Author's Accepted Manuscript

A General, Highly Efficient, High Temperature Thermal Pulse Toward High Performance Solid State Electrolyte

Chengwei Wang, Hua Xie, Weiwei Ping, Jiaqi Dai, Guolin Feng, Yonggang Yao, Shuaiming He, Jamie Weaver, Howard Wang, Karen Gaskell, Liangbing Hu



PII: S2405-8297(18)31184-X DOI: https://doi.org/10.1016/j.ensm.2018.11.007 Reference: ENSM554

To appear in: Energy Storage Materials

Received date: 10 October 2018 Revised date: 9 November 2018 Accepted date: 10 November 2018

Cite this article as: Chengwei Wang, Hua Xie, Weiwei Ping, Jiaqi Dai, Guolin Feng, Yonggang Yao, Shuaiming He, Jamie Weaver, Howard Wang, Karen Gaskell and Liangbing Hu, A General, Highly Efficient, High Temperature Thermal Pulse Toward High Performance Solid State Electrolyte, *Energy Storage Materials*, https://doi.org/10.1016/j.ensm.2018.11.007

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting galley proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

A General, Highly Efficient, High Temperature Thermal Pulse

Toward High Performance Solid State Electrolyte

Chengwei Wang,¹¹ Hua Xie,^{1,1} Weiwei Ping,¹ Jiaqi Dai,¹ Guolin Feng,¹ Yonggang Yao,¹ Shuaiming He,¹ Jamie Weaver,² Howard Wang,¹ Karen Gaskell,³ Liangbing Hu^{1,*}

¹Department of Materials Science and Engineering, University of Maryland College Park, College Park, Maryland, 20742

²Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899

³Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland Accepted. 20742

^{*}Email: binghu@umd.edu

¹ These authors contributed equally to this work.

Abstract

Surface contamination and degradation are two main issues leading to performance decay of ceramic-based solid-state electrolytes (SSEs). The typical strategies used to clean surface contaminants and restore ceramic materials involve mechanical polishing or high temperature thermal treatment. However, mechanical polishing can cause other side reactions and cannot clean contaminants on the grain boundaries of SSEs, while conventional thermal treatment using a furnace is often energy- and time-intensive, as the heating and cooling processes are slow. In this work, we for the first time demonstrate a high temperature thermal pulse technique for rapid ceramic surface processing. As a demonstration, we cleaned a garnet-based Li conductive SSE featuring lithium carbonate surface contamination in less than 2 seconds. The thermal pulsed garnet SSE exhibits an improved ionic conductivity of 3.2×10^{-4} S/cm—a two-fold increase

nanusciik

compared to the starting material. Symmetric cells featuring the thermal pulsed garnet SSE can cycle at current densities up to 500 μ A/cm², while control cells short-circuit at a current density of 100 μ A/cm².

Graphical abstract



Keywords: Rapid thermal Pulse; Garnet solid-state electrolyte; Oxygen vacancy; Lithium carbonate removal; Ceramic; Neutron depth profiling

Surface contamination and degradation are detrimental to the performance of ceramic materials, since many applications involve physical or chemical processes at the interfaces[1,2]. As lithium (Li) conductive ceramic materials, solid state electrolytes (SSEs) are especially plagued with these surface issues due to the high mobility and reactivity of Li ions[3–5]. SSEs have attracted great interest for replacing organic liquid electrolytes in Li-ion batteries due to their nonflammability, which makes it possible to use Li metal anodes without serious safety concerns[6–9]. Cubic garnet phase $Li_7La_3Zr_2O_{12}$ (LLZO) ceramic SSEs are among the most attractive candidates for achieving Li metal batteries due to the material's excellent chemical[10] and electrochemical stability against Li metal and its potential ability to block dendritic Li growth[11–18].

However, surface contamination or degradation of the ceramic leads to poor interfacial Li ion transport properties, which negatively affect electrochemical performance. Recent studies have shown that low ionic conductivity, poor electrolyte-electrode interfaces, and the secondary phase contaminations at grain boundaries of garnet can cause the short-circuit of garnet SSEs at high current densities[19–24]. Because of the high reactivity and mobility of Li ions, lithium carbonate (Li₂CO₃) contamination is one of the main reasons responsible for these problems. Particularly for aged garnet SSEs, Li₂CO₃ can easily accumulate on the surface or even at grain boundaries[25,26], making the storage of garnet SSEs a challenge in practical battery fabrication.

The conventional strategies to remove Li_2CO_3 and other surface contaminations involve mechanical polishing or high temperature thermal treatment to directly decompose the contaminations. However, mechanical polishing can cause other side reactions and cannot clean contaminants on the grain boundaries of SSEs, while conventional thermal treatment using typical thermal equipment (*i.e.*, a furnace) takes at least several hours to conduct the high

temperature treatment, which is too long for practical battery manufacturing. Another issue associated with high temperature treatment of garnet SSEs is the Li loss that occurs due to the volatility of Li₂O at high temperature, which readily vaporizes at 600 °C[27] and can cause a phase change and poor ionic conductivity[12]. To simplify the thermal treatment and prevent Li loss, it is necessary to decrease the heating time while still maintaining the cleaning effect. Therefore, a fast and effective thermal treatment for garnet SSEs would be highly desirable for practical battery manufacturing.

In this work, we for the first time demonstrate a unique thermal pulse process that can successfully remove surface contamination from ceramics and restore aged garnet SSEs in less than 2 s. The maximum pulse temperature can reach up to 1250 °C (higher than the decomposition temperature of Li₂CO₃)[28] in 1 s, fully removing Li₂CO₃ contamination from both the surface and grain boundaries of garnet SSEs. The ultra-short pulse time also successfully prevents Li evaporation loss and the corresponding phase change problem. Because of the high treatment temperature and the inert gas atmosphere, an additional benefit of the thermal pulse process is the generation of oxygen vacancies in the garnet SSE, which recent studies have indicated play an important role in the electrochemical properties of the ceramic. Oxygen vacancies have been demonstrated to affect Li ion transport and therefore the ionic conductivity of garnet SSEs[29,30], which can be a new strategy to further improve the electrochemical performance. The thermal pulsed garnet SSEs turn white and feature a 2-fold increase in the ionic conductivity, which we believe corresponds to the formation of oxygen vacancies. Benefiting from these effects, the thermal pulsed garnet SSE demonstrated improved electrochemical stability.

The schematic in Figure 1 demonstrates the rapid thermal pulse process and its effects on garnet SSEs. In this process, a grayish garnet pellet is placed on top of a carbon-felt heater in an argon-filled glove box. The carbon felt strip is rapidly powered through Joule heating, and the temperature of the garnet pellet increases up to 1250 $^{\circ}$ C, in which the slight evaporation of lithium oxide introduces oxygen vacancies. Since the temperature is much higher than the decomposition temperature of Li₂CO₃[28], and the carbon felt can also act as a reductant at high temperature[31], Li₂CO₃ on the garnet surface and grain boundaries can be thoroughly removed during the thermal pulse treatment. The cleaning effect is important in the real fabrication of garnet-based solid-state Li metal batteries, as the storage of garnet SSEs will inevitably result in the formation of Li₂CO₃ on the surface. The short treatment time ensures the Li loss due to evaporation is not significant, which is critical to maintain the phase and ionic conductivity of garnet SSEs. The unique rapid Joule heating method also enables the potential for a roll-to-roll process to clean garnet SSEs for real applications.

Accepter



Fig. 1. Schematic of the rapid thermal pulse treatment process of garnet SSE. During the treatment, Li_2CO_3 contamination is removed, simultaneously generating oxygen vacancies.

Results and discussion

Fig. 2a shows the thermal pulse treatment of the garnet SSE, in which we can clearly see that the pellet color changes from grayish to white. The cross-sectional image in Fig. S1 demonstrates that this white color is not only on the surface but also in the bulk, indicating a whole pellet change after treatment. The images and the corresponding temperature profile indicate the garnet pellet was rapidly heated up from room temperature (RT) to 1250 °C in about 1 s, and this high temperature lasts for about 0.4 s. The subsequent natural cooling process only takes about 0.3 s, which makes the whole process less than 2 s long. Note that the temperature profile was acquired with a VIS-NIR spectrometer using a previous fitting method[32], which can be used to detect temperatures higher than ~600 °C. Due to the thermal capacity of the garnet pellets, the real temperature of the pellets may be slightly lower than the detected temperature of the carbon felt heating strip.

Cross-sectional scanning electron microscopy (SEM) images of the untreated and treated garnet pellets were used to characterize changes in morphology. Images of the near surface cross-section (Fig. 2b, c) show that the surface contamination was fully removed after the rapid thermal pulse treatment. Higher magnification SEM images of the interior grain boundaries further demonstrate the cleaning effect of the rapid thermal pulse treatment on the garnet SSE, in which the untreated garnet features rough contamination on the grain boundaries (Fig. 2d), while the same interfaces of the thermal pulse-treated garnet are much cleaner and smoother (Fig. 2e).



Fig. 2. Rapid thermal pulse treatment of garnet pellets. (a) Images of the thermal pulse treatment process at different temperatures, and the temperature profile of the process. Cross-sectional

SEM images near the surfaces of the garnet pellets (b) before and (c) after the thermal pulse treatment. (d, e) Cross-sectional SEM images of the interior grain boundaries. The rough contamination of the untreated garnet (d) was removed after the thermal pulse treatment (e).

Besides the morphology change, we also studied potential crystal structural changes of the garnet SSE during the thermal pulse treatment. As previous works have reported[31,33], thermal treatment can remove Li₂CO₃ contamination from garnet. To demonstrate the effectiveness of Li₂CO₃ removal, we applied the rapid thermal pulse treatment to a garnet pellet aged for two weeks in air. Based on the SEM images in Fig. S2, the grain size statistics of the treated and untreated garnet samples are shown in Fig. 3a, in which no obvious grain growth can be observed after treatment. X-ray diffraction (XRD) was used to characterize any phase change of the material (Fig. 3b). Small Li₂CO₃ peaks can be identified in the XRD pattern of the aged garnet, however, the peaks are absent in the pattern of the treated garnet, indicating the cleaning and restoring effect of the thermal pulse process. All the garnet peaks of both the untreated and thermal pulsed samples matched well with the standard cubic garnet phase (PDF#80-0457)[34]. The main difference is the relative intensity of each peak, especially the ones highlighted by the dashed-line box, which indicates a possible slight change in the lattice parameter. According to this XRD analysis, we can eliminate the possibility of a phase change from cubic to tetragonal due to excessive Li loss at high temperature.

Raman spectroscopy was also measured for the garnet SSE before and after the thermal pulse treatment. All the main bands corresponding to LLZO agree with the cubic garnet phase (Fig. 3c), which further confirms there was no phase change after the thermal pulse treatment[35]. The Raman spectra also confirm the cleaning effect of the rapid thermal pulse

treatment. The intense bands in the Raman spectrum at 158 cm⁻¹ and 1091 cm⁻¹ indicate a significant amount of Li_2CO_3 formation in the aged sample[35]. After rapid thermal pulse treatment, no obvious bands corresponding to Li_2CO_3 can be identified, which agrees with the morphology changes of the samples shown in Fig. 2 and the XRD analysis of Fig. 3b.

To characterize the lithium loss during the rapid thermal pulse treatment, neutron depth profiling (NDP) was used to quantitatively measure the lithium change[36,37]. Freshly-made garnet pellets were used to avoid the influence of Li₂CO₃, and the surface was dry-polished with 1200 grit SiC sandpaper[34] for both the untreated and thermal pulse-treated pellets just prior to NDP analysis. The Li depth distribution profiles of the untreated and the thermal pulse-treated garnet pellets are shown in Fig. 3d. The profiles are from the ³H reaction products only. After integrating the counts over the whole energy range, the Li loss was calculated to be 1.59% \pm 0.14% after treatment, much lower than that of other thermal treatments[12,31,38]. The quantitative NDP measurements indicate that Li loss during the rapid thermal pulse treatment is not significant within the bulk, which agrees with the XRD and Raman results.

Accel



Fig. 3. Characterization of the garnet SSE before and after thermal pulse treatment. (a) Grain size distribution of the untreated and thermal pulse treated garnet, indicating no grain size change. (b) XRD patterns and (c) Raman spectra of the garnet pellets before and after the thermal pulse treatment. (d) Li depth profile of the garnet pellets before and after the thermal pulse treatment, as measured *via* NDP analysis. The similar counts indicate that the Li loss to the bulk of the sample during thermal pulse treatment is negligible. Fractional error bars are calculated based on experimental counting statistics.

The color changes of the garnet pellets can be directly characterized by the UV-Vis absorption spectrum. On the UV-Vis spectra (Fig. S3), the untreated garnet has higher absorption than the rapid thermal pulse-treated garnet, especially in the high wavelength range. The UV-Vis measurements indicate that the rapid thermal pulse-treatment increases the band gap of the garnet SSEs, which may potentially increase their chemical stability against Li metal[39]. This color change effect has been previously reported in several works. Goodenough and his coworkers thought the color change was due to the removal of Li_2CO_3 during thermal pulse treatment[31]. However, Doeff *et al.* have demonstrated that the sintering atmosphere can affect the color and the ionic conductivity of garnet pellets, and they proposed that the color change may be due to the formation of oxygen vacancies[40].

To understand the color change, we conducted X-ray photoelectron spectroscopy (XPS) analysis of the garnet pellets before and after the rapid thermal pulse treatment. Data was also collected after Ar ion sputtering to remove the post surface contamination for both the untreated and treated samples, designated as "untreated-S" and "treated-S," respectively. In the C 1s spectra (Fig. 4a), both the treated and untreated garnet SSEs before sputtering have peaks corresponding to Li₂CO₃ and hydrocarbon contaminations. After sputtering all the Li₂CO₃ and hydrocarbon have been removed from the treated-S sample, and most of it from the untreated-S sample, again showing that Li₂CO₃ is found in the form of an overlayer. The absence of the peak at ~290 eV corresponding to Li₂CO₃ by the rapid thermal pulse treatment. The peaks in the O 1s spectra at 529 eV and 531eV correspond to the O from garnet and Li₂CO₃, respectively (Fig. 4b)[31]. Before sputtering, the treated garnet displays a higher O²⁻ intensity at ~529 eV compared to the untreated sample, indicative of the larger attenuation of the carbonate overlayer

after the thermal pulse. After sputtering, as seen by the absence of carbonate in the C 1s spectra (Fig. 4a), there should be no oxygen from carbonate in the O 1s spectra. However, there is still a peak at the higher binding energy (~531 eV) for the treated-S garnet sample. Since there is only one type of oxygen in the cubic LLZO crystal structure, it has been suggested that this peak could be due to oxygen vacancies[41], which is a common defect in garnet SSEs annealed in low oxygen atmospere[29,30]. Even though the intensities of the peaks at ~531 eV for treated-S and untreated-S in the O 1s spectra look equivalent on first glance, for the untreated-S sample there is actually still some carbonate remaining that is contributing to the signal. We calculated based on the C 1s peak that approximately 28% of the O 1s peak at ~531 eV for the untreated-S sample is due to carbonate. If the peak at ~531 eV is due to O vacancy, this would imply a larger number of vacancies in the thermal pulsed sample (treated-S) than the untreated garnet (untreated-S). Besides the difference in intensity, the peak at ~531 eV for the treated-S sample is slightly shifted to lower energy, which may also indicate the formation of O vacancies. In the Zr 3d and La $3d_{5/2}$ spectra, there were no obvious changes after the rapid thermal pulse treatment (Fig. 4c, d). Therefore, the two main possible reasons for the observed color change are the removal of Li₂CO₃ and the formation of oxygen vacancies.

To further exam these two explanations, a control experiment was conducted, in which the white thermal pulsed garnet pellets were re-annealed in pure oxygen atmosphere at 800 $^{\circ}$ C for 10 min. All the white pellets change back to a grayish color after this treatment. The result indicates that the color change during the rapid thermal pulse treatment is due to the formation of oxygen vacancies rather than the removal of Li₂CO₃, which is in agreement with previous reports that garnet SSEs annealed in argon are whiter than those annealed in air or oxygen[40]. Previous studies have shown that white garnet SSEs with more oxygen vacancies typically have better Li

ionic conductivities[30,40]. However, the synthesis of garnet SSE in air is more practical and cost-effective, and the use of oxygen atmosphere can help densify the pellet during annealing[42]. Our rapid thermal pulse treatment can therefore take advantages of both processing conditions. Specifically, garnet SSE synthesized in air or oxygen can be rapidly treated in inert gas to introduce oxygen vacancies and improve the ionic conductivity.

Accepted manuscript



Fig. 4. XPS measurement of garnet SSEs before (Untreated) and after (Treated) thermal pulse treatment, including (a) C 1s, (b) O 1s, (c) Zr 3d, and (d) La 3d spectra. The data was also collected after argon ion sputtering for both the untreated and treated samples, designated as "untreated-S" and "treated-S."

We studied the electrochemical properties of the rapid thermal pulse-treated garnet SSE by measuring the ionic conductivity and cycling performance of Li/SSE/Li symmetric cells. As electrochemical impedance spectroscopy (EIS) shows in Fig. 5a, the ionic conductivity of the thermal pulse-treated garnet ($\sim 3.2 \times 10^{-4}$ S/cm) was about twice that of the untreated material $(\sim 1.6 \times 10^{-4} \text{ S/cm})$ due to the formation of oxygen vacancies, which is in agreement with the literature[29,40]. To further demonstrate the improved electrochemical properties of the thermal pulse-treated garnet, Li-Garnet-Li symmetric cells were assembled to conduct cycling at different current densities. The EIS spectra of the symmetric cells with the thermal pulse-treated garnet are shown in Fig. 5b, and the voltage profile of the cycling behavior is shown in Fig. 5c. The cell was cycled with elevated current densities from 100 µA/cm², and we observed the voltage profile was stable and smooth at current densities up to 300 μ A/cm². At the end of the 300 µA/cm² cycling, the EIS was measured and shown in Fig. 5b, which only featured a slight increase from approximately 250 $\Omega \cdot cm^2$ to 280 $\Omega \cdot cm^2$, indicating excellent electrochemical stability. When the current density was further increased to 500 μ A/cm², the voltage profile of the treated garnet starts to show polarization and becomes noisy at the fourth cycle (Fig. 5c). After 500 μ A/cm², the EIS curve shown in Fig. 5b indicates a short-circuit, however, the current density achieved using the treated sample is comparable to the highest reported in the literature for garnet SSEs[33]. As a comparison, a control cell made with the untreated garnet was cycled at the same condition, and the cell died in the first cycle at a current density of 100 μ A/cm² (Fig. 5c). Note that the starting garnet pellets used in this work only have moderate density and ionic conductivity. If we began with higher quality garnet, we expect the electrochemical performance of the treated material would be even further improved.

The improved electrochemical performance of the treated garnet can be attributed to the increased ionic conductivity and the removal of Li₂CO₃ during the rapid thermal pulse treatment. Therefore, this treatment method can be used to quickly restore and boost the electrochemical properties of garnet SSEs during the practical fabrication of solid-state batteries. Compared with regular thermal treatment, the rapid thermal pulse has much shorter treatment time, which allows it to be integrated in roll-to-roll processes for potential scalable processing of ceramic materials. As the schematic in Fig. 5d shows, the untreated ceramic thin pellet with surface contamination and degradation can be quickly transported through two ultra-fast radiating heaters, in which the ceramic is thermally pulsed, producing a cleaner and more electrochemically stable material for battery application.



Fig. 5. Electrochemical performance of the thermal pulse-treated garnet SSE. (a) EIS measurement of the garnet SSE before and after the thermal pulse treatment. (b) EIS measurement of the symmetric cells with the thermal pulse-treated garnet at different cycling stages. (c) Voltage profiles of the symmetric cells cycled at different current densities. The blue

curve is the cell with the untreated garnet, and the red curve is the cell with the thermal pulsetreated garnet. (d) Schematic of the roll-to-roll process for rapid thermal treatment of ceramic materials.

Conclusion

Acci

For the first time, we have developed a thermal pulse technique for rapid ceramic surface processing that can quickly clean surface contamination and restore the materials in less than 2 s. As a demonstration, we successfully cleaned Li₂CO₃ contamination from the surface and grain boundaries of garnet SSEs. The ultra-short processing time prevented Li loss and any phase change of the garnet SSE at high temperature. We systematically studied the formation of oxygen vacancies by this process, which results in an increase in ionic conductivity of the garnet SSEs from about 1.6×10^{-4} S/cm to 3.2×10^{-4} S/cm. The rapid thermal pulse treatment also significantly improved the electrochemical stability of the material. Additionally, the critical cycling current density in symmetric cells increased from 100 μ A/cm² to 500 μ A/cm² after the thermal pulse treatment. This unique Joule heating method and ultra-fast process enable the potential for roll-to-roll processing for ceramic surface treatment in practical applications.

Methods

Synthesis of the Garnet Solid-State Electrolyte. The Al-doped $Li_{6.75}La_3Zr_2O_{12}$ garnet electrolyte was synthesized via a solid-state reaction method. LiOH·H₂O (99.9%, Sigma Aldrich), La_2O_3 (\geq 99.9%, Sigma Aldrich), and ZrO₂ (99.9%, Sigma Aldrich) were used as precursors. Stoichiometric amounts were adequately mixed in isopropyl alcohol (IPA) for 12 h. 12% excess LiOH·H₂O was added to compensate for the loss of lithium during synthesis. Al₂O₃ nanopowder (~2 wt% of the total material) was added to help the sintering process. The stoichiometrically mixed powders were calcined at 920 °C for 12 h. Then the powders were mixed with IPA and ball-milled for 9 h. The powders were pressed into pellets with diameters of 10 mm at 300 MPa and sintered at 1150 °C for 9 h. After the sintering process, the surface of the pellets was polished with 1200 grit sandpaper in an Ar-filled glovebox.

Thermal pulse treatment. Two tips of the carbon felt heating strip were attached to the edge of glass substrates using silver paste (SPI Supplies). Then a conductive copper tape was used to connect the heating strip with the power supply (VOLTEQ HY6020EX). The garnet pellets were directly placed on the heating strip. A Keithley 2400 power supply unit was used to generate signals that controlled a solid-state relay to control the power on and off. The thermal pulse process was recorded using a digital camera (Canon 60D, 30 frames s⁻¹). The temperature of the heater was calculated by fitting the radiation spectrum following a previous method[32], which was collected by a VIS-NIR spectrometer (USB2000+, Ocean Optics).

Electrochemical Measurement. A Li metal anode was coated on the garnet using a previous method[43]. Electrochemical tests of Li/garnet/Li symmetric cells were conducted on a BioLogic VMP3 potentiostat at room temperature. The EIS was performed with a 20 mV AC amplitude in the frequency range of 100 mHz to 1 MHz for Li/garnet/Li cells. Galvanostatic stripping-plating

of the Li/garnet/Li symmetric cells were recorded at room temperature with various current densities. The cells were placed in an Ar-filled glovebox to conduct all measurements.

Materials Characterization. The morphologies and elemental mapping of the Li alloy-garnet cross sections were conducted on a Tescan XEIA Plasma focused ion beam SEM at 10 kV. XRD spectra were measured on a C2 Discover diffractometer (Bruker AXS, WI, USA) using a Cu Ka radiation source operated at 40 kV and 40 mA. Raman characterization was done with a Horiba Jobin-Yvon equipped with a 532 nm laser and using an integration time of 4 seconds repeated for 4 measurements. The absorbance spectra were measured with a UV-Vis Spectrometer Lambda 35 (PerkInElmer, USA). XPS data was collected on a Kratos Axis 165 operating in hybrid mode using monochromatic Al Kalpha X-ray source (1486.7 eV). Charge neutralization was required to minimize sample charging. Survey spectra and high-resolution spectra were collected with pass energies of 160 eV and 40 eV, respectively. Data was collected both before and after argon ion sputtering. Sputtering was done at 4 kV and 25 ma emission current. The argon ion beam had a spot size of ~ 1 mm and was rastered to create a crater of 7 by 7 mm in size. The current measured at the sample holder when the beam was static (not rastered) was 2.5 µA. Samples were sputtered for 20 minutes. All the XPS spectra were calibrated to the lowest multiplet of the Zr 3d_{5/2} spin orbit split component at 180.8 eV. All samples were transported to the XPS instrument in an Ar environment, in which samples were polished in the glove box prior to transport to the XPS, and a glove bag was attached to the XPS instrument to minimize exposure to oxygen and water in an effort to prevent the formation of a thick Li₂CO₃ layer on the surface.

NDP data was collected at the Neutron Guide 5 (NG5), Cold Neutron Depth Profiling station at the NIST Center for Neutron Research (NCNR) at the National Institute of Standards and

22

Technology (NIST, Gaithersburg, MD). The garnet pellets were dry polished with sand paper right before the measurement to reduce the effect of Li₂CO₃. Samples were mounted with a 3.0 mm circular, Teflon® aperture. Each sample was irradiated at a near constant neutron fluence rate of cold neutrons ($\approx 10^9$ cm⁻² s⁻¹), and all experiments were conducted under vacuum and at room temperature. NDP spectra were collected for ~10 h per sample. ⁶Li nuclear reaction (⁶Li(n,a)³H) product triton particles (³H) were detected using a circular transmission-type silicon surface-barrier detector that was positioned ~120 mm from the sample surface. Each spectrum was corrected for variations in the neutron fluence rate, detector dead time (≈ 0.01 %), and background noise. Li concentrations were calculated in reference to the known concentration of ¹⁰B in a B-implanted concentration standard, according to the following equation. Fractional error was calculated based on experimental counting statistics.

$$[a] = [b] \frac{\sigma_{0,b}}{\sigma_{0,a}}$$

in which [a] and [b] are the concentrations (atoms/cm²) of isotopes a and b being measured in the sample and standard, respectively, and σ_0 is the thermal neutron cross-section for the charged-particle emission. The slight difference in the position of the surface between the two samples is most likely due to the slight depletion of Li from the sample's surface during dry polishing.

Acknowledgements

We acknowledge the support of the Center for Research in Extreme Batteries (CREB) from the Joint Research and Innovation Seed Grant of the University of Maryland (UMD), College Park, the U.S. Army Research Laboratory (ARL), and the National Institute of Standards and Technology (NIST). We also acknowledge the support of the Maryland Nanocenter, its Surface Analysis Center and AIMLab, and the NIST Center for Neutron Research (NCNR). Trade names and commercial products are identified in this paper to specify the experimental procedures in adequate detail. This identification does not imply recommendation or endorsement by the authors or by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose. Contributions of the National Institute of Standards and Technology are not subject to copyright.

Author contributions

L. Hu and C. Wang designed the experiments. C. Wang and W. Ping carried out the thermal pulse treatment experiments, electrochemical measurement, and SEM imaging. H. Xie conducted XRD and Raman measurements. H, Xie, W. Ping, and G. Feng synthesized garnet SSEs. J. Dai created the 3D illustrations. Y. Yao performed the temperature profile measurements. S. He conducted the UV-Vis measurements. H. Wang helped with the NDP measurement. J. Weaver assisted in the collection of the NDP data. K. Gaskell was responsible for XPS measurement and analysis. L. Hu and C. Wang collectively wrote the paper. All authors commented on the final manuscript.

Reference

- N. Tsvetkov, Q. Lu, B. Yildiz, Improved electrochemical stability at the surface of La _{0.8} Sr _{0.2} CoO ₃ achieved by surface chemical modification, Faraday Discuss. 182 (2015) 257–269. doi:10.1039/C5FD00023H.
- [2] N. Tsvetkov, Q. Lu, L. Sun, E.J. Crumlin, B. Yildiz, Improved chemical and electrochemical stability of perovskite oxides with less reducible cations at the surface, Nat. Mater. 15 (2016) 1010–1016. doi:10.1038/nmat4659.
- [3] P. Knauth, Inorganic solid Li ion conductors: An overview, Solid State Ionics. 180 (2009) 911–916. doi:10.1016/j.ssi.2009.03.022.
- [4] S. Hasegawa, N. Imanishi, T. Zhang, J. Xie, A. Hirano, Y. Takeda, O.
 Yamamoto, Study on lithium/air secondary batteries-Stability of NASICONtype lithium ion conducting glass-ceramics with water, J. Power Sources. 189 (2009) 371–377. doi:10.1016/j.jpowsour.2008.08.009.
- [5] W.D. Richards, L.J. Miara, Y. Wang, J.C. Kim, G. Ceder, Interface Stability in Solid-State Batteries, Chem. Mater. 28 (2016) 266–273. doi:10.1021/acs.chemmater.5b04082.
- [6] J. van den Broek, S. Afyon, J.L.M. Rupp, Interface-Engineered All-Solid-State Li-Ion Batteries Based on Garnet-Type Fast Li+Conductors, Adv. Energy Mater. 6 (2016) 1–11. doi:10.1002/aenm.201600736.
- [7] X. Tao, Y. Liu, W. Liu, G. Zhou, J. Zhao, D. Lin, C. Zu, O. Sheng, W. Zhang, H.-W. Lee, Y. Cui, Solid-State Lithium–Sulfur Batteries Operated at 37 °C with Composites of Nanostructured Li7La3Zr2O12/Carbon Foam and Polymer, Nano Lett. 17 (2017) 2967–2972.

doi:10.1021/acs.nanolett.7b00221.

- [8] W. Zhou, S. Wang, Y. Li, S. Xin, A. Manthiram, J.B. Goodenough, Plating a Dendrite-Free Lithium Anode with a Polymer/Ceramic/Polymer Sandwich Electrolyte, J. Am. Chem. Soc. 138 (2016) 9385–9388. doi:10.1021/jacs.6b05341.
- [9] A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes, Nat. Rev. Mater. 2 (2017) 1–16. doi:10.1038/natrevmats.2016.103.
- [10] J. Wolfenstine, J.L. Allen, J. Read, J. Sakamoto, Chemical stability of cubic Li7La3Zr 2O12 with molten lithium at elevated temperature, J. Mater. Sci. 48 (2013) 5846–5851. doi:10.1007/s10853-013-7380-z.
- [11] V. Thangadurai, S. Narayanan, D. Pinzaru, Garnet-type solid-state fast Li ion conductors for Li batteries: critical review, Chem. Soc. Rev. 43 (2014) 4714. doi:10.1039/c4cs00020j.
- [12] I. Garbayo, M. Struzik, W.J. Bowman, R. Pfenninger, E. Stilp, J.L.M. Rupp, Glass-Type Polyamorphism in Li-Garnet Thin Film Solid State Battery Conductors, Adv. Energy Mater. 1702265 (2018) 1–14. doi:10.1002/aenm.201702265.
- Y. Zhu, X. He, Y. Mo, First Principles Study on Electrochemical and Chemical Stability of the Solid Electrolyte-Electrode Interfaces in All-Solid-State Li-ion Batteries, J. Mater. Chem. A. 4 (2015) 1–14. doi:10.1039/C5TA08574H.
- [14] Y. Jin, K. Liu, J. Lang, D. Zhuo, Z. Huang, C. Wang, H. Wu, Y. Cui, An intermediate temperature garnet-type solid electrolyte-based molten lithium battery for grid energy storage, Nat. Energy. (n.d.). doi:10.1038/s41560-018-0198-9.
- [15] J.E. Ni, E.D. Case, J.S. Sakamoto, E. Rangasamy, J.B. Wolfenstine, Room

temperature elastic moduli and Vickers hardness of hot-pressed LLZO cubic garnet, J. Mater. Sci. 47 (2012) 7978–7985. doi:10.1007/s10853-012-6687-5.

- [16] C.-Z. Zhao, X.-Q. Zhang, X.-B. Cheng, R. Zhang, R. Xu, P.-Y. Chen, H.-J. Peng, J.-Q. Huang, Q. Zhang, An anion-immobilized composite electrolyte for dendrite-free lithium metal anodes, Proc. Natl. Acad. Sci. (2017) 201708489. doi:10.1073/pnas.1708489114.
- T. Yang, Z.D. Gordon, Y. Li, C.K. Chan, Nanostructured Garnet-Type Solid Electrolytes for Lithium Batteries: Electrospinning Synthesis of Li7La3Zr2O12 Nanowires and Particle Size-Dependent Phase Transformation, J. Phys. Chem. C. 119 (2015) 14947–14953. doi:10.1021/acs.jpcc.5b03589.
- [18] F. Han, J. Yue, C. Chen, N. Zhao, X. Fan, Z. Ma, T. Gao, F. Wang, X. Guo, C. Wang, Interphase Engineering Enabled All-Ceramic Lithium Battery, Joule. 2 (2018) 497–508. doi:10.1016/j.joule.2018.02.007.
- [19] L. Porz, T. Swamy, B.W. Sheldon, D. Rettenwander, T. Frömling, S. Berendts, R. Uecker, W.C. Carter, Y. Chiang, Mechanism of Lithium Metal Penetration through Inorganic Solid Electrolytes, Adv. Energy Mater. 1701003 (2017) 1–12. doi:10.1002/aenm.201701003.
- [20] F. Aguesse, W. Manalastas, L. Buannic, J.M.L. Del Amo, G. Singh, A. Llordés, J. Kilner, Investigating the dendritic growth during full cell cycling of garnet electrolyte in direct contact with Li metal, ACS Appl. Mater. Interfaces. 9 (2017) 3808–3816. doi:10.1021/acsami.6b13925.
- [21] C.-L. Tsai, V. Roddatis, C.V. Chandran, Q. Ma, S. Uhlenbruck, M. Bram, P. Heitjans, O. Guillon, Li 7 La 3 Zr 2 O 12 Interface Modification for Li Dendrite Prevention, ACS Appl. Mater. Interfaces. 8 (2016) 10617–10626. doi:10.1021/acsami.6b00831.
- [22] Y. Ren, Y. Shen, Y. Lin, C.W. Nan, Direct observation of lithium dendrites

inside garnet-type lithium-ion solid electrolyte, Electrochem. Commun. 57 (2015) 27–30. doi:10.1016/j.elecom.2015.05.001.

- [23] C.L. Tsai, V. Roddatis, C.V. Chandran, Q. Ma, S. Uhlenbruck, M. Bram, P. Heitjans, O. Guillon, Li7La3Zr2O12Interface Modification for Li Dendrite Prevention, ACS Appl. Mater. Interfaces. 8 (2016) 10617–10626. doi:10.1021/acsami.6b00831.
- [24] Y. Shen, Y. Zhang, S. Han, J. Wang, Z. Peng, L. Chen, Unlocking the Energy Capabilities of Lithium Metal Electrode with Solid-State Electrolytes, Joule. (2018). doi:10.1016/j.joule.2018.06.021.
- [25] L. Cheng, E.J. Crumlin, W. Chen, R. Qiao, H. Hou, S. Franz Lux, V. Zorba, R. Russo, R. Kostecki, Z. Liu, K. Persson, W. Yang, J. Cabana, T. Richardson, G. Chen, M. Doeff, The origin of high electrolyte-electrode interfacial resistances in lithium cells containing garnet type solid electrolytes., Phys. Chem. Chem. Phys. 16 (2014) 18294–18300. doi:10.1039/c4cp02921f.
- [26] A. Sharafi, S. Yu, M. Naguib, M. Lee, C. Ma, H.M. Meyer, J. Nanda, M. Chi, D.J. Siegel, J. Sakamoto, Impact of air exposure and surface chemistry on Li–Li ₇ La ₃ Zr ₂ O ₁₂ interfacial resistance, J. Mater. Chem. A. 5 (2017) 13475–13487. doi:10.1039/C7TA03162A.
- [27] M. Nyman, T.M. Alam, S.K. McIntyre, G.C. Bleier, D. Ingersoll, Alternative approach to increasing Li mobility in Li-La-Nb/Ta garnet electrolytes, Chem. Mater. 22 (2010) 5401–5410. doi:10.1021/cm101438x.
- [28] R.P. Rao, W. Gu, N. Sharma, V.K. Peterson, M. Avdeev, S. Adams, In situ neutron diffraction monitoring of Li7La3Zr2O12 formation: Toward a rational synthesis of garnet solid electrolytes., Chem. Mater. 27 (2015) 2903– 2910. doi:10.1021/acs.chemmater.5b00149.
- [29] X. Zhan, S. Lai, M.P. Gobet, S.G. Greenbaum, M. Shirpour, Defect

chemistry and electrical properties of garnet-type Li ₇ La ₃ Zr ₂ O ₁₂, Phys. Chem. Chem. Phys. 20 (2018) 1447–1459. doi:10.1039/C7CP06768B.

- [30] M. Kubicek, A. Wachter-Welzl, D. Rettenwander, R. Wagner, S. Berendts, R. Uecker, G. Amthauer, H. Hutter, J. Fleig, Oxygen Vacancies in Fast Lithium-Ion Conducting Garnets, Chem. Mater. 29 (2017) 7189–7196. doi:10.1021/acs.chemmater.7b01281.
- [31] Y. Li, X. Chen, A. Dolocan, Z. Cui, S. Xin, H. Xu, K. Park, J.B. Goodenough, Y. Li, X. Chen, A. Dolocan, Z. Cui, S. Xin, L. Xue, H. Xu, K. Park, Garnet electrolyte with an ultra-low interfacial resistance for Li-metal batteries Garnet electrolyte with an ultra-low interfacial resistance for Limetal batteries, J. Am. Chem. Soc. 140 (2018) 6448–6455. doi:10.1021/jacs.8b03106.
- [32] C. Wang, Y. Wang, Y. Yao, W. Luo, J. Wan, J. Dai, E. Hitz, K.K. Fu, L. Hu, A Solution-Processed High-Temperature, Flexible, Thin-Film Actuator, Adv. Mater. 28 (2016) 8618–8624. doi:10.1002/adma.201602777.
- [33] A. Sharafi, E. Kazyak, A.L. Davis, S. Yu, T. Thompson, D.J. Siegel, N.P. Dasgupta, J. Sakamoto, Surface Chemistry Mechanism of Ultra-Low Interfacial Resistance in the Solid-State Electrolyte Li7La3Zr2O12, Chem. Mater. 29 (2017) 7961–7968. doi:10.1021/acs.chemmater.7b03002.
- [34] X. Han, Y. Gong, K. (Kelvin) Fu, X. He, G.T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, Y. Mo, V. Thangadurai, E.D. Wachsman, L. Hu, Negating interfacial impedance in garnet-based solid-state Li metal batteries, Nat Mater. 16 (2017) 572–579. doi:10.1038/nmat4821.
- [35] G. Larraz, A. Orera, M.L. Sanjuán, Cubic phases of garnet-type Li7La3Zr2O12: the role of hydration, J. Mater. Chem. A. 1 (2013) 11419. doi:10.1039/c3ta11996c.
- [36] H. Wang, R.G. Downing, J.A. Dura, D.S. Hussey, In Situ Neutron

Techniques for Studying Lithium Ion Batteries, Polym. Energy Storage Deliv. Polyelectrolytes Batter. Fuel Cells. 1096 (2012) 91–106. doi:10.1021/bk-2012-1096.ch006.

- [37] G.P. Lamaze, H.H. Chen-Mayer, D.A. Becker, F. Vereda, R.B. Goldner, T. Haas, P. Zerigian, Cold neutron depth profiling of lithium-ion battery materials, J. Power Sources. 119–121 (2003) 680–685. doi:10.1016/S0378-7753(03)00232-5.
- [38] M. Huang, T. Liu, Y. Deng, H. Geng, Y. Shen, Y. Lin, C.W. Nan, Effect of sintering temperature on structure and ionic conductivity of Li 7 XLa 3Zr 2O 12 0.5x (x = 0.5 ~ 0.7) ceramics, Solid State Ionics. 204–205 (2011) 41–45. doi:10.1016/j.ssi.2011.10.003.
- [39] Y. Suzuki, K. Kami, K. Watanabe, A. Watanabe, N. Saito, T. Ohnishi, K. Takada, R. Sudo, N. Imanishi, Transparent cubic garnet-type solid electrolyte of Al2O3-doped Li7La3Zr2O12, Solid State Ionics. 278 (2015) 172–176. doi:10.1016/j.ssi.2015.06.009.
- [40] L. Cheng, H. Hou, S. Lux, R. Kostecki, R. Davis, V. Zorba, A. Mehta, M. Doeff, Enhanced lithium ion transport in garnet-type solid state electrolytes, J. Electroceramics. 38 (2017) 168–175. doi:10.1007/s10832-017-0080-3.
- [41] K. Wang, Y. Chang, L. Lv, Y. Long, Effect of annealing temperature on oxygen vacancy concentrations of nanocrystalline CeO2film, Appl. Surf. Sci. 351 (2015) 164–168. doi:10.1016/j.apsusc.2015.05.122.
- [42] Y. Li, Z. Wang, C. Li, Y. Cao, X. Guo, Densification and ionic-conduction improvement of lithium garnet solid electrolytes by flowing oxygen sintering, J. Power Sources. 248 (2014) 642–646. doi:10.1016/j.jpowsour.2013.09.140.
- [43] C. Wang, H. Xie, L. Zhang, Y. Gong, G. Pastel, J. Dai, B. Liu, E.D.Wachsman, L. Hu, Universal Soldering of Lithium and Sodium Alloys on

Various Substrates for Batteries, Adv. Energy Mater. 8 (2018) 1701963. doi:10.1002/aenm.201701963.

Accepted manuscript