AGING OF LI-ION BATTERIES AND HOW TO DEAL WITH IT

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AGING OF LI-ION BATTERIES AND HOW TO DEAL WITH IT

- Li-Ion battery
- Aging Mechanisms
- Modelling fresh and aged cells
- Testing
- Parameter estimation
- Using the model
LI-ION BATTERY PRINCIPLE

Cu current collector
Active material $Li_xC_6$
Electrolyte

Al current collector
Active material $LiMeO_z$
Filler, Binder & Electrolyte

Carbon
$Li$
$Li^+$
e$^-$
# KEY BATTERY SPECS FOR STATIONNARY BATTERIES

## A few typical values

<table>
<thead>
<tr>
<th>Battery Specs</th>
<th>Unit</th>
<th>Remark</th>
<th>Home ESS</th>
<th>SME ESS</th>
<th>Utility ESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery Pack</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gross Energy capacity</td>
<td>kWh</td>
<td>Time to deliver power</td>
<td>5 (2-10)</td>
<td>20-200</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Battery pack Weight</td>
<td>kg</td>
<td>Installation location</td>
<td>54</td>
<td>200-2000</td>
<td>&gt; 10000</td>
</tr>
<tr>
<td>Cell gravimetric Energy density</td>
<td>Wh/kg</td>
<td></td>
<td>140 (LFP prism)</td>
<td>170 (NMC prism)</td>
<td></td>
</tr>
<tr>
<td>Cell volumetric Energy density</td>
<td>Wh/l</td>
<td>Required space</td>
<td>280 (LFP prism)</td>
<td>350 (NMC prism)</td>
<td></td>
</tr>
<tr>
<td>Discharge rate</td>
<td>C-rate</td>
<td>Discharging power</td>
<td>0,8C</td>
<td>1,5C</td>
<td></td>
</tr>
<tr>
<td>Charge rate</td>
<td>C-rate</td>
<td>Charging time</td>
<td>0,5C</td>
<td>0,8C</td>
<td></td>
</tr>
<tr>
<td>Operating temperature range</td>
<td>°C</td>
<td>Indoors</td>
<td>v</td>
<td>v</td>
<td>v</td>
</tr>
<tr>
<td>Cycle Lifetime</td>
<td>#EqCyc</td>
<td>Application requirements</td>
<td>10000?</td>
<td>6000?</td>
<td>8000?</td>
</tr>
<tr>
<td>Calendar Lifetime</td>
<td>Years</td>
<td>min 10 years</td>
<td>v</td>
<td>v</td>
<td>v</td>
</tr>
</tbody>
</table>
LIFETIME SPECIFICATIONS

- Examples in datasheets:
  - 10 years performance warranty (EoL capacity 70%) => is this 3650 cycles?
  - 10000 cycles (at ?? which conditions)
  - >3200 Cycles 25°C, 80% EoL, 0.5C/1C
  - 6000 Cycles @ 100% DoD | 70% EoL | 23°C +/-5°C 1C/1C

- Lifetime in number of cycles specified for:
  - Depth of discharge
  - C-rate for charging
  - C-rate for discharging
  - Temperature
  - End of Life condition

- What if my application profile and conditions are different?
DEGRADATION DEPENDS ON ...

- DoD
- C-rate charging
- C-rate discharging
- Temperature

AND Li-Ion batteries degrade, Even if they are not used! => avoid high SoC (and low SoC)

Main degradation mechanisms

▪ SEI growth
▪ Surface cracking
▪ Loss of active material

HOW TO MODEL A FRESH BATTERY? HOW TO ADD AGING?

- **Bucket:**
  degradation usually limited to linear degradation in 1 condition

- **Equivalent Circuits:**
  parameters for each condition degradation modelling requires (non-physics based) additions

- **Empirical/mathematical:**
  usually fitted on a limited data set degradation requires addition of functions

\[ U = f (I, \text{SoC}, T) \]
HOW TO MODEL A FRESH BATTERY? HOW TO ADD AGING?

- Reduced complexity electrochemical models like Single Particle Model (SPM) physico-chemical degradation mechanisms => good compromise between accuracy and complexity

- Accurate high complexity electrochemical models like Doyle–Fuller–Newman (DFN) physico-chemical degradation mechanisms => usually for improving cell design

SINGLE PARTICLE MODEL ELECTROCHEMICAL MODEL

\[
\begin{align*}
\frac{\partial c_i(r,t)}{\partial t} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_i r^2 \frac{\partial c_i(r,t)}{\partial r} \right) \\
D_i \frac{\partial c_i(r,t)}{\partial r} \bigg|_{r=0} &= 0 \\
D_i \frac{\partial c_i(r,t)}{\partial r} \bigg|_{r=R_i} &= -\frac{i_i(t)}{F} = -\frac{I(t)}{V_i a_i F} \\
c_i(r,0) &= c_{i,0}(r)
\end{align*}
\]

Voltage \( \eta_i \)

\[
\eta_i(c_i(R_i,t), I(t)) = \frac{R_s T}{\alpha F} \sinh^{-1} \left( \frac{I(t)}{2V_i a_i i_{i,0}(c_i(R_i,t))} \right)
\]

\[
i_{i,0}(c_i(R_i,t)) = F k_i \sqrt{c_i(R_i,t) c_{el}(c_i^{\text{max}} - c_i(R_i,t))}
\]

+ thermal model + degradation mechanisms
Commercial Battery Kstar BluE-Pack 5.1 S 3680D  5.12kWh 230V 1ph
- Passive air convection cooling. Multi-days test with additional temperature sensors.
- Up to 35°C in room temperature conditions.

CATL cells aging tests
- 18 CATL cells cycling aging tests at 35°C at various C-rates & SoC windows.
- 16 CATL cells calendar aging tests at various temperatures and SoC
Prototype cells with pure Si-anode from LeydenJar
### FLEXINET LI-ION BATTERY CYCLE TESTS

Each test has 2 cells and 2 types of experiments (characterization & cycling)

#### ΔSOC = 50

<table>
<thead>
<tr>
<th>CH\DCH</th>
<th>C/5</th>
<th>C/2</th>
<th>0.8C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/5</td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>C/2</td>
<td></td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

#### ΔSOC = 90

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>C/5</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>C/2</td>
<td>x</td>
<td>x</td>
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#### ΔSOC = 100

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<td>C/5</td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C/2</td>
<td></td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Limits coming from KStar specs.
Across SOCs and C-rates, normalized, **time**

FLEXINET LI-ION BATTERY DEGRADATION
PARAMETER ESTIMATION IN DIFFERENT CONDITIONS – CAPACITY LOSS VS TIME

(a) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(b) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(c) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(d) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(e) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(f) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(g) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(h) \( Q_{\text{loss}} \) vs Time [d] for different conditions.

(i) \( Q_{\text{loss}} \) vs Time [d] for different conditions.
USING THE MODEL

▪ Battery Pack Manufacturers:
  ▪ Predict future degradation of the real battery via simulating the battery degradation model with specific application profiles under specific conditions with the aim to dimension and optimize the Battery Pack
  ▪ Determine warranty conditions & support Battery Pack Integrators
▪ Battery Pack Integrators
  ▪ Anticipate for unforeseen (new) usage of the battery pack
▪ Battery Energy Storage System Operators:
  ▪ Predict future degradation of the real battery via simulating the battery degradation model with various application profiles under various conditions with the aim to make better trade-offs when to use the battery (profit > cost of degradation)
  ▪ Include the model in the control loop
    => both to improve ROI
▪ Battery Cell Manufacturers:
  ▪ Use the model to improve understanding of degradation with specific application profiles under specific conditions with the aim to improve the cell design or cell manufacturing
• Battery usage can help alleviate demand for flexibility and earn a return
• Electricity prices on flex markets are very volatile
• Rapid charging/discharging of battery will lead to high cycling of the battery and impact the aging of the asset
• Aging algorithms such as VITO’s physics-based models will help understand the impact and improve the lifetime or the revenue (within the default lifetime) and thereby the return on investment
CONCLUSIONS

- Li-Ion battery aging depends on many factors
- Little information is publicly available on this
- Battery models help to deal with the aging of Li-Ion batteries
- All models require testing of cells (and modules) or live data acquisition to estimate their parameters
- The Single Particle Model is a good compromise between accuracy and complexity
- Method has been proven for both NMC and LFP batteries
- Method allows to increase ROI

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