

## Lithium Dendrite Suppression for Lithium-Ion Batteries

### Introduction

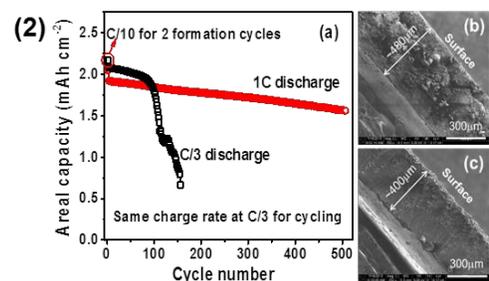
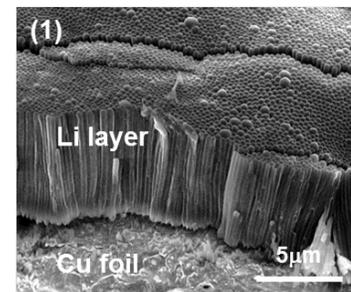
Lithium (Li) metal batteries have been called the “holy grail” of energy storage systems because the Li metal anode has an ultrahigh theoretical specific capacity, the lowest negative electrochemical potential, and low density. However, two major problems—Li dendrite growth and low Coulombic efficiency of Li deposition/stripping—hinder their commercial applications. For a Li-ion battery, Li plating and dendrite formation during overcharging, fast charging, or charging at low temperatures also are serious problems that must be solved. A general solution to form a robust, thin, uniform and compact solid electrolyte interphase (SEI) layer on the Li or graphite anode surface will significantly improve the safety, but also enhance their performance in terms of long-term cycling stability, rate capacity, and a wide operating temperature range.

### Project Objective and Impact

The objective of this project is to enable Li metal as an effective anode in rechargeable Li-metal batteries for long cycle life at a reasonably high current density. The investigation will focus on the effects of various Li salts, additives and carbonate-based electrolyte formulations on Li anode morphology, Coulombic efficiency and battery performances in terms of long-term cycling stability at various temperatures and current densities, rate capability, and low temperature discharge behavior.

### Key Achievements

- Proposed a self-healing electric shield mechanism for dendrite-free Li deposition.
- Developed an effective electrolyte additive based on cesium ion ( $\text{Cs}^+$ ) that can not only smooth the morphology of deposited Li but also result in dendrite-free and well-aligned Li nanorod structure (Figure 1).
- Demonstrated that the  $\text{Cs}^+$  additive in electrolytes can well protect Li metal and greatly improve the cycling stability of Li metal batteries.
- Discovered that  $\text{Cs}^+$  additive can direct the formation of an ultrathin ( $\sim 2 \mu\text{m}$ ), uniform, compact and robust SEI layer on graphite surface in propylene carbonate (PC)-containing carbonate electrolytes. Significantly improved performances of graphite electrode in half cells and full cells under different temperatures have been demonstrated. Formation of Li dendrites on graphite anode has also been suppressed.
- Demonstrated that an appropriate electrolyte formulation with  $\text{Cs}^+$  additive and PC solvent allows the graphite||NCA full cells to release more than



60% of their room-temperature full capacity at  $-40^{\circ}\text{C}$ , while the conventional electrolyte has only 18% capacity retention.

- Demonstrated that long-term stable cycling of rechargeable Li metal batteries can be realized by an appropriate charge/discharge protocol through the formation of a transient high concentration electrolyte layer near the surface of Li metal anode (Figure 2).

**Contact:** Dr. Wu Xu, [wu.xu@pnnl.gov](mailto:wu.xu@pnnl.gov)

**Sponsoring Agency:** DOE/EERE/VTO/BMR program

### Selected Publications

- 1) J. Zheng, P. Yan, D. Mei, M. H. Engelhard, S. S. Cartmell, B. J. Polzin, C.-M. Wang, J.-G. Zhang, W. Xu, “Highly stable operation of lithium metal batteries enabled by the formation of a transient high-concentration electrolyte layer”, *Adv. Energy Mater.*, 2016, **6**, 1502151.
- 2) H. Xiang, D. Mei, P. Yan, P. Bhattacharya, S. D. Burton, A. von Wald Cresce, R. Cao, M. H. Engelhard, M. E. Bowden, Z. Zhu, B. J. Polzin, C.-M. Wang, K. Xu, J.-G. Zhang, W. Xu, “The role of cesium cation in controlling interphasial chemistry on graphite anode in propylene carbonate-rich electrolytes”, *ACS Appl. Mater. Interfaces*, 2015, **7**, 20687-20695.
- 3) L. Xiao, X. Chen, R. Cao, J. Qian, H. Xiang, J. Zheng, J.-G. Zhang, W. Xu, “Enhanced performance of Li|LiFePO<sub>4</sub> cells using CsPF<sub>6</sub> as an electrolyte additive”, *J. Power Sources*, 2015, **293**, 1062-1067.
- 4) F. Ding, W. Xu, X. Chen, J. Zhang, Y. Shao, M. H. Engelhard, Y. Zhang, T. A. Blake, G. L. Graff, X. Liu, J.-G. Zhang, “Effects of cesium cations in lithium deposition via self-healing electrostatic shield mechanism”, *J. Phys. Chem. C*, 2014, **118**, 4043-4049.
- 5) F. Ding, W. Xu, G. L. Graff, J. Zhang, M. Sushko, X. Chen, Y. Shao, M. H. Engelhard, Z. Nie, J. Xiao, X. Liu, P. V. Sushko, J. Liu, J.-G. Zhang, “Dendrite-free lithium deposition via self-healing electrostatic shield mechanism”, *J. Am. Chem. Soc.*, 2013, **135**, 4450-4456.