Lithium-Ion Batteries and Beyond

Prof. Martin Winter, MEET Battery Research Center, Institute for Physical Chemistry, University of Münster, GER
Helmholtz Institute “Ionics in Energy Storage” Forschungszentrum Jülich GmbH, GER
I. Introduction

1. General principles

2. Li-metal chemistry—the ancestor of Lithium Ion

3. Lithium-Ion design overview

4. Battery design trade-offs and limitations
Materials are the Core of the Battery

Good material → inappropriate processing → bad system integration → Bad performance

Bad material → appropriate processing → good system integration → Bad performance

Good material → appropriate processing → good system integration → Excellent performance!
Excerpt from the Periodic System of the Elements with standard reference potentials (Nos. in the figure).

The standard potentials refer to the standard hydrogen electrode (H), abbreviated SHE: potential of 0 Volt (V).

The values of the standard potential relative to each other indicate whether or not the materials are suitable as anode or cathode.

High cell voltages can be achieved with anodes with a very negative potential (blue) and cathodes with very positive potentials (red and pink).

With -3.04V vs. SHE, Li has the most negative potential of all elements.

The potentials of LIB and Li-metal battery materials are typically referred to a Li reference electrode (⇒ Potential vs. Li/Li⁺).

Potentials measured in aqueous electrolyte solution! May vary in non-aqueous electrolyte solutions!
Active Anode and Cathode Materials:

Determine capacity and voltage \( \Rightarrow \) energy

Inactive Materials:

Add, mass + volume \( \Rightarrow \) decrease energy

- **Electrolyte**: ion conduction, interfaces
- **Separator**: safety, electrode separation

Electrode Inactive Components:

- **Current collector**: electron conduction, connection to the ‘outside’
- **Conductive additive**: porosity, ‘inside’ electron current distribution
- **Binder**: The ‘glue’, that holds everything together
- **Processing solvents** (not treated here)
The active material (AM) can be an electron conductor, ion conductor, electron and ion conductor, or does not show ion and electron conductivity at all.

Different electron and ion transport properties of the AM $\rightarrow$ different reaction mechanisms and reaction zone movements $\rightarrow$ cases 1-4 (following 4 slides).

Depending on the reaction mechanism, the electrolyte and electronically conducting agents play an essential role for battery performance.

Legend (for the following 4 slides):

- Active Electrode Material
- Reaction Zone
- Zone Movement
- Electrolyte
**Case 1:**
Electron Conduction: No
Ion Conduction: No
PbSO₄ in aq. H₂SO₄

**Case 2:**
Electron Conduction: No
Ion Conduction: Yes
LiFePO₄ in Li⁺X⁻ (org. solvent)

**Case 3:**
Electron Conduction: Yes
Ion Conduction: No
PbO₂ in aq. H₂SO₄

**Case 4:**
Electron Conduction: Yes
Ion Conduction: Yes
Graphite C₆ in Li⁺X⁻ (org. solvent)
High Energy of Solvation of Li⁺ Causes Li Electrode Potential to be Highly Negative

$\text{M} \xrightarrow{-e^-} \text{M}^+ \xrightarrow{+y \text{ solv}} \text{M}^+(\text{solv})_y$

- **Ionization Energy (IE)** = Invested energy to oxidize alkali metal to alkali ion (in the gaseous state)
- **In gaseous state**: Li is NOT the metal with lowest potential

- **Ion Size**

- **Ionization Energy**

- **Free Energy of Solvation**

- **Free energy of solvation** = Released energy when ions associate with solvent molecules (solution state):
  - **In solution**: Li⁺ is strongly solvated
  - Important role of Li⁺ solvation and desolvation for rate capability

<table>
<thead>
<tr>
<th>M</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>E / V vs. SHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>IE</td>
<td>-3.04</td>
<td>-2.71</td>
<td>-2.93</td>
<td>-2.93</td>
<td>-2.92</td>
<td></td>
</tr>
</tbody>
</table>

Copyright 2017 Total Battery Consulting, Inc.
Rechargeable Li-Metal Cell: High Energy Density, but Dendrite Risk, → Safety Problem

"Vicious Circle": Inhomogeneous SEI
→ Inhomogeneous Li deposition morphology
→ Inhomogeneous SEI →...

- Various Li deposition morphologies
- Needle-like morphology = Dendritic Li
- Dendrites grow to filaments → Short-Circuit
  → Thermal Runaway → ...

- Continuous surface changes, continuous electrolyte decomposition and SEI formation
  → Formation of high-surface-area Li (HSAL)
  → Safety and performance problem!
  ⇒ Li metal replacement necessary!
High-Voltage Batteries Need Thermodynamically and/or Kinetically Stable Electrolytes

- The electrolyte composition has to be tailored to make high-voltage lithium batteries possible.
- Aqueous electrolytes suffer from a low thermodynamic electrochemical stability window (ESW) of 1.23V, which can be extended by specific electrode and electrolyte measures to approx. 2V.
- Nevertheless, beyond 1.23V, electrolyte decomposition and gas evolution (H₂ and O₂) take place.

- Increasing the voltage by using high-voltage cathodes, e.g. LiNi₀.₅Mn₁.₅O₄, LiCoPO₄, etc. asks for new electrolytes, as the typical organic carbonate solvents are not stable enough and/or the CEI is not effective at the higher potentials.
- High-voltage electrolytes can be designed, using fluorinated solvents, nitriles, etc.
- Nevertheless, in the case of high-voltage electrolytes also, an effective SEI is necessary.

*Available with Report purchase*

Magnified figure on the next slide
Without considering the weight of the reaction products, Li and gasoline have similar energy densities (numbers in kWh/kg).

The accumulation of solid Li₂O₂ or Li₂O during discharge of a Li/air battery increases the battery weight and thus decreases the energy density. Values for the fully discharged state are shown.

If, hypothetically, the reaction products (CO₂ or CO₂+H₂O) of gasoline combustion were collected as well, the energy density would correspondingly decrease as indicated.

Gasoline is lightweight compared to oxygen. The heavyweight combustion products CO₂ and water are continuously exhausted from the ICE.

The reaction partner oxygen does not contribute to system weight.
Electrochemical energy storage and conversion devices operate beyond the thermodynamic stability of the electrolyte, i.e., undesired side reactions can occur at the electrode/electrolyte interfaces, e.g., surface reaction and passivation.

- Side reactions deteriorate electrode and thus cell performance.
- Nano-materials possess large surface areas.
- Impact of these side reactions increases with the surface area → ‘bad nano’
- Nano-particles show a larger surface area than nano-structured macro-particles.

Electrolyte-wetted surface reacts with the electrolyte. Passivating films may be formed at the surface.
Battery Material Design is Complex
Example: Active Materials

Active material for lithium-ion batteries

- Particle Morphol.
- Structural Stability
- Redox potential vs. Li/Li⁺
- Thermal stability
- Large Li uptake
- Non Dissolub.
- Size-Effects
- Surface effects
- $\delta_{ionic}$ ($D_{Li}$)
- $\delta_{electronic}$

*↑* indicates increase, *↓* indicates decrease.