Next Generation Batteries: Hopes and Problems

Arnulf Latz and Timo Danner
German Aerospace Center and
Helmholtz Institute Ulm Electrochemical Energy Storage
• Center of Excellence for research in electrochemical energy storage
• Founded in Jan. 2011
• New building on University Ulm campus for 80 scientists (now 103+20 at KIT)
• DLR battery modeling activities are integrated into HIU

http://www.hiu-batteries.de/
Battery modeling at HIU/DLR

Li batteries: Electrochemistry and transport
Understanding and optimization of influence of microstructure on function and life time

Battery safety
Understanding of degradation mechanisms. Theory for electrolytes

Metal-Sulfur cells: Redox-chemistry, Transport and nanostructures
Analysis of cycleability and reversibility

Metal-air cells: Multi-phase Chemistry and reversibility
Improvement of bifunctional air oxygen electrode
Why alternatives to Li?

**Li resources / Cost:**

~13,000 t/a Li are currently produced for world market of Li ion batteries

## TESLA Gigafactory

- 5,000 t/a Li for car batteries
- 8,000 t/a Li for PowerWall batteries

Source: http://tesla.com

Estimated 10 more gigafactories are under consideration worldwide

### United States Geological Survey 2017

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production 2015</th>
<th>Mine production 2016</th>
<th>Reserves 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>3,600</td>
<td>5,700</td>
<td>38,000</td>
</tr>
<tr>
<td>Argentina</td>
<td>14,100</td>
<td>14,300</td>
<td>2,000,000</td>
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<tr>
<td>Australia</td>
<td>200</td>
<td>200</td>
<td>1,600,000</td>
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<tr>
<td>Brazil</td>
<td>10,500</td>
<td>12,000</td>
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<tr>
<td>Chile</td>
<td>2,000</td>
<td>2,000</td>
<td>7,500,000</td>
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<tr>
<td>China</td>
<td>200</td>
<td>200</td>
<td>3,200,000</td>
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<tr>
<td>Portugal</td>
<td>900</td>
<td>900</td>
<td>60,000</td>
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<tr>
<td>Zimbabwe</td>
<td>31,500</td>
<td>35,000</td>
<td>23,000</td>
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<tr>
<td>World total (rounded)</td>
<td>31,500</td>
<td>35,000</td>
<td>14,000,000</td>
</tr>
</tbody>
</table>

Resources

About

49,000,000 t
Why alternatives to Li ion batteries?

The best performing cathodes are based on Nickel Mangan Cobalt (NMC) materials

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production 2015</th>
<th>Mine production 2016</th>
<th>Reserves7</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>6700</td>
<td>690</td>
<td>21,000</td>
</tr>
<tr>
<td>Australia</td>
<td>6,000</td>
<td>5,100</td>
<td>1,000,000</td>
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<tr>
<td>Canada</td>
<td>6,900</td>
<td>7,300</td>
<td>270,000</td>
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<tr>
<td>China</td>
<td>7,700</td>
<td>7,700</td>
<td>80,000</td>
</tr>
<tr>
<td>Congo (Kinshasa)</td>
<td>63,000</td>
<td>66,000</td>
<td>3,400,000</td>
</tr>
<tr>
<td>Cuba</td>
<td>4,300</td>
<td>4,200</td>
<td>500,000</td>
</tr>
<tr>
<td>Madagascar</td>
<td>3,700</td>
<td>3,300</td>
<td>130,000</td>
</tr>
<tr>
<td>New Caledonia9</td>
<td>3,680</td>
<td>3,300</td>
<td>64,000</td>
</tr>
<tr>
<td>Philippines</td>
<td>4,300</td>
<td>3,500</td>
<td>290,000</td>
</tr>
<tr>
<td>Russia</td>
<td>6,200</td>
<td>6,200</td>
<td>250,000</td>
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<tr>
<td>South Africa</td>
<td>3,000</td>
<td>3,000</td>
<td>29,000</td>
</tr>
<tr>
<td>Zambia</td>
<td>4,600</td>
<td>4,600</td>
<td>270,000</td>
</tr>
<tr>
<td>Other countries</td>
<td>11,600</td>
<td>8,300</td>
<td>690,000</td>
</tr>
<tr>
<td>World total (rounded)</td>
<td>126,000</td>
<td>123,000</td>
<td>7,000,000</td>
</tr>
</tbody>
</table>

Resources: 25,000,000 (Congo, Zambia) + 120,000,000 on the floor of Atlantic, Indian and Pacific Oceans

Cobalt supply chain:
Byproduct of Ni or Cu mining
Co production is falling in 2016
Reserves sufficient to run 80,000,000 electric cars

Co is heavily associated with children labour (Estimated 40,000 child miners Amnesty International 2016)
Partly great promises for improving sustainability, cost, safety, energy density → but no system commercialized, yet, due to novelty and scientific/technical obstacles
### Facts about post Li systems

<table>
<thead>
<tr>
<th>Element</th>
<th>Charge of ion</th>
<th>crystal ionic radii /pm$^1$</th>
<th>Earth crustal abundance / ppm by weight$^2$</th>
<th>Price (pure)$^3$ US$ per 100g</th>
<th>specific capacity mA·h·g$^{-1}$</th>
<th>specific capacity mA·h·cm$^{-3}$</th>
<th>Potential vs. NHE/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1</td>
<td>90</td>
<td>20</td>
<td>27</td>
<td>3862</td>
<td>2047</td>
<td>-3.04</td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>116</td>
<td>24000 + 10.8 g/L in seawater</td>
<td>25</td>
<td>1166</td>
<td>1130</td>
<td>-2.71</td>
</tr>
<tr>
<td>Mg</td>
<td>2</td>
<td>86</td>
<td>23300</td>
<td>3.7</td>
<td>2206</td>
<td>3840</td>
<td>-2.37</td>
</tr>
<tr>
<td>Ca</td>
<td>2</td>
<td>114</td>
<td>41500</td>
<td>20</td>
<td>1338</td>
<td>2006</td>
<td>-2.87</td>
</tr>
<tr>
<td>Zn</td>
<td>2</td>
<td>88</td>
<td>70</td>
<td>5.3</td>
<td>820</td>
<td>6845</td>
<td>-0.76</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>68</td>
<td>82300</td>
<td>15.7</td>
<td>2980</td>
<td>8050</td>
<td>-1.66</td>
</tr>
<tr>
<td>Cl</td>
<td>-1</td>
<td>167</td>
<td>145 + 19.4 g/L in seawater</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>used only as shuttle</td>
</tr>
</tbody>
</table>

$^2$David R. Lide, ed., CRC Handbook of Chemistry and Physics, 89th Edition (Internet Version 2009)
$^3$www.chemicool.com
Theoret. storage capacities of electrochemical couples of Li Ion- and post-Li batteries (materials basis)
Mg offers good handling and operational safety.

**No dendrite formation** with Mg metal as anode → major safety issue with Li metal batteries.

Mg is naturally 1000x more abundant on earth than Li.

**Mg/S offers theoretical 3200 Wh/L compared to theoretical 2800 Wh/L for Li/S**

But: Sulfur cathode needs special electrolyte for Mg!

Mg anode is easily passivated with most of the known electrolytes

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### Properties of Magnesium and Lithium

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight</td>
<td>6.9</td>
<td>24.3</td>
</tr>
<tr>
<td>Ionic radius</td>
<td>90 pm</td>
<td>86 pm</td>
</tr>
<tr>
<td>Ionic charge</td>
<td>+1</td>
<td>+2</td>
</tr>
<tr>
<td>Reduction potential</td>
<td>-3.04 V</td>
<td>-2.37 V</td>
</tr>
<tr>
<td>Density</td>
<td>0.53 g/cm³</td>
<td>1.74 g/cm³</td>
</tr>
<tr>
<td>Gravimetric capacity</td>
<td>3861 mAh/g (Li)</td>
<td>2205 mAh/g</td>
</tr>
<tr>
<td></td>
<td>372 mAh/g (LiC₆)</td>
<td></td>
</tr>
<tr>
<td>Volumetric capacity</td>
<td>2061 mAh/cm³</td>
<td>3832 mAh/cm³</td>
</tr>
</tbody>
</table>
**Zinc-Air Batteries**

- **Chemical Reactions**
  
  I. \( \text{Zn} + 4\text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} + 2\text{e}^- \)
  
  II. \( \text{Zn(OH)}_4^{2-} \rightleftharpoons \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O} \)
  
  III. \( \text{O}_2^g \rightleftharpoons \text{O}_2^e \)
  
  IV. \( \frac{1}{2}\text{O}_2^e + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^- \)

- **Specific energy**: 1086 Wh∙kg\(^{-1}\)
  
  **Energy density**: 6090 Wh∙l\(^{-1}\)
  
  **Low cost and safe**

- **Challenges include**: Zn **dendrites**, electrolyte **carbonation**, Zn **passivation**

- **Alternative electrolytes needed** (ionic liquids, neutral electrolytes)
Na-Ion Batteries

Na-ion cell with hard carbon anode made of apple biowaste


http://www.swr.de, Landesschau aktuell: „Forschung am Ulmer Helmholtz-Institut: Batterien aus Apfelresten“
Example: Metal-sulfur battery (Cobalt free)

Global reaction: $S_8 + 16 \text{Li} \rightleftharpoons 8 \text{Li}_2S + 3400 \text{kJ/mol}$

Complex chemistry, complex multi-phase behavior, Redox shuttle
Simplified model: 2 reduction steps

Base model (without degradation)

- S/C composite electrode
- Variation of current amplitude (C-rate)
  - Influence on
    - Transport
    - Kinetics
- Variation of sulfur content
  - Increase in capacity
  - No pore clogging included

$\nu_s = 2 \frac{A}{m^2}$

$10 \text{ vol}\% \text{ sulfur}$

Validated with experiments of Canas et. al (2014) at the DLR in Stuttgart
Loss mechanism: Shuttle effect

- Partial reduction of dissolved polysulfides at negative electrode during charge
- Precipitation of \( \text{Li}_2\text{S} \)

\[ \Rightarrow \] Columbic efficiency ↓
Capacity decay

Infinite charging at small currents

Capacity decay during cycling

Sulfur encapsulation: Nanostructured electrodes

Different approaches to retain sulfur species...

Single particle model

• Model 1
  ➔ Solid carbon shell

• Model 2
  ➔ Microporous sphere

Particle surface:
• $\phi^{ref} = \text{const.}$
• $c_{Li^+} = \text{const.}$

➔ Only Li enters particle
Sulfur encapsulation: Elements of the model

Structural effects

- Nucleation of S₈ / Li₂S
  - Pore space is reduced
  - Li₂S needs much more volume
- Effective transport + pore clogging
  - Hindered diffusion in porous media
    - \( D_i^{\text{eff}} = D_i^0 \varepsilon_{\text{lyte}}^{1.5} \)
- Passivation of active surface area by S₈ / Li₂S
  - Solid reaction products are electronically non-conducting
Results: Surface Defects

Transport overpotential

• Li$^+$ transport into particle

\[ \dot{N}_{Li^+}\big|_{r=R_p} = -D_{Li^+}^{\text{eff}} \frac{\partial c_{Li^+}}{\partial r}\big|_{r=R_p} - D_{Li^+}^{\text{eff}} c_{Li^+} \frac{z_{Li^+}F}{RT} \frac{\partial \phi_{elyte}}{\partial r}\big|_{r=R_p} \]

• Transport against gradient in $c_{Li^+}$

→ Additional transport resistance

→ Additional driving force for polysulfide loss
Results: Cycling properties

Cycling & degradation

- Loss of $S^{2-}$
  → Capacity fade
- Influence of $Li_2S$ solubility
  → Low solubility = long cycle life

→ Suitable choice of electrolyte system

Encapsulation is good idea, but creates additional problems
In the long run alternatives for Li ion batteries are necessary

There are many theoretical alternatives for Li – ion batteries

Each alternative, so far, I plagued with many problems

Working cells do exist only on Lab scale

Counter measures for existing problems very often create additional (interesting) research problems

Theory and simulation helps to improve the understanding of the nonlinear interplay of transport and reactions

Thank you for your attention!
Opportunity

PhD positions available
http://www.hiu-batteries.de
Arnulf.Latz@dlr.de