Field Assisted Sintering of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ Solid State Electrolyte

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Abstract

All solid Li-ion batteries display high stability and longevity, but are hampered by the poor conductivity of most solid electrolytes. The influence of applied electrical fields during sintering on microstructure and electronic properties of lithium aluminum titanium phosphate ($\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$, LATP) electrolyte material was investigated by sintering LATP pellets under DC voltages of 0V, 2V, 10V, and 20V, followed by characterization via Scanning Electron Microscopy (SEM) and impedance spectroscopy. Application of a DC voltage increased the relative density to a maximum of 95.5%. However, unlike reports on other material systems such as zirconia, a high DC voltage induced rather than restrained abnormal grain growth. Resistivity increased with applied voltage from 2.1 $\text{k}\Omega\cdot\text{cm}$ at 0V to 7.8 $\text{k}\Omega\cdot\text{cm}$ at 20V, which was attributed to the high faceting and poor grain to grain contact of the grains sintered under 10V and 20V.

1. Introduction

Environmental and economical concerns about the mass utilization of fossil fuel sources for energy production have led to a search for alternative means of energy production. A vital component for alternate energy to become practical is an improved ability to safely store electricity at large scales and high energy densities.[1] Lithium ion batteries possess high energy

densities, and are already commonly used today in most portable electronic devices. Over the last twenty years, rechargeable lithium-ion batteries have undergone a great deal of development through the introduction of new materials and engineering approaches that have boosted the delivered power densities, bringing them closer to the theoretical ideal.[2, 3] Despite this unprecedented progress, further improvements in storage capacity, lifetime, and stability in extreme environments are still necessary for more widespread utilization.[4] Currently, most commercial Li-ion batteries contain liquid or polymer electrolyte materials, which stand in the way of expanded utilization due to their limited range of operating temperatures and safety concerns related to mechanical rupture of the battery cell and the release of toxic or flammable compounds. All solid Li-ion batteries are a possible safer, longer lasting alternative, but possess poor performance, mainly due to their low solid electrolyte conductivities.[5]

Among the currently known electrolyte materials, the $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) family is one of the most developed and easiest to work with due to their low cost, low toxicity, ease of preparation, and stability in air. Doping LTP with different metallic ions can further improve their Li-ionic conductivity by altering the unit cell volume and carrier concentration.[5] $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) is the most well known of these compounds, and has even been commercialized in thin film batteries.[6, 7] To improve the electronic properties of LTP solid state electrolytes to the point where large scale bulk batteries are practical, novel chemical and processing methods are currently under investigation.[7] Considering the interplay of the effects of porosity, tortuosity, and interfacial phenomena on performance, advancements in the LIB ceramics processing will result not only from a good understanding of electrochemical properties, but also from gaining control over porosity, microstructure, and ultimately sintering mechanisms.

The sintering technique and parameters used when consolidating solid state Li-ion batteries directly influence their microstructure and electrochemical properties.[8] One set of sintering techniques that has produced promising results in multiple systems utilizes electrical currents to aid densification, either by heating the sample or surrounding die with resistive heating at high rates of above 100°C/min in a technique commonly called Spark Plasma Sintering (SPS),[9] or through a much broader range of techniques which apply a voltage exclusively to the sample during sintering, referred to as field assisted sintering (FAST).[10] These techniques are often claimed to enhance sinterability and clean impurities such as oxides from the grain boundaries. However, controversy remains over the exact mechanism behind these beneficial effects; some claim electric discharges are generated at the points of powder contacts, while others assert the improvements are due mainly to the rapid heating rates, localized heating at the grain boundaries, or the electric field enhancing diffusion mechanisms.[7, 9-13]

Spark plasma sintering has been applied to several different systems of solid state Li-ion batteries including LATP to maintain a nano-scale grain size and potentially improve conductivity. A recent review of these efforts by Kali *et al*[7] found that using SPS to densify solid state electrolyte materials can improve their conductivity by as much as two orders of magnitude from the order of $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ to as high as the order of $10^{-2} \text{ S}\cdot\text{cm}^{-1}$, and attributed this to a lowered grain boundary resistance and improved grain to grain contact. For LATP specifically, studies by Duluard *et al*[14] on sintering LATP with SPS over a wide range of hold temperatures found that lower temperature soaks produced a finer microstructure with higher conductivity, which he attributed to better grain to grain contact. Another study by Xu *et al*[15] found that SPS could be used to restrain the grain size to as low as ~100nm, resulting in room temperature conductivities of up to $1.12 \cdot 10^{-3} \text{ S/cm}$. Because the grain boundary resistivity of

solid state electrolytes is far higher than the bulk resistivity,[16] one might expect that reducing the average grain size would decrease conductivity instead of enhancing it. However, the aforementioned studies demonstrate that the opposite is the case for LATP, which the researchers attributed to the SPS mechanism increasing the grain boundary conductivity through some unknown mechanism possibly related to the electric current.

FAST sintering techniques are less developed than SPS, but possess the advantage of not requiring expensive vacuum equipment or sample-contaminating graphite dies. While they have not been used on solid state lithium ion battery materials, recent research has found beneficial effects on similar materials such as yttria-stabilized zirconia (YSZ) solid oxide fuel cells. [17] A small DC voltage of 20V/cm applied during sintering of yttria-stabilized zirconia (YSZ) enhances the sintering rate and restrains grain growth by nearly a factor of two.[18] Application of a larger DC voltage during sintering can also cause a sudden breakdown in resistivity, sintering the sample to densities in excess of 95% in a matter of minutes at temperatures as low as 390°C.[19, 20] This “FLASH” sintering technique has already been extended to other ionic oxides, including titania, yttria, and manganese cobaltite spinel.[21-25]

To our knowledge such sintering techniques have not been applied to any solid state Li-ion battery systems, and it is unclear whether the beneficial effects noted in the SPS research are due to SPS’s high heating rate and low soak time, or an intrinsic effect of the electric field. To isolate the effect of the electric field itself on microstructure and electronic properties outside of the context of SPS, it is necessary to decouple the applied voltage from the system temperature. Such investigation will give a better understanding of the merits of SPS compared to conventional sintering, further expand the ability to control microstructure development and thus

electronic properties of solid state battery materials, and possibly open new routes to sintering bulk solid state batteries with advantageous properties.

2. Experimental

LATP powder was synthesized according to the calcinations procedure first developed by Aono *et al.*[26] LiCO_2 , Al_2O_3 , TiO_2 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed in stoichiometric amounts and ball milled in ethanol for 24 hours using spherical 2.5mm diameter yttria-stabilized zirconia milling media. After milling the powders were reclaimed by evaporative drying and calcined in an alumina crucible at 900°C for 2 hours. The resulting LATP powder was ball milled in ethanol for 24 hours before use. YSZ impurity from the milling media was estimated to be less than 1wt% by weight loss of the media. X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) scans of the finished powder were taken with a Bruker D8 and Technai XL-40 FE-SEM respectively to verify phase composition, measure particle size, and check for impurities.

Sintering was performed in a customized tube furnace setup shown in Figure 1. The sample was suspended in the center of the tube with two nickel electrodes, which also provided electrical contact to the external power supply. LATP pellets were cold pressed at 200MPa for 15s into 12.7mm diameter by 4mm thick cylindrical pellets which were individually inserted in between the electrodes. Samples were sintered at 900°C for three hours with a heating rate of $20^\circ\text{C}/\text{min}$. Once 900°C was reached, a constant DC electric potential of 0, 2, 10, or 20V was applied for the duration of the soak. The power supplied to the samples was below 1W, which is not sufficient to cause any significant resistive heating. Three samples were sintered at each voltage to ensure reproducibility.

After sintering the ceramic pellet was removed from the furnace and any residual contamination from the contact with the electrode ground away. The bulk of the samples were checked again with XRD and energy dispersive spectroscopy (EDS) to verify that no significant contamination was present. Room temperature AC impedance spectroscopy measurements were made using a Solartron SI 1287 Electrochemical Interface and 1252A frequency response analyzer over a frequency range of 300kHz to 1Hz at an amplitude of 25mV. The opposing faces of the samples were painted with a silver suspension (TedPella) to insure good electrical contact and clamped between the leads on the setup. A semicircle with extended tail was observed, which is consistent with the electronic response from other publications.[7, 15] The resistance was calculated with Zview software using a fit to a $R_s - (CPE - R_e)$ equivalent circuit where R_s is the left intercept of the semicircle, representing bulk resistance, R_e the right intercept representing total resistance and CPE a constant phase element, and the total, bulk, and grain boundary resistivities calculated from the real intercepts of the semicircle and the sample dimensions. After the impedance spectroscopy measurements, the samples were broken in half and SEM/EDS scans of the fracture surfaces were performed to check for non-visible metal contamination from the electrodes and to examine the microstructure. The relative density was measured by polishing a fragment with 0.25 μ m diamond paste, imaged the surface with SEM and measuring the areal fraction of porosity at several points across the sample.

3. Results and Discussion

The XRD spectra of the powder produced by solid state reaction (Figure 2) showed a distinct pattern of NASICON peaks slightly offset from that of $\text{LiTi}_2(\text{PO}_4)_3$, [27] verifying that the correct crystal structure had been produced by the reaction and comprised the vast majority of the

powder. EDS spectra of the powder (Figure 3) showed the presence of oxygen, titanium, aluminum and phosphorus, but was unable to detect Lithium as it was below the instrument's range. No unexpected elements were observed, verifying that LATP powder had been produced and that no foreign elements were present in concentrations detectable by EDS. The average powder size after ball milling as measured by direct SEM images was 670 ± 25 nm. Aside from a thin iron/nickel oxide scale at the point of contact with the electrodes which was ground away, XRD and EDS scans of the samples likewise showed no contamination after the sintering process.

The relative densities (Table 1) of the sintered samples ranged between 86% and 95.5%, and scaled with the applied voltage. The samples sintered at 0V and 2V had similar relative densities of 86% and 89%. Likewise, the two samples sintered at the higher voltages of 10V and 20V had similar densities of 94% and 95.5% respectively. Examination of the microstructure through SEM imaging of cross-sectional fracture surfaces (Figure 4) revealed similar effects on the grain size and shape. The samples sintered at 0V and 2V (Figures 4a and 4b) possessed roughly equiaxed grains similarly sized and shaped to that of the green powder (Figure 5). A large amount of porosity is visible, consistent with the density measurements. The microstructures of the samples sintered under 10V and 20V are visibly different (Figures 4c, 4d). Their grains are much more closely packed, reflecting the increase in relative density. Furthermore, their grain size and morphology is different from the 0V and 2V samples, the grains are now highly faceted and several abnormally large grains visible. Overall, application of a DC voltage during sintering lead to an increase in density, altered grain morphology, and induced abnormal grain growth, with the magnitude of these effects being enhanced by an increase in applied voltage.

Room temperature complex impedance spectra, while different between the sets due to varying sample thickness and density, showed the same general trends towards higher resistance at higher applied voltage. Representative spectra from a single set of samples these trends are shown in Figure 6. The resistivity of the samples (normalized for thickness) increased with the applied voltage during sintering from an average of $2.1 \text{ k}\Omega\cdot\text{cm}$ at no applied voltage to a maximum of $7.8 \text{ k}\Omega\cdot\text{cm}$ at 20V as recorded in Table 1. The majority of this difference was from changes in the grain boundary resistivity, which increased from $2.0 \text{ k}\Omega\cdot\text{cm}$ to $7.6 \text{ k}\Omega\cdot\text{cm}$, while the bulk resistivity remained relatively constant varying only from 0.12 to $0.17 \text{ k}\Omega\cdot\text{cm}$. This matches with the previous reports in the literature of LATP's conductivity scaling inversely with grain size in samples sintered by SPS.[7] due to lower grain boundary resistance and increased relative density at smaller grain sizes. A similar increase in relative density was observed in the samples sintered under high applied voltage which should lower the resistivity, but some additional mechanism appears to be increasing the grain boundary resistivity despite the increase in density, which should improve grain to grain contact.

The mechanism behind the increase in grain boundary resistivity can be found with the grain morphology; in the previous literature it is generally accepted that good grain to grain contact is necessary for high conductivity.[14, 15, 28] The large, highly faceted grains in the 10V and 20V samples would reduce the area of contact from the traditional necks between spherical particles in the 0V and 2V samples to intersections between faceted grains and two dimensional planes, causing an increased separation between the grains. Similar behavior has been observed by Duluard *et al*, who concluded that the cohesion of large grains of LATP was less than that of smaller grains, and Xu *et al*, who observed a decrease in conductivity in samples with similarly larger, faceted grains.[14, 15] Thus, even with the increase in relative density, the change in

grain morphology and growth of large, faceted grains causes field assisted sintering of LATP to be a net detriment to its electronic properties unlike the SPS experiments reported in the literature.

To our knowledge, this is the first attempt to study the influence of a steady state DC electric field on sintering of solid state Li-ion battery materials. The effects on microstructure and density are markedly different from comparable experiments in the literature on other materials. Studies by Francis *et al* on the effect of electric fields in FAST and FLASH sintering on Yttria-stabilized Zirconia and other ionic oxides have observed that application of an electric field restrains grain growth, leading to an increase in sinterability due to the inverse relationship between sintering rate and grain size.[10, 19, 20, 29] However, in the presently examined LATP samples, application of an electric field in the absence of high heating rates and pressures during sintering caused abnormal grain growth and alterations to the grain morphology alongside an increase in relative density. This behavior is inconsistent with the model of grain growth retardation via localized grain boundary heating proposed to explain the behavior of YSZ materials under applied voltages.[10]

The abnormally large grains observed in the samples sintered under 10V and 20V could imply that the applied voltage is significantly enhancing surface diffusion, and thus grain coarsening.. However, as surface diffusion is non-densifying, other mechanisms must be at work as well to account for the increased density. One possible mechanism could be electromigration of charged atoms or vacancies, but such a phenomenon would be expected to produce anisotropic grain shape morphologies and atomic concentration gradients along the axis of the electric field, which were not observed. Another could be electric field enhanced mobility of grain boundaries, but this also should lead to enhanced grain growth along the axis of the applied voltage.

Furthermore, enhancement of an overall mass transport mechanism would be expected to uniformly increase the grain size, while in this instance a distinct bimodal grain size distribution was observed. This bimodal distribution may imply that grain features, such as size or orientation, in combination with the applied voltage are responsible for the abnormal growth. Regardless of the mechanisms at work, this different microstructure development under an applied voltage implies that different types of ceramics can have completely different responses to applied electric fields, even within ionic materials. If a complex phosphate such as LATP responds differently from a simpler oxide such as Zirconia or Alumina, the response of other materials such as covalent ceramics such as carbides or nitrides should be expected to be similarly different. In order to fully understand the mechanisms behind FAST, individual examination of each of these classes of materials to ascertain their response and compare is necessary. For LATP and solid state electrolytes in particular, further investigation of the effects of the applied voltage on the in-situ densification over time and temperature along with more extensive microstructure characterization are needed to fully understand their sintering behavior.

4. Conclusion

The effects of applied DC voltages of 0V, 2V, 10V, and 20V during sintering on the densification, microstructure, and resistivity of all solid LATP electrolyte were examined. The applied voltage strongly influenced density, grain size, grain morphology, and conductivity. Higher voltages increased the relative density from 85% at 0V to 95.5% at 20V, but also caused abnormal grain growth and highly faceted grains. This increased the resistivity of the samples sintered at higher applied voltages from 2.1 k Ω ·cm at 0V to 7.8 k Ω ·cm at 20V, which was attributed to poor grain to grain contact in their larger, more angular microstructures. The

microstructure development of LATP under an electric field was different than that of literature reports of conventional oxides such as yttria-stabilized zirconia, with grain growth enhanced instead of restrained alongside the increased densification. This implies that the applied voltage activates a different, currently unknown set of mechanisms in solid state electrolyte materials.

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Figures:

Figure 1: Schematic of the furnace setup used to sinter all samples. The sample is suspended in pellet form between two nickel electrodes in the hot zone and connected to an external power supply

Figure 2: XRD spectra of the LATP powder before sintering

Figure 3: EDS spectra of the LATP samples after sintering

Figure 4: SEM images of the fracture surfaces of samples sintered under a) 0V b) 2V c) 10V d) 20V

Figure 5: SEM image of green LATP powder after ball milling. Acc. Voltage = 10kV, WD = 10mm, magnification = 2500x.

Figure 6: Complex AC impedance spectra for all samples

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1: Density and conductivity of samples

ΔV	ρ_{rel}	ρ (k $\Omega \cdot \text{cm}$)	ρ_{B} (k $\Omega \cdot \text{cm}$)	ρ_{GB} (k $\Omega \cdot \text{cm}$)
0V	86	2.1	0.12	2.0
2V	89	2.3	0.13	2.2
10V	94	7.6	0.17	7.45
20V	95.5	7.8	0.16	7.6