AABC Europe

Volume Change from Materials to Cell Level and Its Influence on Battery Lifetime

31.01.2017 Mainz

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Overview

- Motivation
- Courses of micro-mechanic issues
- From crystal level to cell level
- Strain within electrodes
- Coupled model approach
- Influence on cell design
- Validation and lifetime influence
In cylindrical cells, swelling can shorten lifetime

- The core is more stressed than the outer area
- One reason why upscaling of cylindrical cells is limited

Source: Presentation Prof. T. Takamura “Carbon Material in Power Sources”. June 2005, ZSW Ulm
Investigation of the non linear aging effect

Inhomogeneous plating: Higher compression results in faster li-plating

(a) Outer part of the negative electrode exposed to 6 fast cycles. (b) Inner part of the same electrode showing a stripe pattern. Plating is marked by an ellipsis and arrows.

(a) Computed tomographic crosscut of a pristine cell. The positive (1) and negative (2) current collector tabs are visible. The positive current collector is marked by an ellipsis, resulting deformations to the jelly rolls are marked by arrows. The positive current collector deforms the jelly roll.

Investigation of the non linear aging effect

Forced heterogeneous compression by a hose clamp

- Heterogeneous compression results in Li-plating in the areas with higher pressure.
- Possible reason is the compression of the separator and its local change in diffusion path.

A hose clamp is placed on a cell. (b) Plating is visible on the overlap of the current collector imprints and the clamp which are visualized by black and red rectangles respectively.

Conclusion: Better understanding of volume change and pressure within cells, electrodes and particles is necessary.

First volume change measurements

Our initial investigations: Dilatometry of anode and cathode, displacement and single side laser scanning.

- A commercial pouch cell was selected
- Dilatometry with EL-CELL device
- Two side displacement measurement was set up
- A single side laser scanner was installed.

Measurement of volume change on crystal level of LCO

Left figure: Unit cell parameters during charging for the O3 I and O3 II phases.

Right figure: Comparison of the lattice unit cell volume change and the height change of the electrode during charging

First volume change measurement

Results of graphite-anode

- Non linear volume change
  - 1/3 approx. linear
  - next 1/3 reduced slope
  - last 1/3 increasing
  - at the end fast increase
  → fits to stages in graphite
- Total volume change approx. 7% (reversible)
- Volume increases with lithiation
First volume change measurement

Anode and cathode contribution to the battery thickness change during discharge

\[ \Delta d_{\text{full-cell}} = \Delta d_{\text{graphite}} + \Delta d_{\text{LCO}} \]
Influence of electrode structure

Are structures based on spherical particles representative for real structures?

Measurement of volume change

Modeling setup used in this study.
- a) Representative spherical particle model (RSPM).
- b) Realistic microstructure model (adapted from SEM cross-sectional images of the electrode)
Simulation results with representative spherical particle model
Relationship between volume change and thickness change

Thickness change as a function of volume change and active material fraction:

\[ \Delta h = \Delta V \cdot \xi_{AM} \]
Taking the thermal expansion into account

Total expansion:
\[ \Delta t_{cell} = \Delta t_{int} + \Delta t_{th} \]

Thermal expansion:
\[ \Delta t_{th} = \alpha_{cell} (T - T_0) \]

\[ \alpha_{cell} = 1.1 \frac{\mu m}{K} \text{ for a 6.5 mm thick cell} \]

Determined thermal expansion coefficients \( \alpha_{cell} \) at various SoC.

Simulation results

Overall expansion

Thermal expansion

Intercalation expansion

Simulated and measured displacement curves for different discharge rates.

a) Overall pouch cell displacement $\Delta t_{\text{cell}}$.
b) Thermal displacement $\Delta t_{\text{th}}$.
c) Intercalation displacement $\Delta t_{\text{int}}$

Coupled 3D Cell Model

Comparing of 2 cell designs

Temperature at the end cc of discharge

Measurement (2d) of volume change

- Two 2d laser scanner system: Two 1d laser plus movement of scanner
- Two laser scanners scan the cell from both sides (frontside and backside)
- Inside a temperature controlled chamber
- Post-processing method for highly reproducible local thickness measurement (repeatability of approx. 10 μm between 100 cycles and 2 μm for consecutive measurements)

Measurement (2d) of volume change

- Charging of a cell with 1C rate
- At different temperatures

- At 40 °C volume change is homogeneous and it is as expected (about 160 um)
- At 25 °C there is an additional volume increase in the area of the terminals
- At 17 °C the effect is increased. The volume change increases with decreasing distance to the terminals
- The volume change reaches a peak about cc charge phase is switched to cv charge phase. The thickness is decreasing to the expected value within about 30 minutes.
- Temperature effects have been calculated and are not the reason for the effect.
- We assume increased Li-plating caused by the current density inhomogeneities.
1C charging at different temperature

40 °C  25 °C  17 °C
Reversible and irreversible volume change

• Laser-Checkup” is conducted every 100 cycles inside the laser test bench to detect reversible and irreversible thickness changes

• Displacement overshoot results in faster capacity fade at 1C 25 °C
• Linear aging for homogeneous load cases during charging
Reversible and irreversible volume change during lifetime

- Reversible thickness change (top) and irreversible thickness change (bottom) for aging at 0.5C charging rate

- Irreversible thickness increase is highest in the first 100 cycles and is evenly distributed

Reversible and irreversible volume change during lifetime

- Reversible thickness change (top) and irreversible thickness change (bottom) for aging at 1C charging rate

- Large irreversible thickness increase when lithium plating takes place

Conclusions

- Volume change by intercalation on crystal level has a significant impact on:
  - Forces in electrode and between electrode and current collector
  - Thickness change of electrodes and cells, even inhomogeneous
- Volume is also increased by temperature and by Li-plating
- Inhomogeneous compression, as seen in cylindrical cells, result in inhomogeneous Li-plating inside the cell.
- Li-plating starts first in areas with higher compression
- Volume change can be represented by simplified Electrode models
- Inhomogeneous current distribution results in inhomogeneous SoC, followed by inhomogeneous volume change and mechanical stress.
- During charging, inhomogeneous charge currents result in inhomogeneous Li-plating, including overshooting in thickness.
- First 3D coupled mechanical-chemical-thermal model shows good results
- Further model improvement necessary, taking Li-plating into account