In situ observations of interfacial evolutions in solid-state lithium battery with sulfide-based solid electrolyte

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Abstract — **Solid electrolytes provide for safe rechargeable lithium batteries and allow the batteries with lithium metal anodes to possess higher energy densities than those of traditional liquid electrolyte based batteries. However, the structural evolution-induced interfacial failures during the electrochemical cycling have not been explored at a fundamental level. In this report, a practical setup is developed for *in situ* detection of the electrochemical reaction-induced micro and nanoscale morphological changes along the battery's interface. We have focused on the anode interface with lithium metal as the electrode and solid sulfide as the electrolyte, while monitoring an inflating phenomenon in the electrolyte during the lithium plating. This observation suggests that the lithium dendrite formation as well as the lithium deposition in the porous structures drives the volume expansion of the solid electrolyte. This rare finding offers a fresh perspective, indicating a new impact of the lithium plating in sulfide electrolyte, which does not accord with the conventional structural evolution model at the electrode-solid electrolyte interface. This study contributes significant insights into the mechanism of the interfacial phenomena in sulfide solid-state battery and paves the way for their advanced engineering.**

Index Terms – lithium ion battery, solid-state battery, lithium metal anode, in situ, lithium plating

I. INTRODUCTION

Lithium-ion batteries (LIBs) have undergone significant development and become a popular choice in mobile energy storage devices due to their long lifecycles, high energy density and reliable performance [1-3]. Although the LIBs possess desirable qualities, their volatility has caused safety concerns. This issue has generated interest in developing energy storage devices with alternative materials to develop safer batteries. During this investigation, researchers developed all solid-state battery (ASSB), which consist of non-volatile solid-state electrolytes (SSE) replacing the volatile liquid electrolyte in conventional LIBs [4-7]. The SSE also allows the use of lithium (Li) metal as anode. Combining them is one of the few ways of further improving the energy density of LIB technology [8].

Among various SSEs, sulfide-based solid electrolytes have gained significant interest not only because of its high natural availability and environmentally friendliness, but also due to the desirable properties of sulfide-based ASSBs, such as higher safety, longer life cycles and the much-needed higher energy density (2567 Wh kg^{-1}) [5, 9-11].
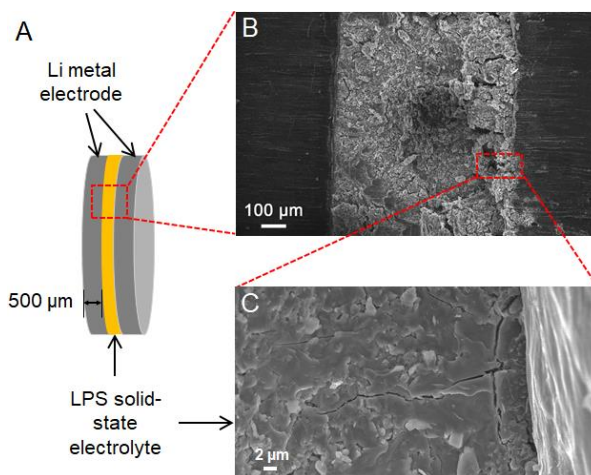

Fig. 1 Symmetric cell setup. (A) Schematic illustration of the LPS-based symmetric solid-state cell. (B) Profile of the symmetric cell. The thickness of the electrolyte layer is 600 µm and the lithium layer reaches 500 µm. (C) The interface between the LPSg electrolyte and Li metal electrode.

These advantages of the sulfide SSE are attractive to the mobile device industry that is constantly trying to develop lighter products. For the transportation industry, the development of the sulfide SSE is rather crucial, as a lower vehicular weight will significantly reduce the energy use per unit distance of travel [12].

Although the ASSB with sulfide-based electrolytes are promising for the energy solutions of the future, they are not the be-all and end-all of energy storage devices. Currently, there are various issues obstructing these batteries' road to success in realizing their true potential. The five major challenges currently faced by ASSB include: 1) high interfacial resistance between electrode-electrolyte

interfaces, 2) SSEs possess low ionic conductivities, especially at low temperatures, 3) degradation of physical stability leading to significant interfacial stress variations, 4) incompatibilities between SSEs and electrodes, 5) growth of Li dendrites causing the battery internal short-circuit [13]. In our study, we developed an *in situ* cell setup for the real-time observation of the interface evolutions at the solid electrolyte interface.
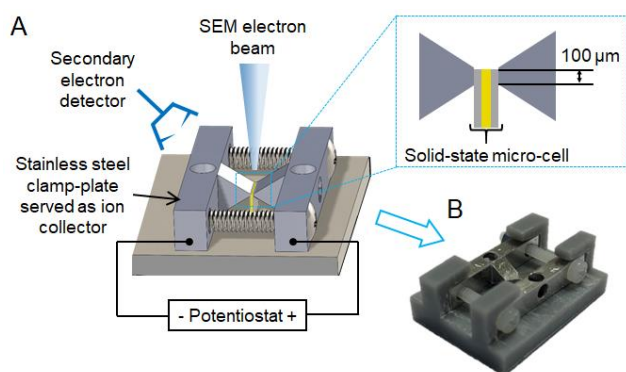

Fig.2 Experimental schematic of the micro-cell setup for the *in situ* SEM characterizations of the cell operations. The setup is composed of two stainless steel clamp vice with the clamp-depth of 100 μm. The vice is served as ion collector for the cell.

Even though a few attempts have been made by researchers to observe the interface evolutions at the solid electrolyte interface using *in situ* setups, the complex and costly setup makes its repeatability rather poor [14, 15]. In contrast, our setup simply consists of a laser-engraving-fabricated micro-scale battery stage and a 3D-printed mount. Once put together, the setup can easily establish a full-cell lamella with the depth equivalent to about 100 μm. As this setup is attached to an electrochemical workstation through a feedthrough, the structural changes during the cell operation can be cross-compared with its electrochemical performances.

II. EXPERIMENT

We used the 61.7% Li_2S – 38.3% P_2S_2, Li_3PS_4 glass (LPSg) as the SSE. The LPSg raw powder was prepared using mechanical ball milling, which is the most popular way for synthesizing sulfide solid electrolytes [4]. The LPSg powder was placed in a Swagelok device and cold-compressed with 360 MPa [16], and a compacted solid electrolyte tablet was fabricated. We placed the LPSg SSE tablet between two Li metal foils for a symmetric solid-state cell setup (Figure 1a). The symmetric cell allowed study of the electrode and electrolyte in a focused area, which is a useful feature for investigating solid electrode/electrolyte interface reactions [17]. The cross-sectional profile of the Li-LPSg-Li symmetric cell is shown in Figure 1b, which has a thickness of the LPSg layer reaches 600 μm. A zoomed-in the interfacial area is shown in Figure 1c, which focuses on the cracks in the solid electrolyte. The pre-

existing micro-cracks were inevitable due to the mechanical compression-based electrolyte tablet fabrication. However, these cracks resulted in two major problems in the stability of the ASSB: increase in the grain boundary impedance and Li dendritic growth [18]. In order to diagnose the impact of these intrinsic defects to the cell performances, we propose an *in situ* setup for the monitoring of the interface evolutions.

As shown in Figure 2a, a pair of stainless-steel clamp-plates (SSCP) were fabricated to vertically support the solid-state cell stacks and conduct the battery test. The SSCP here served as current collectors for the electrode. As shown in the inset of Figure 2a, the clamp edge of the stage is precisely polished using a micro laser engraver, limiting the clamp-depth to 100 μm. We can therefore enable the electrochemical reaction on the exposed cell profile with a maximum depth of 100 μm (Figure 1b), equivalent to an "open" micro-scale full-cell (micro-cell) and avoid the expensive process of nano/micro fabrication. The precise alignment of the protruding clamp edge is implemented by a stereolithography (SLA) 3D-printed scaffold, as shown in Figure 2b. The scaffold is designed to provide a track for the SSCP to slide only along 1 axis, avoiding any possible misalignment of the vice heads, which helped in
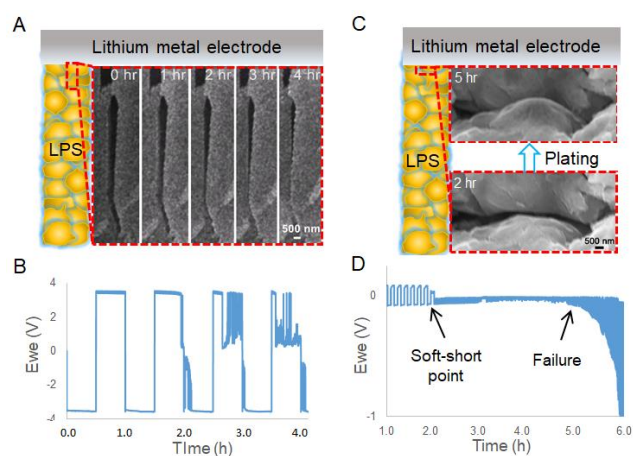

Fig.3 *In situ* observations of the interfacial structural evolutions. (A) The closure of a crack in the LPSg electrolyte during the cycling and the voltage cycling curve of the symmetric cell. The unstable of the curve indicates the soft-short-circuit of the cell. (B) The bumping of a LPSg particle during the discharge and the corresponding voltage curve. As the soft-short occurs, the cycling of the cell switches to the discharging. Then, the plating of the Li^+ induces the LPSg particle bumping up along the discharging direction.

maintaining a constant contact area. Once the SSCP was placed in the scaffold, the micro-cell was placed between the protruding heads and the setup was tightened with non-conductive nylon screws.

The real-time SEM observations of the LPSg electrolyte and its corresponding voltage vs time graphs, during the cell operation, are shown in Figure 3a, b and Figure 3c, d respectively. Figure 3a shows the morphological evolutions

of the LPSg at the interface under the charging and discharging of the symmetric micro-cell. Due to the micro-scale (μm^2) contact area, the applied current for the cycling is correspondingly low. Here, a constant current of 0.3 μA is applied, which corresponds to a current density of 0.8 mA/cm^2. We focused on an intrinsic crack at the interface area for the monitoring, the image sequence shows a gradual closure of the crack. In the meanwhile, the cell failure occurred, a soft short-circuit (soft-short) is indicated in the symmetric cycling curve (Figure 3b). The soft-short will severely deteriorate as the battery keeps cycling, and eventually leads to a hard-short [19]. The synchronization of the internal short circuit and the structural changes we have observed suggests the influence on interfacial properties (e.g., structural, mechanical, and chemical) through the Li stripping and/or plating. In order to identify the exact electrochemical mechanisms during this process, we monitored the crack that is perpendicular to the Li inserting direction (Figure 3c), here the current density was 0.2 mA/cm^2. We have also switched the electrochemical cycling to the discharge after soft-short occurred (Figure 3d), enabling the exclusive Li plating at the interface we observed. As shown in Figure 3c, a bump is raised along the plating direction. No crack filling by the Li metal dendrite was observed [18], the growing of the bump continuous before the complete failure of the cell. By this observation, we can interpret that the gap closure is the result of the volume expansion of LPSg electrolyte, which is induced by the Li insertion during the electrochemical reaction.

III. DISCUSSION

Stripping of lithium occurs in batteries during the charging/discharging cycle, where lithium metal at the anode splits into lithium ion and electron and gets deposited at the cathode once the lithium ion meets the electron [20]. While this process is a part of the normal function of the ASSB, plating on the other hand hinders its normal functioning. Lithium plating tends to occur at cracks and voids at the electrode near the anode, when the battery is subjected to current density that exceeds its critical current density [21]. This progressive infiltration results in the lithium metal internally bridging the anode and the cathode, causing a short-circuit [21]. Additionally, due to the generation of internal stress, lithium plated areas tend to act as dendritic growth sites [22]. Therefore, the lithium plated areas act as an additional channel for the cathode and anode to connect internally and cause short-circuit [22, 23].

The morphological evolution caused by Li plating at the SSE is evident in Figure 3c. The Li plating rate increases when the battery experiences a soft-short [24]. On continuing to apply current that exceeds the battery's critical current density, the SSE steadily increased in volume. This observation corroborates a study conducted by Yang et al. (2017) on modeling of Li plating [24].

According to Yang et al. (2017), as cycling continues, the SSE grows while reducing the anode porosity. Moreover, the cold-press-based manufacturing process induces the crack on the SSE. These cracks and voids are severe at the SSE [13], close to the electrode interface. Therefore, as the Li plating occurs at the SSE, the plating-induced effects,
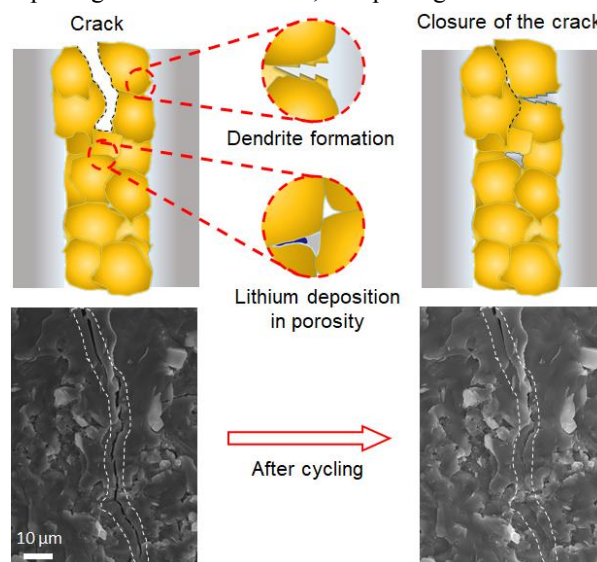

Fig.4 Schematic illustration of the crack closure during the cell operation. As the dendrite growth and the Li metal deposition in the porosity, the volume of the LPSg particle expense, which induced crack squeezing and eventually closed.

such as dendritic growth and Li deposition in the electrolyte [21, 25], occupy these intrinsic defects and expand the electrolyte due to the successive deposition of Li, allowing an "inflation" of the LPSg electrolyte [24]. The pre-existing cracks are then clogged, as shown in Figure 4.

Our observation is contrary to previous reports that crack propagates during the plating [21, 26]. This stark difference in the morphological changes could be attributed either to the difference in deposition mechanism after soft-short or the difference in the mechanical properties of the SSE. In previous investigations focused on the oxide garnet SSE, i.e., single and poly crystallized $Li_6La_3ZrTaO_{12}$ (LLZTO). The LLZTO was prone to fracture due to the high shear modulus, 61 GPa [18, 26]. Thus, when the Li metal penetrated the pristine defects, the crack propagated. Since the shear modulus of LPSg is relatively low (8.3 GPa) [27], the pre-existing voids exhibited elastic expansion rather than crack propagation. More research is need to quantitatively diagnose the Li penetration in the LPSg. The *in situ* SEM characterization results reported in this work suggest a new structural evolution mechanism for the low-modulus solid electrolyte.

V. CONCLUSIONS

In summary, we have demonstrated a feasible micro-cell setup for the detection of the electrochemical reaction-

induced micro and nanoscale morphological changes in situ. The real time monitoring indicates the Li-plating induced structural evolutions of the LPSg SSE. This result suggests that after the soft short-circuit of the cell, the Li-metal penetration effect along the Li-plating direction is significantly enhanced, resulting in the electrolyte volume expansion and thus the closure of the pre-existing crack. The experiment result contradicts previous observations in the high-modulus solid-electrolyte, suggesting a new mechanism after soft-short. In the following investigations, the Li plating in the low-modulus electrolyte will be fundamentally analyzed. In addition, factors such as the applied pressure, current density, and test temperature will be analyzed through the micro-cell setup. Moreover, the micro-cell will incorporate with different diagnostic techniques in the future work, especially the chemical study approaches (e.g., XPS, SIMS, NDP) for the cross-reference of the chemo-structural correlations.

REFERENCES

[1] J. W. Choi and D. Aurbach, "Promise and reality of post-lithium-ion batteries with high energy densities," *Nature Reviews Materials,* vol. 1, no. 4, art. no. 16013, Apr 2016.

[2] N. Nitta, F. X. Wu, J. T. Lee, and G. Yushin, "Li-ion battery materials: present and future," *Materials Today,* vol. 18, no. 5, pp. 252-264, Jun 2015.

[3] J. M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature,* vol. 414, no. 6861, pp. 359-367, Nov 2001.

[4] A. Manthiram, X. W. Yu, and S. F. Wang, "Lithium battery chemistries enabled by solid-state electrolytes," *Nature Reviews Materials,* vol. 2, no. 4, art. no. 16103, Apr 2017.

[5] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, and R. Kanno, "High-power all-solid-state batteries using sulfide superionic conductors," *Nature Energy,* vol. 1, art. no. 16030, Mar 2016.

[6] J. C. Bachman, S. Muy, A. Grimaud, H. H. Chang, N. Pour, S. F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, and Y. Shao-Horn, "Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction," *Chemical Reviews,* vol. 116, no. 1, pp. 140-162, Jan 2016.

[7] Z. G. Xue, D. He, and X. L. Xie, "Poly(ethylene oxide)-based electrolytes for lithium-ion batteries," *Journal of Materials Chemistry A,* vol. 3, no. 38, pp. 19218-19253, 2015.

[8] J. Janek and W. G. Zeier, "A solid future for battery development," *Nature Energy,* vol. 1, art. no. 16141, Sep 2016.

[9] D. H. Kim, D. Y. Oh, K. H. Park, Y. E. Choi, Y. J. Nam, H. A. Lee, S. M. Lee, and Y. S. Jung, "Infiltration of Solution-Processable Solid Electrolytes into Conventional Li-Ion-Battery Electrodes for All-Solid-State Li-Ion Batteries," *Nano Letters,* vol. 17, no. 5, pp. 3013-3020, May 2017.

[10] C. Yu, S. Ganapathy, E. R. H. Van Eck, H. Wang, S. Basak, Z. L. Li, and M. Wagemaker, "Accessing the bottleneck in all-solid state batteries, lithium-ion transport over the solid-electrolyte-electrode interface," *Nature Communications,* vol. 8, art. no. 1086, Oct 2017.

[11] F. Zheng, M. Kotobuki, S. F. Song, M. O. Lai, and L. Lu, "Review on solid electrolytes for all-solid-state lithium-ion batteries," *Journal of Power Sources,* vol. 389, pp. 198-213, Jun 2018.

[12] M. M. Thackeray, C. Wolverton, and E. D. Isaacs, "Electrical energy storage for transportation-approaching the limits of, and going beyond, lithium-ion batteries," *Energy & Environmental Science,* vol. 5, no. 7, pp. 7854-7863, Jul 2012.

[13] S. X. Xia, X. S. Wu, Z. C. Zhang, Y. Cui, and W. Liu, "Practical Challenges and Future Perspectives of All-Solid-State Lithium-Metal Batteries," *Chem,* vol. 5, no. 4, pp. 753-785, Apr 2019.

[14] M. Golozar, P. Hovington, A. Paolella, S. Bessette, M. Lagace, P. Bouchard, H. Demers, R. Gauvin, and K. Zaghib, "In Situ Scanning Electron Microscopy Detection of Carbide Nature of Dendrites in Li-Polymer Batteries," *Nano Letters,* vol. 18, no. 12, pp. 7583-7589, Dec 2018.

[15] P. Hovington, M. Lagace, A. Guerfi, P. Bouchard, A. Manger, C. M. Julien, M. Armand, and K. Zaghib, "New Lithium Metal Polymer Solid State Battery for an Ultrahigh Energy: Nano C-LiFePO4 versus Nano Li1.2V3O8," *Nano Letters,* vol. 15, no. 4, pp. 2671-2678, Apr 2015.

[16] M. Nagao, A. Hayashi, M. Tatsumisago, T. Kanetsuku, T. Tsuda, and S. Kuwabata, "In situ SEM study of a lithium deposition and dissolution mechanism in a bulk-type solid-state cell with a Li2S-P2S5 solid electrolyte," *Physical Chemistry Chemical Physics,* vol. 15, no. 42, pp. 18600-18606, 2013.

[17] J. C. Burns, L. J. Krause, D. B. Le, L. D. Jensen, A. J. Smith, D. J. Xiong, and J. R. Dahn, "Introducing Symmetric Li-Ion Cells as a Tool to Study Cell Degradation Mechanisms," *Journal of the Electrochemical Society,* vol. 158, no. 12, pp. A1417-A1422, 2011.

[18] T. Swamy, R. Park, B. W. Sheldon, D. Rettenwander, L. Porz, S. Berendts, R. Uecker, W. C. Carter, and Y. M. Chiang, "Lithium Metal Penetration Induced by Electrodeposition through Solid Electrolytes: Example in Single-Crystal Li6La3ZrTaO12 Garnet," *Journal of the Electrochemical Society,* vol. 165, no. 16, pp. A3648-A3655, Nov 2018.

[19] X. W. Zhang, E. Sahraei, and K. Wang, "Li-ion Battery Separators, Mechanical Integrity and Failure Mechanisms Leading to Soft and Hard Internal Shorts," *Scientific Reports,* vol. 6, art. no. 32578, Sep 2016.

[20] L. Gireaud, S. Grugeon, S. Laruelle, B. Yrieix, and J. M. Tarascon, "Lithium metal stripping/plating mechanisms studies: A metallurgical approach," *Electrochemistry Communications,* vol. 8, no. 10, pp. 1639-1649, Oct 2006.

[21] L. Porz, T. Swamy, B. W. Sheldon, D. Rettenwander, T. Froemling, H. L. Thaman, S. Berendts, R. Uecker, W. C. Carter, and Y.-M. Chiang, "Mechanism of Lithium Metal Penetration through Inorganic Solid Electrolytes," *Advanced Energy Materials,* vol. 7, no. 20, art. no. 1701003, Oct 25 2017.

[22] X. Wang, W. Zeng, L. Hong, W. W. Xu, H. K. Yang, F. Wang, H. G. Duan, M. Tang, and H. Q. Jiang, "Stress-driven lithium dendrite growth mechanism and dendrite mitigation by electroplating on soft substrates," *Nature Energy,* vol. 3, no. 3, pp. 227-235, Mar 2018.

[23] F. Aguesse, W. Manalastas, L. Buannic, J. M. Lopez del Amo, G. Singh, A. Llordes, and J. Kilner, "Investigating the Dendritic Growth during Full Cell Cycling of Garnet Electrolyte in Direct Contact with Li Metal," *Acs Applied Materials & Interfaces,* vol. 9, no. 4, pp. 3808-3816, Feb 1 2017.

[24] X. G. Yang, Y. J. Leng, G. S. Zhang, S. H. Ge, and C. Y. Wang, "Modeling of lithium plating induced aging of lithium-ion batteries: Transition from linear to nonlinear aging," *Journal of Power Sources,* vol. 360, pp. 28-40, Aug 2017.

[25] F. D. Han, A. S. Westover, J. Yue, X. L. Fan, F. Wang, M. F. Chi, D. N. Leonard, N. Dudney, H. Wang, and C. S. Wang, "High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes," *Nature Energy,* vol. 4, no. 3, pp. 187-196, Mar 2019.

[26] A. Sharafi, H. M. Meyer, J. Nanda, J. Wolfenstine, and J. Sakamoto, "Characterizing the Li-Li7La3Zr2O12 interface stability and kinetics as a function of temperature and current density," *Journal of Power Sources,* vol. 302, pp. 135-139, Jan 20 2016.

[27] A. Sakuda, A. Hayashi, Y. Takigawa, K. Higashi, and M. Tatsumisago, "Evaluation of elastic modulus of Li2S-P2S5 glassy solid electrolyte by ultrasonic sound velocity measurement and compression test," *Journal of the Ceramic Society of Japan,* vol. 121, no. 1419, pp. 946-949, Nov 2013.