

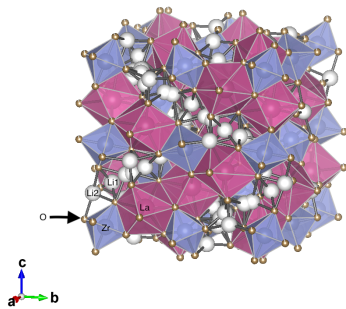
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LLZO as a Solid Electrolyte for Next Generation Batteries and their Potential Application in Electrical Vehicles

Bachelor's thesis in BKJ
Supervisor: Weicheng Hua
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DEPARTMENT OF CHEMISTRY

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Abstract

Solid state batteries are considered to be the sequel to conventional liquid electrolyte batteries, even expected to surpass them in terms of capacity, safety and cycle life. Unfortunately, this technology faces challenges such as the lacking ionic conductivity of solids, unstable solid electrolyte interphase and its dependence on the maintenance of physical contact between electrodes and electrolytes. The garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ has gotten a lot of attention in recent times due to its high ionic conductivity up to $10^{-3} \text{ S cm}^{-1}$, wide electrochemical stability window in the range of 0.0 V-4.3 V vs Li^+/Li and stability against metallic lithium. If the garnet is successfully applied with lithium metal in a battery, the evolution can be expected to especially benefit the transport sector with electrical vehicles being able to increase their driving range. This paper presents the prospects for this new technology and will compare, analyze and dissect the garnet material as a solid electrolyte for next generation batteries.

Contents

1	Introduction	4
2	Theory	5
2.1	Electrochemical cells	5
2.2	Secondary Batteries	6
2.2.1	Conventional lithium-ion batteries	8
2.3	Solid state batteries	8
2.3.1	Ionic transport kinetics	9
2.3.2	Interphases for solid electrolytes	10
2.4	LLZO	10
3	Discussion	11
3.1	LLZO as a solid electrolyte	12
3.1.1	Ionic conductivity and electronic insulator	12
3.1.2	Stability	14
3.2	LLZO with a metallic lithium anode	16
3.2.1	Formation of dendrite	16
3.2.2	Interface	17
4	Conclusion	18
A	Parameters for c-LLZO structure	27

1 Introduction

Although it may be cliché to start of the introduction to a thesis paper with global warming, it is the big, attention seeking elephant in the room that needs to be addressed. Most of the scientific community has agreed that a negative man-made greenhouse effect exists and that it is causing the average temperature on earth to increase. This phenomena is for the most part caused by deforestation and the burning of fossil fuels (oil, gas and coal), which emits large amounts of greenhouse gases, i.e. carbon dioxide, methane etc., to the atmosphere^[1]. Emission of carbon dioxide is a prevalent problem often attributed to the transportation sector, which has since the industrial revolution bloomed in every sense of the word. In fact, nearly 30% of the EU's total carbon emission comes from the transportation sector, with 72% being from road transportation specifically^[2]. The focus in the twenty first century has been on reducing the emission of greenhouse gasses. In the transportation sector, this has presented itself as an effort to move from internal combustion engine vehicles (ICEVs) to electrical vehicles (EVs).

Even with all the effort poured into this relatively new technology, electrical vehicles have not yet become the mainstream. It is estimated that on a global scale only 1 in 250 cars on the road is electric^[3]. This is partially because of the fact that they have struggled to perform as well as the average ICEV. The most talked about shortcoming of EVs has been the driving range on fully charged battery versus full tank^[4]. To indicate the extent of the problem, a term has been coined for the 'fear of running out of electricity before reaching an available charging station'^[5] - range anxiety. Some of the best ICEVs can normally exceed a driving distance of 900km and are the vehicles on today's market with the longest driving distance^[6]. Comparably, the battery powered electrical vehicle with the longest driving distance is the luxury car Tesla Model S with an estimated driving range of 652 km, according to Tesla's own website^[7]. Some of the other problems today's electrical vehicles are facing include safety, low temperature operational range and long charging time.

Solid state batteries (SSBs) are one of the newest and most exciting technology in development today. The expectation for these batteries are enormous and the hope is for them to be able to replace batteries with liquid electrolytes where needed. Conventional lithium-ion batteries on the market today suffer from safety concerns regarding the use of flammable liquid electrolytes. Solid electro-

lytes are intrinsically nonflammable which is expected to make them the safer option^[8]. This paper will focus on the garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, also known as LLZO, as a solid electrolyte in SSBs. It will explore LLZO as an electrolyte and why it has gained so much attention in recent times. More succinct, this thesis will answer the following question:

How does LLZO perform as a solid state electrolyte and what are the prospects of using this technology in electric vehicles?

The main focus of this paper will be the chemistry of LLZO and its inherent abilities that are beneficial as an electrolyte, as well as potential solutions to the drawbacks it presents. Hopefully, that results in SSBs being further developed with the reduction of carbon emissions from the transportation sector being a welcomed effect. However, this paper will not focus on the greenhouse gas emissions associated with the production of EVs nor the batteries themselves. The sustainability of the material and the economic costs associated with the technology will not be regarded as part of the performance of a solid electrolyte, even though solid state batteries in general can be viewed in a bigger context with issues such as recycling and sourcing of material being pressing issues.

2 Theory

2.1 Electrochemical cells

A Galvanic cell is an electrochemical cell that transforms chemically stored energy directly into electrical energy. When there is no need of constant resupply of reactants it is referred to as a battery. In standard batteries two spontaneous reactions happen at each electrode, a reduction and an oxidation. The two electrodes are physically separated by an ionically conductive electrolyte but are connected by an external electronic conductor, such as a wire. An oxidation refers to a chemical reaction where a species loses electrons, whilst in a reduction a species gains electrons. The electrons move from the oxidation electrode to the reduction electrode through the electronic conductor, which converts the chemical energy to an electrical current that can be used to power a device.^[9]

Electrolytes are commonly liquid, but can be solid. They provide a charge balancing mechanism which allows for the reactions to occur continuously in a loop.

To maintain a neutral charge at each electrode, a matching amount of the oppositely charged ions are produced as electrodes gain or lose electrons. At the oxidation electrode, a matching amount of cations, positive ions, are produced. These cations travel through the ionically conductive electrolyte to the reduction electrode to neutralize the negative charge accumulated through reduction. Through this accumulation of positively charged ions, the reduction electrode can therefore be regarded as the positive pole. Oftentimes the positive pole also produces negative ions, called anions, which travel through the electrolyte to the negative pole.^[9]

This paper will annotate the electrode where the reduction occurs as the cathode and the electrode where the oxidation occurs as the anode, although this is only partially correct as it only aligns for a secondary battery during discharge^[9]. A visualization of a standard galvanic cell with a zinc anode and a copper cathode is shown in figure 2.1.

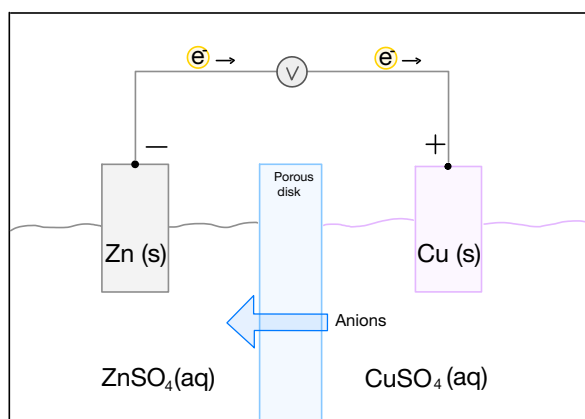


Figure 2.1: Galvanic cell with a zinc anode and a copper cathode.

2.2 Secondary Batteries

The chemical potential, μ , refers to the inert ability a substance has to undergo a physical or chemical change and it is a driving force in chemistry. It is defined as the partial Gibbs energy, ∂G , divided by the partial number of moles, ∂n_i , for a species, i . The equation is given by,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{p,T,N_j}, \quad (2.1)$$

for constant temperature and pressure. The number of all species, other than i , are also kept constant.^[10]

The driving force becomes defined by the electrochemical potential, $\tilde{\mu}_i$, rather than chemical potential, when the species in question are charged. It is defined by,

$$\tilde{\mu}_i = \mu_i + z_i \cdot F \cdot \phi, \quad (2.2)$$

where ϕ is the inner electric potential, z_i is the charge valency of substance i and F is the Faraday constant.^[11]

Furthermore, the cell potential for a electrochemical cell, ΔE_{cell} , is defined as the difference in inner electric potential, ϕ , for the cathode and the anode. The equation is given by,

$$\Delta E_{cell} = \phi_{cat} - \phi_{an} = -\frac{\Delta G}{nF}, \quad (2.3)$$

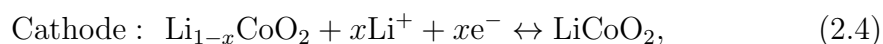
so that the difference in electric potential for the electrodes is equal to the negative change in Gibbs energy, ΔG , divided by the number of electrons transferred, n , and Faraday constant, F ^[9]. A larger potential difference between the cathode and anode therefore means more energy to do work per mole of electrons transferred.

A secondary battery, or a charge accumulator, is an electrochemical cell where the cell reactions are reversible. To charge a battery, there needs to be a supply of opposite potential larger than the ΔE_{cell} . This reverses the flow of electrons so that they move from the cathode to the anode, storing the electric energy as chemical potential. If the supplier of electric energy is replaced with a device, then the battery transforms the built up chemical potential into electric energy and is able to apply work. This is referred to as the discharging of a battery.

Safety, capacity, cycle and calendar life, and cost of fabrications are all important factors that need to be considered for a rechargeable battery^[12]. Whilst the cycle life of a battery refers to its degradation with repeated charge-discharge cycling, the calendar life gives its degradation with time^[13].

2.2.1 Conventional lithium-ion batteries

Conventional lithium-ion batteries (LIB) is usually a term used for LIBs with liquid electrolytes. Typically, electrolytes used are LiBF_4 or LiPF_6 in organic liquids such as dimethyl carbonate (DMC), diethylene carbonate (DEC), ethylene carbonate (EC) etc. LIBs use the principle of intercalation chemistry, where both the anode and cathode material have layered structures that allow for reversible insertion and extraction of Li^+ between the layers. Lithium ions therefore move from the anode to the cathode through the liquid electrolyte during discharging and in the opposite direction during charging. Lithium is an excellent reduction agent and has a low molar mass which allows for design of LIBs with high cell voltages and energy densities^[14]. Active cathode materials often used in commercial lithium-ion batteries are for example LiMO_2 ($M = \text{Co}, \text{Mn}, \text{Ni}$). Graphite is a common choice for the anode material^[15]. For batteries with a LiCoO_2 cathode and a graphite anode, the electrochemical half reactions can be described as follows^[16],



with the overall reaction being,



2.3 Solid state batteries

Whilst electrolytes are usually liquid, they can be solid. Solid electrolytes are an exciting new area of research and the batteries that use these are referred to as solid state batteries. The solid materials used have to be ionically conductive for the ions to be able to perform their charge balancing objective. A solid electrolyte, like an aqueous one, has to meet four critical criteria to be able to perform in batteries. These are^[17]:

1. High ionic conductivity, for lithium-ions in LIBs of above 10^{-3} Sm/cm .
2. Being compatible with the anode and cathode material, chemically.

3. Low electronic conductivity.
4. Having a wide electrochemical stability window.

2.3.1 Ionic transport kinetics

Ionic transportation, at the atomic scale, occurs as mobile cations diffuse through the solid electrolyte. Mobile cations hop between vacant or partially occupied sites in the electrolyte's crystal structure, sometimes by even displacing a lattice ion.^[17] In LIBs, mobile Li^+ move through the immobile crystal structure by point defects such as the Frenkel defect, Schottky defect and antisite disorders. The Frenkel defect refers to a interstitial and vacancy pair^[18]. The Schottky defect however, refers to the excitation of ions leaving their original lattice point vacant. This defect happens in pairs of oppositely charged ions to preserve the charge neutrality^[19]. Antisite disorders describe different ionic species that change place in a crystal structure^[20].

Ionic transportation in a solid electrolyte can be described by the function for ionic conduction, σ , as a modified Arrhenius relationship, given by,

$$\sigma = (A/T) \exp(-E_a/K_B T), \quad (2.7)$$

where A is the pre-exponential factor, T is temperature, E_a is the activation energy and k_B is the Boltzmann's constant. The activation energy indicates how likely it is for an ion to move to a neighboring lattice point, with higher activation energy being more unlikely and indicating a higher energy barrier for transport.^[21]

Structural and compositional inhomogeneities in electrolytes affect the ionic conductivity. Oftentimes, solid electrolytes are doped in order to increase the ionic conductivity of the material. Doping refers to the controlled introduction of impurities into the structure of a material in hopes of better performance^[17]. Furthermore, poly-crystalline structures have regions of contact between crystalline sections with different crystallographic orientations. These regions are referred to as grain boundaries. Grain boundaries have been found to oftentimes increase the resistance for ion transportation, negatively affecting the ionic conductivity^[22].

Inadequate physical contact between the solid particles in the electrolyte has also

been found to affect the ionic conductivity negatively. Porous materials exhibit this as they have been found to have a increase in resistance to ionic migration. This is a result from the pathways for ionic conduction becoming tortuous and the current densities becoming inhomogeneous^[17].

2.3.2 Interphases for solid electrolytes

At the area of contact between the solid electrolyte and electrode, known as the interface, electrochemical reactions can be observed which cause degradation and the formation of a new stable interphase. These interphases serve as a passivating layer that protect the electrodes from degrading completely^[17]. Sometimes interphases that are ionically resistive or electrone-conductive can be formed if the electrodes and electrolytes are not compatible. This is a major problem facing solid state batteries, but the negative effect of an interphase can range from negligible to dominating^[23]. Various studies have found that many solid electrolytes exhibit too narrow electrochemical stability windows and are therefore not thermodynamically stable when used with various cathode and anode materials^[17]. The stability window of an electrolyte refers to the range of voltage it can endure without undergoing redox decomposition. It is defined as the gap between the oxidation and reduction potential, where the LUMO of the electrolyte needs to be higher than the chemical potential of the anode and the cathode potential needs to be above the HOMO of the electrolyte. Otherwise, the electrolyte will be reduced at the interface with the anode and oxidized at the cathode side, forming the passivating interface^[24].

2.4 LLZO

The garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, also known as LLZO, is a ceramic material often used as the electrolyte in solid state batteries. LLZO comes with two structures, cubic and tetrahedral. The cubic Li-stuffed garnet, c-LLZO, adopts the space group $\text{Ia}\bar{3}\text{d}$ (no. 230), has a high ionic conductivity at between 10^{-3} and 10^{-4} S/cm and a wide electrochemical stability window ranging from 0.0V to 6.0 V^[8]. Its structure is shown in figure 2.2 and was computed in VESTA using parameters referenced from Momma et al.^[25], shown in table A.1 and table A.2 found in Appendix A. The material is considered to be the most promising solid electrolyte as there are promising potential benefits in energy density, high temperature stability, general stability and safety^[26].

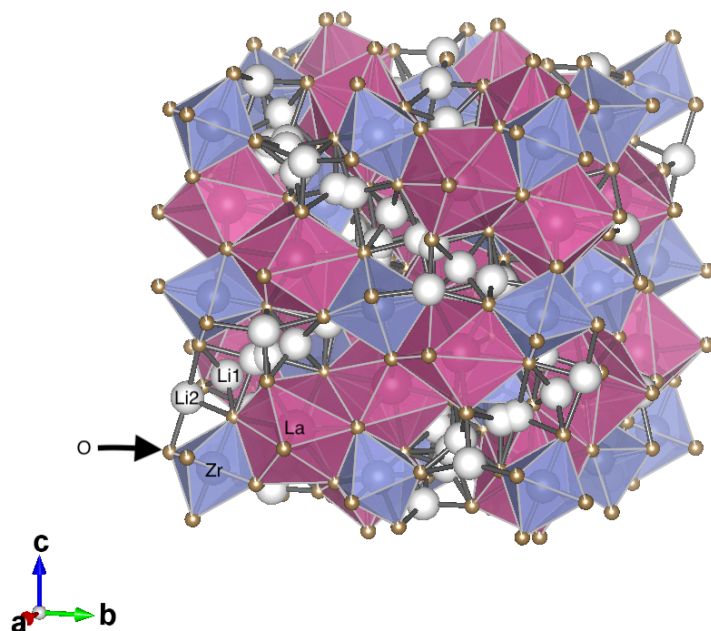


Figure 2.2: The structure of c-LLZO computed in VESTA with structural parameters and lattice parameters referenced from Momma et al.^[25]

3 Discussion

Although solid state batteries have not yet hit the market in a remarkable way, there are certain benefits to solid state batteries that make them a desired development of today's mainstream batteries, especially for the transportation sector. Conventional lithium-ion batteries typically use flammable liquid electrolytes. By implementing solid electrolytes, which in general are not very flammable, it has been proposed that a battery would increase in safety^[27]. The hope for SSBs is that even if the batteries were to experience mechanical, electrical or thermal abuse, the cases of fires and explosions would be lower than for LIBs. Furthermore, it is also assumed that since solid electrolytes in general are less reactive than liquid electrolytes, there should be an increase in device lifetime^[28]. Solid electrolytes are expected to open up for high-performance electrodes which would increase the overall energy density. If the expectations for SSBs are met, EVs should be able to compete with ICEVs and even potentially outperform them.

3.1 LLZO as a solid electrolyte

Currently, there are no solid state batteries on the market using ceramics as electrolytes that are good enough to power an electrical vehicle. There is one EV model that uses PEO-based polymers, known as Bolloré's Bluecar, but the narrow electrochemical stability of the electrolyte restricts the choice of cathodes to rather low voltage materials and have therefore lower energy densities. For comparison, the Bolloré Bluecar has a driving distance of reportedly 250km at maximum on urban terrain^[29], which is not even half of the driving range of Tesla Model S. By comparing its inherent abilities to the demands mentioned in section 2.3, this section will argue that c-LLZO is a good solid electrolyte and might help EVs outperform ICEVs.

3.1.1 Ionic conductivity and electronic insulator

An electrolyte needs to be an electronic insulator, just as much as it needs to be ionically conductive. For an electrochemical cell to work, the electrons and the ions need to migrate through separate parts of the battery^[30]. The electrolyte should transport ions, but be resistive to electrons. LLZO is both an electronic insulator and an ion conductor^[31], and it also fulfills the role of a separator. This means that the batteries can increase in energy density. For the transportation sector, increasing energy densities is one of the main priorities as it will directly affect the driving range of an EV.

High ionic conductivity is an important trait for an electrolyte, be it solid or liquid. Although the conductivity of an electrolyte does not affect the theoretically maximum capacity of a battery, which is determined by the electrochemical reactions at the electrodes, it can affect the rate behavior and might alter the experimental capacity of the battery at specific charging and discharging rates^[32]. As stated, c-LLZO has a high ionic conductivity due to its unique structure. In theory there are many different Li-diffusion pathways that are possible for garnet structures that would allow for charge transfer in the electrolyte^[33]. Xu et al.^[34] suggested, based on *ab initio* calculations for cubic garnets with lithium contents of above 5 per unit cell, two distinct pathways for lithium-ion migration. Pathway A proposes that lithium-ions migrate via the interstice between neighboring octahedral sites, bypassing their common tetrahedral neighbor. Pathway B proposes, however, that the ions move through the shared triangular faces of the octahedral and tetrahedral sites, known as the "bottleneck". For LLZO, which

has a high lithium content, pathway B is preferred and is associated with lower activation energy, in this case 0.26 eV^[33]. This low-energy barrier makes it easy for mobile cations to migrate and elucidates why c-LLZO has such a high ionic conductivity.

Tetragonal LLZO (t-LLZO) has a lower ionic conductivity by two orders of magnitude compared to c-LLZO with an ionic conductivity of 10^{-6} S cm⁻¹. This is ascribed to the difference in ordering of Li atoms and occupation of lithium sites, with the tetragonal distortion present in t-LLZO affecting lithium distribution remarkably. Furthermore, the migration of lithium-ions in t-LLZO has been found by Meier et al.^[35] to be synchronous, meaning several ions collectively moving at the same time. c-LLZO, however, exhibited migration of mobile lithium ions dominated by jumps of single ions and induced collective motion, therefore described as asynchronous and demanding less energy than synchronous movement. The large number of vacancies and disorders in c-LLZO compared to t-LLZO also promotes migration. Although cubic LLZO has a high ionic conductivity, it is unstable at room temperature with the tetragonal counterpart being stable^[33]. A considerable amount of effort has therefore been put into stabilizing the c-LLZO with dopants and by using various methods of synthesis. It has been successfully stabilized at room temperature by incorporation of elements such as gallium and aluminium. This is referred to as aliovalent doping where for example Al³⁺ substitutes Li⁺, creating two lithium vacancies to maintain charge neutrality, which furthermore stabilizes the high conductivity cubic phase. For Ga-doped c-LLZO, the ionic conductivity remained very high at 5.4×10^{-4} S cm⁻¹ meaning that the benefits of having an electrolyte with high conductivity would not be compromised^[36].

If the ionic conductivity of c-LLZO was to be compared to liquid electrolytes favored in LIBs, c-LLZO can be said to be on par. For LiBF₄ and LiPF₆, the literature shows a maximum ionic conductivity of 3.9×10^{-3} S cm⁻¹ and 6.1×10^{-3} S cm⁻¹ respectively^{[37][38][39]}. With the maximum ionic conductivity measured for Ga doped c-LLZO being at 10^{-3} S cm⁻¹, it is not quite as high as the values for LiBF₄ and LiPF₆, but it is in the same order of magnitude. Compared to other solid electrolytes, LLZO outperforms most of the other materials currently being studied. Other solid electrolytes that have gotten a lot of attention are Li₁₀GeP₂S₁₂, also known as LGPS, and the NASICON-types such as LATP and LAGP. LGPS, LATP and LAGP all have ionic conductivities in the range of 10^{-4} S cm⁻¹ - 10^{-3} S cm⁻¹^{[40][41][42]} at room temperature nor-

mally, with the bulk ionic conductivity of LATP being the maximum. However, like LLZO, LATP has a grain boundary conductivity of almost two orders of magnitude lower than that of the bulk and they can compare in performance. Although LGPS has been shown to perform at higher ionic conductivities for certain cathode and anode materials, it also has had issues with severe vulnerability to oxygen and water. Even if the other ceramic electrolytes were to be able to compete in ionic conductivity, they present further issues with stability and safety not making them ideal as a solid electrolyte^[43].

3.1.2 Stability

c-LLZO has been shown to have good general stability and is therefore one of the better performing solid electrolytes. It has been confirmed via thermogravimetric and differential thermal analysis (TG-DTA) that c-LLZO has a good thermal stability. Data collected in air showed negligible weight loss and no detectable phase transition of the material in a temperature range of 20°C to 900°C^[44]. This is very promising, as it could be fatal if a solid electrolyte that was not thermally stable was employed in any battery, but especially for those in electrical vehicles. If this was to be compared to liquid electrolytes typically used in LIBs, such as LiBF₄, LiPF₆ etc., which have very low thermal stability and decompose at high temperatures, even going up in flames, the benefits of c-LLZO become clear. c-LLZO was furthermore found to also be stable against molten lithium and chemically stable for several weeks if exposed to air and moisture^[45]. Although rarely, moisture can leak into batteries in EVs and that can affect their performance. For c-LLZO, the performance deteriorates as the electrolyte reacts with humid air to produce lithium carbonate which lowers ionic conductivity. It is hard to conclusively say anything about the spontaneity and probability of fire after collisions for EVs compared to ICEVs because of the lacking data^[46], but solid state batteries with c-LLZO as an electrolyte will certainly reduce the risk.

Furthermore, LLZO reportedly has a wide electrochemical stability window (EW). Cyclic voltammetry (CV) studies have found the electrochemical window to be >6 V vs Li⁺/Li. The stability found by CV studies seems to be an overestimation of the EW as the electrodes used in these studies were semiblocking and therefore more stable than normal electrodes^[47]. On the other hand, computational analyses have found the EW to be 0.05 V- 2.9 V^[26]. The computational analyses done were based on density functional theory (DFT) and the range found corresponds to the thermodynamic intrinsic electrochemical window. DFT does

not explicitly capture stabilizing kinetic effects for LLZO^[17], so the theoretical range for electrochemical stability is expected to be lower than experimentally found data^[47]. The experiments conducted by Smetaczek et al.^[47] were conducted with the idea of reducing the sources of error mentioned above, resulting in rather accurate estimations, and found that LLZO has an EW of 0.0 V-4.3 V vs Li⁺/Li. This wide electrochemical stability window makes LLZO one of the better performing electrolytes in terms of stability.

If the electrochemical stability window of LLZO was to be compared to other solid electrolytes, LLZO still has a significant advantage. When CV studies with semiblocking electrodes were performed on LGPS the EW was determined to be about the same as for LLZO. When further investigated with computational analyses however, the EW was found to be 1.7 V - 2.1 V^[8]. Even if the theoretical calculations for LGPS do not account for its kinetic stabilization, there is a significant difference in values for LGPS and LLZO. It indicates that LGPS has a narrower electrochemical stability window than LLZO. LATP and LAGP have been estimated to have EWs of 2.65 V- 4.6 V and 1.85 V- 4.9 V respectively vs Li⁺/Li^[48]. Again, LLZO performs better in terms of stability. There appears to be trade-off between high ionic conductivity and stability as exhibited by the different solid electrolyte materials. LLZO appears to be a good middle ground, being both stable enough while having a high enough ionic conductivity.

Why is the wide EW of LLZO good for further development of batteries? It opens up for high-performance electrodes, including metallic anodes such as lithium and high-voltage cathodes. If applicable in large-scale systems, this might lead to batteries with very high energy densities and therefore also to better performing EVs. The best of LIBs today have reached the upper limit of capacity allowed by intercalation chemistry at 300 Wh kg⁻¹. To increase the driving range on a single charge, the transport industry should increase the capacity of batteries to 500 Wh kg⁻¹. Metallic lithium is one of the most investigated high-performance electrodes with the highest specific capacity of 3860 mAh g⁻¹, which is significantly higher than graphite at 372 mAh g⁻¹^[49]. Efforts have been put into implementing them into batteries with liquid electrolytes, but issues such as low coulombic efficiency and significant dendrite formation have been dominating^[50]. c-LLZO is one of the few solid and liquid electrolytes with apparent stability in contact with lithium metal^[51], as its lower limit in the EW range needs to be at most 0 V^[52]. The most challenging aspects of lithium metal batteries with c-LLZO as electrolyte is still dendrite formation, unstable interface and loss of physical contact between

electrodes and electrolyte.

3.2 LLZO with a metallic lithium anode

Whilst the prospects of SSBs are great, there are practical issues still at hand that need further research before they can be implemented in any device, but especially EVs. There has been a shift in the scientific community with now a lot of the focus being given to high-performance electrodes such as metallic lithium, in the hopes of solving the lacking driving range EVs present today. This section will delve into the challenges with implementing metallic lithium in the context of LLZO and propose solutions that could be interesting for further development.

3.2.1 Formation of dendrite

Although there are clear advantages to SSBs in regards to safety even without the use of high-performance electrodes, the biggest benefit to some solid electrolytes would be their compatibility with metallic anodes. Metallic lithium anodes work on the principle of plating and stripping interphases, where during charging lithium builds on the anode, i.e. plating, and during discharging that layer is removed, i.e. stripping. In LIBs where metallic Li has been implemented, short-circuiting has been a problem because of the deposition of lithium during plating as filament-like structure which has grown through the separator and reached the cathode. This filament-like structure is commonly known as dendrite. At first it was believed that SEs would be able to mechanically restrain the formation of dendrite, but new reports have indicated that metallic lithium has been able to penetrate even solid electrolytes^[17]. When metallic lithium reacts with a solid electrolyte, a solid electrolyte interphase (SEI) layer forms on the Li surface. Oftentimes the brittle SEI layer cannot tolerate the volume changes in the metallic anode and therefore breaks and recovers continuously. This causes there to be an uneven spread of current distribution on the anode, with the dendrite forming at sites with locally high current densities^[53]. This has been demonstrated even for garnets which have very high shear moduli, as this deposition can happen in grain boundaries or flaws above a certain critical current density. Cheng et al.^[54] demonstrated that there was a correlation between the microstructure of aluminium doped c-LLZO and how it performed. Densified LLZO pellets showed a higher resistance to dendrite formation, although it did not solve the problem entirely. Some of the efforts put into hindering Li dendrite formation have been

focused on artificial SEI layers, mechanical protective layers and nanostructure designs, among others^[53].

One of the solutions to dendrite formation has been found to be Li_2CO_3 free LLZO. Li_2CO_3 forms on the surface of LLZO during the production process and is an unwanted byproduct. Wu et al.^[53] investigated *in situ* formed Li-deficient shields and their role in producing Li_2CO_3 free LLZO with an intrinsic lithiophilicity characteristic. Li_2CO_3 was found to be what causes the inadequate contact between the metallic anode and LLZO in the Li|LLZO interface, which furthermore causes the uneven current densities which facilitate dendrite formation. By high-temperature calcination at 900°C , formation of Li_2CO_3 can be restrained giving rise to lithium deficient compounds. The study showed that by removing the lithium deficient compounds, the Li_2CO_3 free LLZO showed increased physical contact with the metallic Li resulting in very low interfacial resistance and an even current distribution which moreover suppressed dendrite formation.

3.2.2 Interface

Another problem plaguing this new technology is the formation of compounds on the interface between the electrodes and the electrolytes that are either ionically resistive or electronically conductive, leading to performance issues by hindering ion transport. For LLZO with metallic Li, the formation of Li_2CO_3 has been found to cause the high interfacial resistance. The literature shows that the interfacial resistance between metallic Li and LLZO electrolytes for the most part is far larger than $100 \Omega \text{ cm}^2$, with the highest being $2500 \Omega \text{ cm}^2$ ^{[55][56][57]}. With such high resistivity the capacity of the batteries were not only significantly below theoretical capacities, but there was also high capacity degradation which is very undesirable^[58].

Wu et al.^[53], with the Li_2CO_3 free LLZO, were able to reduce the interfacial resistance of the Li | LLZO interface to $49 \Omega \text{ cm}^2$ without any surface modifications by using Li_2CO_3 free LLZO. There have also been other studies focusing on reducing the interfacial resistivity such as Han et al.^[59] with a Al_2O_3 layer and Goodenough et al.^[60] with the aid of carbon. They were able to reduce the interfacial resistivity to $1 \Omega \text{ cm}^2$ and $28 \Omega \text{ cm}^2$ respectively. Those are promising values and the respective batteries showcase that in the found values for their battery capacities. Although they also presented with promising cycling per-

formances, they did not have the stability of performance needed for commercial application. Loss of physical contact between the electrodes and the electrolytes was one of the main reasons^[53].

SSBs rely on physical contact between the solid electrodes and electrolytes for ionic diffusion. It is essential for the batteries that the contact between solid particles is maintained, even with the stresses developed through their cycle life. This is prominent problem for all SSBs in development. These stresses include the electrode materials cracking and the delimitation of interfaces due to volume changes of electrodes during cycling^[17]. When there is inadequate contact between solid particles in SSBs, the ionic conductivity becomes affected negatively further hindering the performance of the battery. For Wu et al.^[53], with the Li_2CO_3 free LLZO, the high capacity degradation was attributed to the volume change undergone by the cathode used. To counteract the loss of contact, high external pressures have been applied on cells and this has at times reduced the interfacial impedances^[61].

4 Conclusion

LLZO was evaluated as a solid electrolyte in batteries and the prospects of using them in electrical vehicles were analyzed. The electrolyte performs very well when compared to other solid electrolytes in terms of stability and ionic conductivity. When compared to liquid electrolytes frequented in LIBs, LLZO is in the same order of magnitude for ionic conductivity whilst being much more thermally stable. The most promising aspect of LLZO as an electrolyte with electrical vehicles in mind, is its apparent stability when in contact with metallic lithium. Although electrochemical cells with LLZO and a metallic lithium anode faced issues such as dendrite formation, unstable interface and loss of physical contact, there have been studies that have proposed promising solutions to these issues.

This technology is headed in the right direction with progress being made everyday, but further investigation needs to be employed into solutions that solve these challenges at the same time. Further research into high-performance cathode materials is needed and would be beneficial in hindering capacity degradation. All of this indicates that LLZO has a promising future in terms of high capacity batteries that are needed in EVs. Their application on a large commercial scale

in the transport sector would propel electrical vehicles into a future of better driving ranges. The hope is for these batteries to solve the range anxiety established as a reason for the lack of popularity electrical vehicles have today. Even though it is cliché to end by mentioning global warming, if driving electrical were to become the new norm, then maybe we would be one step closer to solving the climate crisis and saving our planet.

Trondheim, 29th April 2022

Ivana Zlatic

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A Parameters for c-LLZO structure

The lattice parameters for c-LLZO are shown in table A.1 and were referenced from Momma et al.^[25]. These values were used to compute the structure for c-LLZO in VESTA, shown in figure 2.2.

Table A.1: Unit-cell volume [\AA^3], axial relationship [\AA] and interaxial angles for c-LLZO referenced from Momma et al.^[25].

Lattice parameters	c-LLZO
Unit-cell volume [\AA^3]	2156.6891
Axial relationship [\AA]	$a = b = c = 12.92$
Interaxial angles	$\alpha = \beta = \gamma = 90^\circ$

The structural parameters for c-LLZO are shown in table A.2 and were referenced from Momma et al.^[25]. These values were used to compute the structure for c-LLZO in VESTA, shown in figure 2.2.

Table A.2: Site, occupancy value (g), and fractional coordinates for atoms in c-LLZO referenced from Momma et al.^[25].

Atom	Site	g	x	y	z
Li1	24 d	0.750	0.375	0.000	0.250
Li2	96 h	0.250	0.147	0.176	0.439
La	24c	1.000	0.125	0.000	0.250
Zr	16a	1.000	0.000	0.000	0.000
O	96 h	0.927	0.103	0.197	0.280

