The Coupling between Voltage Profiles and Mechanical Deformations in LAGP Solid Electrolyte During Li Plating and Stripping

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ABSTRACT

Chemo-mechanical degradation at the solid electrolyte – Li metal electrode interface is a bottleneck to improve cycle life of all-solid state Li-metal batteries. In this study, in operando digital image correlation (DIC) measurements provided temporal and spatial resolution of the chemo-mechanical deformations in LAGP solid electrolyte during the symmetrical cell cycling. The increase in strains in the interphase layer was correlated with the overpotential. The sudden increase in strains coincides with the mechanical fracture in LAGP detected by Micro CT. This work highlights the mechanical deformations in LAGP / Li interface and its coupling with the electrochemical behavior of the battery.

Keywords: solid electrolyte, LAGP, interfacial deformations, strains, chemo-mechanical instabilities, overpotentials, fracture

MAIN TEXT

Rechargeable Li-ion batteries with organic liquid electrolytes have been widely used in portable electronics since their first commercialization in the early 1990s¹. However, demanding applications such as electrical vehicles require batteries with much higher energy density than Li-ion batteries. Replacing organic liquid electrolytes with the solid electrolyte helps to eliminate the fire hazard to improve the safety, and in addition, it offers a promising way to increase the energy density by allowing the utilization of Li metal as an anode material. Despite the growing interest in solid electrolyte-based Li metal batteries, the utilization of the technology is still hindered by solid-solid interactions and chemo-mechanical instabilities in all-solid-state batteries^{2,3}.

Chemo-mechanical instabilities may originate from penetration of Li metal towards solid electrolyte, the formation of interphase layer in the vicinity of solid electrolyte – electrode, and void formation and associated contact loss between electrode and electrolyte²⁻⁴. Understanding the driving forces behind these instability mechanisms and their coupling with the electrochemical performance of the all-solid-state batteries is required to engineer the properties of solid electrolytes and the interface between electrode – solid electrolytes. However, the buried nature of the solid-solid interface makes it a challenge to probe the so-called chemo-mechanical deformation using in operando techniques. Various characterization techniques have been adopted to investigate these chemo-mechanical deformations in the solid electrolyte – electrode interface such as optical microscopy⁵, X-ray computed tomography⁶⁻⁸, Raman spectroscopy⁹, scanning electron microscopy¹⁰, transmission electron microscopy¹¹, in situ X-ray photoelectron spectroscopy¹², and in situ neutron diffraction¹³.

Here, we demonstrate a new experimental approach to monitor dynamic physical changes and their resultant mechanical variations in solid electrolytes by utilizing in operando strain

measurements via digital image correlation (DIC). These in operando experiments are supported by electrochemical measurements and ex-situ micro X-ray computed tomography (Micro-CT) analyses. $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}\text{P}_3\text{O}_{12}$ (LAGP) solid electrolyte is selected as a model system. DIC technique has been used to investigate reversible and irreversible strain generation in the battery electrodes due to phase transformations¹⁴⁻¹⁶ and a formation of solid-electrolyte interface^{17,18}. Recently, Koohbor et al. applied DIC technique to monitor spatial deformations in the solid electrolyte – Au electrode interface¹⁹. Building on it, we utilized the DIC technique to monitor strain generation in LAGP solid electrolyte and at the interface between LAGP – Li metal electrode during Li plating and stripping. In operando DIC measurements provided spatial and temporal development of the chemo-mechanical strains in the interphase layer. The study provides experimental evidence for the relationship between mechanical deformations in the interphase layer and the overpotential. Fractures in the solid electrolyte were found by ex-situ Micro-CT analysis and the location of the fractures coincides with the areas wherein large shear strains were generated. Counterintuitively these shear bands were formed away from the SE/electrode interface but near the middle of the solid electrolyte.

Figure 1 demonstrates the schematics of the experimental setup for in operando strain measurements on LAGP solid electrolytes during battery cycling and the details of the system can be found in Supp. Figure S1. A symmetrical $\text{Li} \mid \text{LAGP} \mid \text{Li}$ cell was cycled by applying constant current density. In operando strain measurements were performed to monitor deformations in electrode-solid electrolyte interface during battery cycling. Details of the sample preparation can be found in the Experimental Section in Supp. Info. Figure 2 shows the galvanostatic voltage profiles during 3rd (at $1 \mu\text{A}/\text{cm}^2$), 6th (at $2 \mu\text{A}/\text{cm}^2$), 17th (at $8 \mu\text{A}/\text{cm}^2$) and 21st (at $16 \mu\text{A}/\text{cm}^2$) stripping cycles where Li is stripped from the upper Li metal electrode and plated on the bottom

one in Figure 1. The voltages showed a flat profile at around 0.04 and 0.08V when Li was stripped at 1 and 2 $\mu A/cm^2$, respectively. When cycled at 8 $\mu A/cm^2$ for 4 hours, the voltage profile demonstrated an increase from 0.32 to 0.38V with the total 32 $\mu Ah/cm^2$ charge being transferred. At 16 $\mu A/cm^2$, the voltage profile rapidly increased from 1.27 to 2.56 V.

Figure 1: Schematic of in operando strain measurement for solid electrolytes.

Figure 2B shows the corresponding contour plots for normal vertical strains, ϵ_{yy} on the LAGP solid electrolyte at the end of the stripping cycles. A negligible amount of strains development was observed at the end of the third stripping cycle at 1 $\mu A/cm^2$. When the current density was increased to 2 $\mu A/cm^2$ while keeping the total charge transferred to be the same, interphase formation and associated chemo-mechanical strains were detected in the interface of LAGP – Li metal electrodes. Non-homogeneously distributed negative strains were generated at the top interface, while positive strains were observed on the bottom interface. At 8 $\mu A/cm^2$, strains further propagated towards the solid electrolyte and a strain generation in the middle of the

solid electrolyte was observed. Propagation of mechanical deformation and the interphase formation towards the solid electrolyte became more pronounced when current was $16 \mu\text{A}/\text{cm}^2$.

Figure 2: A) Voltage evolution profile with respect capacity when Li was stripped from the top Li metal electrode at 1, 2, 8 and $16 \mu\text{A}/\text{cm}^2$. B) Contour plots of normal strain, ϵ_{yy} at the end of the corresponding stripping cycle. C) normal strains, ϵ_{yy} along the line A and line B for four different current densities from figure 2B. D) normal strains, ϵ_{yy} along the horizontal lines I, II and III. Line I and II are 50 and 100 μm away from the upper Li metal / LAGP electrolyte, respectively. Line III is 50 μm away from the below Li metal / LAGP electrolyte.

To demonstrate the chemo-mechanical strains quantitatively, the strain evolution along the thickness of solid electrolyte (vertical lines A and B) and along the width of the solid electrolyte (horizontal lines I, II and III) are plotted in Figure 2C and D, respectively. Normal strains on the vertical line A and B demonstrate the evolution of the interphase formation when the symmetrical cell was cycled under different current densities. As the current density was increased, the interfacial deformations reached almost -2.25% in some areas in the LAGP – top Li metal interface. The negative strains could be associated with the formation of voids at the top Li-LAGP interface as a result of the Li stripping process. The presence of these voids will possibly weaken the mechanical load-bearing capacity of LAGP at areas close to the top interface and reduce the

contact area between LAGP SE and Li electrode^{10,11}. At the same time, positive strains at the opposite side indicate the expansions in the interphase of LAGP – bottom Li metal which could be due to Li penetration and / or amorphization in LAGP. Li plating can penetrate in ceramic solid electrolytes, causing the expansions in the interphase of solid electrolyte – Li metal^{3,5,10}. Reaction between Li and LAGP solid electrolyte causes volume expansions due to amorphization of the LAGP interphase^{8,20}. The depth profile of strains on the vertical lines suggests that the interphase formation is about 75 micron-thick. Previous studies on LLZO and LAGP solid electrolytes also reported around 50-90 micron-thick interphase formation between Li metal and solid electrolyte^{8,20}. Generation of normal strains in the center of the solid electrolyte was recorded at higher current densities in the vertical lines. We will discuss these deformations in the solid electrolyte and how it impacts the electrochemical behavior in the later section.

The strain profiles on the horizontal lines in Figure 2D provide information about the strain magnitudes 50 and 100 microns away from the interface of LAGP-Li metal electrodes. Strains measured at the end of the 3rd stripping cycle at $1 \mu A/cm^2$ were negligible. Normal strains, ε_{yy} along the horizontal line I, II and III became noticeably large at the 6th cycle at $2 \mu A/cm^2$. Normal strains, ε_{yy} further increased by the end of the 17th cycle at $8 \mu A/cm^2$. The strain patterns on the horizontal lines show heterogenous Li plating and stripping in the LAGP / Li metal interface. The interfacial deformations became more heterogenous by increasing the applied current density. For example, on line III, the minimum strains are on the same location regardless of the applied current density and cycle number. However, the magnitude of the strains in the neighboring areas increased with increasing current density. This demonstrates the impact of the early non-uniform

deformations on the spatial distribution of Li plating and stripping on the solid electrolyte – electrode interface^{10,21}.

Figure 3: A) Voltage evolution during stripping cycles at 8 μA/cm². B) Contour plots of normal strain, ϵ_{yy} , at the end of the corresponding stripping cycle. C) Average voltages from Fig 3A and average normal strains, ϵ_v , along the horizontal lines I, II, III and IV. Line I and II are 50 and 100 μm away from the upper Li metal / LAGP electrolyte, respectively. Line III and IV are 50 and 25 μm away from the bottom Li metal / LAGP electrolyte, respectively.

To understand the relationship between overpotential and the chemo-mechanical strains in the interphase, Li ions were stripped and plated at the same current density for consecutive cycles at 8 μA/cm². Figure 3A shows an increase in the voltage with the cycle number. The average value of the voltage during each stripping cycle also increases with subsequent cycles. Contour

plots of normal strain, ε_{yy} at the end of the corresponding stripping cycles are shown in Figure 3B. The depth of the strained layers near Li metal / LAGP interface increases slightly with the subsequent cycles (Supp. Figure S4 and S5). Strains profiles for ε_{xx} and ε_{yy} components on the horizontal lines I, II and III were plotted in Supp. Figure S6-S8. Assuming symmetry about the y-axis, the strain components ε_{xx} and ε_{zz} can be taken to be equal (or at least close) in value. Volumetric strains developed at any given location across the SE thickness could then be calculated $\varepsilon_V = 2\varepsilon_{xx} + \varepsilon_{yy}$. Considering the dominance of ε_{yy} values over those of ε_{xx} , volumetric strain is expected to have the same sign as ε_{yy} strain component. The calculated volumetric strains along the horizontal lines are plotted in Supp. Figure S9. The average ε_V is calculated along each horizontal line for each cycle as shown in Figure 3C. Overall, both average voltage and average strains increased with the subsequent cycles. This suggests a direct correlation between the interfacial deformations and the mechanical overpotential.

At the LAGP – Li electrode interface, the electrochemical redox reactions are $Li \leftrightarrow Li^+ + e^-$. In Figure 3, the Li metal is oxidized at the top Li metal / LAGP interface, and it is reduced at the bottom Li metal / LAGP interface. The overpotential is the summation of the electrical overpotential, η_ϕ and the mechanical overpotential, η_σ . The electrical potential can be defined as.

$$\eta_\phi = \phi_s - \phi_e - U$$

where ϕ is the electrical potential and U is the equilibrium potential. The contribution of stress on the overpotential has been discussed for alloy-type anodes and lithium iron phosphate cathode in organic liquid electrolytes for Li-ion batteries^{22–25}. Recently, Mistry and Mukherjee²⁶ developed the mathematical expressions for the mechanical overpotential, η_σ by also considering deformations in solid electrolyte particles as well as the electrode.

$$\eta_\sigma = \{\Omega_{Li^+}\sigma_{h,e} - \Omega_{Li}\sigma_{h,Li}\}/F$$

where Ω_{Li^+} is the partial volume of Li^+ in the solid electrolyte, Ω_{Li} is the molar volume of Li and σ_h is the hydrostatic stress. The Butler-Volmer relationship correlates the overpotential, η with the Faradaic reaction current. If the electrical overpotential impacts the anodic and cathodic reactions equally but mechanical overpotential selectively contributes to the anodic reaction, then the Butler-Volmer relationship becomes^{27,28};

$$i = i_o \left(\exp\left(\frac{F\eta_\sigma}{RT}\right) \exp\left(\frac{F\eta_\phi}{2RT}\right) - \exp\left(\frac{-F\eta_\phi}{2RT}\right) \right)$$

where i_o is the exchange current density, α_a and α_c are the charge transfer coefficients, F is the Faraday's constant, R is the gas constant, and T is temperature. The mathematical model based on the updated Butler-Volmer relationship predicted the contribution of the hydrostatic stress in the solid electrolyte particles in overpotentials for all-solid-state batteries²⁶. While the present results only show the evolution of chemo-mechanical strains, a simple stress analysis can be conducted to highlight the role of hydrostatic stresses as well. A correlation between volumetric strain and hydrostatic stress can be easily established using the well-known linear elastic mechanics as $\sigma_h = K\varepsilon_V$ where K denotes the bulk modulus of the solid electrolyte material. Bulk modulus can be calculated via $K = E/[3(1 - 2\nu)]$. Elastic modulus, E and Poisson's ratio, ν for LAGP were reported as 144 GPa and 0.25, respectively²⁹. When considering the relationship between stress and strains, our experimental measurements on the correlation between overpotential and strains in the interphase layer aligns very well with the predictions in the mathematical model. The nonuniform growth of the interphase layer accelerates at higher currents, which leads to the chemo-mechanical failure in the solid electrolytes^{5,20}. The surface overpotentials can also be impacted by the contact loss between solid electrolyte and Li metal electrode, charge transfer resistance at the interface, and transport rate of Li ions in the solid electrolyte^{11,30}.

Figure 4: A) Voltage evolution during stripping cycles at $16 \mu\text{A}/\text{cm}^2$, B) 3-D X-ray microcomputed tomography (Micro-CT) image of the Li metal - LAGP solid electrolyte - Li metal after cycling. Large cracks and flaws are observed in the LAGP electrolyte. C) Contour plots of normal strains, ϵ_{yy} and ϵ_{xx} and shear strains ϵ_{xy} at the end of the corresponding stripping cycle.

In order to quantitatively analyze the role of strains on the mechanical failures at higher current densities, the Li metals were stripped and plated at $16 \mu A/cm^2$ for four consecutive cycles. The voltage was set to 5V upper limit. A rapid increase in the voltage profile was observed in the first two consecutive cycles at $16 \mu A/cm^2$ (cycle 21 and 22). In the last two consecutive cycles, the voltages reached to 5V upper limit. After the electrochemical cycling, an ex-situ Micro-CT image of the solid electrolyte was taken without disassembling the cell. The Micro-CT image in Figure 4B shows evidence of cracks and flaws in the LAGP solid electrolyte after cycling.

The associated counter plots for ε_{yy} , ε_{xx} and ε_{xy} strains at the end of each stripping cycle are plotted in Figure 4B. The strain evolutions along the thickness of the solid electrolyte (vertical lines A and B) are shown in the Supp. Figure S10 and S11. Generation of positive normal strain, ε_{yy} in the middle of the LAGP solid electrolyte is recorded in the 21st stripping cycle. However, the magnitude of the ε_{xx} normal strains and ε_{xy} shear strains were much smaller compared to the ε_{yy} normal strain. In the subsequent cycles, the magnitude and size of the ε_{yy} normal strain became much greater. The ε_{yy} normal strain could be associated with the formation of voids in the solid electrolyte, which can disturb the conduction of the Li ions in the solid electrolyte. At the same time, the magnitude of the shear strains increased dramatically in the middle of the LAGP electrolyte. These mechanical deformations in the middle of the solid electrolyte correspond well with the cracks observed in the Micro CT analysis in Figure 4.

In conclusion, in operando DIC measurements provided temporal and spatial analysis of the chemo-mechanical strains in LAGP solid electrolyte during battery cycling. The depth of the interphase layer was about 75 microns and the normal strains progressively increased with consecutive cycles and increasing current density. An increase in the average strains in the interphase layer corresponds to the increase in overpotential. The DIC measurement suggests the

generation of large normal strains and shear strains in the middle of the solid electrolyte, which coincides with the mechanical fracture detected by ex-situ Micro CT. In operando DIC measurements offer promising capabilities to study interfacial instabilities in solid-solid interfaces by probing spatial and temporal resolution of mechanical deformations during all-solid-state battery operation.

Supplementary Information

The supplementary information includes details of experimental setup, sample preparation, material characterization and figures showing contour plots and strain evolutions.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Ö. Ö. Ç conceived the idea and supervised the work. B. O. and A. T. prepared LAGP solid electrolytes and performed surface roughness measurements. B. O. performed in situ strain measurements. All authors discussed the results. The authors declare that they have no competing interests. All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supporting information. Additional data related to this paper may be requested from the authors.

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