Next Generation Batteries: Hopes and Problems

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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
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></th>
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<tbody>
<tr>
<td>United States</td>
<td>3,600 W</td>
<td>5,700 W</td>
<td>38,000</td>
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<td>Argentina</td>
<td>14,100 W</td>
<td>14,300 W</td>
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<td>200 W</td>
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<td>48,000</td>
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<td>World total (rounded)</td>
<td>31,500 W</td>
<td>35,000 W</td>
<td>14,000,000</td>
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Resources
About 49,000,000 t
Why alternatives to Li ion batteries?

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

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

![Cobalt mining image]

**Cobalt (Co) resources:***
- **25,000,000** (Congo, Zambia)
- **120,000,000** on the floor of Atlantic, Indian and Pacific Oceans

**Mine production and reserves:**

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production 2015</th>
<th>Mine production 2016</th>
<th>Reserves</th>
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<tbody>
<tr>
<td>United States</td>
<td>6700</td>
<td>690</td>
<td>21,000</td>
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<tr>
<td>Australia</td>
<td>6,000</td>
<td>5,100</td>
<td></td>
</tr>
<tr>
<td>Canada</td>
<td>6,900</td>
<td>7,300</td>
<td></td>
</tr>
<tr>
<td>China</td>
<td>7,700</td>
<td>7,700</td>
<td></td>
</tr>
<tr>
<td>Congo (Kinshasa)</td>
<td>63,000</td>
<td>66,000</td>
<td>3,400,000</td>
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<tr>
<td>Cuba</td>
<td>4,300</td>
<td>4,200</td>
<td>500,000</td>
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<tr>
<td>Madagascar</td>
<td>3,700</td>
<td>3,300</td>
<td>64,000</td>
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<td>New Caledonia</td>
<td>3,680</td>
<td>3,300</td>
<td>130,000</td>
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<tr>
<td>Philippines</td>
<td>4,300</td>
<td>3,500</td>
<td>290,000</td>
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<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><strong>World total (rounded)</strong></td>
<td><strong>126,000</strong></td>
<td><strong>123,000</strong></td>
<td><strong>7,000,000</strong></td>
</tr>
</tbody>
</table>

Co is heavily associated with children labour (Estimated 40,000 child miners, Amnesty International 2016)
Systems Beyond Li

Cationic Shuttles

- Sodium Ion Battery
- Magnesium Battery
- Zinc Battery
- Calcium Battery
- Aluminum Battery

„multivalent shuttles“

Anionic Shuttles

- Chloride Ion Battery
- Fluoride Ion Battery

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&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Earth crustal abundance / ppm by weight&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Price (pure)&lt;sup&gt;3&lt;/sup&gt; US$ per 100g</th>
<th>specific capacity</th>
<th>Potential vs. NHE/V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>mA·h·g&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>mA·h·cm&lt;sup&gt;-3&lt;/sup&gt;</td>
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<tr>
<td>Li</td>
<td>1</td>
<td>90</td>
<td>20</td>
<td>27</td>
<td>3862</td>
<td>2047</td>
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<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>
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<tr>
<td>Mg</td>
<td>2</td>
<td>86</td>
<td>23300</td>
<td>3.7</td>
<td>2206</td>
<td>3840</td>
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<tr>
<td>Ca</td>
<td>2</td>
<td>114</td>
<td>41500</td>
<td>20</td>
<td>1338</td>
<td>2006</td>
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<tr>
<td>Zn</td>
<td>2</td>
<td>88</td>
<td>70</td>
<td>5.3</td>
<td>820</td>
<td>6845</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>
</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>
</tr>
</tbody>
</table>

<sup>1</sup>For coordination number 6, from R. D. Shannon "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides". Acta Crystallogr A. 32 (1976) 751–767.

<sup>2</sup>David R. Lide, ed., CRC Handbook of Chemistry and Physics, 89th Edition (Internet Version 2009)

<sup>3</sup>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.
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“
Theory and Simulation for next generation batteries

Example: Metal-sulfur battery (Cobalt free)

Global reaction: $S_8 + 16 \text{ Li} \rightleftharpoons 8 \text{ Li}_2\text{S} + 3400 \text{ kJ/mol}$

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

→

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 \( Li_2S \)

\[ \text{Polysulfide shuttle} \]

Columbic efficiency ↓
Capacity decay

Consequences of Polysulfide shuttle at HIU

Infinite charging at small currents

Capacity decay during cycling

Sulfur encapsulation: Nanostructured electrodes

Different approaches to retain sulfur species…

Modeling of nanostructured electrodes

Goal: Investigation of fundamental limiting effects

Single particle model

• Model 1
  ➞ Solid carbon shell

• Model 2
  ➞ Microporous sphere

Particle surface:
• $\phi_{\text{ref}} = \text{const.}$
• $c_{\text{Li}^+} = \text{const.}$
  ➞ Only Li enters particle
Structural effects

- Nucleation of $S_8 / Li_2S$
  - Pore space is reduced
  - $Li_2S$ needs much more volume
- Effective transport + pore clogging
  - Hindered diffusion in porous media
    - $D_{i}^{eff} = D_{i}^{0} \varepsilon_{elyte}^{1.5}$
- Passivation of active surface area by $S_8 / Li_2S$
  - Solid reaction products are electronically non-conducting
Results: Surface Defects

Transport overpotential

- Li$^+$ transport into particle

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

- 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 $\text{Li}_2\text{S}$ 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

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