Supplementary Materials for

The void formation behaviors in working solid-state Li metal batteries

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Supplementary Text
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I. Supplementary Text

The calculation towards the phase diagram of contact loss

The quantification of the contact loss coefficient is calculated as follows:

The active area after Li stripping is equivalent as a circle with a diameter of \( a \). The initial area before Li stripping is the circle with diameter \( b \). The thickness of SSEs is defined as \( L \). The schematic show of the calculation is displayed in Figure S5, S6.

With the reduced active area at the Li anode side, the effective area for the SSE will be reduced into a frustum of a cone. It is ensured in the main text that the intrinsic impedance of solid-state electrolytes can be distinguished by DRT. The effective impedance of SSE after active contact loss can be calculated as:

\[
r = a + \frac{b-a}{L} x
\]

\[
k = \frac{b-a}{L}
\]

\[
r = a + kx
\]

\[dR = \rho \frac{dx}{\pi(a+kx)^2}\]

\[
R_{\text{strip}} = \frac{\rho}{\pi} \int_0^L \frac{dx}{(kx+a)^2} = \frac{\rho L}{\pi ab}
\]

\[
R_{\text{initial}} = \frac{\rho L}{\pi b^2}
\]

Because the relationship of \( R \) and the active area is listed as: \( R = \frac{\rho L}{S} \). (\( \rho \) resistivity, \( L \) length or thickness, \( S \) area), The evolution ratio of the active area after Li stripping can be calculated and defined as contact loss coefficient \( m \).

\[
\frac{R_{\text{strip}}}{R_{\text{initial}}} = \frac{b}{a} = \sqrt{\frac{S_{\text{initial}}}{S_{\text{strip}}}}
\]

\[
m = \frac{S_{\text{initial}}}{S_{\text{strip}}} = \left(\frac{R_{\text{strip}}}{R_{\text{initial}}}ight)^2
\]

Each stripping capacity with a specific current density will be related to a contact loss coefficient. A series of Li stripping GEIS measurement with different current densities will form a group
vectors of (current density; stripped current density; contact loss coefficient). These vectors will be drawn as a contour phase diagram with an axis of current density, stripped capacity, and contact loss coefficient.

**Mathematical deduction for the formulas**

The calculation of void induced surficial energy is stated as follows. In the equations, ∆G_v is the free energy per unit of void. V_void means the total volume of the void. γ_{Li} represents the free surface energy of Li metal. S_void is the free area of void derived from Li stripping. γ_{SSE} represents the surface energy of solid-state electrolyte. γ_{Li-SSE} represents the energy of Li-SSE interfaces. S_{contact} represents the contact area before the Li stripping. R is the radius of the void.

\[
\Delta G_{\text{nucleation}} = -V_{\text{void}} \Delta G_v + S_{\text{void}} y_{Li} - (y_{SSE} - y_{Li-SSE}) S_{\text{contact}} \tag{9}
\]

\[
\Delta G_{\text{nucleation}} = -R^3 F_\alpha \Delta G_v + R^2 F_\beta y_{Li} - (y_{SSE} - y_{Li-SSE}) R^2 F_\gamma \tag{10}
\]

The critical radius of void R_{crit} is given as:

\[
R_{\text{crit}} = \frac{2y_{Li}}{\Delta G_v} \tag{11}
\]

\[
F_\alpha = \frac{\pi}{3} (2 - 3\cos \alpha + \cos^3 \alpha) \tag{12}
\]

\[
F_\beta = \pi (1 - \cos \alpha) \tag{13}
\]

\[
F_\gamma = \pi \sin \alpha^2 \tag{14}
\]

The total nucleus area S_{nucleus total} is given as follows, where the n_{nucleus} means the total nuclei amounts and the S_{nucleus} is the surface area per nuclei.

\[
S_{\text{nucleus total}} = n_{\text{nucleus}} \times S_{\text{nucleus}} \tag{15}
\]

\[
R_{\text{crit}} \propto \frac{1}{i} \tag{16}
\]

The total areal stripping capacity is fixed, where the amount of nucleus is \( \propto i^3 \) considering the nuclei size \( \propto \frac{1}{i} \)

\[
S_{\text{nucleus}} \propto R^2 \propto i^{-2} \tag{17}
\]

\[
S_{\text{nucleus total}} \propto i \tag{18}
\]
II. Supplementary Figures

Fig. S1. The GEIS result reflects time consumption and stripping capacity. (A) The voltage–time profile of the GEIS measurement at the current density of 1, 2, 5, 10 mA cm$^{-2}$. (B) The stripping capacity and overpotential evolution until contact loss failure at the current density of 1, 2, 5, 10 mA cm$^{-2}$. Each point of the curves in Figure S1A represents the position for impedance measurement.
Fig. S2. Typical EIS of contact loss failure at 1.0 mA cm\(^{-2}\). The complete contact loss results in a total impedance of over 2000 Ohm.
Fig. S3. The interpretation of the EIS of Li\textvert Li_7P_3S_{11}\textvert Li–In half cell. (A) Typical EIS of Li–In half cell. (B) The DRT plot of (A). (C) The equivalent circuit of the battery model. The basic interpretation of EIS in a Li–In half cell is shown in Figure S3A. Due to the limitation of the highest frequency, the RGB exhibit an incomplete semi-circle. The frequency of turn-point between the two major semi-circle is 25.1 kHz. After the DRT transition, it is ensured that the time constant of RGB of SSEs located at 10^{-6} s, and those of Li kinetics such as R_{SEI}, R_{Li–In}, and R_{Li} are located at 10^{-4}, 10^{-2}, and 10^{-1}–1 s, respectively. R_{SEI} means the impedance of solid-electrolyte interphase. R_{Li–In} means the charge transfer impedance of Li–In alloying process. R_{Li} means the charge transfer impedance of Li metal.
Fig. S4. The impedance evolution of interfaces without contact loss phenomena. (A) The impedance evolution of LiIn | Li7P3S11 | In half symmetric cells during single side Li stripping. (B) The DRT plots of (A). The impedance increase in half symmetric cells is only displayed at the second semi-circle. The impedance of SSE R\text{GB} remains stable, proving that no obvious contact loss is observed. The changes of impedance only derive from the charge transfer of Li–In alloy.
Fig. S5. The schematic show of equivalent calculation for contact loss by impedance result.
Fig. S6. The schematic illustration for calculating the contact loss coefficient/active area ratio.
Fig. S7. The DRT calculated contact loss coefficient (1.0 mA cm\(^{-2}\)) comparing with conventional impedance calculating by the simulated R\(_{GB}\).
**Fig. S8. The morphology of Li metal anode.** The morphology comparison among (A, C) Xe ion milling at room temperature (RT), (B) Ga ion milling at RT (D) and Ga ion milling at −170°C. Figure B and D are derived from prof. Meng’s research. Reproduced with permission Ref. 39 in the main text. Copyright 2019, American Chemical Society. Firstly, the FIB-SEM in our experiments used the plasma Xe ion as an ion source, which is significantly different from conventional FIB-SEM using Ga ion beams. As known, Ga will form alloy with Li metal during the long-term milling, which is one of the most crucial reasons that the Li metal was damaged by conventional FIB. In sharp contrast, the milling rate and efficiency of Xe ion can reach 30–40 times higher than that of the Ga ion. The radiation time is significantly reduced by using PFIB with Xe ion source. More importantly, the Xe ion is inert against Li metal. The chemical reaction between the ion beam and Li metal will be eliminated, which can maintain the morphology to a large extent during the short milling time. It has also been proved that the inert Xe ion can significantly reduce the surficial damage during the milling. Hence, we ensured that the Xe ion equipped PFIB-SEM can maintain the morphology character for SEM observations. Frankly, the Xe ion milling can minimize the surficial damage delivering similar milling results comparing with the cryo-FIB. We compare our Xe ion milled Li metal at room temperature with the Ga ion cryo-FIB milled Li metal reported by Prof. Meng’s team. The sample for evaluation is Li metal pressed on the solid-state electrolyte without any Li stripping. The interface is the original status without artificial void or gap. It is shown that the Xe ion beam doesn’t introduce particular morphology, including the new gaps or voids at the interface during the milling at room temperature (Figure S8A). Besides, intimate contact can be well maintained at the interfaces after the fine milling (Figure S8C), with no void and pores detected. As aforementioned, the Ga ion milling at RT will damage the Li morphology (Figure S8B), which makes the cryogenic working condition necessary to suppress the parasitic reaction with the Ga ion sources. On the contrary, the inert Xe ion can help to maintain the morphology during the PFIB-milling at room temperature, showing the same results as that by cryo-FIB (Figure S8D). Hence, we think the PFIB-SEM using Xe ion beam at room temperature can satisfy the demand for morphology observation in this research.
Fig. S9. The morphology and composition of residual Li on the SSE surface. The left SEM image with EDS mapping of N (green), P (red), and S (yellow). The residual Li can be distinguished by the following methods. The samples have exposed in the air for 3 min. The surface of residual Li will react with N\textsubscript{2} and be transformed into Li\textsubscript{3}N. The scale bar for the right column is 100 μm.
Fig. S10. The identification of interfacial defects. (A) The SEM images and (B) the Li elemental distributions of TOF-SIMS scanning for the white dash square region in (A). The intensity figure proves the existence of the Li voids at the interfaces.
**Fig. S11. The SEM image of residual Li.** The morphology of residual Li after 1 mA cm$^{-2}$ for TOF-SIMS measurement in Figure 4B. The lithium exhibits a porous and dense morphological character.
Fig. S12. The P and S signals of TOF-SIMS in Figure 4B.
Fig. S13. Ascertainment for the possible surficial damage by TOF-SIMS measurement. (A) SEM image of pristine Li metal anode of 33 μm. (B) The SEM images of surficial Li metal anode in (A) after TOF-SIMS measurement for 100 frames. It is ensured that the TOF-SIMS measurement cannot form a fine porous structure on Li metal.
Fig. S14. The SEM image of Li metal after complete contact loss. The Li metal is automatically separated from the interfaces.
Fig. S15. The critical Li void features induced by different current loadings. The top view of low scale SEM images about residual failure Li measured with current density of 1 mA cm\(^{-2}\), 2 mA cm\(^{-2}\), 5 mA cm\(^{-2}\) and 10 mA cm\(^{-2}\).
**Fig. S16. EBSD results of Li metal.** (A) The SEM images of typical Li metal. (B) specific area for EBSD evaluations. (C-E) The EBSD images of the initial result, IPFY color, and IPFZ color, demonstrating the grain size of Li metal is ~100 μm.
Fig. S17. SEM image of typical nucleus embryos.
**Fig. S18. The morphology of Li stripped morphology.** The low-magnification SEM images (×300) of the Li stripped morphology under the current density of (A) 1, (B) 2, (C) 5, (D) 10 mA cm\(^{-2}\) in a liquid electrolyte system. Herein we measure Li anode stripping in the liquid electrolyte system. The stripping current densities range from 1, 2, 5, and 10 mA cm\(^{-2}\) with a fixed stripping capacity of 2 mAh cm\(^{-2}\). The stripping parameters are completely the same as that used in solid-state systems. As shown in the low magnification SEM (Figure S18), clear pits and holes are exhibited on the Li surface after the stripping. The pits morphologies become concentrated with the increased current density. These phenomena demonstrate that the Li void formation will also determine the interfacial morphology and the influence by current density also shows similar features as that shown in solid-state systems. The low current density (1–2 mA cm\(^{-2}\)) forms concentrated big pits and the high current density (5–10 mA cm\(^{-2}\)) forms dispersed little voids.
Fig. S19. The morphology of Li stripped morphology. The enlarged SEM images (×10k) of the Li stripped morphology under the current density of (A) 1, (B) 2, (C) 5, (D) 10 mA cm\(^{-2}\) in a liquid electrolyte system. The microscopic morphology can help to demonstrate the void behaviors further. From the SEM images of the surface of the pinholes (×10k, Fig. S19) at high magnification, we can observe a similar honeycomb like morphology in the pits on the Li metal surface after the stripping. It is clearly shown that the sizes of the “void honeycomb” shrink with the increased stripping current density. The size of the “void honeycomb” formed at 1 mA cm\(^{-2}\) remains at 2 μm. The size of the voids will reduce to 400–500 nm at 10 mA cm\(^{-2}\). The sizes of voids are similar to that formed in the solid-state system. These results demonstrate that the void formation theory is partly applicable in both solid and liquid systems. However, according to the location of the formation of the voids, the void behaviors exhibit obvious discrepancies. The Li void morphology remains on the solid-state electrolyte, while the Li void morphological features stand on the bulk Li metal. Therefore, we can distinguish the void formation behaviors in the liquid-based systems and the solid-state systems.
Fig. S20. The schematic illustration of the void behavior during Li stripping at solid-state interfaces and in liquid electrolyte systems. Moreover, the discrepancies on Li void behaviors in solid-state batteries and liquid electrolytes have been clearly shown in Fig. S20. Similar with the case in solid-state batteries, the voids are also formed at the interfaces between Li metal and liquid electrolyte. However, the liquid electrolyte can replenish the interfacial voids, resulting in the continuous shifting of the solid-liquid interface. Subsequently, the continuous Li stripping occurred, accompanied with the continuous growth of old voids as well as the nucleation of new voids at the fresh interfaces, exhibiting a new void behavior in liquid electrolytes.
Fig. S21. The *operando* optical facility for interfacial void observation.