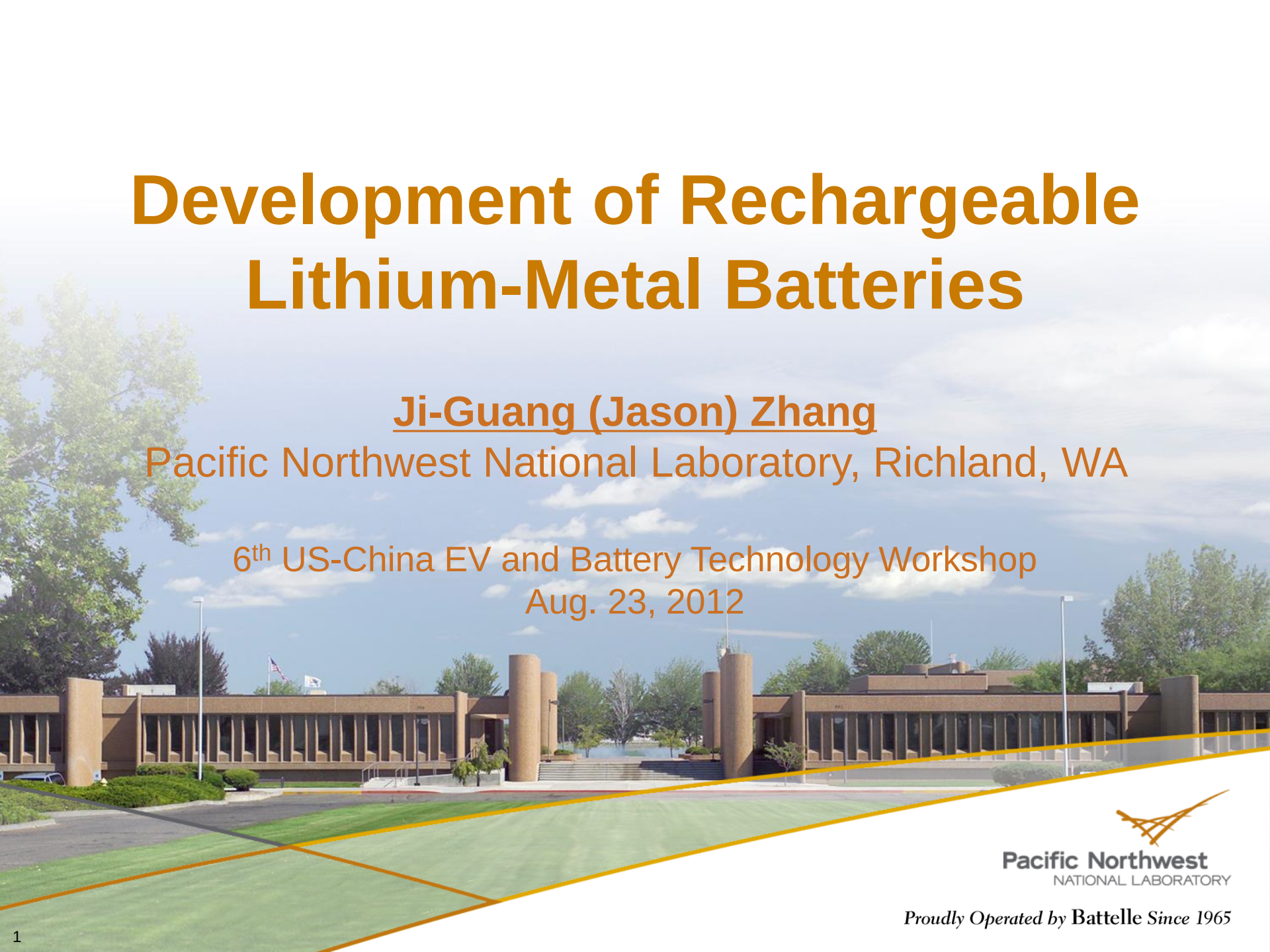
Development of Rechargeable Lithium-Metal Batteries

Ji-Guang (Jason) Zhang
Pacific Northwest National Laboratory, Richland, WA

6th US-China EV and Battery Technology Workshop
Aug. 23, 2012



Pacific Northwest
NATIONAL LABORATORY

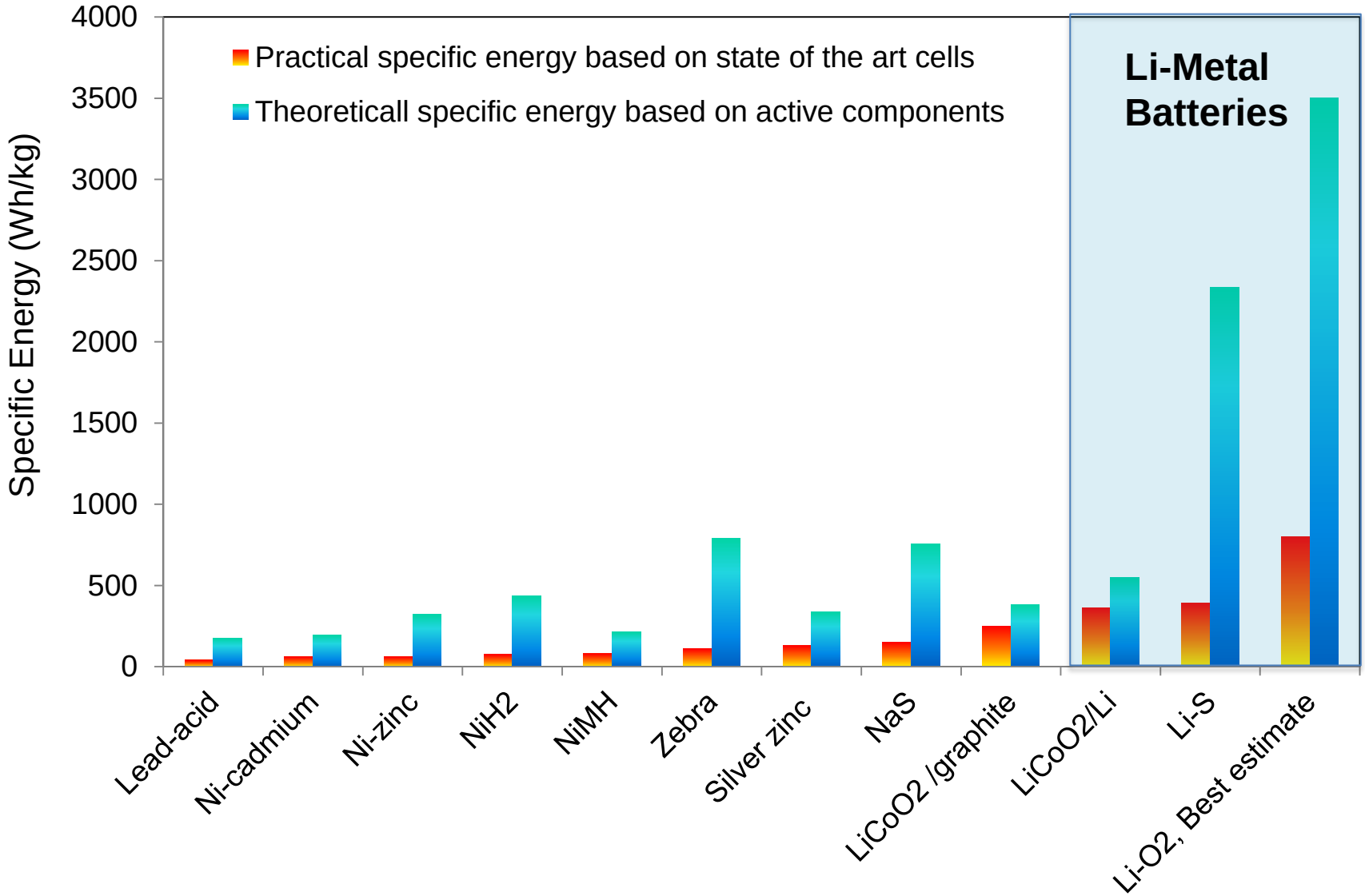
Proudly Operated by Battelle *Since 1965*

Outline

1. Introduction
2. Effects of Novel Additive on the Morphology of Li Deposition
3. Long Term Cycling Stability of Li-Metal Batteries
4. Summary

1. Introduction

Comparison of Specific Energy of Various Batteries



Opportunities and Challenges

- Rechargeable Li-metal batteries are considered the “holy grail” of energy storage systems due to the high energy density.

GM estimate on HE NMC/Li metal system: 540 Wh/kg, 1050 Wh/L in cell level (2012)

- However, Li dendrite growth in these batteries has prevented their practical applications inspect of intensive works in this field during the last 40 years.

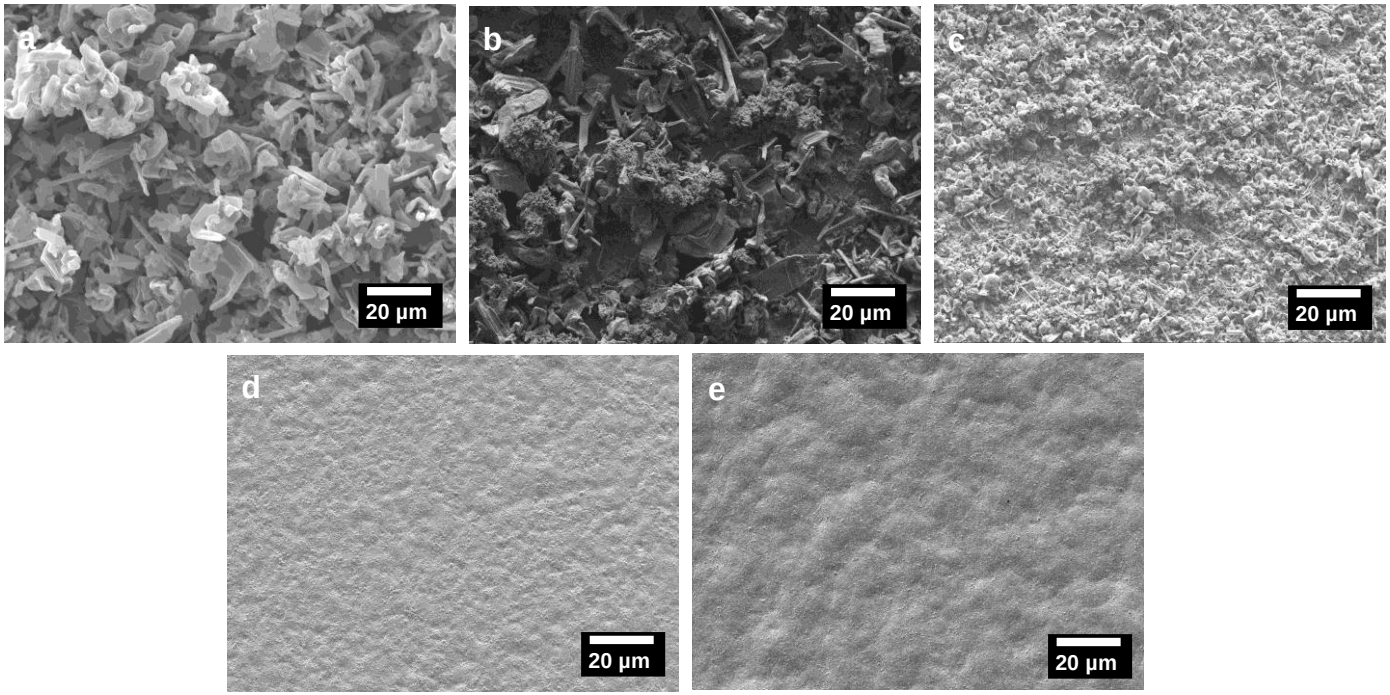
Classical Li dendrite growth (Chianelli, Exxon, 1976)

➢ Dendrite-free Li metal deposition is needed for rechargeable Li-metal batteries, Li-S batteries, Li-air batteries.

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

2. Effect of PNNL Additive on The Morphology of Li Deposition

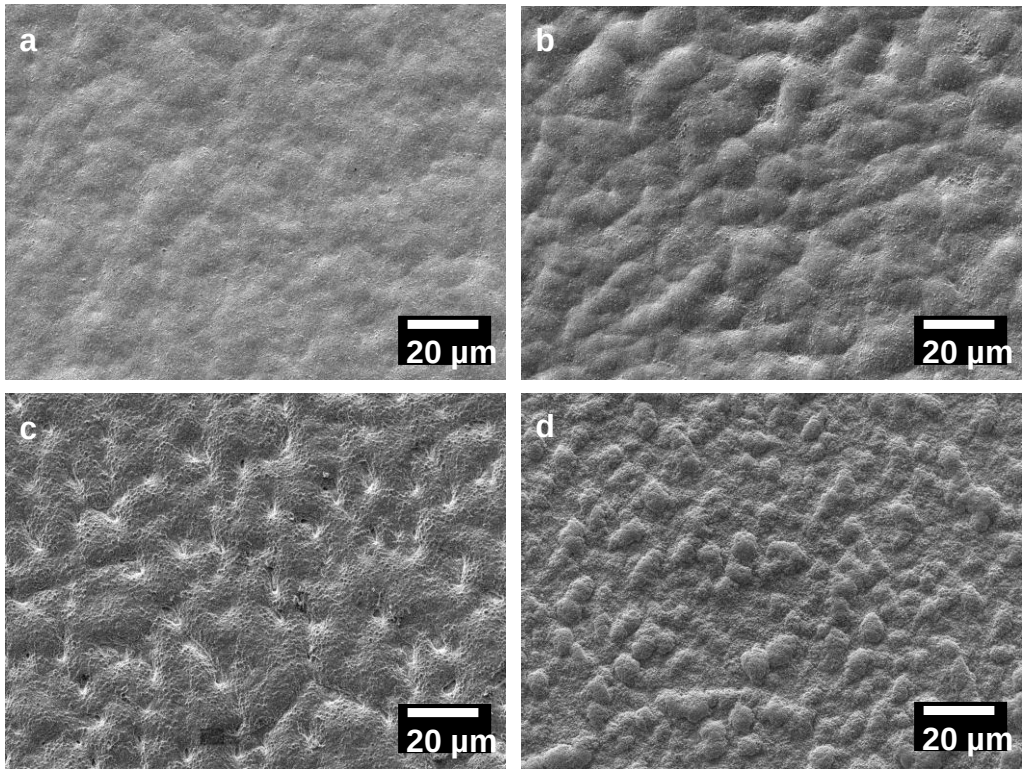


- **PNNL additive can effectively suppress Li dendrite growth.**

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Effect of Current Density on Li Deposition



- Current density (mA cm^{-2}): (a) 0.1, (b) 0.2, (c) 0.5, and (d) 1.0.

➢ **PNNL additive is effective at different current densities.**

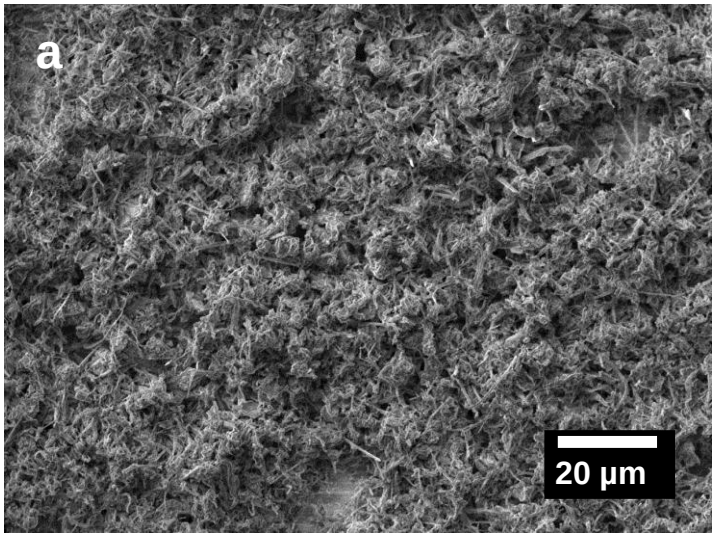
Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Effect of PNNL Additive on Li Film Grown on Dendritic Surface

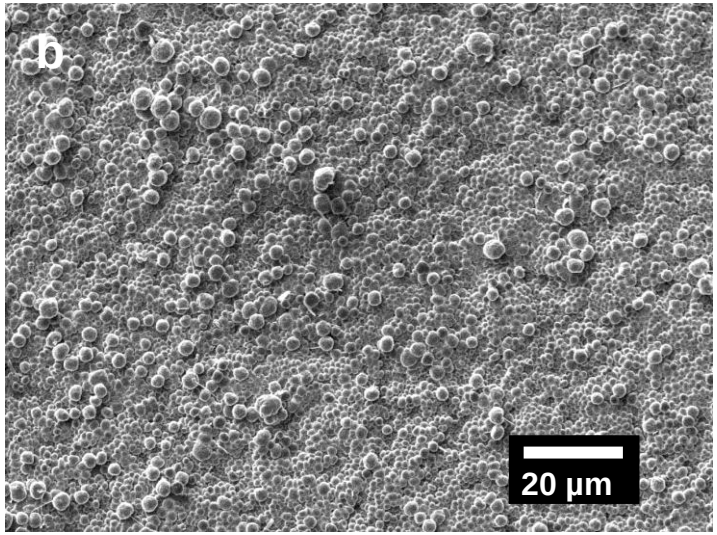
Self-amplification of chaotic/dendritic growth

Self-healing of ordered/smooth growth



(a) 1 hr deposition in the control electrolyte.

Significant Li dendrite was formed.



(b) Additional 14 hr in the electrolyte with PNNL additive.

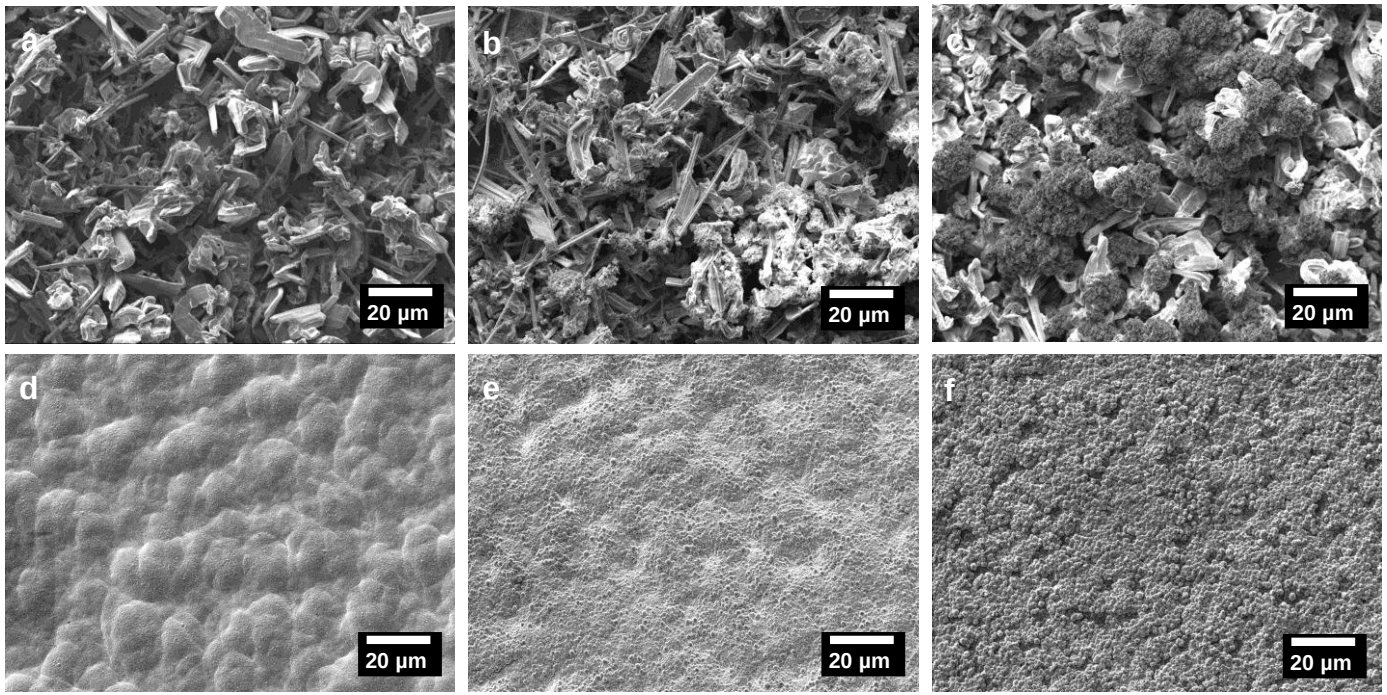
All Li dendrite was soothed.

- **PNNL additive can effectively smooth the existing dendrite.**

3. Long Term Cycling Stabilities of Li-Metal Batteries

No additive

With PNNL additive



2th deposition 3th deposition 10th deposition

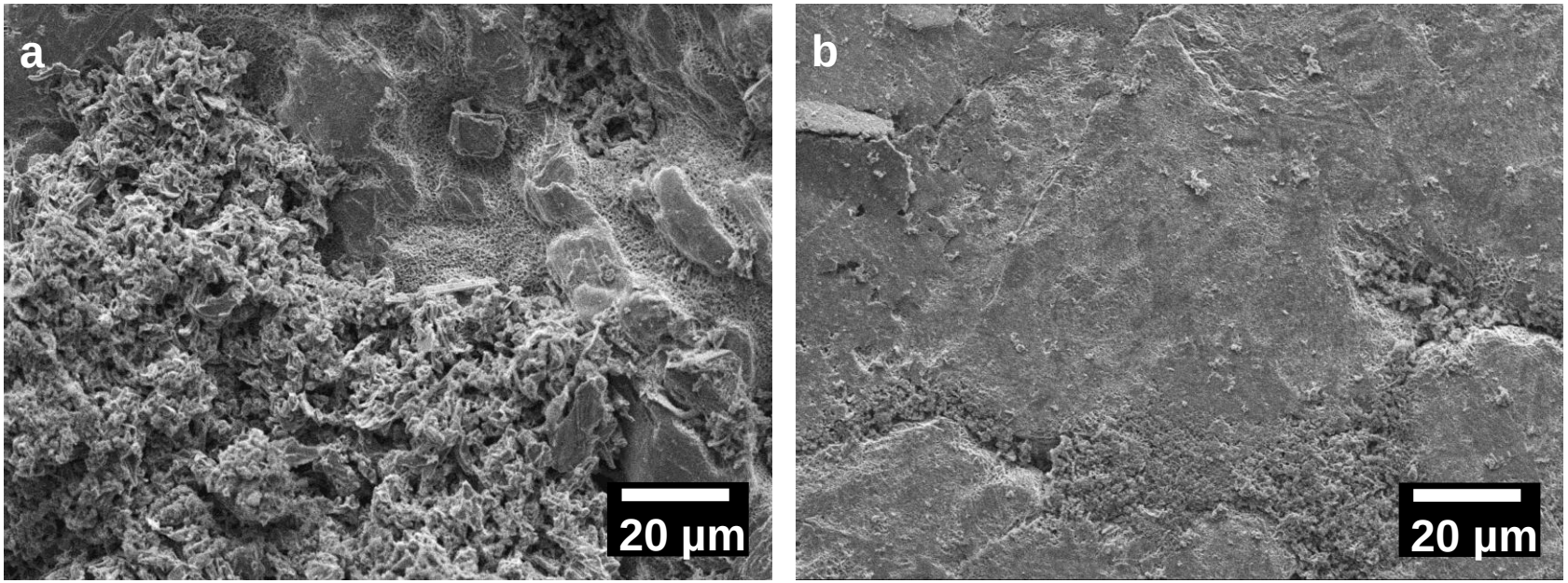
Li electrodes after repeated deposition/stripping cycles in beaker cells.

➢ **PNNL additive is effective during cycling.**

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Morphology Changes During Long Term Cycling of Li Electrode in Li/LTO Cells



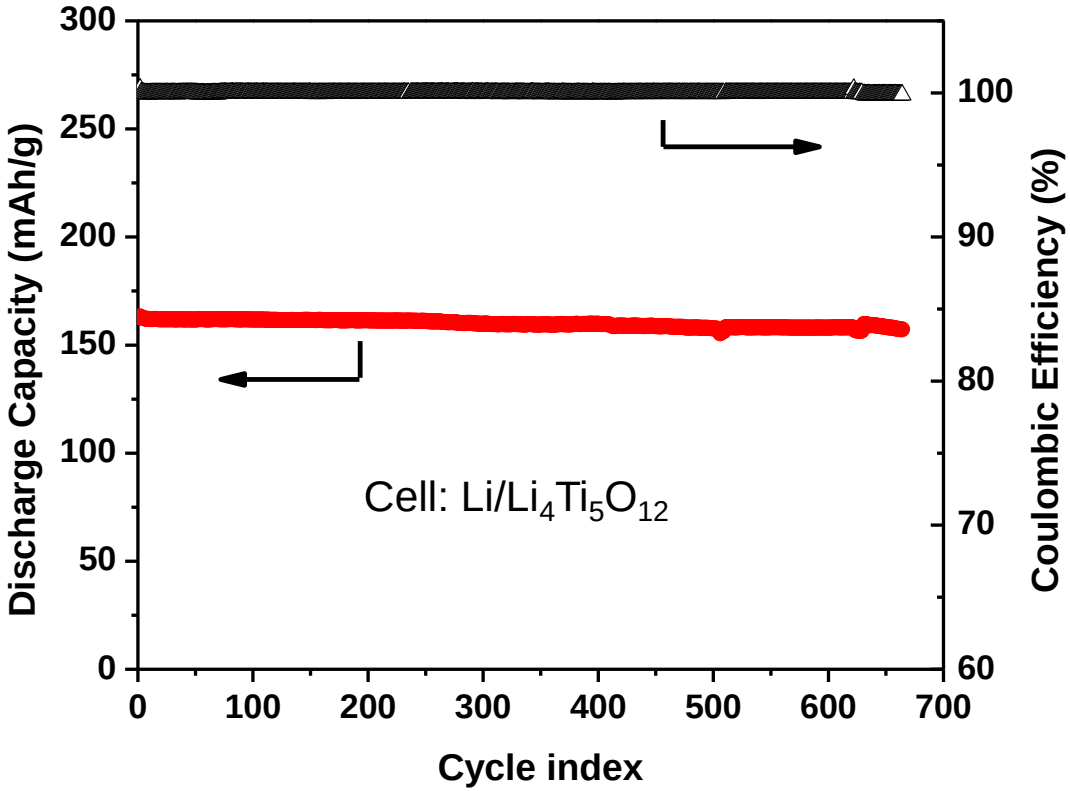
Surface morphologies of Li electrodes after 100 cycles in coin cells of $Li|Li_4Ti_5O_{12}$ system containing electrolytes without (a) and with (b) PNNL additive.

- **PNNL additive is effective during long term cycling.**

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Excellent Long Term Stability of Li-Metal Batteries Using PNNL Additive



- **Columbic efficiency: 99.97%**
- **Cycling stability: Only 3.3% capacity fade in 660 cycles**

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

4. Summary

- A novel mechanism has been proposed to suppress Li dendrite growth.
- Two most critical barriers on Li-metal batteries have been addressed:
  - PNNL additives can effectively suppress Li dendrite growth on Li metal batteries.
  - Smooth deposition largely reduces the surface area of Li film and leads to much smaller Li/electrolyte depletion.
- ~99.97% Coulombic efficiency and ~4.2% capacity fade in 660 cycles for Li-metal batteries.

Acknowledgment

Technical Teams:

Fei Ding,[a,b] Wu Xu,[a,*] Gordon L. Graff,[a] Jian Zhang,[a] Maria Sushko,[a] Xilin Chen,[a] Yuyan Shao,[a] Mark H. Engelhard,[a] Zimin Nie,[a] Jie Xiao, [a] Xingjiang Liu,[a] Peter V. Sushko,[a,c] Jun Liu,[a] and Ji-Guang Zhang[a,*]

a. Pacific Northwest National Laboratory, U.S.A.
b. Tianjin Institute of Power Sources, China
c. University College London, London, UK

Financial supports:

- DOE/EERE/Office of Vehicle Technology (Tien Duong)
- Laboratory Directed R&D Program of PNNL (Transformational Materials Science Initiative)

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*