

Lithium anode protection for safe and efficient Li-metal batteries

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EMISTRY: MOLECULES-TO-MATERIALS

Introduction

Strategies [3]

The ever-increasing demand of electronic devices or electrical vehicles has greatly promoted the research and development of high energy batteries. Lithium metal has always been interesting because of its low redox potential (-3.04 V vs SHE) and its very high theoretical specific capacity (3860 mAh.g⁻¹). However, during the battery discharge, dendrites are formed, which can create short-circuit or fire hazards. To overcome these safety issues, some strategies have been investigated, such as electrolyte formulation or optimization of the electrode/electrolyte interface. Indeed, additives or highly concentrated electrolytes modify the SEI nature preventing or delaying dendrites growth [4]. Another way to reduce dendrite formation is to protect the Li surface by forming an alloy on top of it, to reduce electrolyte decomposition [5].

Li metal main issues [2]



 \succ Chaotic increase of overpotential with 1M electrolyte \rightarrow dendrites growth

- Polarization more stable with 5M electrolyte for 150 cycles



- > 0 to 100h: Higher polarization with 5M (125 mV vs. 89 mV) due to higher viscosity > 5M very stable for 250h
- \succ For 1M electrolyte: appearance of dendrites from 250h \rightarrow DOL addition changes the SEI and increases electrolyte stability



CI Κα1 Sn K α 1

> Sn and Cl are only on the top of the electrode

Both of them are on the same layer

CARNOT CHIMIE BALARD

Cycling conditions:

Electrolyte: LiTFSI (1M) + DOL/DME (Celgard + 100 μL) Current rate: 1 mA/cm² (=1.27 mA) for 1h



 \succ Lower overpotential with 10mM SnCl₄ modified Li and better stability for 250h \succ Modification of Li with too 50 mM SnCl₄ does not work well as 10 mM solution

Conclusion

> Concentrated electrolytes:

- Better stability with high concentrated electrolytes
- Adding DOL in the electrolyte allows delaying the appearance of dendrites for 1 M _ electrolytes \rightarrow formation of different SEI on the Li surface

> Surface modification:

- Alloy on the surface of Li \rightarrow improvement of the polarization stability
- 10mM SnCl₄ solution is the optimized concentration

> Concentrated electrolytes:

Operando ATR-FTIR + GC-MS → Behavior and degradation of electrolytes as function of the concentration

M

- $XPS \rightarrow Study$ of the different SEI formed on the Li surface
- $EIS \rightarrow Evolution of the electrolyte/SEI conductivity$

> Surface modification:

- Mössbauer spectroscopy \rightarrow evolution of tin species during charge/discharge - XPS + EIS \rightarrow Study of the alloy layer
- Full cell with LiFePO₄ as positive electrode

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