Rational Design of Lithium Metal Matrix and its Protective Solid Electrolyte Interphase

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Rechargeable Battery Technology

<table>
<thead>
<tr>
<th>Technology</th>
<th>Electrolyte</th>
<th>Overall reaction</th>
<th>Cell voltage (V)</th>
<th>Specific energy (Wh/kg)</th>
<th>Operating temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb/acid</td>
<td>Sulfuric acid (aq.)</td>
<td>Pb + PbO₂ + 2H₂SO₄ → 2PbSO₄ + 2H₂O</td>
<td>2.04</td>
<td>30</td>
<td>-25 to +50</td>
</tr>
<tr>
<td>Ni/Cd</td>
<td>Alkali hydroxide (aq.)</td>
<td>2NiOOH + Cd + 2H₂O → 2Ni(OH)₂ + Cd(OH)₂</td>
<td>1.3</td>
<td>50</td>
<td>-40 to +60</td>
</tr>
<tr>
<td>Ni/MH†</td>
<td>Alkali hydroxide (aq.)</td>
<td>NiOOH + MHₓ → Ni(OH)₂ + MHₓ-x</td>
<td>1.35</td>
<td>65</td>
<td>-20 to +60</td>
</tr>
<tr>
<td>Li ion</td>
<td>LiPF₆ (organic solvents)</td>
<td>Liₓ₋ₓMoO₂ + LiₓC₆ → LiₓMO₂ + 6C</td>
<td>3.6⁵</td>
<td>150 to 270⁷</td>
<td>-30 to +60¹</td>
</tr>
<tr>
<td>Li polymer#</td>
<td>Li salt** (polyethyleneoxide)</td>
<td>xLi + V₂O₅ → LiₓV₂O₅†</td>
<td>3</td>
<td>140</td>
<td>60 to 100</td>
</tr>
</tbody>
</table>

Beyond Li-ion Battery

- Na-ion battery
- Li-S battery (2600 Wh kg⁻¹)
- Li-oxygen battery (3500 Wh kg⁻¹)
Li Metal Based Batteries

Li dendrite

- Short Circuit
- Fire/Explosion
- Side Reaction
- Dead Li
- Low efficiency

Adv. Mater 2014, 27, 284

Nat. Commun. 2014, 5, 5195
J. Cryst. Growth, 1976, 34, 239
Strategy to Suppress Li Dendrites

**Lithiophilic coating**

A) Porous Object

- CVD Si
- Li Melt
- Infusion

B) Uncoated Porous Object

- Molten Li
- Carbon Framework
- Metal Foam
- Si - Coated Porous Object

C) Lithiophilic

- 0s, 3s, 6s, 9s

Y Cui *PNAS* 2016, 113, 2862

**Artificial SEI**

1. Li electrode
2. Pristine film
   - (Li2CO3, LiOH, Li2O)
   - Li melt
   - Infusion

3. SEI break and repair

4. LiPO4 SEI film

a) Pristine film
   - PPA in DMDS solution

b) LiPO4 SEI film

- Li2CO3, LiOH, Li2O

No Protection Porous surface

Y G Guo et al *Adv Mater* 2016, 28, 1853
Strategy to Suppress Li Dendrites

Y Lu and L Archer Nat Mater 2014, 13, 961

Y Cui Nat Commun 2015, 6, 7436

JG Zhang Nat. Commun. 2015, 6, 6362

S Xiong, J. Power Sources 2014, 246, 840
Outline

1. Why Li is not stable in most electrolyte?

2. What is the SEI on a working Li metal?

3. How to guide Li deposition?
   - Nucleation
   - Kinetic
   - Ion diffusion regulation
1. The importance of Li metal anode

Scheme of pouch cells

Pouch cells vs coin cell
- High sulfur loading
- Small uptake of electrolyte
- Small amount of Li metal
- Large current density
- Short cycling life

Electrochemical cycling of Li-S pouch cells

Energy Storage Mater. 2017, 6, 18
1. The importance of Li metal anode

Both dead Li and Li powdering caused by Li dendrite growth on the Li metal at large current
Renaissance Li-S cells: Fresh Li vs cycled S

Li metal anode with stable SEI to prevent Li powdering and increase Li ion diffusion is urgently needed
1. The importance of Li metal anode

1.0 M LiTFSI dissolving in DOL/DME without LiNO₃

Adsorption-to-reaction route

Energy Storage Mater. 2017, 8, 194
ab initio molecular dynamics

(a-d) Complete sequence of DOL molecule decomposition obtained from AIMD simulation for Li (110) + 9DOL model.

At 1866 fs, a carbon-oxygen bond of a DOL molecule was broken with the interaction of a lithium atom.

(e) Time evolution of another DOL molecule decomposition in the Li (110) + 9DOL model.

Unpublished results
1. The importance of Li metal anode

- Less DOL benefits for stable long cycling
- Electroplating a protective film on the reactive lithium anode was proposed to separate solvent molecule from reactive Li surface and protect Li anode in a working cell

Unpublished results
2. Electrolyte with polysulfides/LiNO$_3$/LiTFSI
Sulfurized SEI on Li metal

**mosaic structure**

- 0.258 nm Li$_2$O (111)
- 0.271 nm LiNO$_3$ (104)
- 0.291 nm Li$_2$S (200)
- 0.315 nm Li$_3$N (100)
- 0.328 nm Li$_2$S (111)

**high conductivity structure**

Sulfurized SEI on Li metal

LiTFSI

LiTFSI-LiNO₃

LiTFSI-LiNO₃-Li₂S₅

(a) Mono-salt, S 2p

(b) Dual-salt, S 2p

(c) Ternary-salt, S 2p

(d) Mono-salt, N 1s

(e) Dual-salt, N 1s

(f) Ternary-salt, N 1s

(g) Mono-salt, Li 1s

(h) Dual-salt, Li 1s

(i) Ternary-salt, Li 1s

(j) Mono-salt, O 1s

(k) Dual-salt, O 1s

(m) Ternary-salt, O 1s

Li₂S₅ leads to Li₂S in the SEI

S 2p

N 1s

Li 1s

O 1s

Unpublished results
Short circuit time test

Local short circuit: A short circuit happens locally but the cell can work well

Cell short circuit: The cell cannot work

\[ \sqrt{0.1 \text{M} \ [S]} + 5\% \text{ LiNO}_3 \]
LiF-riched SEI

Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Li Metal Batteries
Implantable SEI in working batteries with different electrolytes

Li metal

Implantable SEI

Chem 2017, 2, 258
Implantable SEI in working batteries

Sulfur cathode

NCM cathode

Pouch cell
SEI is NOT Enough

Li metal → SEI layer → After cycling → Dead Li → Dendrites

SEI

Matrix

Li⁺

Solvent

e⁻

Li

Adv. Sci. 2016, 3, 1500213

Nat. Rev. Mater. 2016, 13, 16013

Adv. Sci. 2016, 3, 1500213
Li bonds in Li-S batteries

- No charge transfer:
  electrostatic dipole-dipole interaction
- NMR test vs ab initio calculation

Angew Chem Int Ed 2017, 56, 8178, VIP paper

Blue and red denote the positive and negative phase of the orbital, respectively.
Lithiophilic Sites Guide Li Nucleation

The pyridinic and pyrrolic nitrogen in the N-doped graphene is lithiophilic, which guide Li nucleation to distribute on anode surface uniformly.

Lithiophilic Sites Guide Li Nucleation

Nucleation overpotential. a) The V vs t during Li nucleation at 0.05 mA cm\(^{-2}\) on Cu foil, G, and NG electrodes. b) The Li nucleation overpotentials (\(\mu_n\)) on Cu, G, and NG electrodes.

Li metal nucleates onto the lithiophilic sites

Lithiophilic Sites Guide Li Nucleation

The N-containing functional groups like pyridinic and pyrrolic nitrogen in the N-doped graphene is lithiophilic, which guide Li nucleation to distribute on anode surface uniformly.
Lithiophilic Sites Guide Li Nucleation

CE of Cu foil and NG with a cycling capacity of a) 1.0 mA h cm\(^{-2}\), b) 2.0 mA h cm\(^{-2}\) at the same current density of 1.0 mA cm\(^{-2}\).

c) Voltage profiles of the 10\(^{th}\), 50\(^{th}\), and 100\(^{th}\) cycle of Cu foil and NG with a cycling capacity of 1.0 mA h cm\(^{-2}\) at 1.0 mA cm\(^{-2}\).

d) Voltage-time curves in 150 cycles of Cu foil and NG electrode at 1.0 mA cm\(^{-2}\).
Mechanism 1: Larger Sand’s time

Sand’s time: The time from Li depositing to dendrite growth

\[ \tau = \pi D \left( \frac{eC_0(\mu_a + \mu_{Li^+})}{2J\mu_a} \right)^2 \]

Surface area (S) \[ \uparrow \]
Effective current density (J) \[ \downarrow \]
Sand’s time (\( \tau \)) \[ \uparrow \]
Safer battery \[ \uparrow \]

Surface area: 1666 m² g⁻¹
Electrical conductivity: 435 S cm⁻¹

CVD Graphene

Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China
Conductive matrix

Mechanism 1: Larger Sand’s time

![No dendrites](4×10^{-5} \text{ mA cm}^{-2}, \text{Cu foil})

![Increasing current](200 \text{ nm})

![Increasing current](Dendrites, 0.5 \text{ mA cm}^{-2}, \text{Cu foil})

![Large dendrites](0.5 \text{ mA cm}^{-2}, \text{Cu foil})

![Graphene](0.5 \text{ mA cm}^{-2})

![Graphene](1.0 \text{ mA cm}^{-2} & 2.0 \text{ mA cm}^{-2})

Adv. Mater. 2016, 28, 2155
Conductive matrix

Free Li in Li$_7$B$_6$ nanostructured matrix

(a) 0.3 mA cm$^{-2}$ for 40h
(b) 10 mA cm$^{-2}$ for 40h

Li-S battery

Discharge capacity
- LIB
- Li

Coulombic efficiency
- LIB
- Li

(a) Standardized capacity vs. Cycle number
(b) Voltage vs. Capacity (mAh g$^{-1}$)

Small 2014, 10, 4157
Li ion diffusion: Matrix adsorbing Li

(a) Conventional Cu foil electrode

(b) GF-modified Cu foil electrode

b1: Cu foil
b2: Glass fiber with polar groups

Uniformly distributed Li ions

Dendrite-free morphology

Adv. Mater. 2016, 28, 2888
Li ion diffusion: Matrix adsorbing Li

1 ev difference in binding energy

Uniformly distributed Li ions
Li ion diffusion: Matrix adsorbing Li

Relatively high long-cycle stability
Conclusions

- Li metal anode is a key element in pouch Li-S cell
- Polysulfides: The critical role for robust SEI on Li metal
- No matrix, no safe Li metal anode
- Conductive nano/micro-structured matrix
  - Low effective current density
  - Self-limited Li deposits
- Matrix strongly adsorbing Li
  - Uniformly distributed Li ions
energy storage materials

Special Issue: Li Metal Anode

Editor in Chief
Prof. Dr. Hui-Ming Cheng

Guest Editor
Prof. Dr. Qiang Zhang & Prof. Dr. Xiaogang Han

Important dates
Final Submission deadline: August 31, 2017
Acceptance deadline: October 31, 2017
2018 National Conference on Li-S Batteries

- 2018.06 Beijing, China
- 20 Invited talk + 80 Poster
- 400 participants
- Topic
  - Anode
  - Electrolyte
  - Cathode
  - Mechanism
  - Modelling
  - Cell assembly
  - Module technology
  - Battery Management System
  - Applications

Photo of 2016 Li-S batteries
June 11-12, Tsinghua University, Beijing, China
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