Aging of Lithium-Ion Batteries

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Ageing Processes and Lifetime Prediction of Batteries (Helmholtz - FZJ)

In total:
~ 110 full time scientists, engineers, technicians
~ 100 students
Aging and Lifetime of Batteries

Electrochemical Energy Conversion and Storage Systems

Modeling & Life Time Prediction

Battery System Design and Vehicle Integration

Grid Integration and Storage System Analysis

Sauer

Figgemeier

Analytics & Materials

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5 MW grid service

>1000 test benches
Aging of lithium-ion batteries
Motivation

battery costs
1% - 5%
lifetime
2 years

battery costs
30% - 50%
lifetime
10 years (even better 15)
Battery technologies

2030:
- 450 Wh/kg
- < 75 €/kWh
- 12 years lifetime
- 1000 cycles
- > 3C charging rate

around 260 Wh/kg today
Technology Development – LIB Evolution

- LMO (NMC111/4.2 V)
  - Graphite

- HE-NMC(622/4.4 V)
  - Graphite/Si (>20 %)
  - LNMO
  - Graphite/Si (>20 %)

- HE-NMC(622/811/4.4 V)
  - >4.5 V / Si- or lithium anode + solid state electrolyte / Separator

- HE-NMC(>4.6 V)
  - Graphite/Si (>40 %)

Increase in energy density → new aging mechanisms

Stability & Safety Issues

Energy Density

Year

199X - 2010

2016

2018

2020

2022
The trouble with metal anodes – volume expansion

Graphite anode without Silicon!

Large volume variations need to be accommodated!


A. Pfrang , E. Figgemeier et al., Journal of Power Sources 392 (2018), 168-175
Agenda

1 Introduction
2 Motivation
3 Aging behavior
4 Material aging
5 Modeling
6 Conclusions
Calendaric aging – SOC dependency

Calendaric aging at 35 °C

- Pouch-Cell: 20 Ah
- Energy density: 174 Wh/kg
- Cathode: NMC (4:4:2)
- Anode: Graphit

A. Warnecke, Degradation Mechanisms in NMC-Based Lithium-Ion Batteries, Dissertation, 2017
Cyclic aging – DOD dependency

Cyclic aging at 35 °C, 1 C current rate

Assumption:
- 80 kWh pack
- 25 kWh / 100 km

Same battery, same conditions, different aging


- Sanyo/Panasonic UR18650E
- 1.85 Ah
- Graphite / NMC111
- Operation 3.9 V to 3.5 V
- Current 4.1 A (~2 C)
- 48 cells, identical operating conditions

~ 700

~ 900

80% $C_N$
3 stages of aging & aging processes

Phase 1: Geometry

Phase 2: Material aging

Phase 3: Crash

relative capacity in %

aging duration in days

100%
Phase 1 – Geometry

Phase 1
Geometry

Phase 2
Material aging

Phase 3
Crash

relative capacity in %

100%

aging duration in days
State of charge history influences usable capacity

Passive electrode effect:

\[ \text{SOC}_{\text{test}} < \text{SOC}_{\text{start}} (50\%) \]

Calendaric aging at 35 °C

Also see: Lewerenz et al., J. Power Sources., vol. 345, pp. 254–263, 2017
State of charge history influences usable capacity

Passive electrode effect:

\[ \text{SOC}_{\text{test}} > \text{SOC}_{\text{start}} \ (50\%) \]

Calendaric aging at 35 °C

also see: Lewerenz et al., J. Power Sources., vol. 345, pp. 254–263, 2017
3 stages of aging

Phase 1: Geometry

Phase 2: Material aging
- Capacity loss
- Aging rate
- Time

Phase 3: Crash

Aging duration in days

relative capacity in %
Aging effects of the cathode

- Electrolyte decomposition & cover layer formation
- Structural effects
- Conductive additive
- Aluminum corrosion
- NMC
- Microcracks
- Oxidation of binder and conductive additives
- Dissolution & precipitation
Known anode aging mechanisms

- Exfoliation of graphite
- Current rate, corrosion phenomena, ...

- Continuous SEI growth
- Mechanical damage to SEI, material expansion, ...

- Chemical deterioration of SEI
- Transition metal dissolution on cathode, electrolyte composition, ...

- Deposition of metallic Lithium (Plating)
- Uncontrolled layer growth
- Charge temperature, high charge currents, ...

Inhomogeneity on the anode

Inhomogeneous lithium distribution causes:

- Locally increased current densities
- Locally varying potentials
- Different load stress on particles
- Varying production parameters

Inhomogeneous aging on the microscale before it becomes observable!

also see: Lewerenz et al., J. Power Sources., vol. 368, pp. 57-67, 2017
Impedance and Physics based Concepts for battery modelling / lifetime prediction

Network for Current Distribution and Potentials
- Charge transfer resistance (SEI)
- Electrode resistance
- Electrochemical Open Circuit Potential
- Contact and Current Collector Resistance
- Solid Resistance

Input Signal: $U_{in}$
Output Signal

Local currents

Particle Diffusion
Electrolyte Diffusion

Potential vs. Li/Li$^+$

Re($Z$) / mΩ
Im($Z$) / mΩ
$
\begin{array}{c}
1\text{ kHz} & 1\text{ Hz} & 100\text{ Hz} & 10\text{ Hz} & 0.1\text{ Hz} & 0.01\text{ Hz}
\end{array}$

$L$ $R_{ser}$ $R_{SEI}$ $R_{ct}$ $C_{SEI}$ $C_{dl}$ $Z_W$
Battery Modeling

• Electrical & physical models
  – Impedance based for dynamic simulations
  – Physical/chemical for representation and understanding occurring processes
  – According to application usage of simple or spatially-resolved models

• Thermal models for cells and stacks incl. cooling strategies
Lifetime Prediction

Load profile \((I, P, T_{\text{environment}})\)

Spatially-resolved thermoelectrical model

Electrical and thermal characterisation

Systematic calendaric and cycle ageing tests

Model of ageing processes

Parameter adaption of electrical model

Post mortem analysis for identification of aging processes and speed

Lifetime prediction
Verification Profiles

- Verification of the models
- Realistic driving profiles

Charge

- Verification Profiles
- Realistic driving profiles

Power / W vs. Time (min)
Verification Profiles

Profil 1

Profil 2

Profil 3

+0°C

+10°C

+20°C
Summary

Understanding of aging processes
- Separate reversible and irreversible aging
- New materials $\rightarrow$ new processes
- Optimization of all relevant parameters simultaneously (probably) not possible

Modelling and lifetime assessment
- Understand what you want to simulate $\rightarrow$ needed level of detail and computational power
- Single cell behaviour determines overall system performance
- Influences of inhomogeneities and pack topology can be significant
Vielen Dank für Ihre Aufmerksamkeit

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