High-Spatial-Resolution Quantitative Chemomechanical Mapping of Organic Composite Cathodes for Sulfide-Based Solid-State Batteries

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Cite This: ACS Energy Lett. 2023, 8, 1107−1113

ABSTRACT: Understanding the chemomechanical behaviors of electrodes, particularly at electrode/electrolyte interfaces, is critical for improving the performance of all-solid-state batteries. However, due to the instability of electrolyte materials under ambient conditions, such characterizations are challenging, particularly for sulfide-based all-solid-state batteries. Herein, by combining time-of-flight secondary-ion mass spectroscopy (ToF-SIMS) and in-SEM nanoindentation measurements, a systematic quantitative investigation of the chemomechanical behaviors of pyrene-4,5,9,10-tetraone (PTO)/Li$_6$PS$_5$Cl composite cathodes is carried out. Chemical and quantitative mechanical information on the composite cathode was collected with high spatial resolution after developing and implementing an air-free characterization protocol. By directly connecting the Young’s modulus and hardness with the Li distribution in the composite cathode, a comprehensive chemomechanical mapping of the PTO/Li$_6$PS$_5$Cl composite cathode has been established. This work improves our knowledge of the critical chemomechanical phenomena that occur at the cathode/electrolyte interfaces in all-solid-state batteries.

All-solid-state batteries (ASSBs) have been considered as promising candidates for next-generation batteries due to their improved safety and energy density compared to lithium-ion batteries.1 Lacking the relatively homogeneous stress distribution in liquid-based lithium-ion batteries, mechanical behaviors of both electrode and electrolyte materials, particularly at the electrode/electrolyte interfaces, in ASSBs play a more dominant role in determining their reliable operation during the electrochemical charging and discharging cycles. The contact and the porosity of solid battery materials are known to be affected by the stress applied to the entire battery, which impacts the battery performance.2−4 The stress concentration in the active materials generated during cell operation may deteriorate solid–solid interfaces and hinder ion transport.5,6 Therefore, understanding and engineering mechanical properties of electrode/electrolyte composites and their interfaces are therefore essential for constructing intimate solid–solid contact in ASSBs and ensuring robust performance.4

Because of their favorable contribution to cell performance, the mechanical properties of various components in solid-state lithium batteries, including active electrode materials and electrolytes, have attracted a lot of attention.7−16 Sulfide-based electrolytes, for example, have garnered notable interest because of their high ion conductivity (>10$^{-3}$ S cm$^{-1}$ at room temperature), inexpensive starting materials, and excellent mechanical properties for facile processing. Sulfide-based solid electrolytes have Young’s moduli in the 10s of GPa, which is substantially lower than those of oxide-based solid electrolytes (100−200 GPa), allowing for great processability in the manufacture of solid-state batteries.7,8,13,14

Received: October 28, 2022
Accepted: January 20, 2023
electrode materials, on the other hand, have sparked the curiosity of researchers due to their moderate redox potential, mechanical compliance, and comparatively little volume variation during cycling when compared to their inorganic counterparts. A more favorable electrode/electrolyte interface between the mechanically compliant organic electrode and solid electrolytes in the ASSBs has been proposed.

It is worth noting that the majority of mechanical characterizations in ASSBs reported so far have been performed on individual components in the bulk form rather than the composite of active electrode materials and electrolytes. Various forms of chemical degradations have also been observed at the electrode/electrolyte interface during the charge and discharge cycles of ASSBs.

As a result, under realistic battery operation conditions, the mechanical properties of components in composite electrodes evolve, and the evolution may be rather nonuniform based on their local chemical composition variations, particularly at the electrode/electrolyte interface. Understanding the chemomechanical behaviors of composite electrodes by concurrently analyzing chemical composition change and monitoring mechanical characteristics with high spatial precision is vital in this respect.

In this work, a home-built air-free transfer vessel and corresponding sample transfer protocols were developed and implemented to enable high-spatial-resolution quantitative chemomechanical mapping of a PTO/Li₆PS₅Cl composite cathode using an in-SEM nanoindenter system with time-of-flight secondary-ion mass spectroscopy (ToF-SIMS) (PTO, pyrene-4,5,9,10-tetraone). This type of characterization method has been utilized to investigate the mechanical properties of pristine active materials, pristine electrolytes, and composite cathodes in ASSBs. Because of its ultralow (ppm–ppb level) detection limit, ToF-SIMS has been shown to be a powerful instrument for probing lithium-related species.

As a result, the composition-dependent mechanical properties of the organic composite cathode may be measured with great spatial resolution. Such an innovative diagnostic method offers a great benefit for the development of ASSBs with superior mechanical stability and interfacial compatibility.

**Development of an Air-Free Chemical and Mechanical Characterization Technique.** Characterization of battery materials remains challenging due to their high sensitivity to air and moisture, especially for sulfide-based electrolytes. An air-free characterization approach was devised here to tackle the air-sensitivity issue of battery materials. First, an argon ion polishing was used to generate a clean and smooth cross-section of the battery sample, which was then maintained in a glovebox, as schematically shown in Figure 1a. The sample was then transported from the glovebox to a ToF-SIMS instrument using an air-free transfer vessel (ION-TOF GmbH), as shown in Figure 1b. ToF-SIMS analysis (schematically shown in Figure 1c) is capable of obtaining a chemical mapping at ~150 nm spatial resolution with an appropriate sensitivity for lithium-related species (see more details in Figure S1). Figure 1d shows secondary ion (SI) images with an overlaid RGB image of PTO fragments (blue), Li₆PS₅Cl fragments (red), and interfacial products fragments (green).

The sample was held under a vacuum in the sealed transfer vessel after the ToF-SIMS analysis before being brought back to the glovebox for further analysis.

Several methods have been developed to tackle the air-sensitivity issue for mechanical characterizations of battery materials, such as ultrasonic sound velocity measurement with plastic glove-bag protection or nanoindentation testing protected by mineral oil or in a glovebox environment. It would be difficult to measure mechanical properties of each phase in the composite cathode using the ultrasonic sound approach. Even for the nanoindentation measurements reported in prior studies, tests were carried out using optical microscopes with poor spatial resolution. In the current study, a Bruker PI85L in-SEM nanoindenter system was employed.
to conduct the test in the region of interest with submicron spatial resolution. Another home-built transfer vessel, shown in Figure 1e, was developed to accommodate the nanoindenter system and provide air-free sample transfer between the glovebox and SEM. The transfer vessel loaded in the SEM chamber is shown in Figure 1f (see more details in Figure S2). Following vacuum pumping of the SEM chamber, the cover of the transfer vessel could be opened for subsequent in situ nanoindentation tests. Figure 1g shows an SEM image of the composite cathode and nanoindenter tip, which helps in locating the region of interest during mechanical measurement.

Preparation and Characterization of an Organic Composite Cathode. Taking advantage of the above air-free characterization technique, the chemical and mechanical properties of pristine PTO, pristine Li$_6$PS$_5$Cl electrolyte, and composite cathode were investigated. The PTO/Li$_6$PS$_5$Cl composite cathodes for chemomechanical characterizations were prepared by cold pressing the as-prepared powders into pellets, as illustrated schematically in Figure 2a. The PTO powders have a rodlike shape with a diameter around 5 μm as shown in Figure 2b. The particle size of Li$_6$PS$_5$Cl powders is within 1–10 μm (Figure 2c). Figure 2e reveals no apparent boundaries in the cold-pressed PTO pellet cross-section, suggesting its

![Figure 2](https://example.com/figure2.png)

Figure 2. Microstructure of PTO, Li$_6$PS$_5$Cl, and composite cathode samples. (a) Schematic illustration of composite cathode preparation. (b) SEM image of PTO powders. (c) SEM image of Li$_6$PS$_5$Cl powders. (d) Cross-section SEM image of the composite cathode pellet. (e) Cross-section SEM image of the PTO pellet. (f) Cross-section SEM image of the Li$_6$PS$_5$Cl pellet.

![Figure 3](https://example.com/figure3.png)

Figure 3. ToF-SIMS analysis indicates the redox behaviors between PTO and Li$_6$PS$_5$Cl. (a) Detailed mass spectra of pristine PTO, Li$_6$PS$_5$Cl electrolyte, and composite cathode. (b) SI images of Li$_6$PS$_5$Cl fragments ($S^-$ and $Cl^-$), PO$_x$- fragments (PO$_2^-$, PO$_3^-$), PTO fragments (C$_2$H, C$_4$H), and LiOH$^+$ fragments in a composite cathode.
excellent malleability. On the contrary, a considerable number of defects such as particle boundaries and pores were found in the cross-section image of the cold-pressed Li$_{x}$PS$_{6}$Cl pellet (Figure 2f). The cross-section image of the composite cathode is shown in Figure 2d, with low- and high-contrast domains corresponding to the PTO and the Li$_{x}$PS$_{6}$Cl regions, respectively, as validated by energy-dispersive X-ray spectroscopy (EDS) (Figure S3). The Li$_{x}$PS$_{6}$Cl particles are clearly surrounded by PTO with smooth and continuous interfaces. The excellent contact between Li$_{x}$PS$_{6}$Cl electrolyte and PTO cathode materials enables the preferred ion transport kinetics at the interface, which we believe originates from the softness and high malleability of PTO active material.

Next, ToF-SIMS analyses were performed to detect the chemical changes in PTO electrode materials and Li$_{x}$PS$_{6}$Cl electrolytes for a better understanding of the spontaneous redox behaviors between PTO and Li$_{x}$PS$_{6}$Cl phases in the composite cathode as reported in our previous study. The mass spectra of the pristine PTO, the pristine Li$_{x}$PS$_{6}$Cl, and the composite cathode have been compared to identify the chemical characteristic ions of PTO and Li$_{x}$PS$_{6}$Cl species as shown in Figure 3a. Li$_{x}$PTO fragments (LiOH$^{+}$ at m/z of 25.0253 and LiC$_{x}^{-}$ at m/z of 55.0166) can be clearly identified in the composite cathode sample, confirming the lithiation of PTO species as in our previous observation. Small peaks at m/z of 25.0253 and 55.0166 in pristine Li$_{x}$PS$_{6}$Cl and pristine PTO samples, respectively, may originate from contaminations during sample preparation. Additionally, the peak intensity ratio between PO$_{2}^{−}$ and PS$^{−}$ is dramatically larger in the composite cathode as compared to the pristine Li$_{x}$PS$_{6}$Cl, which implies the occurrence of the oxidation of the Li$_{x}$PS$_{6}$Cl electrolyte in the composite cathode. Similar intensity changes in the peak ratio were also observed between PO$_{3}^{−}$ and PSO$^{−}$ fragments. Small amounts of PO$_{2}^{−}$ (PO$_{2}^{−}$, PO$_{3}^{−}$) fragments were also observed in the pristine Li$_{x}$PS$_{6}$Cl sample, which can be explained by the high reactivity of Li$_{x}$PS$_{6}$Cl with a trace amount (ppm) of oxygen and water, leading to the slight oxidation of the electrolyte during storage in the glovebox or transportation through the transfer vessel. ToF-SIMS spectra were then used to confirm the chemical evolution in the composite cathode. To spatially identify the chemical changes in the composite cathode, ion mapping of the composite cathodes from the same region as shown in Figure 2d was also performed. Figure 3b shows the 2D distribution of fragments corresponding to the Li$_{x}$PS$_{6}$Cl (red, S$^{−}$, Cl$^{−}$), PTO (blue, C$_{3}$H$^{+}$, C$_{2}$H$^{+}$), interphase component (green, PO$^{−}$), and Li$_{x}$PTO (gold, LiOH$^{+}$). The oxidation fragments (PO$^{−}$) from Li$_{x}$PS$_{6}$Cl have enhanced signals at the interface, which indicates the chemical reactions between PTO and Li$_{x}$PS$_{6}$Cl electrolyte at the contact point. Meanwhile, Li$_{x}$PTO-related fragments can also be found inside the PTO domains, which indicates the lithiation of PTO particles. We believe that these originated from the spontaneous redox reactions between PTO and Li$_{x}$PS$_{6}$Cl. In summary, the ToF-SIMS analysis highlights the chemical evolution of the PTO electrode and Li$_{x}$PS$_{6}$Cl electrolyte with a sufficient spatial resolution.

**In Situ Chemomechanical Characterization of an Organic Composite Cathode.** Effects of such important chemical evolution on mechanical properties of composite cathodes have seldom been reported, mainly due to the limited spatial resolution of nanoindentation tests under an optical microscope. To overcome this limitation, in-SEM nanoindentation tests were performed on the composite cathodes, and mechanical properties of different phases were measured with much higher spatial resolutions as shown in Figure 4a. Mechanical properties of pristine PTO and pristine Li$_{x}$PS$_{6}$Cl were also tested as references (Figure S7). More details about in-SEM nanoindentation measurements on different phases are demonstrated in the Supporting Information (as shown in Movies S1 and S2). Typical load–displacement curves of PTO and Li$_{x}$PS$_{6}$Cl in the composite cathode are shown in Figure 4b, c, respectively. The average Young’s moduli (using the Oliver-Pharr method) of PTO and Li$_{x}$PS$_{6}$Cl in the composite cathode were measured as 15.0 ± 2.5 and 30.3 ± 4.5 GPa, respectively. The average hardnesses of PTO and Li$_{x}$PS$_{6}$Cl in the composite cathode were measured as 0.92 ± 0.29 GPa, respectively, which is on the same order as the theoretical value reported by Deng et al. The average
Young’s modulus and hardness of pristine PTO, pristine Li$_6$PS$_5$Cl, PTO in a composite cathode, and Li$_6$PS$_5$Cl in a composite cathode are shown in Figure 4d. The Young’s modulus and hardness value of PTO in a composite cathode dramatically increased compared to the pristine PTO, while the Li$_6$PS$_5$Cl did not. We hypothesize that the dramatic modulus and hardness increase in the PTO in the composite cathode should originate from the partial lithiation of PTO in the composite cathode during the sample preparation process. As mentioned in the previous ToF-SIMS analysis, chemical reactions did occur in the composite cathode. In this regard, the average Young’s modulus and hardness statistics of different phases in the composite cathodes are not sufficient to reflect the real composition changes in such cathodes.

Chemomechanical Mapping of a PTO Cathode. Figure 5a,b shows the Young’s modulus and hardness mapping of the PTO phase at a specific location of interest. Figure 5c shows the lithium distribution in the same area by ToF-SIMS analysis. The SI image of the Li$^+$ fragment in PTO domains confirmed the lithiation of PTO even before the electrochemical operation of the cathode. It is worth mentioning that the normalized lithium intensity from ToF-SIMS measurement is positively correlated with Li concentration in PTO although the two are not identical. Figure 5d shows the Young’s modulus and hardness of the pristine PTO and the Li$_x$PTO with different Li concentrations. All Li$_x$PTO phases are stronger than the pristine PTO, and the Li$_x$PTO with higher Li concentration shows higher Young’s modulus and hardness. The above trend effectively illustrates that the chemical reaction affected mechanical properties of PTO domains and potentially provides a new dimension for understanding the chemomechanical behaviors in ASSBs.

In conclusion, we presented a well-designed air-free characterization technique for acquiring chemical and mechanical information on battery materials. A transfer vessel was also designed to accommodate the in-SEM nanoindenter, which allows mechanical testing of air-sensitive samples in an SEM instrument. PTO/Li$_6$PS$_5$Cl composite cathodes were subjected to quantitative chemomechanical studies. The spontaneous chemical reaction between PTO and Li$_6$PS$_5$Cl was shown by ToF-SIMS analysis. Inside the SEM instrument, nanoindentation quantitatively mapped the mechanical properties of both components in the composite. The average Young’s moduli of the PTO and Li$_6$PS$_5$Cl in the composite cathode were measured to be 15.0 $\pm$ 2.5 and 30.3 $\pm$ 4.5 GPa, respectively. The average hardnesses of the PTO and Li$_6$PS$_5$Cl in the composite cathode were 0.92 $\pm$ 0.27 and 1.56 $\pm$ 0.27 GPa, respectively. Lithiation was discovered to increase the modulus and hardness of PTO in the composite cathode, and the PTO domains with greater lithiation level are stronger. Our state-of-the-art chemomechanical characterization protocol offers enormous potential for understanding the important chemomechanical behaviors of composite electrodes, particularly at the electrode/electrolyte interfaces in ASSBs, which can provide critical insights into future battery performance improvements through rational structure design, material selection, and material modification.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c02430.

Additional data and figures including setup diagrams and photographs, EDS spectra, ToF-SIMS spectra, SI images, mass spectra, SEM images, load–displacement curves, 

Figure 5. Chemomechanical mapping of a composite cathode. (a) Young’s modulus mapping results in the PTO domains of the composite cathode, scale bar 5 $\mu$m. (b) Hardness mapping results in the same PTO domains of the composite cathode, scale bar 5 $\mu$m. (c) Lithium distribution mapping in PTO domains overlapping with the indented area; the intensity is normalized by the total ion counts from ToF-SIMS analysis, scale bar 5 $\mu$m. (d) Mechanical properties of PTO domains with different lithium concentration.
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Academy of Sciences of the United States of America, National Science Foundation CBET-1626418. This work was mainly supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under Contract DE-EE000886. The ToF-SIMS analyses were carried out with the support provided by the National Science Foundation CBET-1626418. This work was conducted in part using resources of the Shared Equipment Authority at Rice University.

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Movie S2: indentation of Li2PS5Cl phase in a composite cathode (MP4)

Notes
The authors declare the following competing financial interest(s): Y. Yao and Y. Liang have equity interest in LiBeyond LLC. Z. Fan and Y. Yao have equity interest in Solid Design Instruments LLC. The University of Houston reviewed and approved their relationship in compliance with its conflict-of-interest policy.

ACKNOWLEDGMENTS
This work was mainly supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under Contract DE-EE000886. The ToF-SIMS analyses were carried out with the support provided by the National Science Foundation CBET-1626418. This work was conducted in part using resources of the Shared Equipment Authority at Rice University.


