Flash Sintering of Li-Ion Conducting Lithium Lanthanum Titanate for Li–Air Batteries

by Victoria L Blair, Selva Vennila Raju, Aubrey L Fry, Michael Kornecki, Jeffrey Wolfenstine, and Raymond E Brennan
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Flash Sintering of Li-Ion Conducting Lithium Lanthanum Titanate for Li–Air Batteries

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The US Army needs high energy density, lightweight batteries, which can reduce Soldier load by up to 14 lb. One potential method to reduce the load is to replace disposable, alkaline batteries with lithium (Li)–air batteries, which weigh less due to high energy density and a porous “air” cathode. Li–air battery performance is limited by the electrolytic membrane, which must have an extremely high Li-ion conductivity. Li₀.₃₃La₀.₅₅TiO₃ (LLTO) is a promising electrolytic membrane material due to its high lattice conductivity; however, the total conductivity of LLTO is lowered by its grain-boundary properties. Previous work shows careful structural modification and processing can improve the grain-boundary conductivity. For the current work, flash sintering densifies LLTO at temperatures well below the conventional sintering temperature. Excessive volatilization of Li could be avoided by reducing the time of exposure to high temperatures to improve grain-boundary conductivity. X-ray diffraction of the flashed specimens showed no significant phase change among specimens processed by other methods. Electrochemical-impedance-spectroscopy measurements were taken and results modelled to understand the nature of conductivity within the flashed samples. The effects of flash sintering on the microstructure and conductivity in comparison with conventionally sintered samples are discussed.
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1. Introduction

Lithium (Li)-ion batteries are currently one of the leading energy-storage-device technologies, and the US Army is interested in continuing to develop novel battery materials to aid the warfighter. The technologies employed by Soldiers (radios, surveillance equipment, etc.) require portable energy supplies, and current lithium ion batteries can only supply 6–8 h of continuous power before needing to be replaced or charged. If novel battery devices were developed and implemented, potential benefits for extending the supply energy beyond 72 h and expanding to multiple devices could be possible. Additionally, the number and total weight of batteries could be reduced if the energy density was higher, leading to lower risk of musculoskeletal injuries sustained by the Soldier. Li–air batteries have been the focus of recent research, as they can supply up to 10× higher energy due to the porous “air” cathode, which reduces the weight of the device.1

Both low electrical conductivity and high Li-ion conductivity are required for efficient battery operation, while the chemical stability and mechanical robustness are necessary to support the reliability and safety of the battery, respectively. One of the most promising candidates for this membrane material is lithium lanthanum titanate, Li$_{3x}$La$_{(2/3)-x}$TiO$_3$ (LLTO), due to its high theoretical lattice conductivity.2 This study will focus on LLTO with $x = 0.11$ (Li$_{0.33}$La$_{0.55}$TiO$_3$), as previous work indicates LLTO ceramics with this composition exhibit the maximum lattice conductivity.$^{3,4}$

1.1 Methods to Improve Conductivity in LLTO

The low total conductivity observed in LLTO ceramic materials is believed to arise from three main factors: lithium deficiency, low density, and high resistivity at the grain boundaries. All three of those factors influence each other; for example, sintering at higher temperatures may increase the density (thus increasing conductivity) but may also lead to Li loss through volatilization of Li$_2$O and simultaneously decrease conductivity due to loss of the main charge carriers.2

Recently, there has been significant effort toward improving the grain-boundary conductivity in LLTO and related ceramic-membrane materials. One method for increasing the grain-boundary conductivity is to maximize the density of the part such that it approaches the theoretical density (TD), as explored by Weiss Brennan et al.5 Density optimization is expected to enhance grain-boundary conductivity, since recent transmission-electron-microscopy results on LLTO indicate the majority of porosity exists at the grain boundaries.6
Increasing the surface area at the grain boundaries by improving the density should enhance the Li-ion diffusion pathways at the grain boundaries. Minimization of the detrimental grain-boundary second phase (i.e., air) should increase the total conductivity as well. These ideas were partially investigated by Weiss Brennan et al. Additionally, US Army Research Laboratory (ARL) researchers studied the effects of hot isostatic pressing (HIP) of LLTO and found the material could remain in the cubic phase at near TD. In this case, however, the conductivity of the material was similar to that of a non-HIPed part. It was possible the extended period of time at the sintering temperature led to significant volatilization of Li. This type of loss could lead to a lower concentration of charge carriers, reducing the ionic conductivity of the material. ARL researchers have also concluded that a combination of grain-boundary engineering, high density, and maintenance of the concentration of the charge carriers could also improve the grain-boundary conductivity by a factor of three.

LLTO, a perovskite, comes in two different polymorphs: tetragonal ($P4/mmm$) or cubic ($Pm\bar{3}m$). The tetragonal structure is stabilized upon slow cooling from a sintering temperature of 1200 °C. If a rapid-cooling regime is used, such as quenching into liquid nitrogen, the cubic phase ($Pm\bar{3}m$) is stabilized. Harada et al. determined that LLTO tends to crystallize with a ratio of both phases, depending on the cooling schedule and the A-site composition. Additionally, Harada showed that the lattice conductivities ($\sigma$) for the tetragonal phase was 60% lower than that of the cubic phase. The change in lattice conductivity from one phase to the next may have been due to the symmetry of the cubic space group. In the cubic phase, the angle between the octahedra (as shown in Fig. 1) was slightly larger than the angle in the tetragonal phase. This tilting of the octahedra may have resulted in a lower activation energy for Li-ion conduction through the cubic lattice, leading to a higher lattice conductivity.

![Image of cubic and tetragonal lattices](image)

Fig. 1  Idealized cubic lattice (left) shows tilting of the octahedral causing a larger space for Li-ion conduction in comparison to the idealized tetragonal structure (right)

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1.2 Flash Sintering

Flash sintering is a relatively new technique gaining traction in the ceramic-sintering community due to its ability to rapidly sinter materials at significantly lower furnace temperatures than conventional sintering methods. The technique was first examined by Cologna et al. in 2011, demonstrating sintering of yttria stabilized zirconia (YSZ) in a matter of seconds by applying an electric field across the sample and ramping the furnace to 750 °C. Since its discovery, the academic and research communities have expanded the research to include understanding the fundamental mechanisms that enable densification of these high melting-temperature (T_m) materials in a short period of time.

The flash-sintering process has been described as a dynamic one in which a green ceramic part sinters quickly due to a transition in electrical conductivity, leading to joule heating within the part. This joule heating enables the part to reach the sintering temperature very quickly. Typically, the DC power supply switches from voltage-driven to current-driven to prevent electrical runaway, which could damage the power supply. As the material sinters, the electrical resistance decreases and eventually reaches steady state once densification is complete. However, this occurs in a matter of seconds. Much of the early research on this phenomena was explored by Raj et al. at the University of Colorado at Boulder. The mechanism of flash sintering is still under academic debate, and the materials to which flash sintering can be applied are still being examined.

1.3 Motivation and Research Objective

This ongoing work will examine the effectiveness of flash sintering, as opposed to conventional pressureless sintering, when applied to LLTO. As described earlier, the crystal structure of LLTO is extremely sensitive to heating and cooling rates, which can affect grain conductivity. The lower furnace temperatures and shorter times could greatly reduce the amount of lithium volatilization and also influence the final conductivity. Therefore, it is hypothesized that flash sintering will lead to dense LLTO materials with ionic conductivity rivalling conventionally sintered samples due to the high heating rates and short exposure times to high temperatures.

2. Experimental Procedure

2.1 Materials Processing

LLTO powder was synthesized by the same method described by Weiss Brennan et al., in which reagent-grade oxides and carbonates were mixed together and
calcined at 1100 °C in air for 1 h. The prereacted LLTO powder was then consolidated into green parts by making a slurry from the calcined powder and pouring it into a plastic mold to produce approximately 3- × 3- × 12-mm rectangular bars. All results from the conventionally sintered specimens were derived from previous ARL technical reports.5,7,8

By using two different sample geometries, the application of voltage and the resulting voltage per area could be altered. Figure 2 shows the experimental setup in parallel-plate configuration, in which a bar or disk is placed between two metallic electrodes connected to the power supply.

Fig. 2 Experimental schematic of the tube furnace (purple box), electrical leads and electrodes (blue lines), and sample (orange): setup uses pressed disks between two metal plates as electrodes that are connected to wires going to the power supply; atmosphere in the furnace can be adjusted (e.g., argon [Ar] or Ar–oxygen [O2] mixes)

Figure 3 shows the experimental setup for a slip-cast rectangular bar, which can be placed directly on top of the nickel–chromium-alloy (nichrome) wire electrodes that connect to the power supply. In this case, the sample length is greater than that of a pressed disk but the overall sample volume is smaller, which could lead to a larger power density.

Fig. 3 Experimental schematic of the tube furnace (purple box), electrical leads (blue lines), and sample (orange): setup uses slip-cast bars laid on two metal wires that go to the power supply; furnace can be back-filled with gases such as Ar and Ar–O2 mixes

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The experiments were documented by tracking the voltage drop across the sample during ramping of the furnace temperature. The furnace temperature at which the voltage suddenly dropped was defined as the flash temperature. The flash event was accompanied by a bright orange or yellow emission from the sample, in contrast to the dull-red background color in the furnace. Table 1 lists experiment configurations from four flash sintering cycles.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Configuration</th>
<th>( V_{\text{applied}} ) (volts)</th>
<th>Furnace gas</th>
<th>Flash temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W parallel plate (bar)</td>
<td>125</td>
<td>Ar</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>Nichrome wires (bar)</td>
<td>125</td>
<td>Ar</td>
<td>768</td>
</tr>
<tr>
<td>3</td>
<td>Pt Parallel plate (bar)</td>
<td>60</td>
<td>Ar</td>
<td>636</td>
</tr>
<tr>
<td>4</td>
<td>Pt Parallel plate (disk)</td>
<td>75</td>
<td>5.18% O\textsubscript{2}–Ar</td>
<td>1000</td>
</tr>
</tbody>
</table>

Note: W = tungsten; Pt = platinum.

### 2.2 Characterization of Parts

In order to complete work with a scanning electron microscope (SEM), the samples were freshly fractured and set onto sticky carbon tape. Fresh fracture of the specimens was completed to reduce any potential contamination of the sample during handling. They were then imaged using a Hitachi S-4700 SEM. A small fragment of sample was crushed in an agate mortar and pestle, mixed with alcohol, and dripped onto silicon zero-background sample holders to determine the phase content via powder X-ray diffraction (XRD). Specimens from previous research (described in a 2016 ARL technical report\textsuperscript{8}) were also crushed and measured with a Bruker D2 Phaser to obtain data for Rietveld-refinement calculation of the phases. The data were imported into TOPAS software (Bruker AXS, Inc.) and modeled assuming both the cubic (\( Pm\bar{3}m \)) and tetragonal (\( P4/mmm \)) structures were present.

Specimens from Experiments 3 and 4 were measured by electrochemical impedance spectroscopy (EIS) to calculate the ionic conductivity of the grains and grain boundaries. The specimens were gently polished using water and diamond-impregnated films and shaped into parallelepips, which were coated with 30-nm-thick gold electrode. The conductivity was measured from 0.1 Hz to 1 MHz with a potential amplitude of 100 mV. Figure 4 shows idealized data expected from either an ionic conducting material (expected result for LLTO) or an electronic conducting material (expected result for a metal such as copper).
Fig. 4 Example of a) EIS data from an ionic conducting material and b) an electrical conducting material

These data were fit to an equivalent circuit to provide the bulk resistance \( R_b \), grain-boundary resistance \( R_{gb} \), and capacitance. The values were then plugged into the conductivity equations (Eqs. 1 and 2) along with the specimen dimensions to obtain the conductivity of either the bulk \( (\sigma_b) \) or the grain boundaries \( (\sigma_{gb}) \), where \( l \) is the specimen length and \( A \) is the cross-sectional area.

\[
\sigma_b = \frac{l}{R_b A} \tag{1}
\]

and

\[
\sigma_{gb} = \frac{l}{R_{gb} A} \tag{2}
\]

3. Results

3.1 Microstructure and the Flash Event

Experiment 1 was the first attempt at flash-sintering LLTO. The sample was a rectangular fragment (bar shaped) from a uniaxially pressed and cold isostatically pressed “dog bone” specimen (description of dog-bone die included in Cologna et al.\textsuperscript{13}); the bar was placed between parallel-plate W electrodes. The bar had starting dimensions (length × width × height) of 12.5 mm × 3.7 mm × 1.6 mm. The furnace was heated at 10 °C/min up to 1000 °C under flowing Ar. The sample flashed as the power supply was discharged in current-control mode. The data logger malfunctioned and did not collect any voltage data during the experiment.

Figure 5 shows an SEM image from the fracture surface of a specimen from Experiment 1. An apparent density gradient was observed from the edge closest to the W electrode (Region 1) through the thickness to the green compact-like microstructure (Region 3), following the arrow in green.
Fig. 5 SEM image of specimen from Experiment 1 taken on edge near W electrode (100-micron scale bar): yellow lines represent approximate areas where microstructure changes were observed; Region 1 is densest with limited porosity, Region 2 has more porosity, and Region 3 is essentially a green compact; green line indicates direction of decreasing density.

Figure 6 shows the SEM images from Regions 1 and 2 of Experiment 1. While both regions exhibit porosity, Region 2 appears to have significantly more than Region 1. The grains in Region 2 appear to have formed necks and exhibit partial densification, as there is limited interconnectivity in the remaining porosity.

Fig. 6 SEM images of Region 1 (left) and Region 2 (right) from Experiment 1

The sample underwent 11% volumetric shrinkage (by measuring the geometry before and after flash) during the flash experiment. However, considering these
parts had a green density that was approximately 45% of the TD, to get to a final density of 95% of TD the parts should shrink by approximately 50%. This indicates that 11% volumetric shrinkage on this part would lead to a density that is approximately 56% of the TD.

Experiment 2 was conducted in a similar manner to Experiment 1, but with a different geometry. The sample was a slip-cast bar of geometry 12.5 mm × 3.9 mm × 3.1 mm laid onto two nichrome wires. Figure 7 shows the furnace temperature and sample voltage versus time in minutes. From these data, the flash temperature (T_f) was estimated as 768 °C, which was significantly lower than the conventional sintering temperature of 1200 °C. After the initial voltage drop, the furnace was held at the flash temperature for 5 min with the current applied.

![Graph showing furnace temperature and sample voltage vs. time in minutes](image)

**Fig. 7** Graph shows furnace temperature and sample voltage vs. time in minutes (data were recorded manually and do not indicate full furnace cycle); flash onset occurs at ~ 18 min as indicated by voltage drop

Figure 8 shows an SEM image of the specimen from Experiment 2. The grain size of this specimen appeared to be smaller than the grain sizes from Experiment 1. This was likely due to the amount of time the sample was at high temperature. One of the drawbacks to the experimental set-up was the sample temperature could not be accurately measured during the flash event, making it difficult to assess the heating rate or how long the sample was at the densification temperature.
Another observation from Experiment 2 was that the nichrome wires were melted at the point where the sample made contact. Nichrome wire has a $T_m$ of 1400 °C; therefore, it is possible the maximum temperature of the sample was approximately 1400 °C. Despite the high sample temperature, which should have led to significant densification, the short exposure time resulted in a final grain size of approximately 1 micron.

Experiment 3 was also run on a rectangular bar of size 11 mm × 3.5 mm × 2.5 mm, but when the sample was pressed between the metallic electrode plates it broke in half. While the experiment was continued the two pieces of the sample remained separated by an air gap, effectively creating two specimens. One specimen was imaged in the SEM while the other was used for XRD analysis. This experiment used Pt-plate electrodes as opposed to W, since they had a higher melting temperature and were less reactive than W. The distance between the electrodes (length “L” in Fig. 3) was the same for both specimens in Experiment 3. Figure 9 shows the furnace temperature and voltage versus time, with the flash temperature estimated as 636 °C. Once the initial voltage dropped, the furnace was held at the flash temperature for 5 min with the current applied.
Fig. 9  Furnace temperature and sample voltage vs. time for Experiment 3

Figure 10 shows an SEM image of the specimen from Experiment 3. Region 1 indicates the surface of the specimen that was in contact with the Pt electrode, while Region 2 is a fracture surface in which a chip of material broke off during sample handling after the flash event.

Fig. 10  SEM image of Experiment 3’s specimen, whose Region 1 is the surface that was against the electrode while Region 2 is a fracture surface (1-mm scale bar)

Figure 11 shows Regions 1 and 2 at higher magnifications. Region 1 exhibits a different microstructure than the fracture surface in Region 2. It was possible the sample reacted with the electrode even though it was Pt. Region 2 shows grain-necking and some interconnected porosity. It is possible this specimen did not have as high of a density as the sample in Experiment 2. However, a true evaluation of density could not be made because the specimens were too small to get precise density measurements (via pycnometry or geometric calculations).
In Experiment 4, a disk with a thickness of 3.18 mm and diameter of 12.8 mm was pressed in a similar manner to the samples sintered by conventional means. The goal was to make a dense part through the thickness as a direct comparison to the conventional method. Instead, it was found that a significantly higher furnace temperature was required to observe a flash under these conditions, as shown in Fig. 12. Once the temperature of the furnace was maximized, the voltage was manually increased until the power supply switched to current control and the voltage dropped. The current was applied for 5 min after the voltage drop.

Figure 13 shows an SEM image of the fracture surface from Experiment 4. The microstructure exhibits intergranular fracture with some remaining porosity. However, this SEM image was not consistent with the rest of the specimen, which
exhibited a significant amount of remnant porosity and some interesting features at the surfaces closest to the electrodes, as shown in Fig. 14.

![SEM image of a fracture surface on the specimen from Experiment 4](image1)

**Fig. 13**  SEM image of a fracture surface on the specimen from Experiment 4

![SEM image of the specimen from Experiment 4 showing the area nearest the Pt electrode](image2)

**Fig. 14**  SEM image of the specimen from Experiment 4 showing the area nearest the Pt electrode

### 3.2 Evaluation of the Phases Present

The phase content of the LLTO materials was calculated from powder-XRD data using the Rietveld method (via TOPAS). The goodness of fit (GOF) was calculated by the software, which indicated how well the calculated pattern matched the measured pattern. In TOPAS, a GOF value between 1 and 2 was considered to be an acceptable correlation. Table 2 shows the calculated phase content for the cubic and tetragonal structures. The variation between the specimens was within 10% of the mean. The data from Table 2 are depicted in Fig. 15.
Table 2  Phase content as calculated by Rietveld method from powder-XRD data along with the GOF value from TOPAS

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tetragonal P4/mmm (%)</th>
<th>Cubic Pm3m (%)</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting powder</td>
<td>38.4</td>
<td>61.6</td>
<td>1.24</td>
</tr>
<tr>
<td>Pressureless sintered</td>
<td>43.7</td>
<td>56.3</td>
<td>1.28</td>
</tr>
<tr>
<td>Sintered and quenched</td>
<td>34.4</td>
<td>65.6</td>
<td>1.32</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>44.3</td>
<td>55.7</td>
<td>1.33</td>
</tr>
<tr>
<td>Experiment 3</td>
<td>45.2</td>
<td>54.8</td>
<td>1.23</td>
</tr>
<tr>
<td>Experiment 4</td>
<td>56.7</td>
<td>43.3</td>
<td>1.49</td>
</tr>
</tbody>
</table>

It was expected the specimen with the highest percent of cubic structure was conventionally sintered and quenched in liquid nitrogen. Since all of the flash-sintered specimens had a lower percent of cubic structure than the quenched sample (from previous work), it was possible the rate of temperature change in the flash experiments was unable to preserve the cubic polymorph. The furnace temperature of Experiment 4 was a maximum of 1000 °C, which is lower than the expected cubic-to-tetragonal-transition temperature of approximately 1100 °C; hence, the greater proportion of the tetragonal phase in Experiment 4.

Fig. 15  Bar graph of phase content of Experiments 2–4 and the comparison specimens from previous work

3.3 Comparing the Ionic Conductivity

The flash-sintered LLTO specimens were very fragile and typically broke into small fragments over time. However, two specimens from Experiments 3 and 4 were polished down to parallelepipeds for EIS measurements. Figure 16 shows the

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raw and modelled data for the specimen from Experiment 3. While the specimen exhibited stronger electronic than ionic conduction, grain and grain-boundary resistances were still calculated. Figure 17 shows the raw and modelled data for the specimen from Experiment 4.

Fig. 16 Imaginary impedance vs. real impedance in ohms for the specimen from Experiment 3; solid line represents measured data and dashed line represents the model of an equivalent circuit

Fig. 17 Imaginary impedance vs. real impedance in ohms for the specimen from Experiment 4; solid line represents measured data and dashed line represents the model of an equivalent circuit

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Figure 18 shows the calculated lattice ionic conductivity in Siemens per centimeter (S/cm). The pressureless-sintered and sintered-and-quenched samples exhibited higher lattice conductivity than the flash-sintered samples. One possible explanation was the lower percent of cubic structure resulted in a lower conductivity. Figure 19 shows the grain-boundary ionic conductivity of the specimens. Recall that the grain-boundary ionic conductivity was the limiting contribution to the total ionic conductivity of the material. The specimen from Experiment 3 had the highest grain-boundary conductivity among the measured specimens, even though the raw data appeared to be more electronically conducting (movement of electrons through the lattice). It was possible the lower temperature of the furnace reduced the amount of lithium volatilization, leading to more lithium ion charge carriers available for transport at the grain boundaries.

Fig. 18 Calculated ionic conductivity of the grain for four different specimens: two flash-sintered specimens (Experiments 3 and 4) compared with conventionally sintered samples
4. Conclusions and Ongoing Work

Four experiments were completed using a flash-sintering procedure to produce sintered LLTO specimens. Microstructural, physical, and electrical characterization were conducted on the sintered samples. The flash-sintered specimens were compared to conventionally processed materials. All flash-sintered specimens exhibited the typical “flash” behavior and demonstrated varying degrees of densification. All of the samples exhibited nonuniform densification, which could have been a result of the sample size. Since all of the specimens were larger than those mentioned in the literature, it was possible that once the current pathways were formed on the outside of the specimen, the sample became conductive and densification no longer occurred. These experiments have indicated a few different processing parameters can affect the onset of the flash event, including sample size, green density, and electrode configuration. The grain-boundary conductivity from Experiment 3 was higher than the conventionally sintered control specimen but with a trade-off on the lattice conductivity.

Future efforts will focus on carefully controlling the specimen size and green density and observing changes in the flash temperature (furnace temperature at the onset of the flash event) and ionic conductivity as the applied voltage is varied. The

Fig. 19  Calculated grain-boundary ionic conductivity for four different specimens: two flash-sintered specimens (Experiments 3 and 4) compared with conventionally sintered samples

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goal will be to consistently produce parts with uniform density. Based on the results of this study, some of the challenges will include reaction with the electrodes and potentially reducing atmospheres. Future experiments should also examine the effects of the furnace atmosphere on the composition; an oxidizing atmosphere could be beneficial to retaining the Ti$^{4+}$ cation. Finally, significant understanding of the fundamental mechanisms could be gained by further incorporation of in-situ characterization methods.
5. References


11. Sommariva M, Catti M. Neutron diffraction study of quenched Li0.3La0.567TiO3 lithium ion conducting perovskite. Chem Mater. 2006;18(9):2411–2417.


<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_b$</td>
<td>conductivity of the bulk boundaries</td>
</tr>
<tr>
<td>$\sigma_{gb}$</td>
<td>conductivity of the grain boundaries</td>
</tr>
<tr>
<td>$A$</td>
<td>cross-sectional area of the specimen</td>
</tr>
<tr>
<td>$\text{Ar}$</td>
<td>argon</td>
</tr>
<tr>
<td>ARL</td>
<td>US Army Research Laboratory</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>GOF</td>
<td>goodness of fit</td>
</tr>
<tr>
<td>HIP</td>
<td>hot isostatic pressing</td>
</tr>
<tr>
<td>$l$</td>
<td>specimen length</td>
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<tr>
<td>$\text{Li}$</td>
<td>lithium</td>
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<tr>
<td>LLTO</td>
<td>Li$<em>{0.33}$La$</em>{0.55}$TiO$_3$</td>
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<td>oxygen</td>
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<td>$R_b$</td>
<td>bulk resistance</td>
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<td>$R_{gb}$</td>
<td>grain-boundary resistance</td>
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<td>SEM</td>
<td>scanning electron microscope</td>
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<td>TD</td>
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<td>$T_f$</td>
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<tr>
<td>$T_m$</td>
<td>melting temperature</td>
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<tr>
<td>$\text{W}$</td>
<td>tungsten</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>YSZ</td>
<td>yttria stabilized zirconia</td>
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