Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Lithium Metal Anode for Rechargeable Battery Applications

Introduction

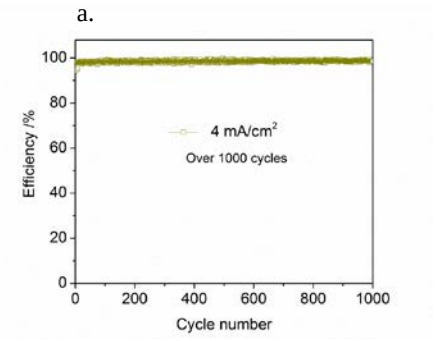
Lithium (Li) metal is an ideal anode material for rechargeable Li batteries, including Li-S, Li-air, and other rechargeable batteries using Li intercalation compounds as cathode materials. However, dendrite growth and limited Coulombic efficiency (CE) during cycling have prevented its practical application in rechargeable batteries.

Project Objective and Impact

The main objective of this project is to improve the stability of Li metal anode in rechargeable batteries, especially in Li-S batteries where the dissolution of polysulfide is corrosive to Li metal anode and lead to fast capacity fade of the batteries.

Key Achievements

Recently, we have developed highly concentrated electrolytes composed of ether solvents and the lithium bis(fluorosulfonyl)imide salt that enables the high rate cycling of a lithium metal anode at high Coulombic efficiency (up to 99.1 %) without dendrite growth. With 4 M lithium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane as the electrolyte, a Li|Li cell can be cycled at 10 mA cm^{-2} for more than 6000 cycles, and a Cu|Li cell can be cycled at 4 mA cm^{-2} for more than 1000 cycles with an average Coulombic efficiency of 98.4% as shown in Fig. 1.



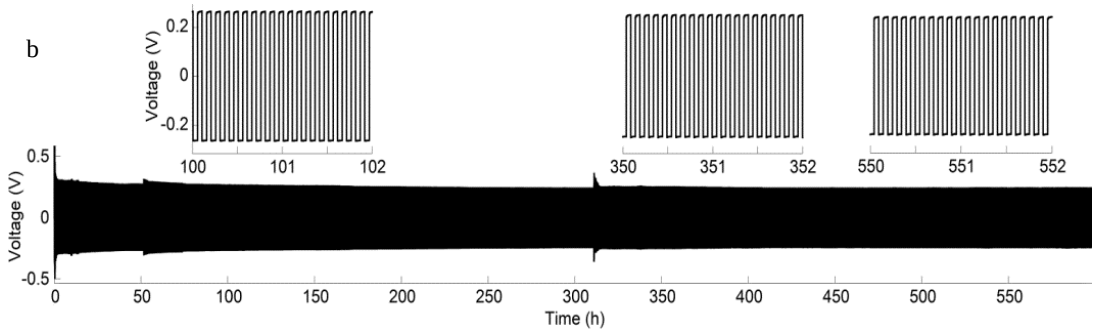


Figure 1. (a) CE of Li deposition/striping in 4 M LiFSI-DME. (b) Li metal plating/stripping from a Li|Li cell cycled at 10.0 mA cm^{-2} with a 4 M LiFSI-DME electrolyte. The top plots are expanded views from the bottom plot.

These excellent performances can be attributed to the increased solvent coordination and increased availability of lithium ion concentration in the electrolyte. Further development of this electrolyte may enable practical applications for lithium metal anode in rechargeable batteries. In a separate effort, we found that Li-S batteries using LiTFSI-based electrolytes are more stable than those using LiFSI-based electrolytes. The decreased stability is because the N-S bond in the FSI^- anion is fairly weak and the scission of this bond leads to the formation of lithium sulfate ($LiSO_x$) in the presence of polysulfide species. In contrast, in the LiTFSI-based electrolyte, the lithium metal anode tends to react with polysulfide to form lithium sulfide (LiS_x) which is more reversible than $LiSO_x$ formed in the LiFSI-based electrolyte. This fundamental difference in the bond strength of the salt anions in the presence of polysulfide species leads to a large difference in the stability of the anode-electrolyte interface and performance of the Li-S batteries with electrolytes composed of these salts. Therefore, anion selection is one of the key parameters in the search for new electrolytes for stable operation of Li-S batteries.

Contact: Dr. Ji-Guang Zhang, jiguang.zhang@pnnl.gov
Sponsoring Agency: Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the Department of Energy, Office of Science, Basic Energy Sciences

Selected Publications

1. "High Rate Cycling of Stable Lithium Metal Anode," Jiangfeng Qian, Wesley A. Henderson, Wu Xu, Priyanka Bhattacharya, Mark Engelhard, Oleg Borodin, Ji-Guang Zhang, Nature Communications, | 6:6362 | DOI: 10.1038/ncomms7362.
2. "Dendrite-free Li deposition using trace-amounts of water as an electrolyte additive," Jiangfeng Qian, Wu Xu, Priyanka Bhattacharya, Mark Engelhard, Wesley A. Henderson[a], Yaohui Zhang, Ji-Guang Zhang, Nano Energy, Nano Energy(2015) 15, 135–144.
3. "Anodes for Rechargeable Lithium-Sulfur Batteries," Ruiguo Cao , Wu Xu , Dongping Lv , Jie Xiao , and Ji-Guang Zhang, Adv. Energy Mater. 2015, 1402
4. *"In situ* ^{7}Li and ^{133}Cs nuclear magnetic resonance investigations on the role of Cs^+ additive in lithium-metal deposition process," Jian Zhi Hu, Zhenchao Zhao,Mary Y. Hu, Ju Feng, Xuchu, Xilin Chen, Wu Xu, Jun Liu, Ji-Guang Zhang, Journal of Power Sources 304 (2016) 51–59.
5. Wu Xu,* Jiulin Wang, Fei Ding, Xilin Chen, Eduard Nasybulin, Yaohui Zhang and Ji-Guang Zhang,* "Lithium metal anodes for rechargeable batteries," ***Energy Environ. Sci.***, 2014, 7 (2), 513 – 537.