

## **Supplementary Information**

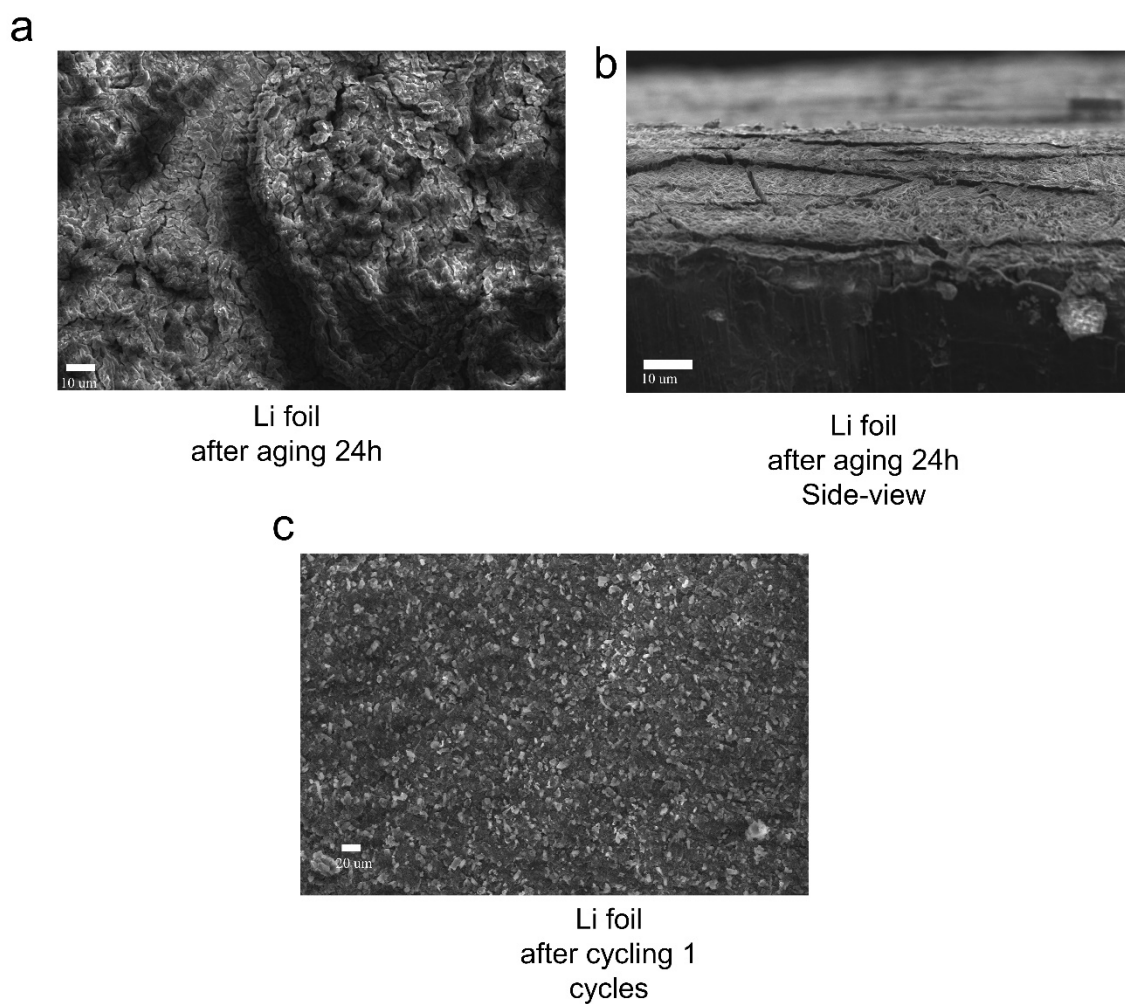
# **Self-sufficient metal-air battery systems enabled by solid-ion conductive interphases**

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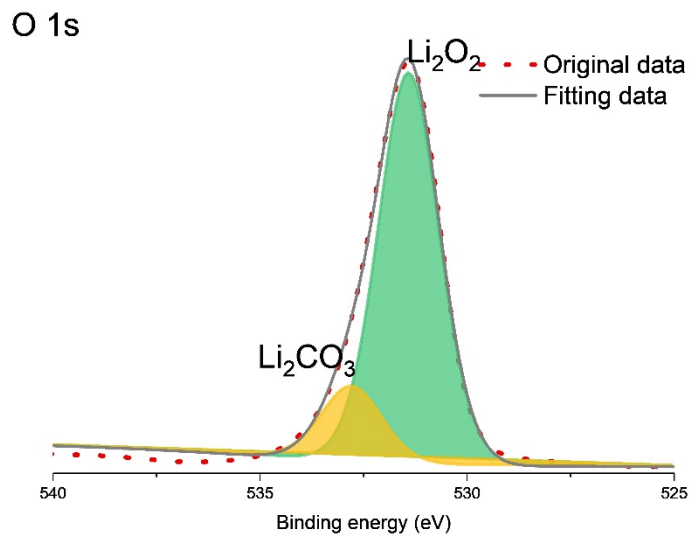
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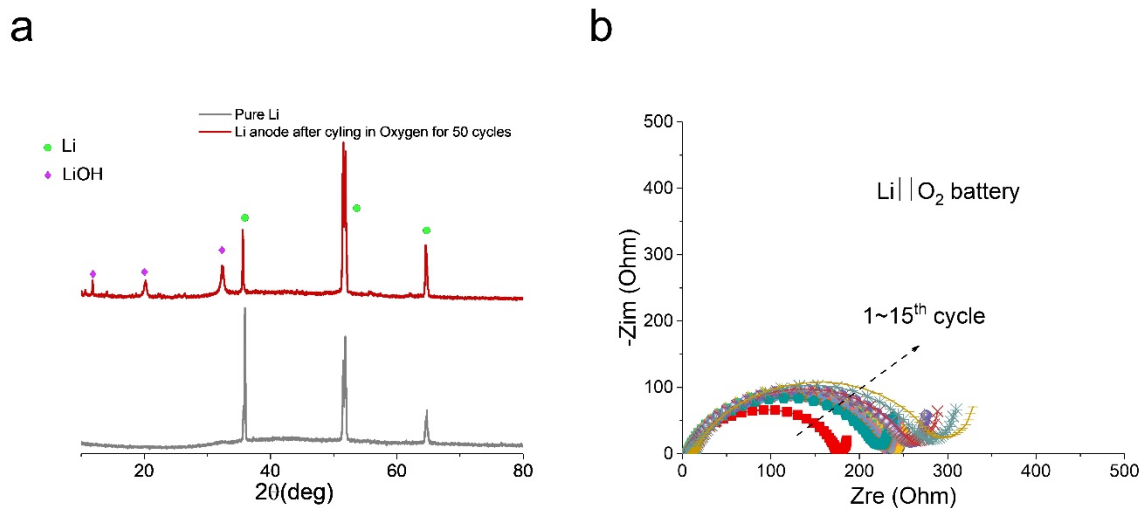
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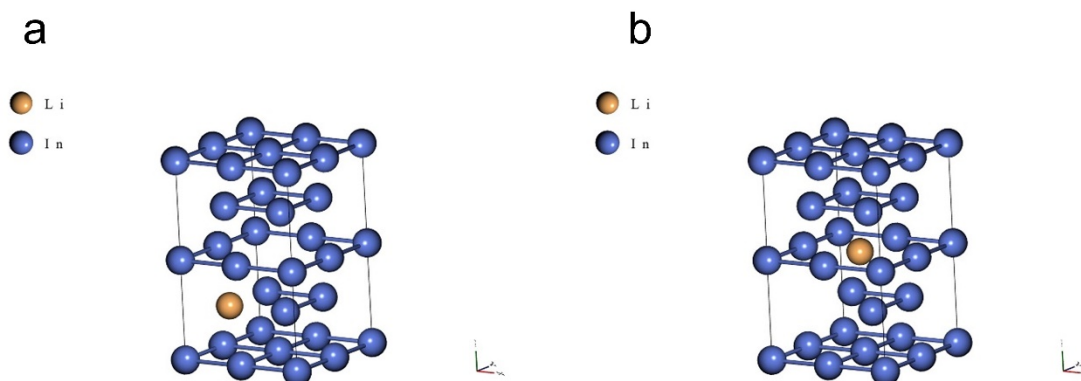
**Figure S1.** Morphology of Li foil after aging 24 hours (a) Top view, (b) Side view; (c) after cycling 1 cycle.



**Figure S2.** XPS results of O 1s for Li foil after cycling 8 cycles.



**Figure S3.** (a) XRD of pure Li foil and Li foil after cycling in the Li-O<sub>2</sub> (Pure Oxygen environment) for 50 cycles. (D) EIS of Li-O<sub>2</sub> during 1~15 cycles.

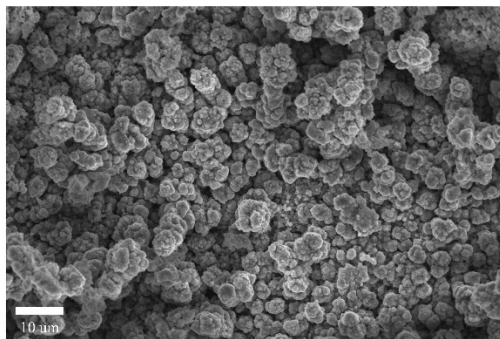


**Figure S4.** Diffusion pathway of lithium in bulk metal indium via vacancy mechanism in first-principle calculations. (A) Starting position and (B) ending position of diffusion.

The Li:In ratio in our simulation was as low as 1:14, much lower than the lowest known ratio ( $\text{LiIn}_3$ ) of Li-In alloys, and thus can be viewed as a good approximation of lithium diffusion in bulk indium metal.

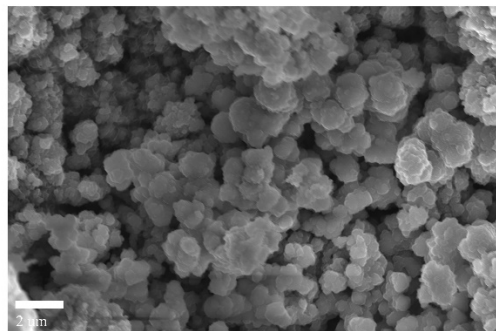
Also, among the two common diffusion pathways (vacancy vs. interstitial), we mainly focused on the vacancy mode because (1) it is easier to be initiated, (2) it typically renders a lower diffusion energy barrier, and (3) it often shows high symmetry.<sup>7</sup> For (1), lattice defects are typically the most vulnerable location of bulk metal – intuitively, it is easier for a lithium atom to enter a lattice vacancy than forcefully enter a perfect unit cell. In other words, when a lithium atom encounters bulk indium metal, it is more possible to reach the starting location of vacancy diffusion than reaching the starting location of interstitial diffusion. For (2), the extra diffusant atom in the interstitial mode often imposes strong tensile stress on the lattice, repels its surrounding atoms, and leads to unstable crystal structures. Meanwhile, the crowded lattice in the interstitial mode typically requires relocating more atoms to make space for lithium migration, thus resulting in a higher diffusion energy barrier. Apparently, when multiple pathways exist for an atom to diffuse to similar locations, atoms tend to choose the one with lower energy barrier. For (3), vacancy structures are typically more symmetrical than interstitial ones due to the larger void space.<sup>7</sup> This avoids a high-energy transition state and lowers the diffusion energy barrier.

a



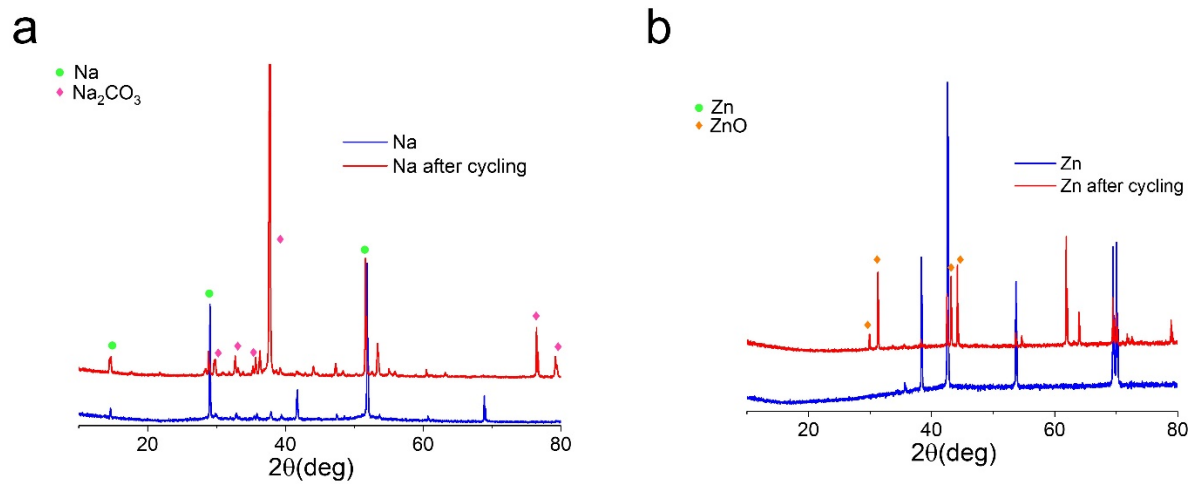
Li@In foil before cycling

b

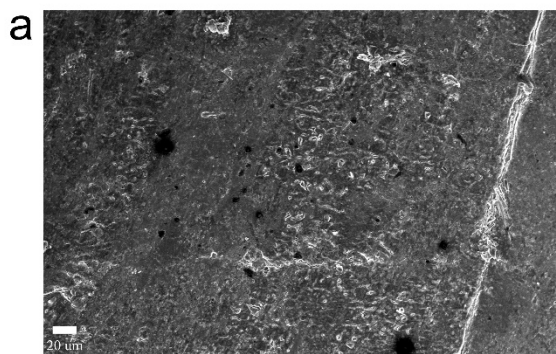


Li@In foil before cycling

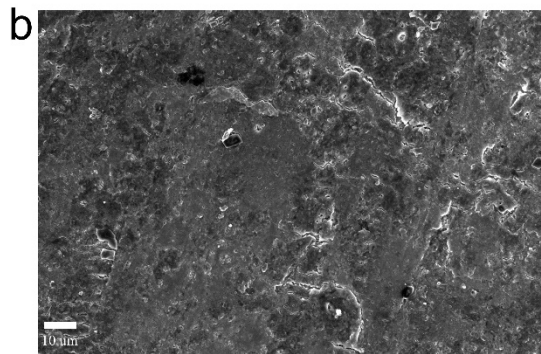
**Figure S5.** SEM images of Li@In anode before cycling.



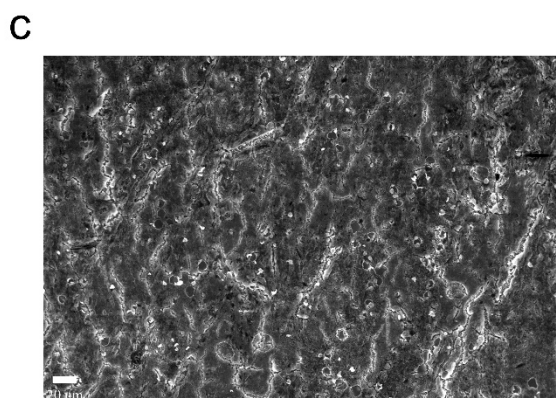
**Figure S6.** XRD of Na foil and Zn foil before and after cycling in the Na-Air and Zn-Air batteries, respectively.



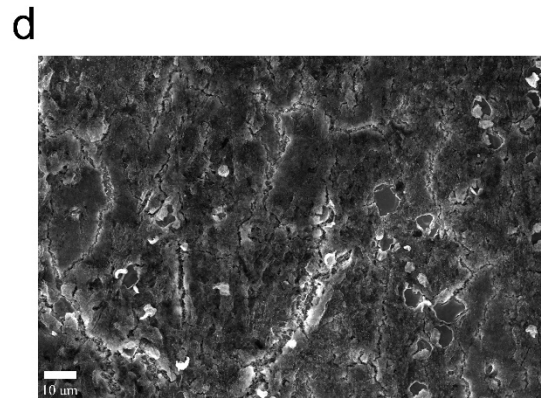
Na foil before  
cycling



Na foil before  
cycling

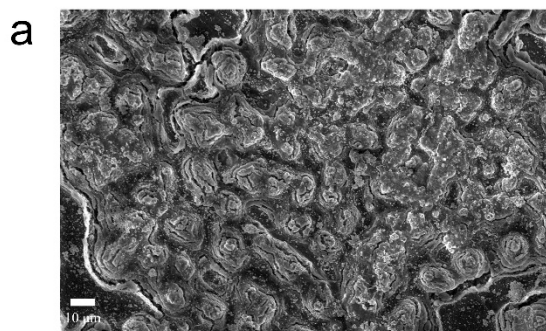


Na foil after  
cycling

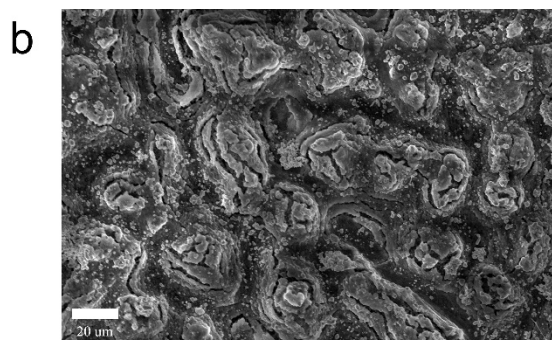


Na foil after  
cycling

**Figure S7.** SEM images of Na foil before and after cycling in the Na-Air.



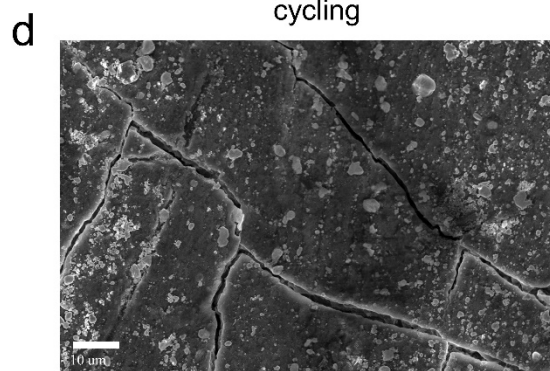
Na@In before  
cycling



Na@In before  
cycling



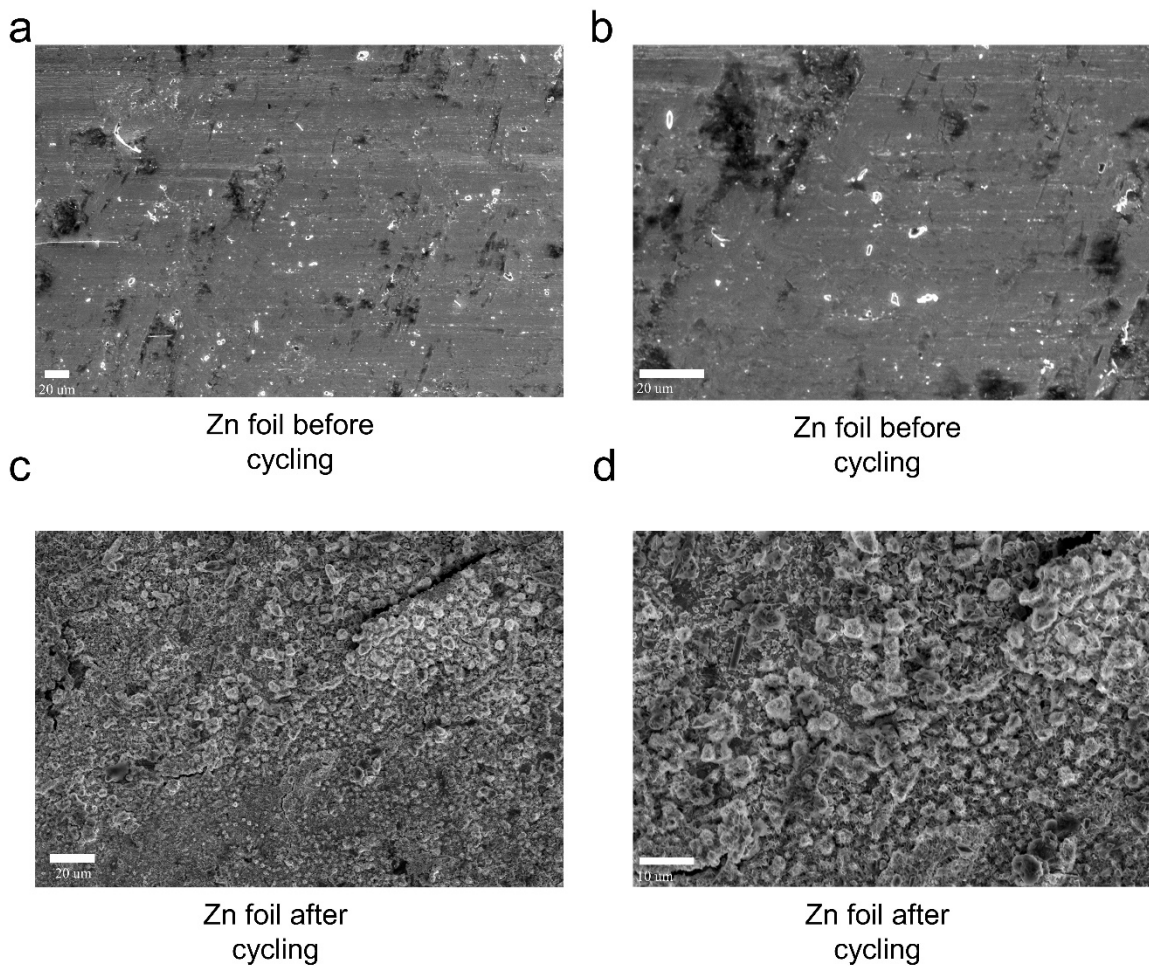
Na@In after  
cycling



Na@In after  
cycling

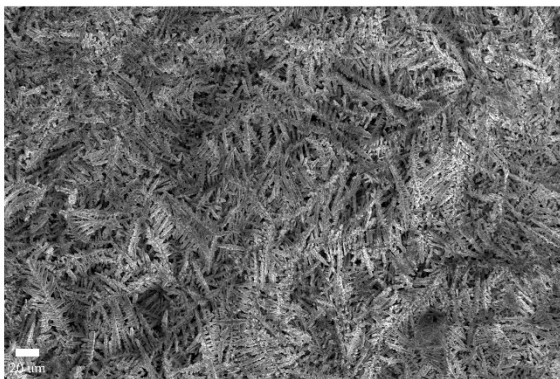
**Figure S8.** SEM images of Na@In anode before and after cycling in the Na-Air.





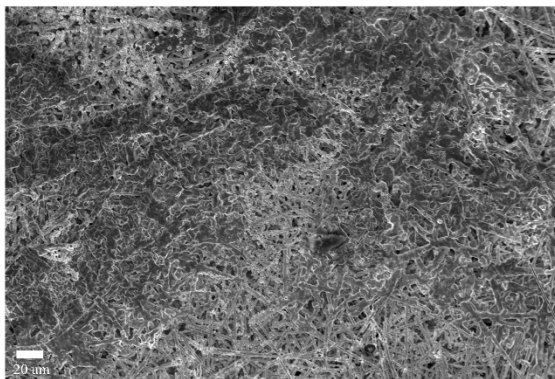
**Figure S9.** SEM images of Zn foil before and after cycling in the Zn-Air.

a



Zn@Sn before  
cycling

b



Zn@Sn after  
cycling

**Figure S10.** SEM images of Zn@Sn before and after cycling in the Zn-Air.