte inhibited sintering at 1150 °C. When sintering temperature was elevated to 1250 °C, the effect of the additives became less visible, and regardless of the composition relative density was close to 94%. It is worth noting that the average grain size in the obtained sinters is relatively low and close to each other, as compared to other reports concerning LLTO [46, 47]. Furthermore, some cracks appeared at the surface of the Cu-

Figure 4 Scanning electron micrographs showing $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ cross-sections for samples with and without additives, sintered at 1150 °C (L) and 1250 °C (H).

Table 4 Numerical average grain diameter and relative density for $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with 2 mol.% additives sintered for 12 h at 1150 °C and 1250 °C. Error in average grain diameter can be roughly estimated as $\pm 30\%$ while for relative density as $\pm 1\%$. Numbers in brackets denote uncertainty expressed in terms of the least significant digit

Sample name	Average grain diameter d (μm)	Relative density (%)
Sintering temperature 1150 °C		
Ref_L	2.7(6)	83(1)
LBO_L	3(1)	86(1)
LF_L	2.5(7)	80(1)
Co_L	3(1)	87(1)
Cu_L	2.4(5)	85(1)
Sintering temperature 1250 °C		
Ref_H	3(2)	94(1)
LBO_H	3.4(9)	92(1)
LF_H	4(1)	94(1)
Co_H	2.6(7)	95(1)
Cu_H	2.9(9)	94(1)

Figure 5 EDX analysis of chemical composition across a grain boundary in the Cu_H sample.

modified sample (Fig. S2) sintered at 1250 °C, pointing to the build-up of stress, when this additive is used.

EDX analysis of chemical composition revealed considerable enrichment of grain boundary zone in copper for both, Cu_L and Cu_H samples. A line scan across a grain boundary of the Cu_H sample is presented in Fig. 5, whereas point spectra for Cu_L at several locations on the cross-section are shown in Fig. S2.

The concentration of copper in the grain boundaries reached 4.4 wt% (3.5 at.%) for Cu_L and 8.3 wt% (6.5 at.%) for Cu_H samples, whereas inside the grains it was below a limit of detection. These results indicate that the desired enrichment of the grain boundaries in copper was indeed achieved. However, ca. two times higher concentration of Cu at the grain boundaries of the Cu_H sample can be regarded as indicating increased aggregation of the modifier as a result of higher sintering temperature.

This was also further confirmed as a relative number of the enriched places was lower in the Cu_H sample, despite the same used amount of the additive. Moreover, it was detected that some of the grain boundaries remained in their pristine state (see Fig. S2, point 1). Probably this is because the additives were introduced only to the outer surface of the powder particles, exposed during the impregnation step, while other grain boundaries, located inside the aggregate parties, remained unaffected. For all other samples, EDX spectra did not allow to unambiguously identify regions with enhanced levels of the introduced elements, neither as separate grains, nor as the continuous phase at grain boundaries. Nevertheless, the lack of any detectable regions enriched with Co (for Co_L and Co_H samples) suggests that cobalt rather is introduced as a bulk defect, likely taking place of titanium. This can be additionally supported by more similar radii of Ti^{4+} and Co^{2+} (in relation to Cu^{2+}). For LBO and LF additives, EDX studies were inconclusive, due to low atomic numbers of lithium and boron, and small separation of the fluorine spectral line from the oxygen line which makes them difficult to analyze quantitatively.

When introducing 3d metal ions into the oxide matrix of a solid electrolyte, concerns often arise about the level of electronic component conductivity. In order to evaluate the effect of the introduced additives on ionic transference number, DC polarization measurements on sintered LLTO samples with Au electrodes were carried out. The obtained polarization curves are presented in Supplementary Information Fig. S3 and calculated ionic transference numbers are gathered in Table S1. Except for the Co_L sample, the ionic transference number did not

drop below 0.98–0.99, indicating that the additive in the applied amount did not disturb the dominating ionic character of the electrical conductivity. Even for LLTO modified with Co (likely forming bulk defects), the ionic transference number remained above 0.9, pointing to the dominant ionic component of the charge transport.

Now, let us move to the main topic of this article, which is the evaluation of the true specific grain boundary conductivity and space charge potential of LLTO doped with Li_3BO_3 , LiF, as well as Co^{2+} and Cu^{2+} ions. A technique allowing for insight into electrical properties of grain bulk and grain boundaries is impedance spectroscopy. Figure 6a, b shows Nyquist plots for the LLTO samples with additives. The observed spectra consisted of two semicircles located at high and medium frequency range, above 300 kHz and between 300 kHz and 100 Hz, respectively, and a linear part below 100 Hz. According to the standard interpretation of the impedance spectrum of polycrystalline solid electrolyte [48], the high-frequency semicircle is associated with the bulk ionic conductivity, while the medium frequency one originates from the grain boundary region; the linear part is related to the electrical response from the Au electrode. The spectra were modeled with the equivalent circuit used by Chen et al. [32] (Fig. 6c), where R1 and CPE1 describe bulk, R2 and CPE2 grain boundary, and CPE3 the electrode response. Next, corresponding specific bulk and specific grain boundary conductivities were calculated according to Eqs. 1–4, average grain sizes were determined from

the SEM images as presented in Table 4. The obtained values of bulk and grain boundary specific conductivities for all the samples measured at 30 °C were gathered in Fig. 7.

Bulk ionic conductivity at 30 °C in the reference samples sintered without additives at 1150 °C and 1250 °C was determined to be 0.57 mS cm^{-1} and 1.1 mS cm^{-1} respectively, and the values are among the highest reported in the literature [8, 12, 32, 48]. In order to gain deeper insight into the observed changes in ionic conductivity of the LLTO samples, the activation energy of bulk and specific grain boundary components was calculated from their dependences on temperature. Corresponding Arrhenius plots are gathered in Supplementary Information Figs. S4 and S5, and the calculated activation energy values are presented in Table 5.

Discussion

As can be seen in Table 2, a small amount of precipitate was observed in the modified samples. However, as refined by the Rietveld method, the respective quantities of the secondary phases were considerably lower than the equivalent amount of the introduced additives. This indicates that the modifiers existed also beside the crystalline precipitates, forming either the desired enriched grain boundary zones, or (unwanted) solid solution with the LLTO perovskite. Furthermore, the obtained results showed that the higher sintering temperature generally

Figure 6 Nyquist plots of impedance spectra of $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with 2 mol.% additives sintered at **a** 1150 °C and **b** 1250 °C. Inset graphs present medium frequency regions corresponding to the grain boundary response. **c** Equivalent circuit modeling frequency response.

Figure 7 **a** Bulk and **b** specific grain boundary conductivity measured at 30 °C for $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with 2 mol.% additives sintered 1150 °C and 1250 °C.

Table 5 Activation energy of Li^+ ion conductivity in bulk and in grain boundaries as function of additive and temperature. Numbers in brackets denote uncertainty expressed in terms of the least significant digit

Sample name	$E_{a \text{ bulk}}$ (eV)	$E_{a \text{ gb}}$ (eV)
Sintering temperature 1150 °C		
Ref_L	0.32(1)	0.43(1)
LBO_L	0.33(1)	0.41(1)
LF_L	0.33(1)	0.39(1)
Co_L	0.34(1)	0.39(1)
Cu_L	0.34(1)	0.38(1)
Sintering temperature 1250 °C		
Ref_H	0.33(1)	0.39(1)
LBO_H	0.33(1)	0.33(1)
LF_H	0.32(1)	0.38(1)
Co_H	0.32(1)	0.53(1)
Cu_H	0.33(1)	0.45(1)

avored a lower amount of the precipitated phases, plausibly indicating enhanced dissolving of the additives in the host LLTO crystallites as sintering temperature raised to 1250 °C. Two main trends could be observed for the samples sintered with additives. Firstly, when lithium-containing compounds were introduced, nearly zero changes of the unit cell volume took place versus the reference, which indicates that these additives prevent lithium

loss and provide desirable simultaneous enrichment in lithium at grain boundaries. Secondly, samples containing Co^{2+} and Cu^{2+} additives exhibited a much more pronounced tendency of expansion of the unit cell volume. As no enrichment of grain boundary zone with Co was detected, for this material it could be explained by a partial substitution of Ti^{4+} with larger Co^{2+} cations. As a consequence of the electroneutrality condition, such bulk defects are expected to lead to an effective depletion of the grain boundaries with lithium, due to a reversed effect in relation to the one depicted in Fig. 1 i.e., formation of Co_{Ti}'' and an equivalent number of Li_i' point defects in the grain bulk. This is expected not to be beneficial in terms of ionic transport at the grain boundary region.

In the case of the Cu-modified sample, lattice expansion can be regarded as being a result of the depletion of bulk LLTO with lithium ions. Here, grain boundaries were pronouncedly enriched with copper, as confirmed by SEM/EDX analysis (Figs. 5 and S2), which requires displacement of lithium ions from grain interior, in order to maintain electroneutrality. The existence of Cu_{Ti}'' and in consequence, an equivalent number of Li_i' point defects at the grain boundaries, should help to mitigate the blocking effect at the grain boundaries, as more lithium is located in this area (cf. Fig. 1).

Bulk lithium-ion conductivity

As for bulk ionic conductivity, it is important to emphasize that increased sintering temperature significantly improved the conduction, and what is remarkable, this effect could not be explained solely by the reduced porosity of the ceramic polycrystalline sinter. Further discussion in this work contributes to a better understanding of this observation. For samples sintered with additives at 1150 °C, bulk ionic conductivity remained virtually unaffected by the addition of Li_3BO_3 , LiF and Co^{2+} ions, whereas Cu^{2+} caused its degradation to 0.33 mS cm^{-1} . Such effect can be explained by lowered bulk lithium concentration inside grains of Cu-modified LLTO (as was explained before on a basis of electrostatic interactions of the defects). When sintering temperature increased to 1250 °C, Co^{2+} and Cu^{2+} additives diminished bulk conductivity in relation to the reference sample, whereas Li_3BO_3 and LiF additive resulted in unchanged bulk conductivity. Comparing to the lower sintering temperature, only Co-modified material shows different behavior, which is likely due to an increased amount of $\text{LiCo}_{0.5}\text{Ti}_{1.5}\text{O}_4$ precipitate, also depleting bulk with lithium.

Grain boundary lithium-ion conductivity

Similarly, as in the case of bulk, increased sintering temperature improved also LLTO reference sample specific grain boundary conductivity, more than doubling its value from $1.2 \cdot 10^{-8} \text{ S cm}^{-1}$ to $3.1 \cdot 10^{-8} \text{ S cm}^{-1}$. To put the observed effects into a proper perspective, some of the studied additives

Figure 8 Grain boundary specific conductivity measured at 30 °C as a function of grain boundary thickness for $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with 2 mol.% additives sintered 1150 °C and 1250 °C.

introduced into LLTO sintered at 1150 °C allowed to obtain similar effect as elevating the sintering temperature (to 1250 °C), with the highest improvement in the grain boundary conductivity with the addition of Cu^{2+} and LiF , allowing to reach $2.1 \cdot 10^{-8} \text{ S cm}^{-1}$ and $1.7 \cdot 10^{-8} \text{ S cm}^{-1}$, respectively.

Another important issue is possible dependence or its lack of the specific grain boundary conductivity on the thickness of the grain boundaries (δ_{gb}). Fig. 8 shows the considered relationship calculated according to Eq. 2.

What could be noticed is that the temperature of sintering is a factor considerably affecting grain boundary thickness: δ_{gb} is around 15–35 nm for samples sintered at 1150 °C and around 10–15 nm for samples sintered at 1250 °C. Li_3BO_3 is the additive which reduces the grain boundary thickness, most notably at the lower sintering temperatures, whereas all the other investigated additives resulted in increased δ_{gb} . Remarkably, Cu_L sample possessed the highest specific grain boundary conductivity among all the samples sintered at 1150 °C, despite the thickest grain boundaries (ca. 20 nm). It seems that except for these observations, no further dependences could be deduced from this plot, which suggests that there should be another factor more strongly influencing specific grain boundary conductivity.

As previously discussed factors, such as the presence of the precipitated phases, changes of the unit cell parameters, porosity and grain size, could not

Figure 9 Grain boundary specific conductivity measured at 30 °C as a function of space charge potential for $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3$ samples with 2 mol.% additives sintered 1150 °C and 1250 °C. The dashed lines present relation between σ_{gb} and $\Delta\phi$ calculated directly from Eq. 7 for σ_{bulk} conductivity averaged for samples sintered at 1150 °C (dash line) and 1250 °C (dash-dot line).

convincingly explain the observed effect of additives on the electrical properties of grain boundaries, we kept looking for more suitable factors. Among them, the space charge potential proposed by Wu and Guo [22, 44] appears to be one of the key factors governing the concentration of lithium ion and therefore conductivity across the grain boundary region (cf. Eq. 7). Fig. 9 depicts the dependence of the grain boundary specific conductivity on the space charge potential for LLTO samples sintered with 2 mol.% additives at 1150 °C and 1250 °C.

The resulting dependence approximately follows the formula given in Eq. 7, as denoted by the dashed lines in Fig. 9, with samples having lower space charge potential exhibiting higher grain boundary specific conductivity for both sintering temperatures. Deviation from the theoretical behavior can be related to varying microstructure of the samples and other uncontrolled factors. At lower sintering temperature, the Cu and LiF modified samples exhibited lower space charge potential in comparison with the reference sample. As initially assumed, it indeed allowed to enhance Li^+ conduction at grain boundaries (higher values of specific conductivity). In the case of the Cu_L material, the microscopic nature of this effect can be linked to the presence of Cu_{Ti}'' substitution at the grain boundaries. According to the model described in the introduction, such modification leads to the raised lithium concentration at the grain boundaries. Nature of interactions of LiF with the grain boundaries could not be unequivocally explained, as its concentration in the grain boundaries was not confirmed by elemental analysis, however, possibly even a low concentration of Li^+ and F^- ions at the grain boundaries was sufficient to prevent lithium evaporation during sintering, and provide a reduction of the space charge potential. On the other hand, the presence of lithium and cobalt-containing secondary phase in the Co_L sample (Table 2) and simultaneous partial existence of Co_{Ti}'' defects in the bulk of LLTO crystallites remains in accordance with depleted grain boundaries in lithium. This results in raised Schottky potential and, as a consequence, decreased lithium ion conductivity. The unfavorable effect of LBO additive for the sample obtained at lower temperature likely stems from a presence of some amount of amorphous phase, not detectable on XRD (boron oxide is known as a glass-forming agent). Also, only in this case, the sintering

curve (Fig. 3) indicated liquid phase-assisted sintering.

For the reference sample, increased sintering temperature led to decreased space charge potential, showing the beneficial effect at higher temperature. This can be explained by the increased grain size, similarly as it was observed by Wu and Guo [44]. On the contrary to the Cu-addition at 1150 °C, sintering of the Cu_H sample at 1250 °C did not allow to achieve enhancement of the σ_{gb} (Fig. 9). This can be explained by the discussed aggregation of Cu-containing precipitates, as evidenced in the EDX analysis, not fulfilling their role as initially expected. The other 3d-metal (cobalt) behaves the same at 1250 °C as at the lower sintering temperature. While the addition of LBO at higher temperatures did not allow to enhance grain boundary conductivity, LiF seems to be the only one effective modifier, likely due to its role as a lithium loss preventing agent.

Overall it can be stated that for enhancement of transport properties of LLTO, selection of the proper additives and the optimal (as low as possible) sintering temperature is crucial. Modification of the Schottky barrier is possible, but it is very sensitive to the conditions of the preparation route. Comparing Figs. 8 and 9, it can be stated that smaller $\Delta\phi$ is highly preferable, while the thickness of the grain boundaries plays a secondary role.

Noticeably, for all investigated samples, the activation energy for bulk conductivity remained approximately constant, irrespectively of sintering temperature and the additive, at a level of 0.33 ± 0.1 eV. This value is in good agreement with previous reports [22], and suggests that the additives hardly affected bulk migration enthalpy. Interestingly, for the modified samples, the activation energy value is not dependent directly on the sintering temperature, but it is lower for the material which shows lower $\Delta\phi$ (Table 5). This corresponds with the easier mobility of lithium ions crossing the grain boundary area if the Schottky barrier is decreased.

Conclusions

In this work, we discussed factors influencing grain boundary contribution to ionic conductivity in modified $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ lithium conducting solid electrolytes. It was shown that among multiple parameters, which have to be taken into account to

achieve low grain boundary resistance, sintering temperature and modification of chemical composition plays a crucial role. A series of lithium- and 3d-metal-containing additives were investigated revealing that the most important mechanism linking the grain boundary ionic conductivity and properties of the additive is a modification of the Schottky potential at the grain boundaries. However, to obtain the desired effect for the particular additive, the sintering temperature must be optimized. Among the investigated additives, 2 mol.% Cu²⁺ for LLTO sintered at 1150 °C resulted in the space charge potential reduced by 32 mV in relation to the reference sample. As a result, the material showed grain boundary specific conductivity increased by 80%. It should be highlighted that for the optimized modifications, it is possible to obtain similar effects as elevating sintering temperature, which can be highly beneficial from the practical point of view.

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Compliance with ethical standards

Conflicts of interest There are no conflicts of interest to declare.

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