## Supporting Information

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

Han Wu,<sup>†,‡</sup> Zhenguo Yao,<sup>†</sup> Qingping Wu,<sup>†</sup> Shengsheng Fan,<sup>†,‡</sup> Congling Yin <sup>‡\*</sup> Chilin Li<sup>†\*</sup>

<sup>†</sup>State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China. Email: chilinli@mail.sic.ac.cn

<sup>‡</sup>School of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China. Email: congling.yin@gmail.com



**Figure S1.** Surface SEM morphologies of (a) pristine Li and (b) PVA-Li after 10 cycles at 1 mA cm<sup>-2</sup> with an areal capacity of 1 mAh cm<sup>-2</sup>.



Figure S2. Surface SEM morphologies of (a) pristine Li and (b) PVA-Li after 10

cycles at 5 mA cm<sup>-2</sup> with an areal capacity of 1 mAh cm<sup>-2</sup>.



**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<sup>-2</sup> with an areal capacity of 1 mAh cm<sup>-2</sup>.



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<sup>-2</sup>. The thickness of Cu foil is about 10  $\mu$ m.



**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<sup>-2</sup> and (b) 3 mA cm<sup>-2</sup> with a fixed capacity of 1 mAh cm<sup>-2</sup>.



**Figure S6.** Voltage hysteresis comparison of Li/Cu cells during Li plating/stripping at a current density of 1 mA cm<sup>-2</sup> with a capacity of 2 mAh cm<sup>-2</sup>.



**Figure S7.** CEs of Li/Cu cells based on pristine Cu and PVA-Cu electrodes with a high areal capacity of 4 mAh cm<sup>-2</sup> at 2 mA cm<sup>-2</sup>.



**Figure S8.** Voltage gap comparison of Li/Li symmetric cells during Li plating/stripping at a high current density of 5 mA cm<sup>-2</sup> with 2 mAh cm<sup>-2</sup>.



**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<sup>-2</sup>.



**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.