

Electronic Supplementary Information

Dual-Phase Li-Ca Alloy with Patternable and Lithiophilic 3D Framework for Improving Lithium Anode Performance

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Additional details

After the Ca metal and the CaLi₁₀ alloy had been soaked in both carbonate and ether based electrolyte for 6 days, their surface color did not change significantly and the metallic luster remained. It indicates that the Ca metal is compatible with the electrolyte and thus performs stably in it. The as-prepared CaLi₂ alloy is hard and brittle, but the hardness and brittleness of the Li-Ca alloy decrease and the flexibility increases with the increase of Li content. After delithiation, the as-prepared CaLi₂ alloy keeps the state of bulk without porous, which indicates that it is a single phase. The Li-Ca alloy with high Li content is firmly attached to the substrate of stainless steel sheet and it is difficult to separate the Li-Ca alloy from stainless steel. Besides, the experiment has proved that the stainless steel is very difficult to be corroded by molten Li, which is the reason for stainless steel sheet to be selected as the substrate. In order to test the mechanical properties of the pristine Li foil and CaLi₁₀ alloy foil by an electromechanical universal testing machine, the CaLi₁₀ alloy without stainless steel sheet was obtained by using polyimide film as substrate. The Li foil was heated to be molten on a polyimide film at 300 °C, and the Ca metal was added to form Li-Ca alloy. After cooling down to room temperature, the polyimide film was peeled off. And then the as-prepared CaLi₁₀ was cut to 10 mm×100 mm rectangles.

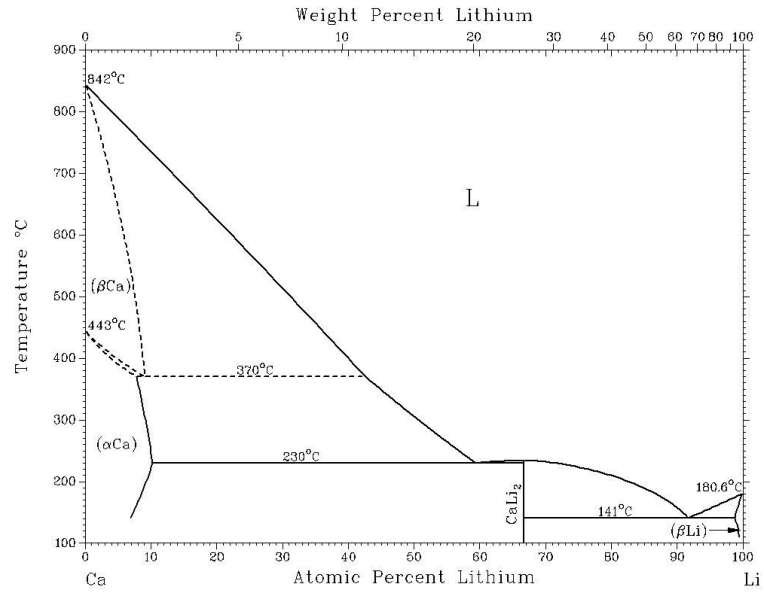


Fig. S1. Li-Ca binary phase diagram.^{S1}

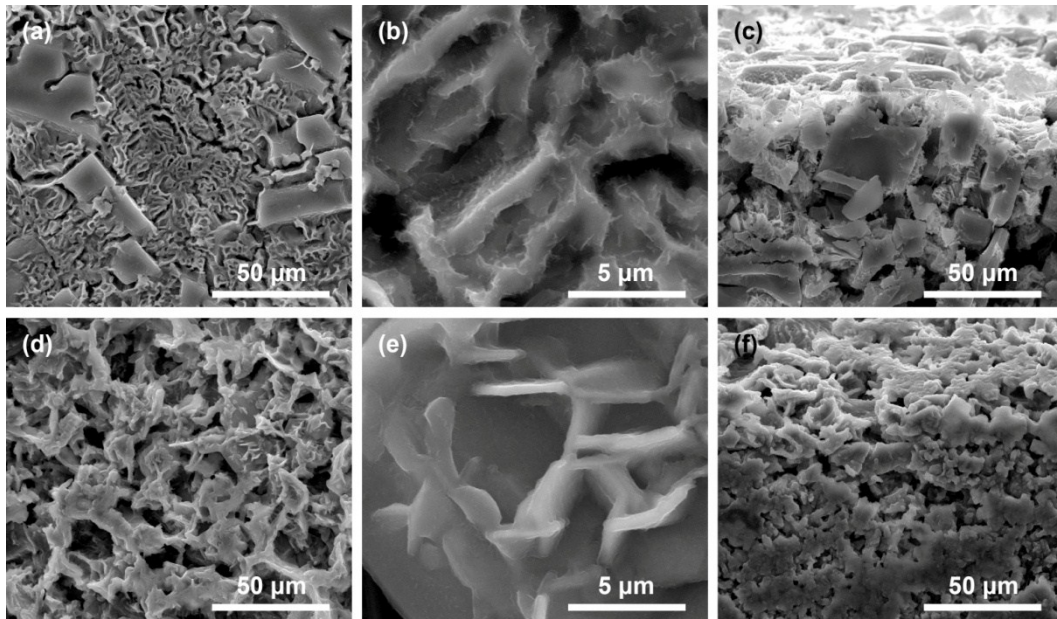


Fig. S2. The SEM images of (a-c) CaLi5 and (d-f) CaLi50 after electrochemical delithiation for 20 mAh cm⁻².

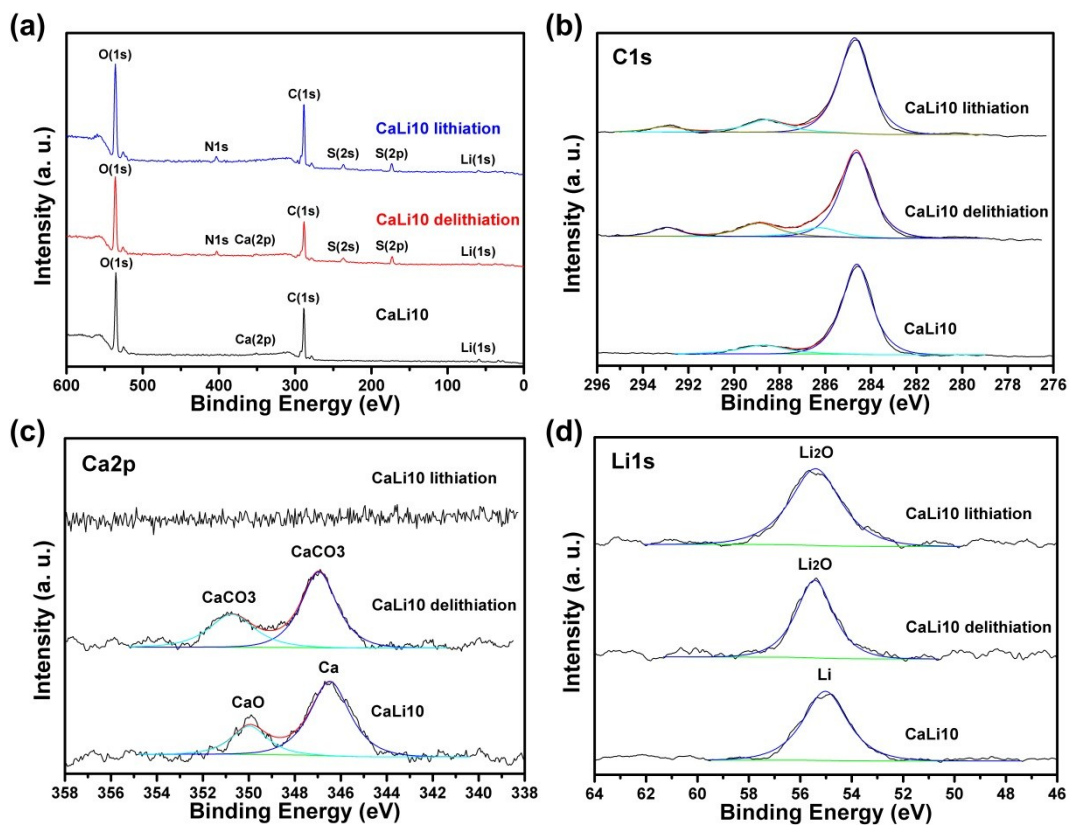


Fig. S3. (a) X-ray photoelectron spectroscopy (XPS) survey spectra of CaLi10 at different delithiation-lithiation states, and the corresponding (b) C1s spectra, (c) Ca2p spectra, and (d) Li1s spectra.

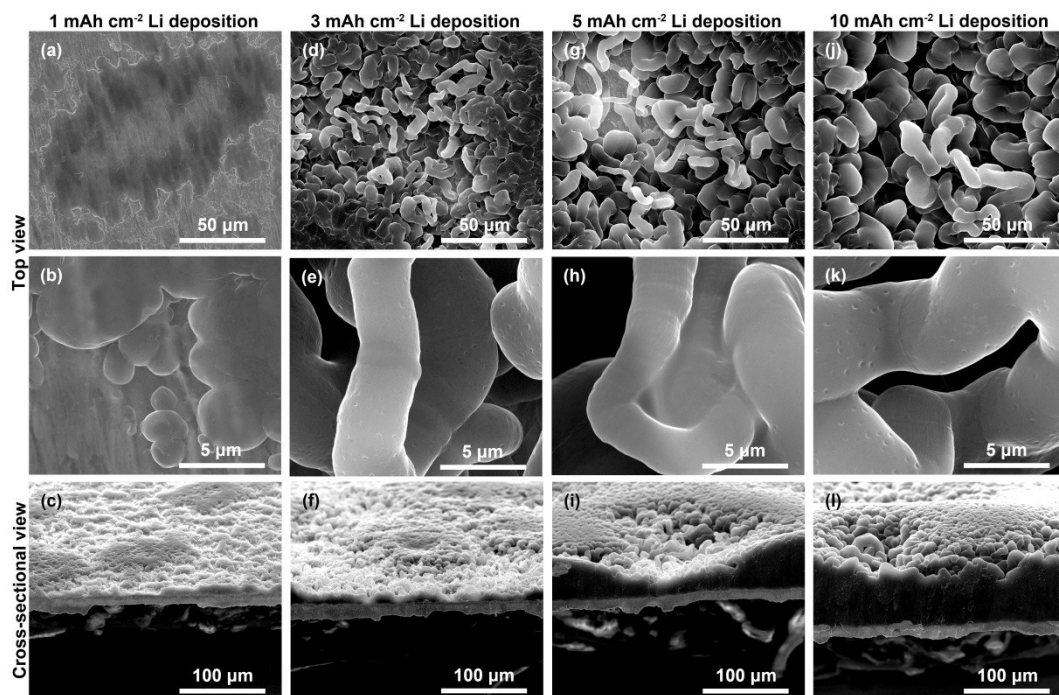


Fig. S4. The top view and cross-sectional SEM images of (a-c) 1 mAh cm⁻², (d-f) 3 mAh cm⁻², (g-i) 5 mAh cm⁻², and (j-l) 10 mAh cm⁻² Li deposited on bare Cu foil at a current density of 1 mA cm⁻².

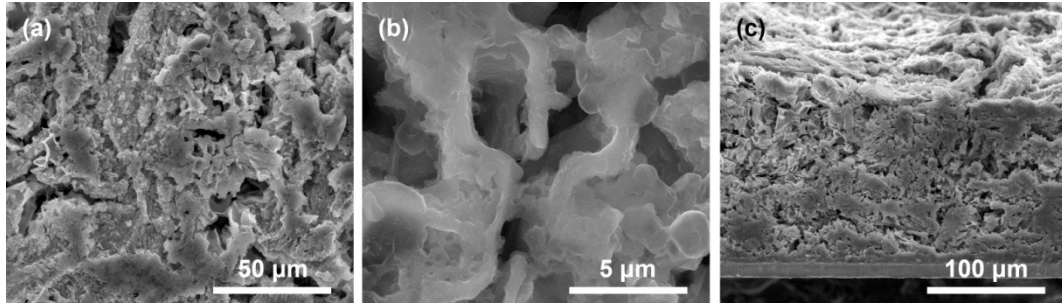


Fig. S5. The (a-b) top view and (c) cross-sectional SEM images of Ca foam after 100 cycles at 1 mA cm^{-2} for 1 mAh cm^{-2} .

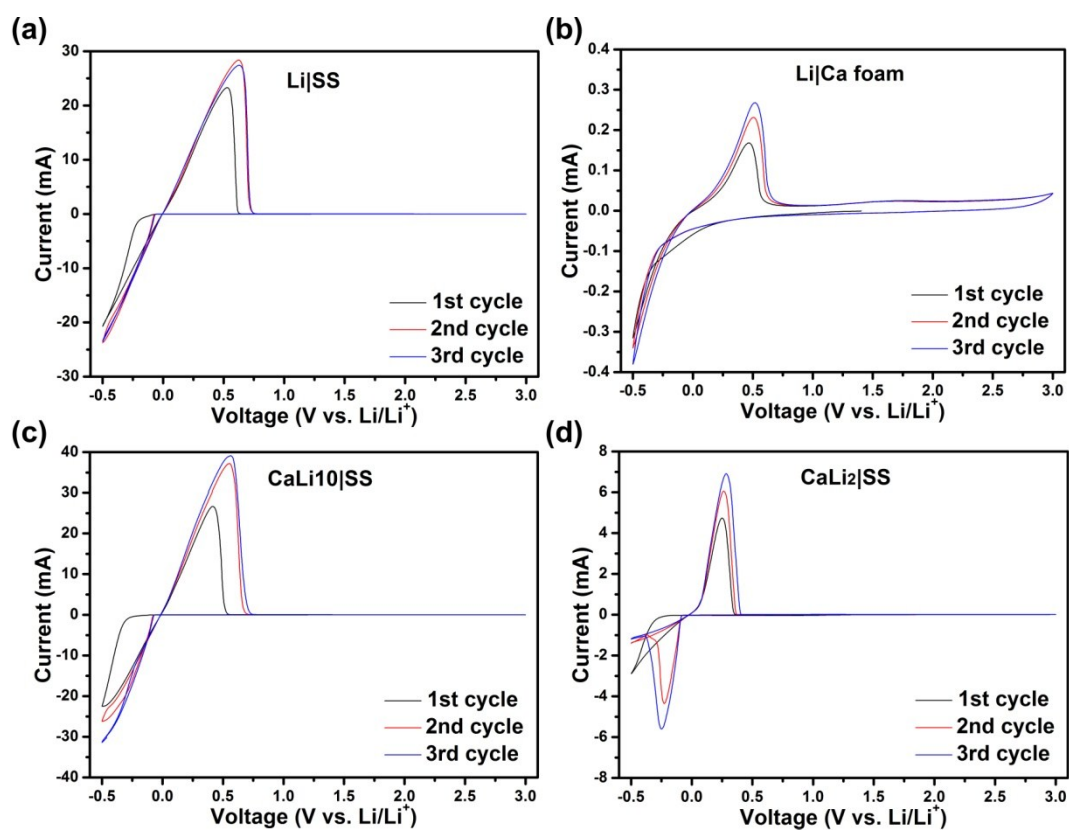


Fig. S6. Cyclic voltammetry curves of (a) Li|SS cell, (b) Li|Ca foam cell, (c) CaLi₁₀|SS cell, and (d) CaLi₂|SS cell over a voltage range of -0.5 to 3 V (vs. Li/Li⁺) at a scan rate of 1 mV s⁻¹.

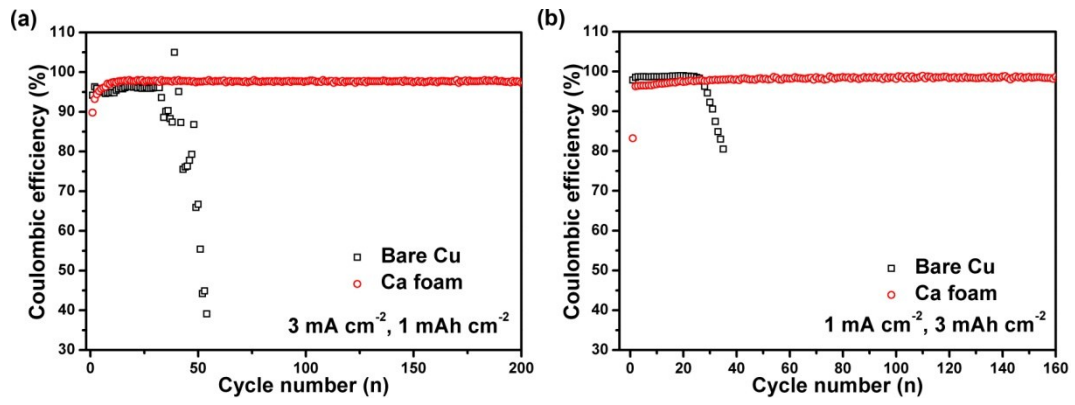


Fig. S7. The comparison of Coulombic efficiencies of Li deposition on bare Cu and Ca foam electrode at (a) 3 mA cm^{-2} for 1 mAh cm^{-2} and (b) 1 mA cm^{-2} for 3 mAh cm^{-2} .

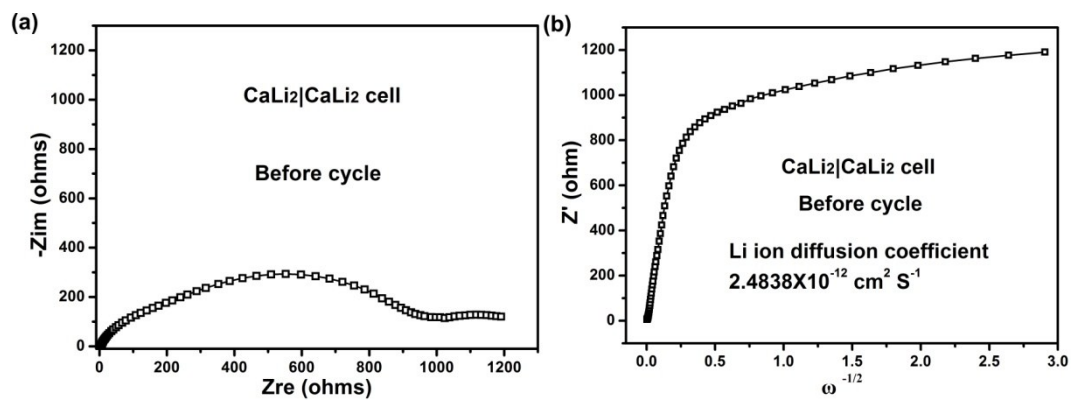


Fig. S8. (a) The AC impedance plots of symmetric $\text{CaLi}_2|\text{CaLi}_2$ cell before cycling; and (b) the corresponding Li ion diffusion coefficient.

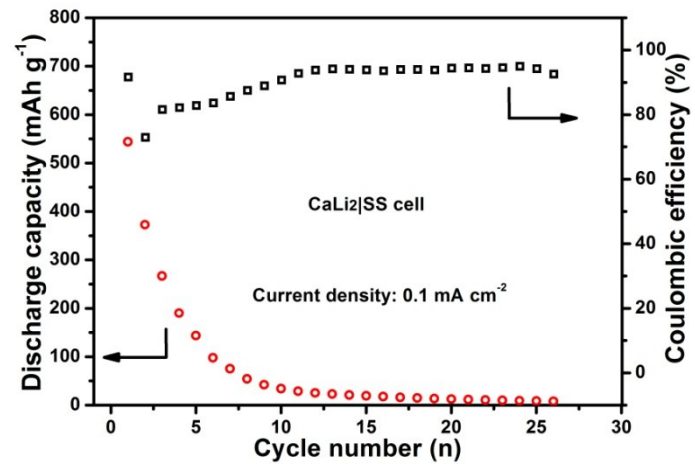


Fig. S9. Cycling stability performance of the CaLi₂|SS cell at current density of 0.1 mA cm⁻².

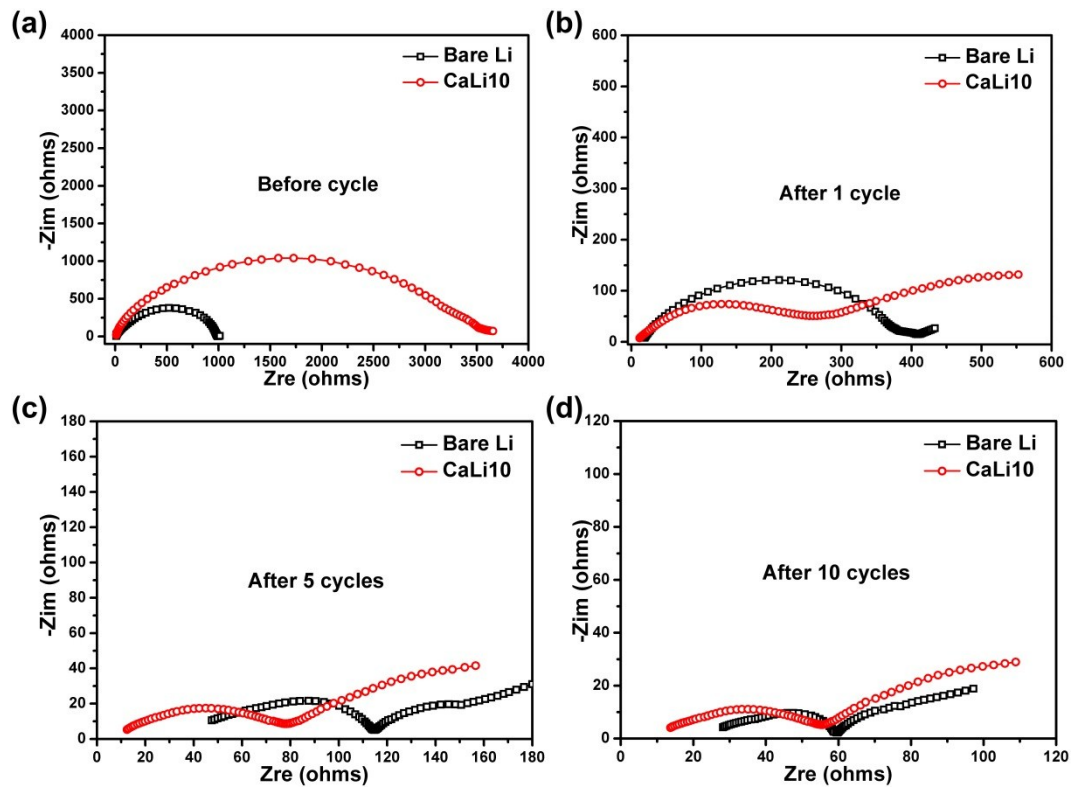


Fig. S10. The AC impedance plots of symmetric Li|Li cells with different electrodes (a) before cycle, after (b) 1 cycle, (c) 5 cycles, and (d) 10 cycles.

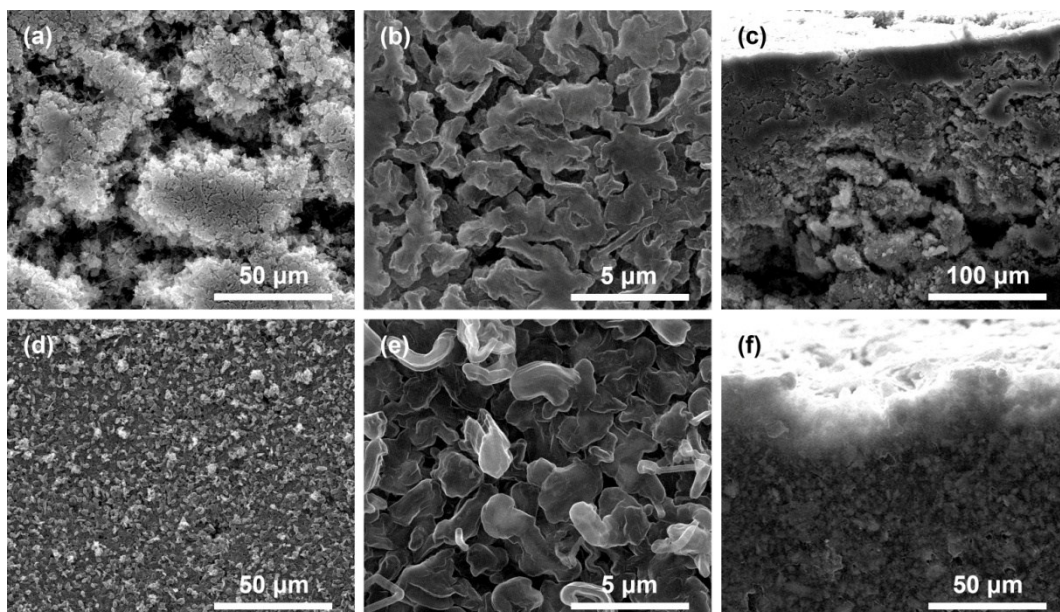


Fig. S11. The (a-b) surface and (c) cross-sectional SEM images of pristine Li after 100 cycles; and the (d-e) surface and (f) cross-sectional SEM images of CaLi10 alloy electrode after 100 cycles. The current density of the symmetric cell was 3 mA cm^{-2} , and the capacity was 1 mAh cm^{-2} .

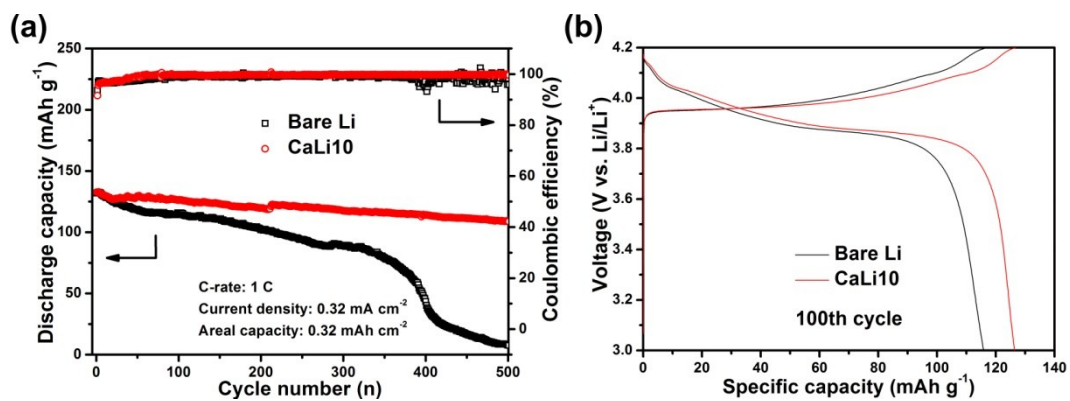


Fig. S12. (a) Cycling stability performance of LCO cell using pristine Li foil and CaLi10 tested at 1 C rate, and (b) the corresponding voltage profile comparison at the 100th cycle.

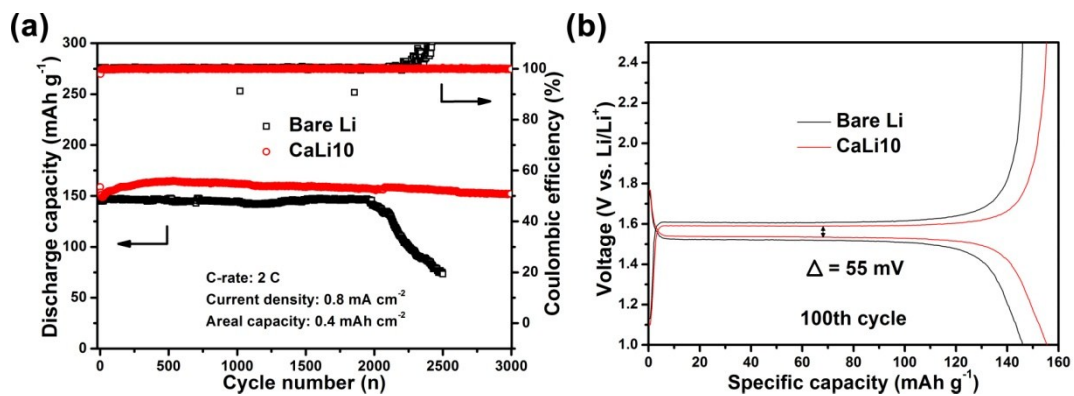


Fig. S13. (a) Cycling stability performance of LTO cell using pristine Li foil and CaLi10 tested at 2 C rate, and (b) the corresponding voltage profile comparison at the 100th cycle.

Reference

S1 C. W. Bale and A. D. Pelton, *J. Phase Equilib. Diff.*, 1987, 8, 125-127.