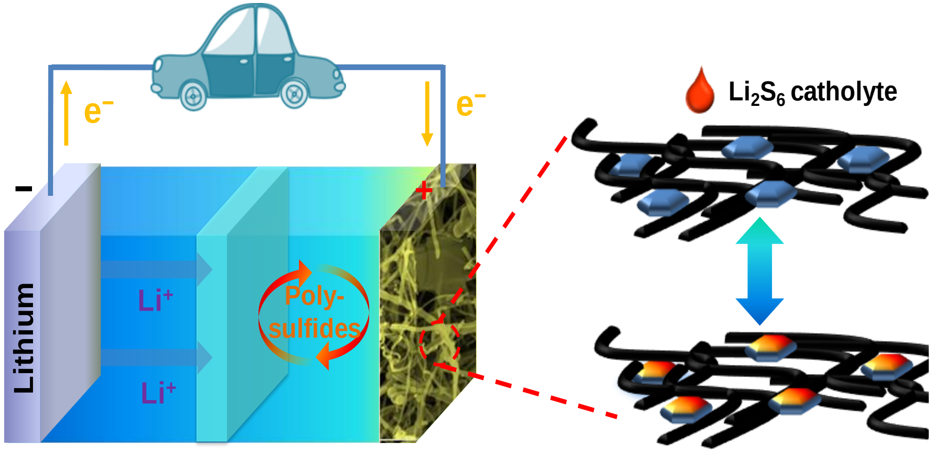
Self-Heating Induced Healing of Metal Dendrites



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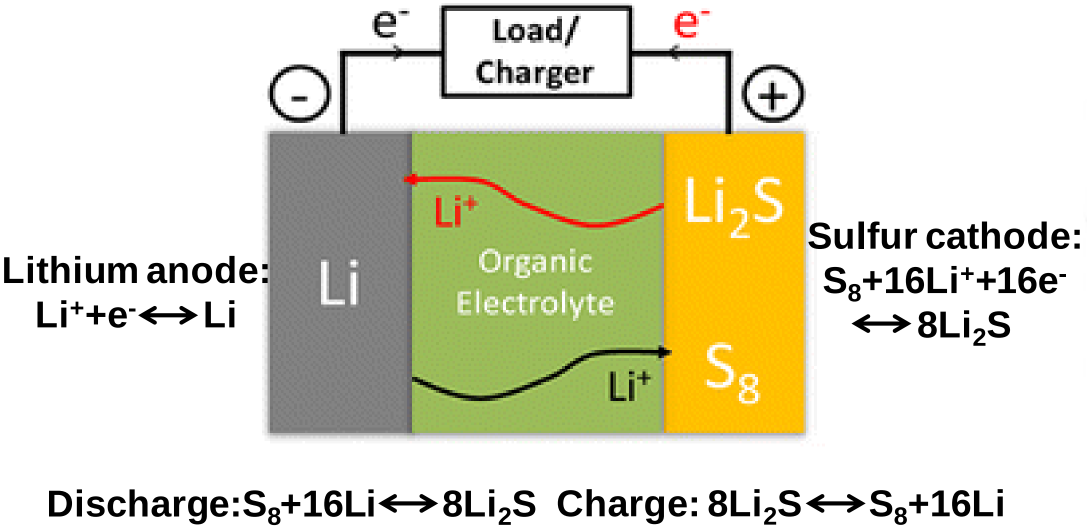
The genesis of this work started about 3 years back when we began working on Lithium-Sulfur (Li-S) Batteries

$S_8 + 16Li \leftrightarrow 8Li_2S$

2 electron transfer per S atom !



Theoretical specific capacity ~1675 mAh/g

Maximum energy density of ~2,600 Wh/kg

5X higher than Lithium-ion batteries (~387 Wh/kg)

Source: Chem. Soc. Rev. 2016, 45, 5605–5634.

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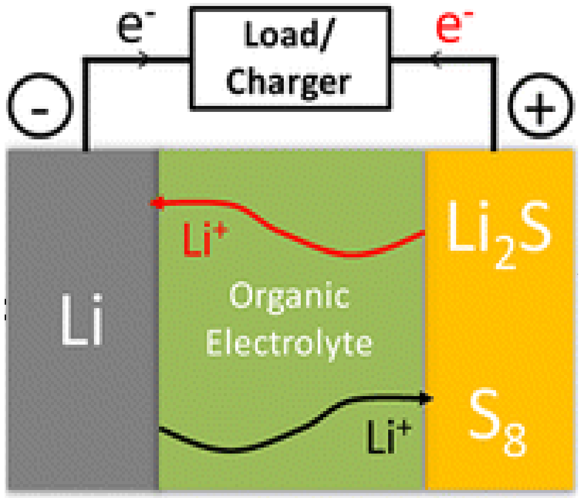
Challenges with Li-S Technology

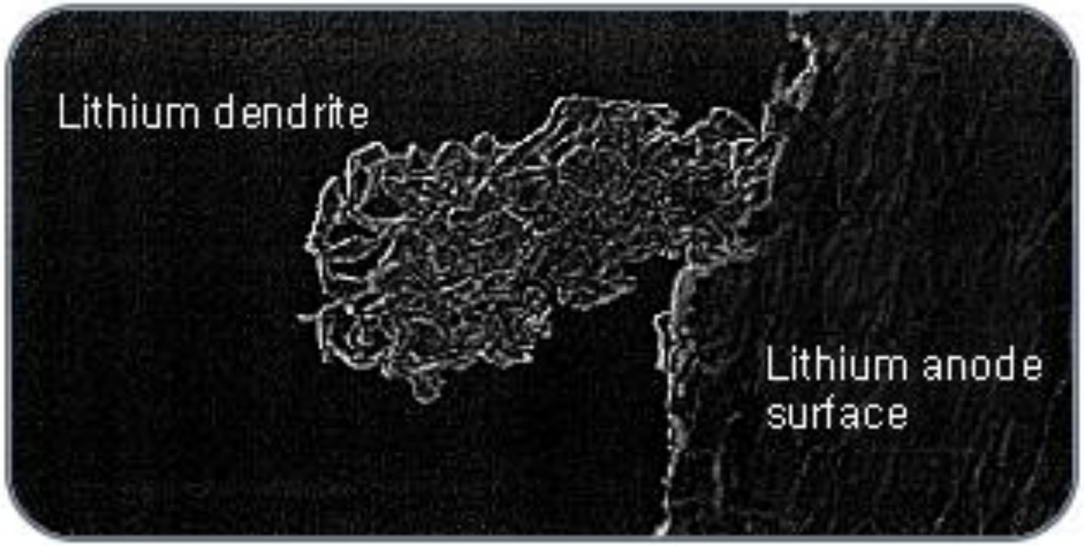
- **Poor Stability**
  Rapid fade in capacity with charge/discharge cycling

- **Safety Concerns**
  Lithium Dendrites Cause Cell Shorting and Fire Hazard

Dendritic Growth is Unavoidable in Li Metal Electrodes

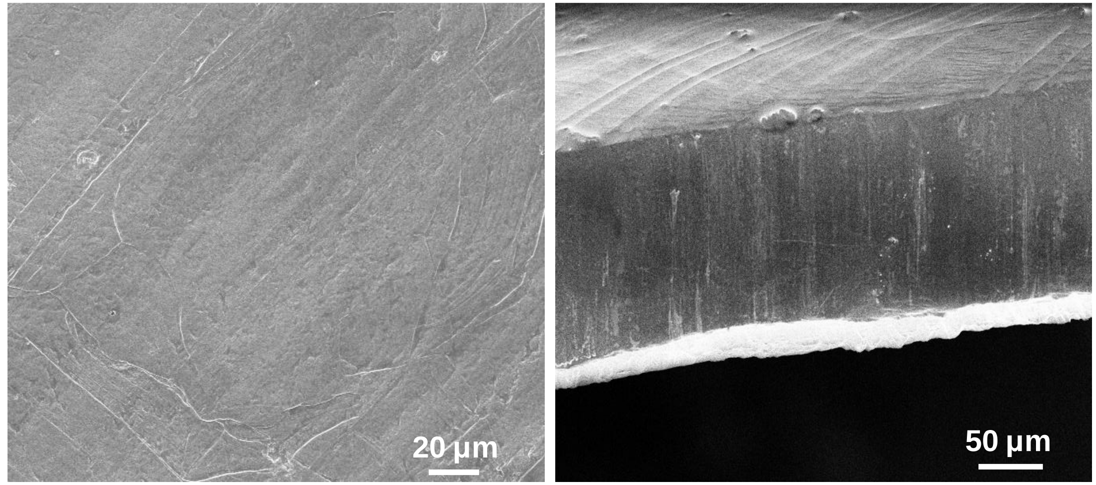
- **Non-uniform plating of Li+ at defects, edges, steps, grain boundaries due to high local field and/or a thinner solid electrolyte interface (SEI)**
- **Once dendrites are nucleated, Li+ is preferentially deposited at dendrite tips, causing the dendrites to grow sharper and longer till they pierce the membrane separator and short the cell.**
- **Resultant current spike (associated with shorted cell) raises the temperature of the cell and causes fire hazard (electrolyte is flammable).**



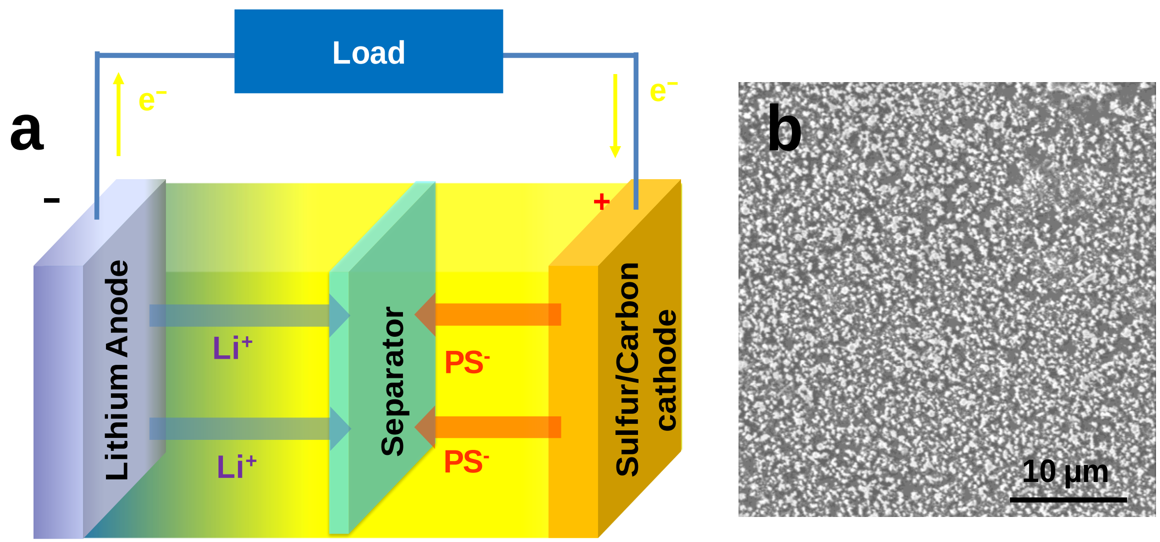


Dendrite Evolution on Li-Anode

Initial State



After only 50 charge-discharge cycles at 0.75 mA/cm^2



Electrolyte: 1.0 M lithium bis(trifluoromethylsulfonyl)imide in 1,3-dioxolane and 1,2-dimethoxyethane (1:1 by volume) with 0.1 M $LiNO_3$ additive

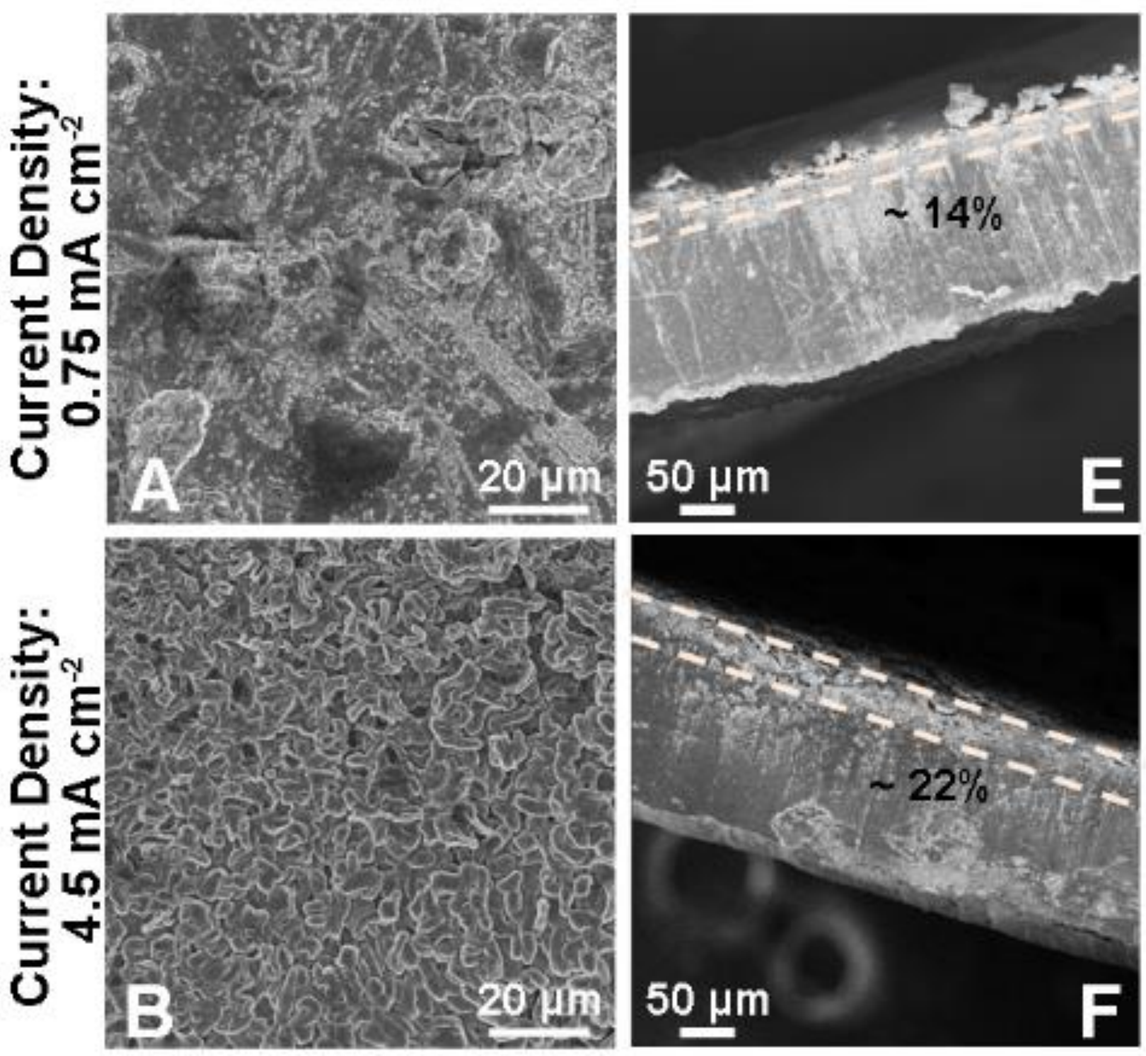
Research Question:

Can we exploit battery self-heat to heal the dendrites in situ ?

Distinct from previous approaches which focused on various coatings applied to the Lithium metal anode as well as varying solid electrolyte interface (SEI) properties

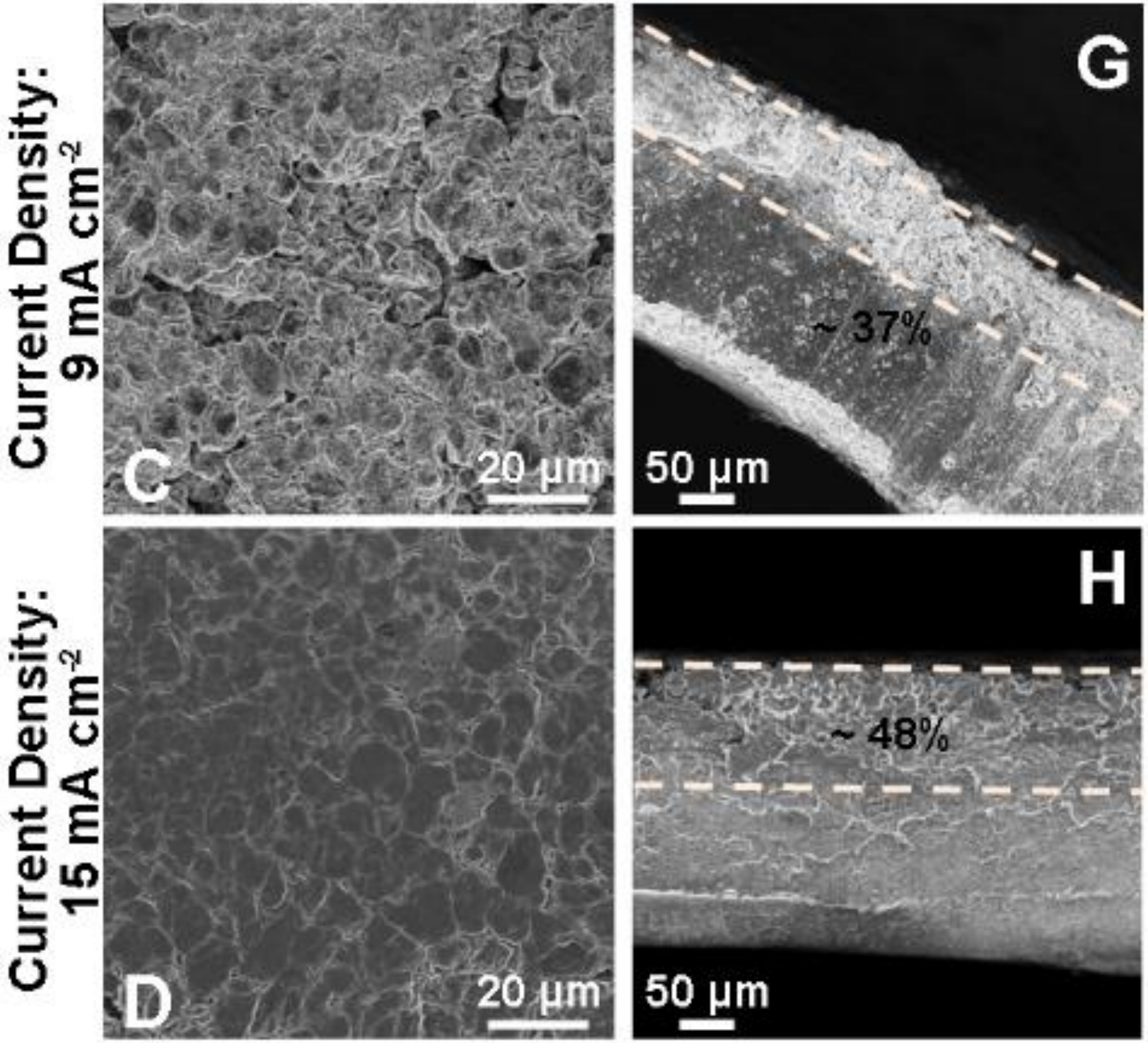
Generate battery self-heat (Joule heating) by controlling the current density or the charge-discharge rate (C-rate) of the battery

Dendritic evolution at different current densities of the Electrochemical cell

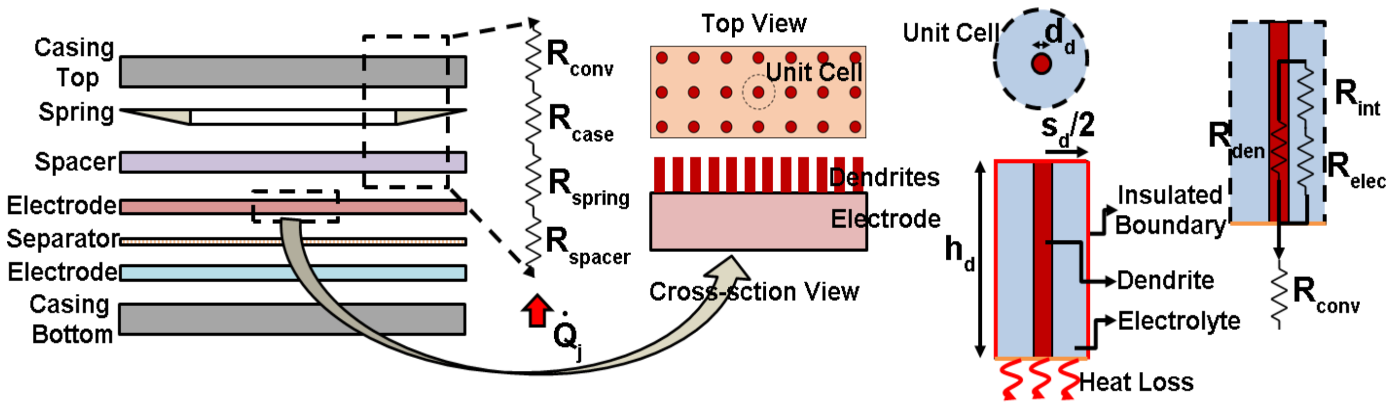


Generate battery self-heat (Joule heating) by controlling the current density or the charge-discharge rate (C-rate) of the battery.

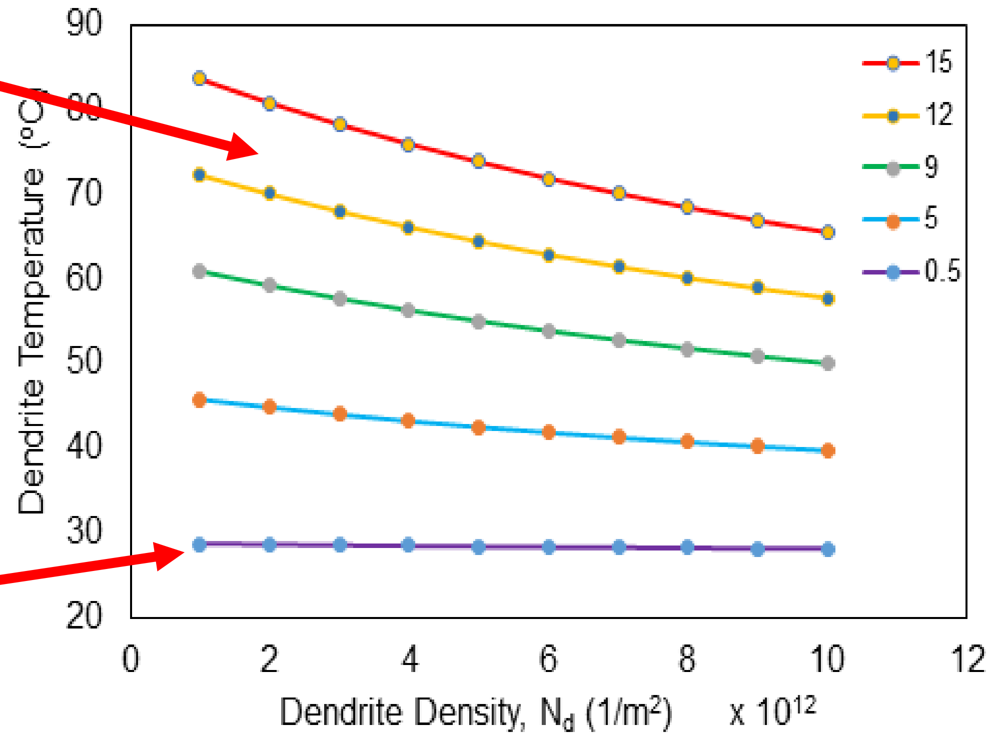
Healed morphology of Li dendrites for > 10 mA/cm^2 current density



Computational Thermal Modeling



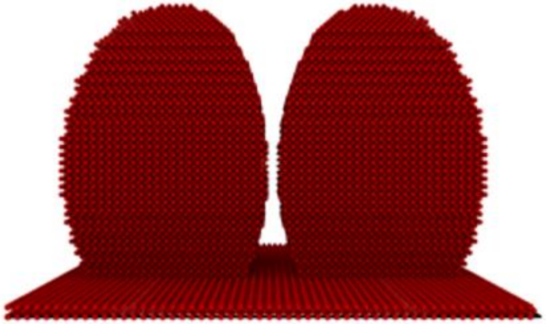
@ 10-15 mA/cm²
Dendrite temperatures of 60 to 80° C are possible



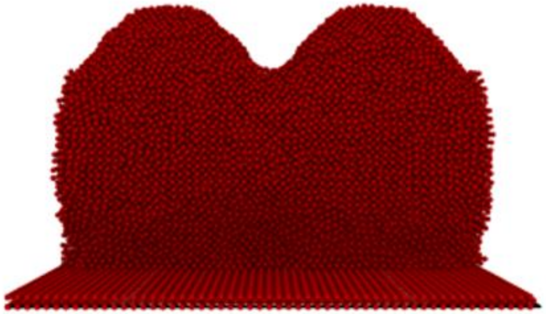
Normal Operation- 0.5 mA/cm²
Large temperature rise is not possible

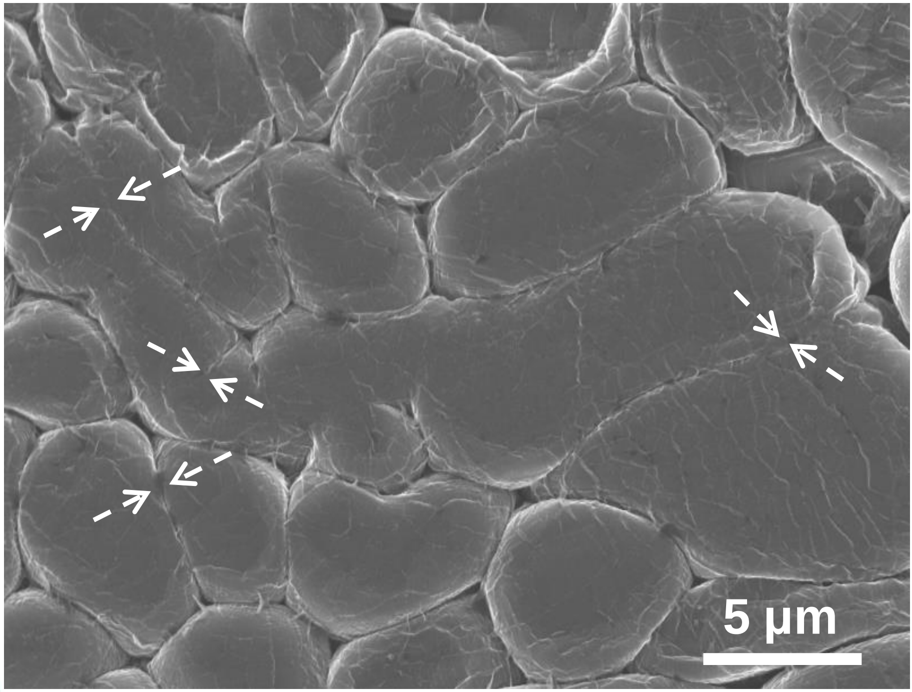
Likely Mechanism- Surface Migration of Li

Time = 0 sec
@ ~80 deg C



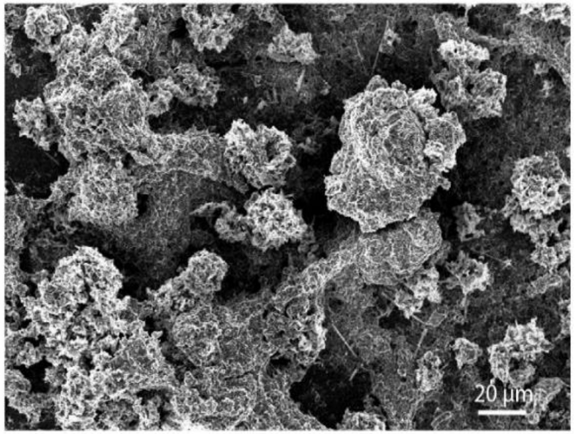
Time = 100
pico-secs
@ ~80 deg C

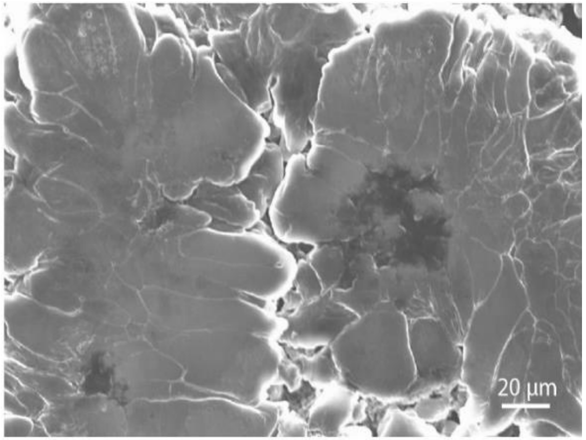


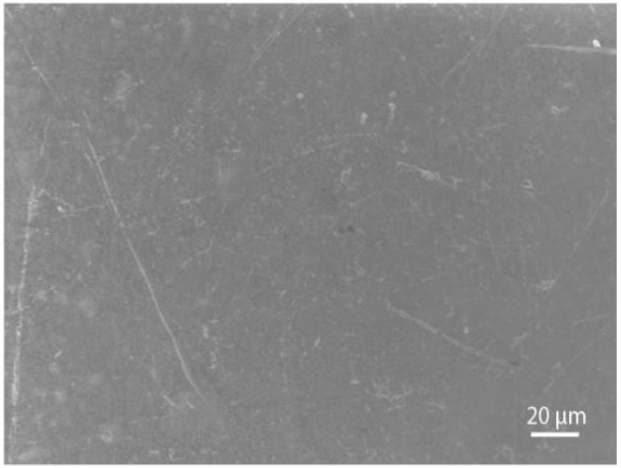


MD Simulations: Lithium-lithium interaction described by the second nearest-neighbor modified embedded atom method interatomic potential (2NN MEAM) and implemented in LAMMPS software.

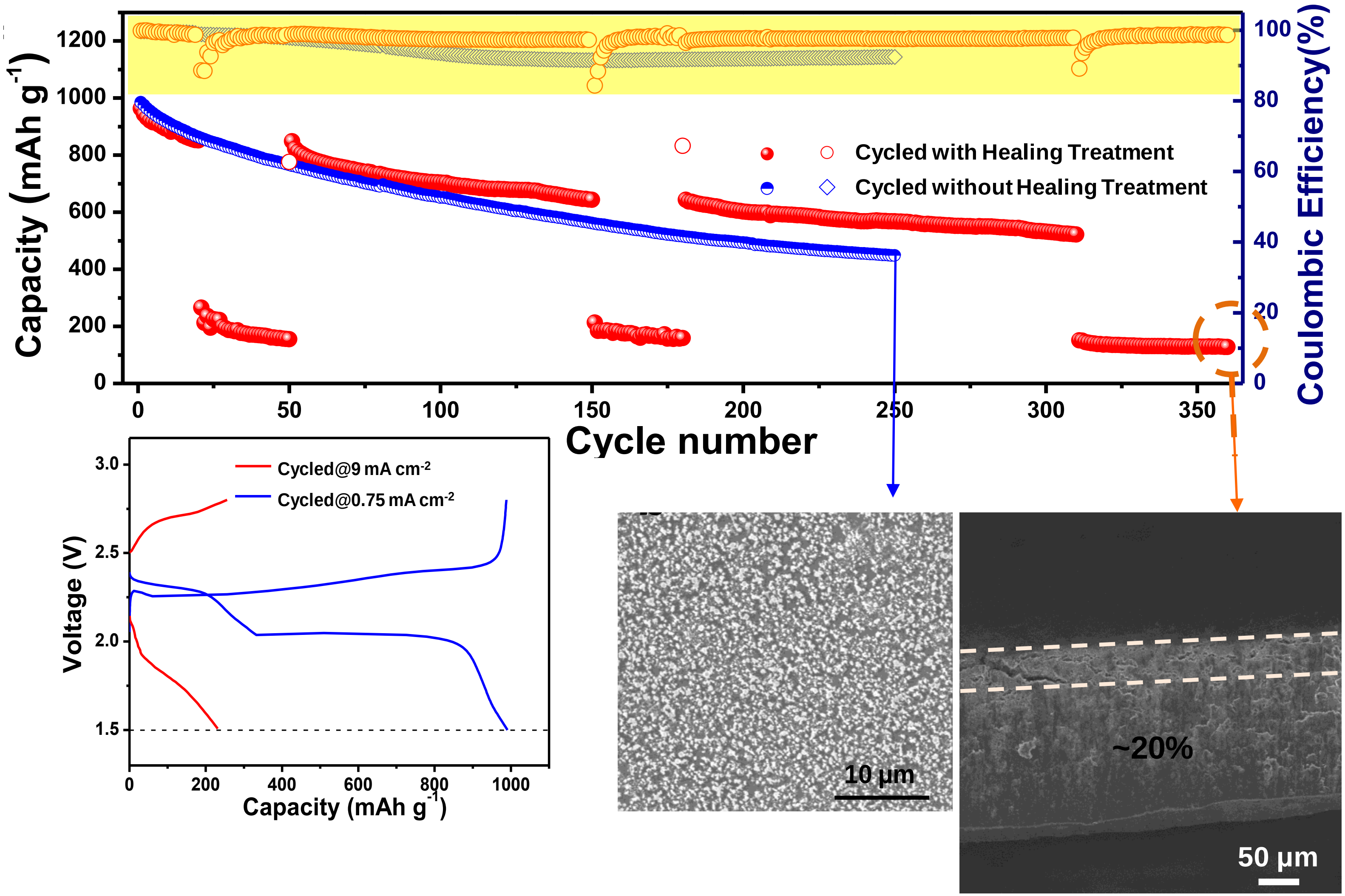
Thermal Annealing Experiment @80°C to Confirm The Surface Diffusion Mechanism



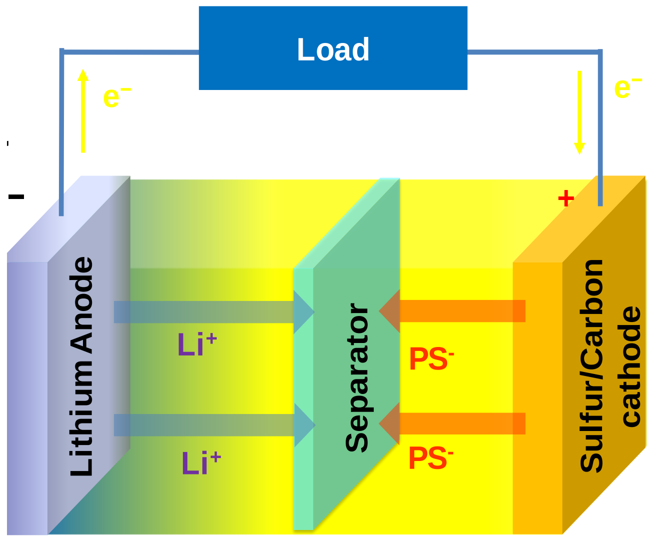




Healing Strategy: Periodic bursts of high current density applied by the Battery Management System (BMS)

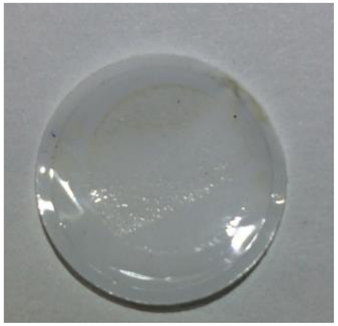


Evidence of Dendrite Healing: Membrane Separator

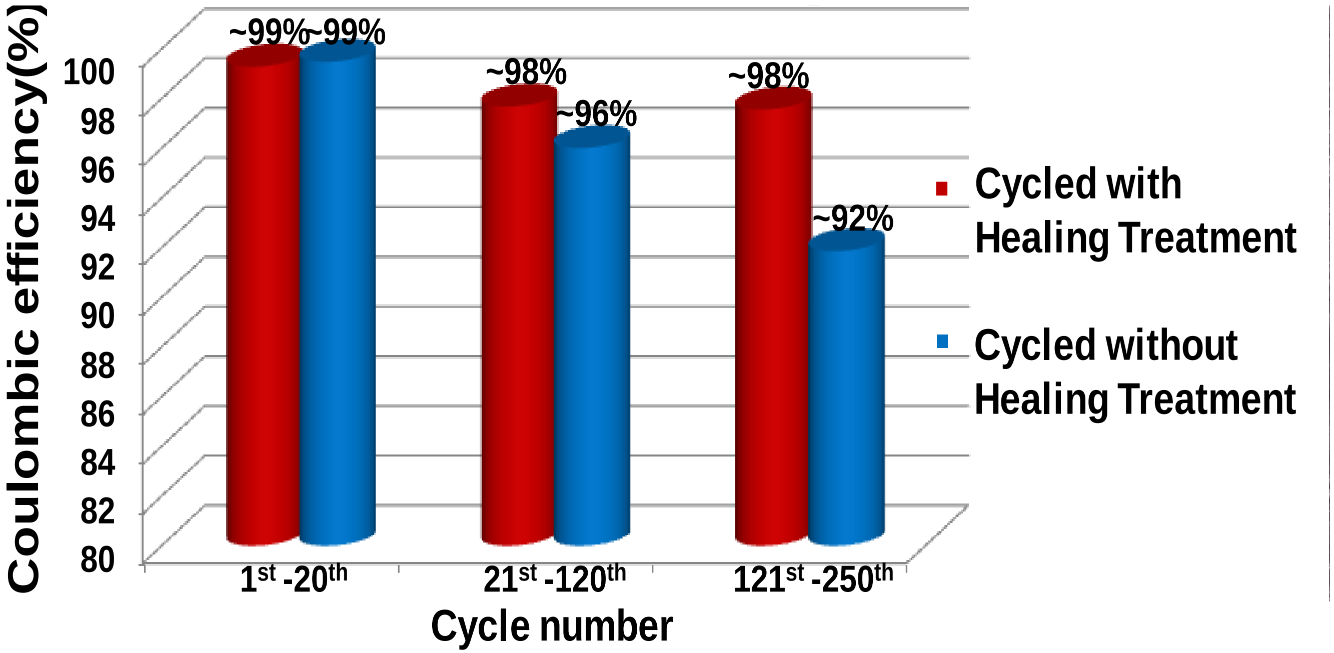


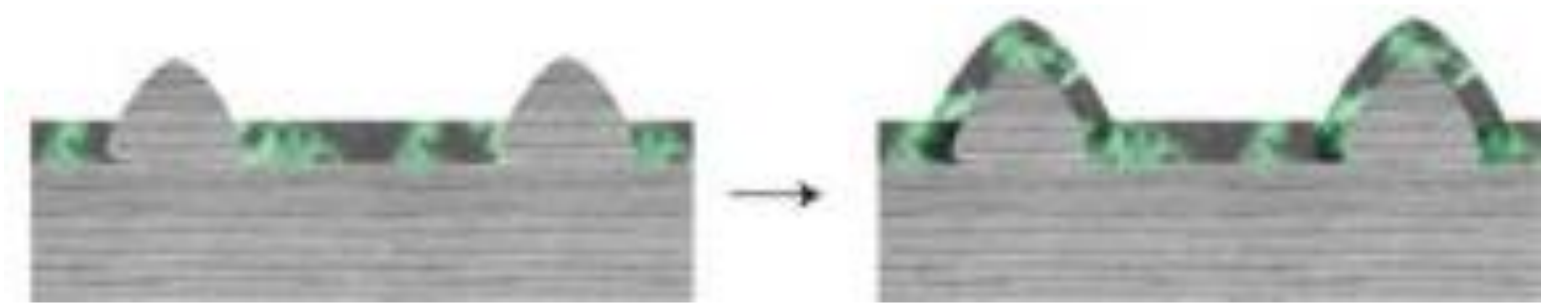
Without Healing Treatment

With Healing Treatment



High coulombic efficiency (i.e., ratio of Li plated to Li stripped) also confirms dendrite healing





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BATTERIES

Self-heating–induced healing of lithium dendrites

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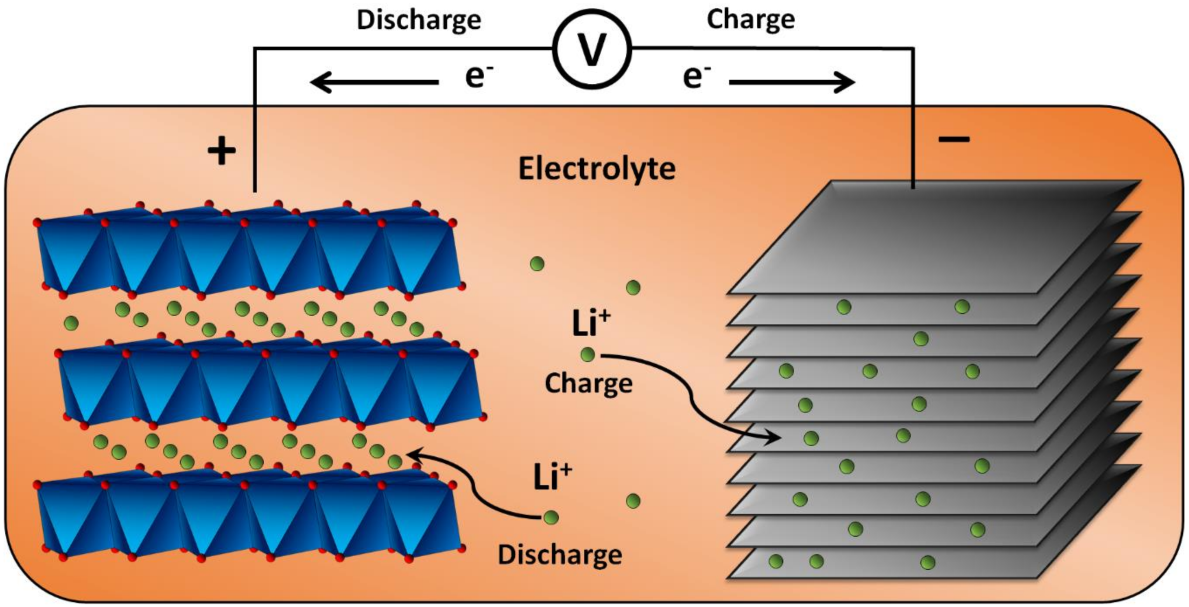
Lithium (Li) metal electrodes are not deployable in rechargeable batteries because electrochemical plating and stripping invariably leads to growth of dendrites that reduce coulombic efficiency and eventually short the battery. It is generally accepted that the dendrite problem is exacerbated at high current densities. Here, we report a regime for dendrite evolution in which the reverse is true. In our experiments, we found that when the plating and stripping current density is raised above ~9 milliamperes per square centimeter, there is substantial self-heating of the dendrites, which triggers extensive surface migration of Li. This surface diffusion heals the dendrites and smoothens the Li metal surface. We show that repeated doses of high-current-density healing treatment enables the safe cycling of Li-sulfur batteries with high coulombic efficiency.

current densities of ~15 mA cm^{-2}, an order of magnitude higher.

To corroborate the electrochemical evidence, we carried out ex situ scanning electron microscopy (SEM) imaging of the surfaces of the Li metal foils used in the experiments. Before cycling, the Li foils displayed a relatively smooth appearance and were completely free of dendrites (fig. S3). Shown in Fig. 1, A to D, are SEM images of the Li metal electrode surface after 50 cycles of charge and discharge at current densities of ~0.75, ~4.5, ~9.0, and ~15 mA cm^{-2}. Under low current density (~0.75 mA cm^{-2}) (Fig. 1A), a few isolated but large-diameter dendritic particles can be observed. With the increase of current density (Fig. 1B), the diameter of Li dendrites decreases, but the packing density of the protrusions has increased substantially. However, when the current density was increased all the way up to ~15 mA cm^{-2} (Fig. 1D), the dendrites tend to fuse (merge) together. As a consequence, the surface of the Li electrode becomes much smoother, which substantially lowers the risk of dendrite penetration through the separator. At

Applicable to other battery chemistries

Traditional Li-ion Battery:
Anode → Graphite; Cathode → Lithium Cobalt Oxide (LCO)
Our Configuration:
Anode → Li Metal; Cathode → Lithium Iron Phosphate (LFP)



Electrolyte: 1M $LiPF_6$ in EC : DEC (1:1 vol %)

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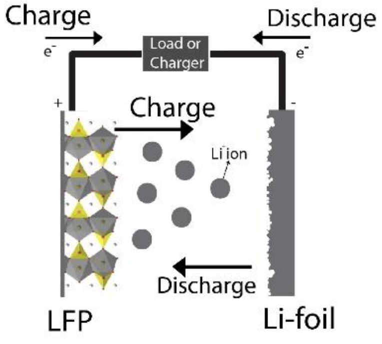
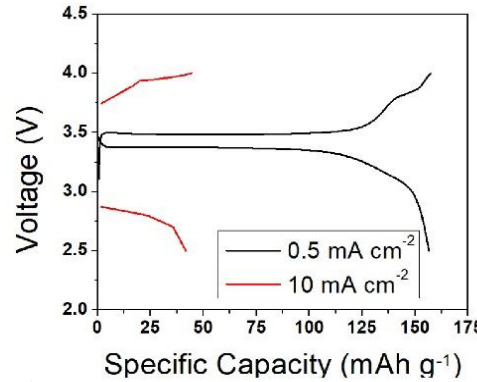
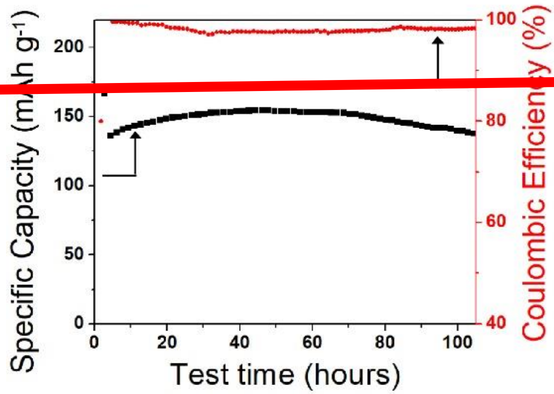
Applicable to other battery chemistries

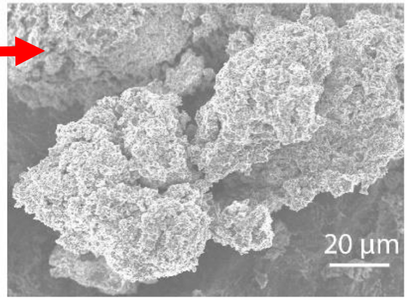
Li-ion Battery
with
ANODE: Li-metal foil
CATHODE: $LiFePO_4$ (LFP)



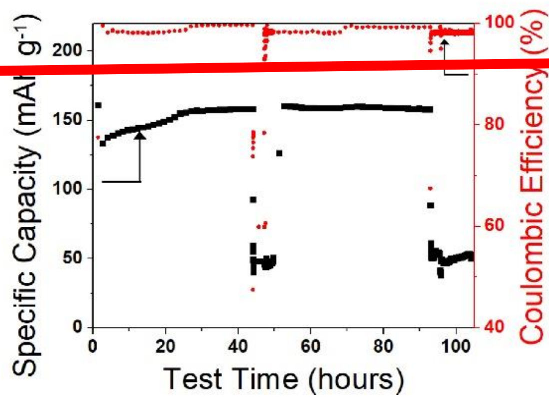


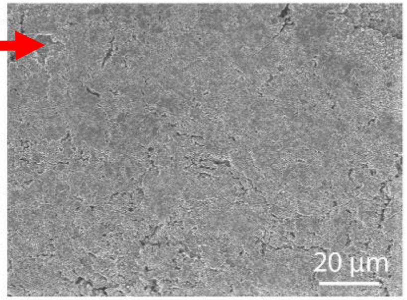
Without healing treatment
Dendrites Flourish





With healing treatment
Dendrite get Healed





Takeaway Points

- **Lithium dendrites can be healed by battery self-heating**

  → Required healing current density > 10 mA/cm^2

- **Battery Management System (BMS) could be programmed to heal dendrites**

  → By periodically applying high current density healing treatment, when the battery is off-line

- **Healing concept is not limited to Li-S batteries**

  → Applicable to Li-ion chemistries with Li metal anodes and Lithium Iron Phosphate (LFP) based cathodes.

- **Applicable to other Alkali Metals (beyond Li)**

  → In fact healing of Potassium (K) dendrites is much more potent and efficient than for Li dendrites

  → Healing current density for K is 1 to 2 mA/cm^2, about 10-fold lower than for Li

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