Water-induced Influences on Active Materials in Lithium Ion Batteries

Werner Bauer
Manufacturing of Lithium Ion Batteries

Slurry Processing
Electrode Fabrication
Cell Assembling
Electrochemical Characterization
Electrode Components

- Active material
- Conductive Additives
- Binder
- Porosity
Aqueous Processing of Electrodes

- Substitution of the harmful and expensive N-Methyl-2-Pyrrolidone (NMP) by inexpensive and eco-friendly water

since 2011 on SVHC candidate list
(Substances of Very High Concern)
Cathode Materials

140 mAh/g 3,3 V
LiFePO$_4$

160 mAh/g 3,7 V
LiCoO$_2$

180 mAh/g 3,6 V
Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$)O$_2$

120 mAh/g 3,8 V
LiMn$_2$O$_4$

190 mAh/g 3,6 V
Li(Ni$_{0.8}$Co$_{0.15}$Al$_{0.05}$)O$_2$
Interaction of Cathode Materials with Water

- Hydroxylation
- Leaching of cations
- Proton exchange

Source: Zhang et al, J. Power Sources 196 (2011)
Leaching of Cations from NMC

Li(Ni$_{0.33}$Mn$_{0.33}$Co$_{0.33}$)O$_2$

- After 30 min leaching time
  - Lithium loss 0.5%
  - Leaching layer $\approx$ 7 nm thick

Recommendations
- Crucial for nano materials
- Store in dry chamber
- Coating of active materials

5 wt.% NMC111 in water
pH 11 (native), T = 21 °C
ICP-OES
Corrosion of Aluminum Foils

- Stability range of aluminum between pH 4 – 8.5
- Problems caused by extreme pH
  - Dissolution of protective oxide layer
  - Formation of water soluble Al species
  - Pitting of aluminum foil
  - Formation of hydrogen gas bubbles
  - Foaming of electrodes
Impact on pH of Aqueous Slurry

- Formation of LiOH leads to an increase of the pH
- Native pH depends on product and storage conditions
- Does a metastable range exist? (depending on exposure time and temperature)
Countermeasures

- pH reduction by acid addition
  (Li et al., JMaterSci 42 (2007) 5773–5777)

- Addition of amphoteric oxidic additives

- Pressurized CO$_2$ Gas Treatment

- Carbon coating on aluminum current collector
  (I. Doberdò et al., JPowerSources 248 (2014) 1000-1006)

- Particle coating with VO$_x$

- In-situ coating by adding of phosphoric acid
  (N. Loeffler et al., ChemSusChem 9 (2016) 1112 – 1117)
Adjustment of pH by Addition of Acid

- Acetic acid (HAc)
- Polyacrylic acid (PAA) (MW = 2.000, 450.000 and 1.250.000 g/mol)
- Phosphoric acid (PA)
- Citric acid

**Slurry composition**

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(Ni$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$)O$_2$</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black (Super C65)</td>
<td>3</td>
</tr>
<tr>
<td>CMC (CRT2000PA)</td>
<td>2</td>
</tr>
<tr>
<td>Latex binder (TRD202A)</td>
<td>3</td>
</tr>
<tr>
<td>+ Acid</td>
<td>x</td>
</tr>
</tbody>
</table>

Rule of thumb: 0.5 – 1 wt.% of acid required for pH 7
Impact of pH Reduction on Cation Solubility

- Lithium leaching is minimal at native pH
- Dissolution of transition metal ions is detectable at lower pH

![Graph showing the impact of pH reduction on cation solubility.](image)

5 wt.% NMC in water pH modified by HCl Leaching time 10 min
Impact of Acetic Acid on Slurry Rheology

- Moderate decrease of viscosity
- Viscosity rises again at neutral zone

Electrode topography

- pH 11
- pH 8
- pH 7

- Decrease of surface roughness
  -> Deletion of agglomerates from carbon black
Impact of Acetic Acid on Coating Resistivity

- Increase of DC (electrode) and AC (cell) resistance at low pH
- Formation of small carbon black fragments
  - Unfolding of CMC chains → more entanglement and bridging
  - Loss of electrical connection for isolated fragments

![Graph showing resistivity and cell impedance vs. pH with data points for before and after calendaring.]

**Source:** Strümpler & Glatz-Reichenbach, J. Electroceramics 3:4 (1999) 329-346

NMC particles with homogeneously distributed carbon black fragments at pH7
Adhesion Strength after Acid Addition

- Massive loss of adhesion strength with most acids
- Good adhesion with high molecular weight PAA (binder capability!)
- Besides pH, adhesion drop depends on composition and processing
Adhesion Failure

- Below the IEP, the alumina surface has a positive charge.
- Anions from the dissociated acids are strong Lewis bases, replacing existing interactions.

- Small PAA molecules adhere as a thin layer preventing straight interaction with functional binder groups.
- Extended PAA molecules form loops and tails, which enable diffusion bonding by creating an interdiffusion layer with the binder.
Electrochemical Properties with Acetic Acid

- Maximum of specific capacity at pH 9

pouch cells, 11.4-14 mg/cm², graphite anode, LP 30, CC, 3.0 – 4.2 V

Values corrected for different mass loadings
Electrochemical Results

- Higher initial capacity for acetic acid, but also high degradation
- Best long-term stability for acid free slurry

![Graph showing specific capacity over cycles for different electrolytes and conditions.]

- CC: Current Control
- CC/CV: Current Control/Cycle Voltage

Pouch cells, 10.9-12.3 mg/cm², graphite anode, LP 30, 3.0 – 4.2 V
Summary

- Challenges for aqueous processing of cathode materials
  - Leaching of lithium ions, lithium loss by formation of $\text{Li}_2\text{CO}_3$
  - Corrosion of aluminum foil due to high pH value of slurry
- Investigated approach: Decrease of pH by addition of acids
  - Lowering of corrosion effects
  - Significant drop of adhesion strength (for acids with low molecular weight)
  - Acetic acid gives high initial capacity, but strong degradation
  - Best long-term stability without acid addition
    - Better understanding of the influence of the acid required
    - Invest more effort in the minimization of lithium leaching
Co-Authors
Ulrike Kaufmann
Marcus Müller
Fatih Çetinel (now BASF)

Thank you for your attention.