Supporting Information

Confinement effect and air tolerance of Li plating by lithiophilic poly(vinyl alcohol) coating for dendrite-free Li metal batteries

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Figure S1. Surface SEM morphologies of (a) pristine Li and (b) PVA-Li after 10 cycles at 1 mA cm$^{-2}$ with an areal capacity of 1 mAh cm$^{-2}$. 
Figure S2. Surface SEM morphologies of (a) pristine Li and (b) PVA-Li after 10 cycles at 5 mA cm$^{-2}$ with an areal capacity of 1 mAh cm$^{-2}$.

Figure S3. Surface SEM morphologies of PVA-Li with broken surface and large hole in (a) overview, (b) low magnification and (c) high magnification after 10 cycles at 5 mA cm$^{-2}$ with an areal capacity of 1 mAh cm$^{-2}$.

Figure S4. Cross-section SEM morphologies of Li deposited on (a) pristine Cu
and (b) PVA-Cu electrodes after 30 cycles at a high current density of 5 mA cm\(^{-2}\). The thickness of Cu foil is about 10 μm.

**Figure S5.** Comparison of CEs of Li/Cu cells based on PVA-coated Cu electrodes of different PVA thickness at current densities of (a) 1 mA cm\(^{-2}\) and (b) 3 mA cm\(^{-2}\) with a fixed capacity of 1 mAh cm\(^{-2}\).
Figure S6. Voltage hysteresis comparison of Li/Cu cells during Li plating/stripping at a current density of 1 mA cm$^{-2}$ with a capacity of 2 mAh cm$^{-2}$.

Figure S7. CEs of Li/Cu cells based on pristine Cu and PVA-Cu electrodes with a high areal capacity of 4 mAh cm$^{-2}$ at 2 mA cm$^{-2}$. 
**Figure S8.** Voltage gap comparison of Li/Li symmetric cells during Li plating/stripping at a high current density of 5 mA cm$^{-2}$ with 2 mAh cm$^{-2}$.

**Figure S9.** Electrochemical impedance spectra of Li/Li cells based on (a) pristine Li and (b) PVA-Li electrodes after the 1st and 10th cycles at a current density of 2 mA cm$^{-2}$. 
Figure S10. Charge and discharge profiles of Li-S cells based on pristine Li or PVA-Li anodes at different cycling stages at (a) 0.2 C and (b) 1 C.