Effects of Temperature on the Crystal Structure of Lithium-Lanthanum Zirconate

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ABSTRACT Lithium-lanthanum zirconate (LLZ) can potentially be used as a solid electrolyte in lithium-metal batteries. Li-metal batteries offer superior charge capacities and higher energy densities compared to currently used Li-ion batteries. Lithium is highly reactive, which can be dangerous in consumer electronics, but a layer of LLZ electrolyte inserted alongside the Li-metal electrode greatly stabilizes its reactivity. The cubic phase structure of LLZ ($Li_7La_3Zr_2O_{12}$) has the highest conductivity of its crystalline phases, making it the most promising crystal form of LLZ for this application. Samples of LLZ were doped with different amounts of aluminum and heated to high temperatures in a furnace while measuring *in-situ* x-ray diffraction data. The aim of this project was to calibrate and integrate the data. Preliminary results show that different crystallographic phases form as the samples are heated. The amount of aluminum present plays a major role in stabilizing the cubic phase.

1. INTRODUCTION

The past few decades have been marked by an ever-increasing ubiquity of consumer electronics in our world. As electronic devices continue to become more sophisticated, affordable, and indispensable to everyday life, research relating to electronics technology is persistently driven by demand for higher-performing electronic devices. In most cases, a crucial aspect of a device’s quality is its battery performance.

Currently, commercial rechargeable batteries are lithium-ion based. This technology offers high-energy density and charge capacity, and can be mass-produced within the necessary safety requirements. These batteries most often use lithiated graphite as their anode, meaning that the anode is comprised of a graphite plating with lithium deposited onto it [1]. Generally, in lithium batteries, the more lithium an anode stores, the more energy the battery can output overall. So in principle, the ideal anode for such a battery would simply be a lithium-metal anode. Li-metal electrodes boast a specific energy density several times higher than lithiated graphite.

Unfortunately, such Li-metal electrodes come with a major complication. Because lithium is so reactive, over several charge-discharge cycles, the anode can start to form growths of branch-like structures called dendrites, which can eventually span across to the cathode and cause a catastrophic short circuit or explosion. This is unacceptable for most applications where safety is a priority, especially in consumer electronics. Due to this problem, development in Li-metal rechargeable batteries was largely abandoned by the late 1980s [2].
However, recent research has shown that certain solid-electrolyte components can greatly reduce the tendency for Li-metal anodes to form dendrites, and may allow the Li-metal battery to function safely and effectively in the long term. In particular, a candidate for this electrolyte is lithium-lanthanum zirconate ($Li_7La_3Zr_2O_{12}$), also known as LLZ.

The purpose of this project was to examine the behavior of LLZ samples as they were subjected to steadily increasing temperatures ranging from room temperature to 1000°C. Observations regarding what phases (crystal structure configuration) formed at various temperatures were particularly relevant. Previous research has indicated that the phase structure most well-suited for this application is the cubic structure, since it has the highest conductivity of any LLZ phase. One of the main objectives of this project was to determine what temperatures maximize the formation and stability of cubic LLZ in a sample.

2. METHODS

The starting samples consisted of LLZ precursors prepared by a sol-gel method [3]. Aluminum dopants were added in order to stabilize the cubic structure. The doping amounts were 0%, 0.3%, 0.5%, and 1%, by weight percent. Synchrotron x-ray diffraction data of these samples were measured at Sector 1 of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The data were collected in transmission geometry, starting at room temperature up to 1000°C in static air or flowing helium gas using a two-dimensional detector. Above approximately 700°C each sample began to fuse with its glass capillary, eliminating all cubic LLZ phase and rendering the data irrelevant. Thus, only data below 700°C were analyzed. The incident x-ray beam had an energy of 20.076 keV. Over the course of this project, the raw data images were calibrated, integrated, and analyzed with the Rietveld method to examine the crystalline phase composition and atomic structures of the sample through the heating cycle.

The data set taken at the APS was very large, with over 800 raw diffraction images to process and analyze. To effectively process this large collection of data, the analysis process was completed in three main steps, using a different software program for each stage. First, GSAS-II, an open-source python program, was used to calibrate and integrate the raw diffraction images into one-dimensional intensity plots [4]. Next, a MATLAB script, developed in another student’s undergraduate research project, converted the resulting files into a format suitable for the final step. Finally, the FullProf suite was used to fit the data with crystallographic models [5].

**Figure 1.** A glass capillary filled with LLZ powder is held between two heating coils in this high-temperature cell configuration.

**Figure 2.** The experimental setup at the APS synchrotron. Here the sample is being heated. The detector is found behind the sample toward the left of the picture.
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The data images were calibrated using the 640c NIST silicon reference material [6]. The exact wavelength of the incident beam, the position of the beam center at the detector, the sample-detector distances, and the tilt and rotation of the detector were determined. These parameters were then stored and used by GSAS II to precisely and accurately process and integrate all the images.

As seen in Figures 3 and 4, the post holding the beam stop left a shadow in the data images. This was easily left out by selecting the appropriate azimuthal range of values to be integrated over, such that the range containing the shadow of the post was not included. The other main source of undesirable data was the glass capillary itself. Its imprint was removed from the data by taking a diffraction image of the empty capillary. Then those data were subtracted from each image during integration (subject to some multiplier factor), as seen in Figure 5. Finding this multiplier was somewhat difficult because the factor changed throughout the data set, and had to be manually redetermined. Once this was rectified, the images were integrated.

The GSAS-II output files were converted, using a MATLAB script, into data files compatible with FullProf, the software used to obtain crystallographic information about the samples. In order to analyze the data, the FullProf Rietveld software needed initial crystallographic information for the phases in the sample and other refinement parameters. FullProf used this information to automatically and continuously optimize the fits of the crystal structure of the LLZ sample via the Rietveld refinement method [7].

3. RESULTS AND DISCUSSION

The resulting models can provide us with a wealth of information (including unit cell size, atomic positions, and compositional distribution of the crystalline phases) about the crystal structure of each sample throughout each heating step. Figure 6 is an example of a Rietveld refinement on a sample with 0.3% Al-dopant that contained mostly cubic LLZ. The complete Rietveld analysis of the full data set is still in progress, but some basic conclusions can be made at this stage.

The temperatures at which the cubic phase is most dominant varies between samples with different aluminum doping levels. Aluminum is a key dopant that stabilizes the cubic phase. These results can be used to decide the doping level and appropriate temperature that optimize the cubic phase. LLZ samples can be quickly cooled to preserve the phase composition in the optimal state.

4. CONCLUSION

This research analyzed x-ray synchrotron data of lithium-lanthanum zirconate samples with different aluminum doping levels, collected at high temperatures. The raw two-dimensional diffraction data were calibrated and integrated. Complete analysis of these data and refinement of the models is ongoing. The data are being fitted to crystallographic models which provide much more detailed information about the crystal structure of the LLZ sample as it undergoes heating. Preliminary results show that different crystallographic phases form as the samples are heated. The amount of aluminum present plays a major role in the stability of the cubic phase.
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Figure 4. The diffraction image of the empty glass capillary. This broad, continuous ring is due to the amorphous structure of the silica capillary and stands in contrast to the sharp, discrete rings diffracted from the crystalline LLZ. The capillary contribution to each image was subtracted.

Figure 5. The effect of background subtraction. The blue plot is an intensity integration with the capillary data included, seen as a broad hump. The capillary data was subtracted in the green plot.

Figure 6. The experimental data from one image (in red) is fitted with the Rietveld method (in black). The green vertical lines indicate the positions of fitted peaks, and the difference between the fit and the data is show in blue at the bottom.

role in stabilizing the cubic phase. Full analysis of these data may provide information about the optimum heating conditions that maximize the presence of the cubic LLZ phase. This information will be valuable to researchers studying this material for possible applications in next-generation battery technology.

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REFERENCES


