Investigation of a degradation-induced charging anomaly in commercial lithium-ion batteries

BATTERIE INGENIEURE by UL Solutions

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Key take aways

- Previously unreported charging anomaly observed in cylindrical high-energy NCA/C-Si cells, occurring during aging study.
- Charging anomaly is marked by a significant charging surplus and a pronounced temperature rise (up to 95 °C observed here).

→ **Detailed investigation of operational conditions, degradation & post-mortem analysis, reveals that the anomaly is triggered by high-SOC degradation and a preceding discharge to low SOC levels.**
→ **Most plausible explanation are pressure- and degradation-induced soft short circuits, involving localized lithium plating.**
→ **Need for further research into aging- and format specific stress effects and for real-time anomaly detection strategies to improve battery reliability & safety.**

Observed phenomenon

Commercial 21700

NCA / C-Si
Si: ~1 wt%
3.63 V, 4.9 Ah
Max. C_{rate} CHA: 1 C
Max. C_{rate} DCH: 2 C

Calendar

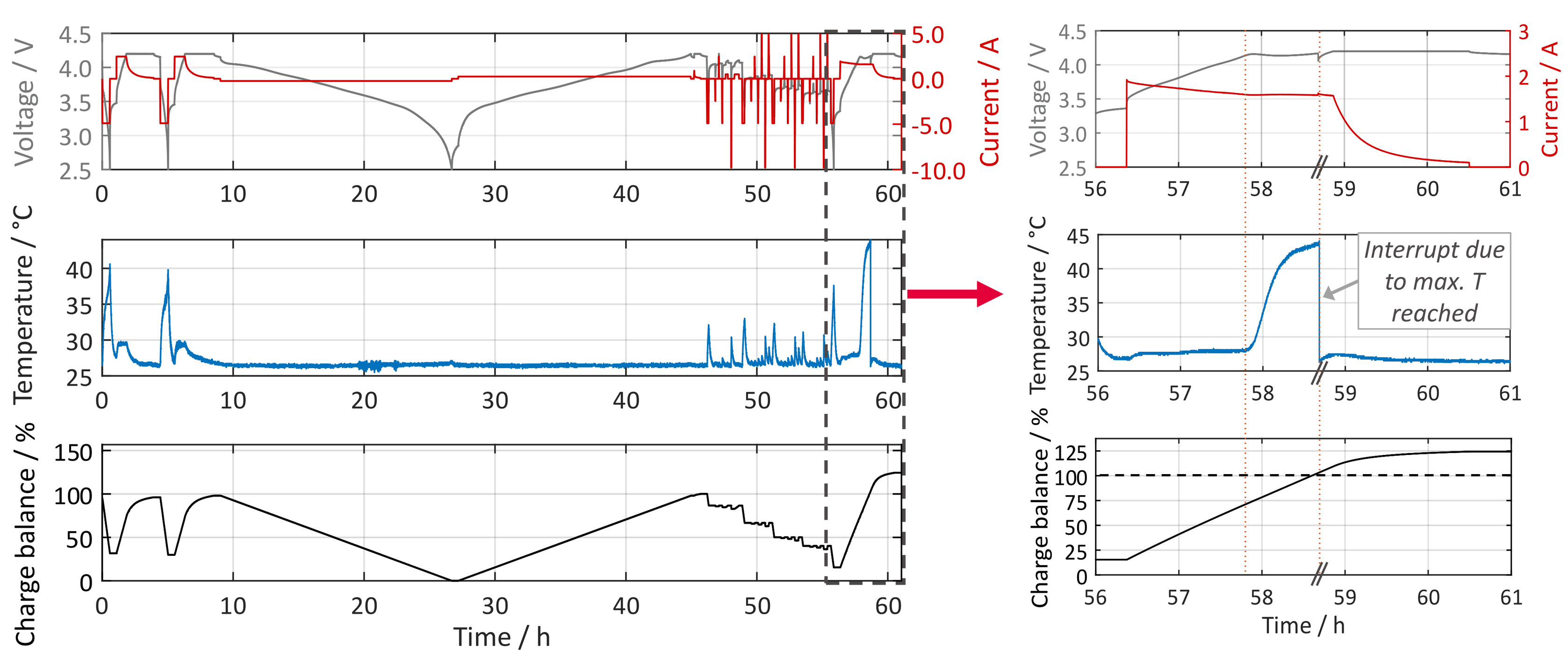
Calendar	Temperature / °C		
SOC / %	35	45	55
100		2	
96		2	
92	2	3	3
80		2	
…		…	
6		3	

Cyclic

Cyclic, 25°C	DOD / %					
SOC_{mean} / %	100	90	75	50	20	5
90					3	
75				3	3	3
65					3	
50	3	3	2	2	3	3
25				2	3	2
15					2	

> 20 cells

Checkup – Charging anomaly during last charge (Constant power with 75% $P_{nominal}$)



- Calendar and cyclic aging study conducted
- Charging anomaly emerged for > 20 cells during constant power charge of checkups
- Characterized by pronounced temperature rise & significant charging surplus

Goals
→ Characterize the charging anomaly and its occurrence
→ Identify the root cause of the charging anomaly
→ Understand the potential consequences

Methodology

Analysis of operational conditions

- Tests of anomaly without interrupt A
- Tests varying preceding depth-of-discharge B
- Tests monitoring voltage behavior directly after interrupting charging during anomaly (not shown here)

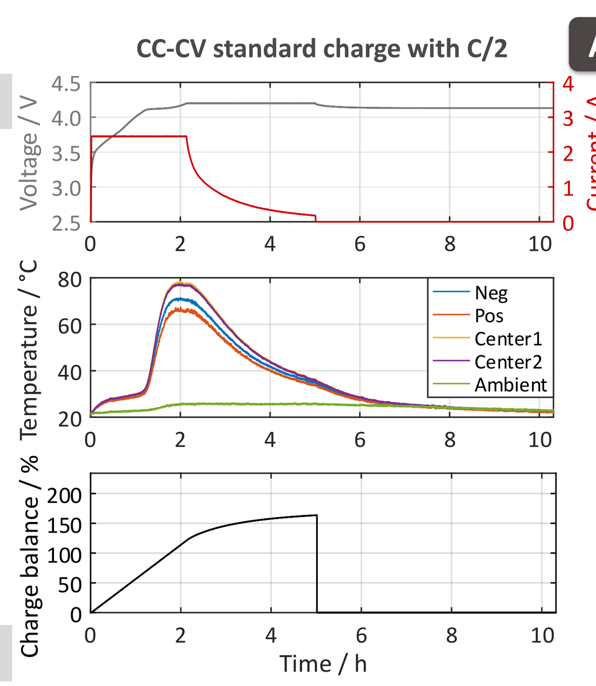
Degradation analysis

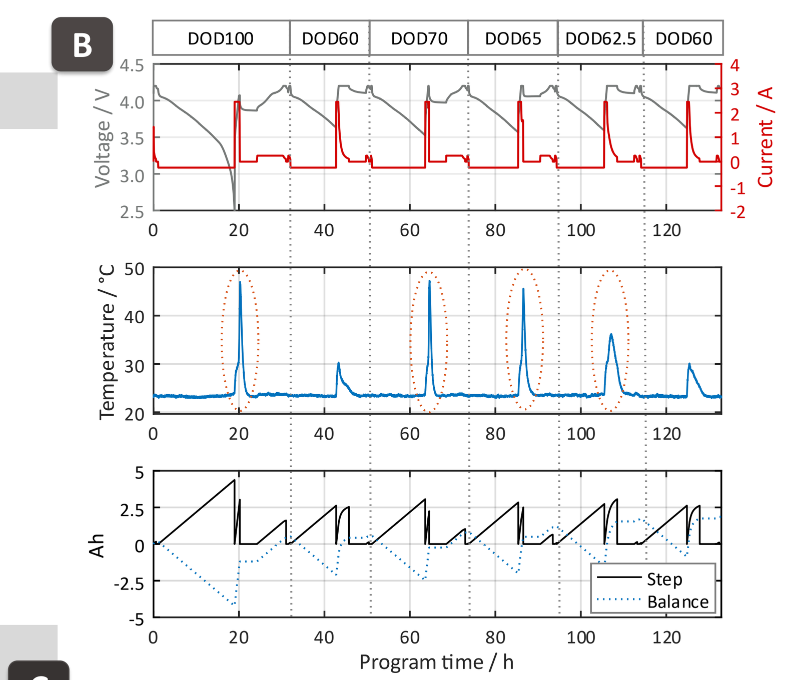
- Aging conditions of affected cells: Highlighted in test matrices shown above
- Degradation trajectories: When does the anomaly occur? → Ah-balance as indicator
  - Charge balance vs. Checkup-number / DC-IR / C/20 capacity C
- Impedance, DVA (not shown here)

Post-mortem analysis

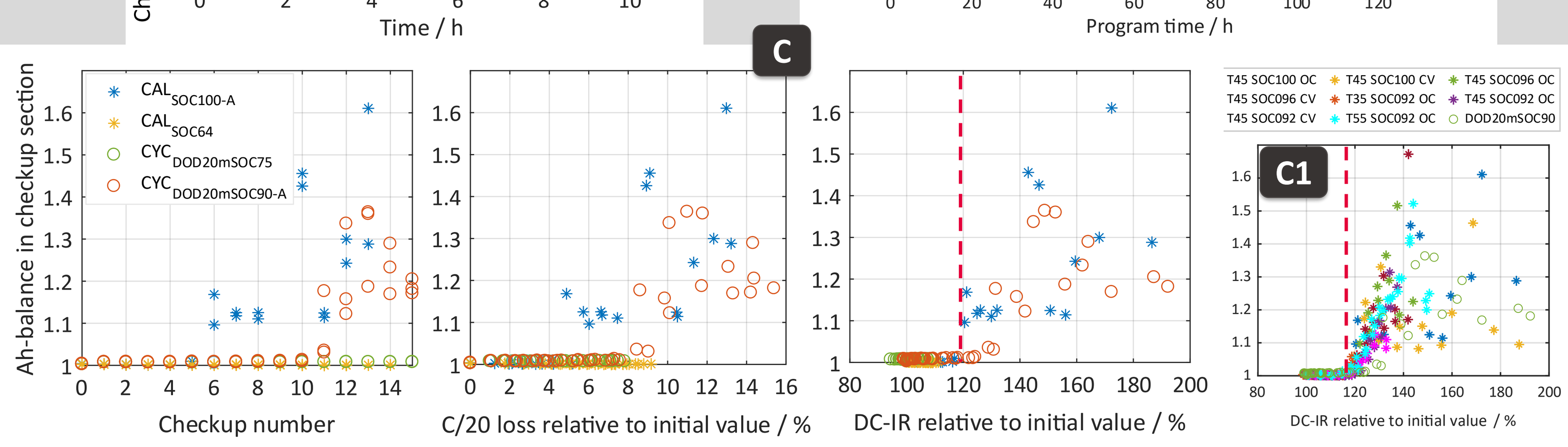
- Selected cells opened under inert gas atmosphere
  - in during-anomaly state D
  - In discharged state
- Inspection of electrodes and separators E
- Lasermicroscope & SEM/EDX F

Results

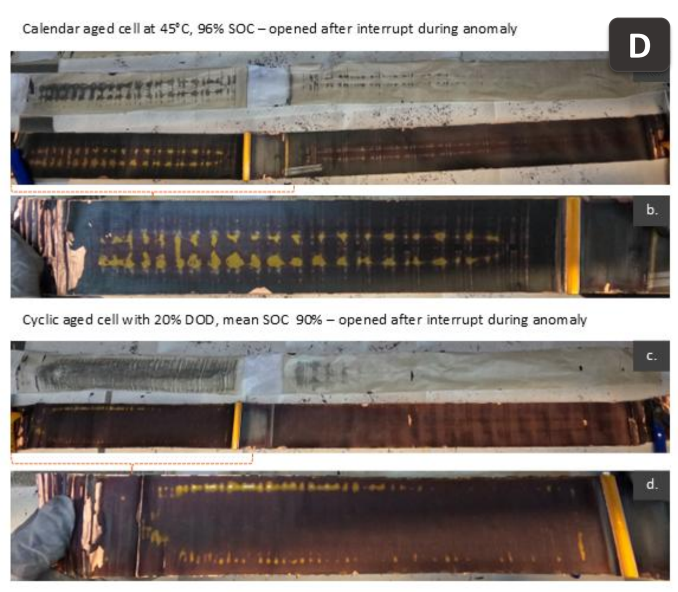


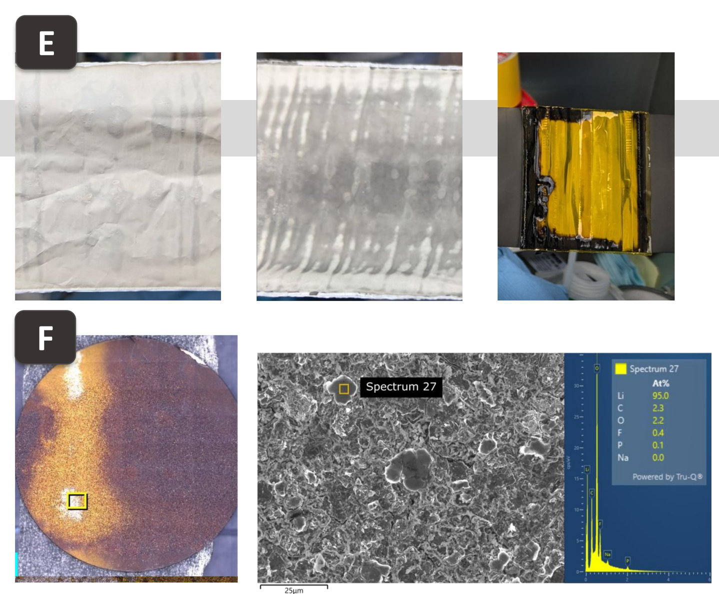


- Up to 95 °C during 1C charging reached
- Self-resolving effect observed → stabilizing at high temperatures
- Preceding discharge to low SOC level required
- Depending on charging current rate (not triggered during C/20 charging)
- no lithium-stripping observed directly after anomaly



- Degradation at high SOCs: DC-IR reaching ~125% → emerging of anomaly
  - → valid for all affected cells C1
  - → Certain passivation degree is required
- Charging surplus of up to 163 % of nominal capacity, but capacity does not collapse → process must be largely non-lithium consuming
- Impedance & DVA indicate cathode degradation & electrolyte decomposition in affected cells



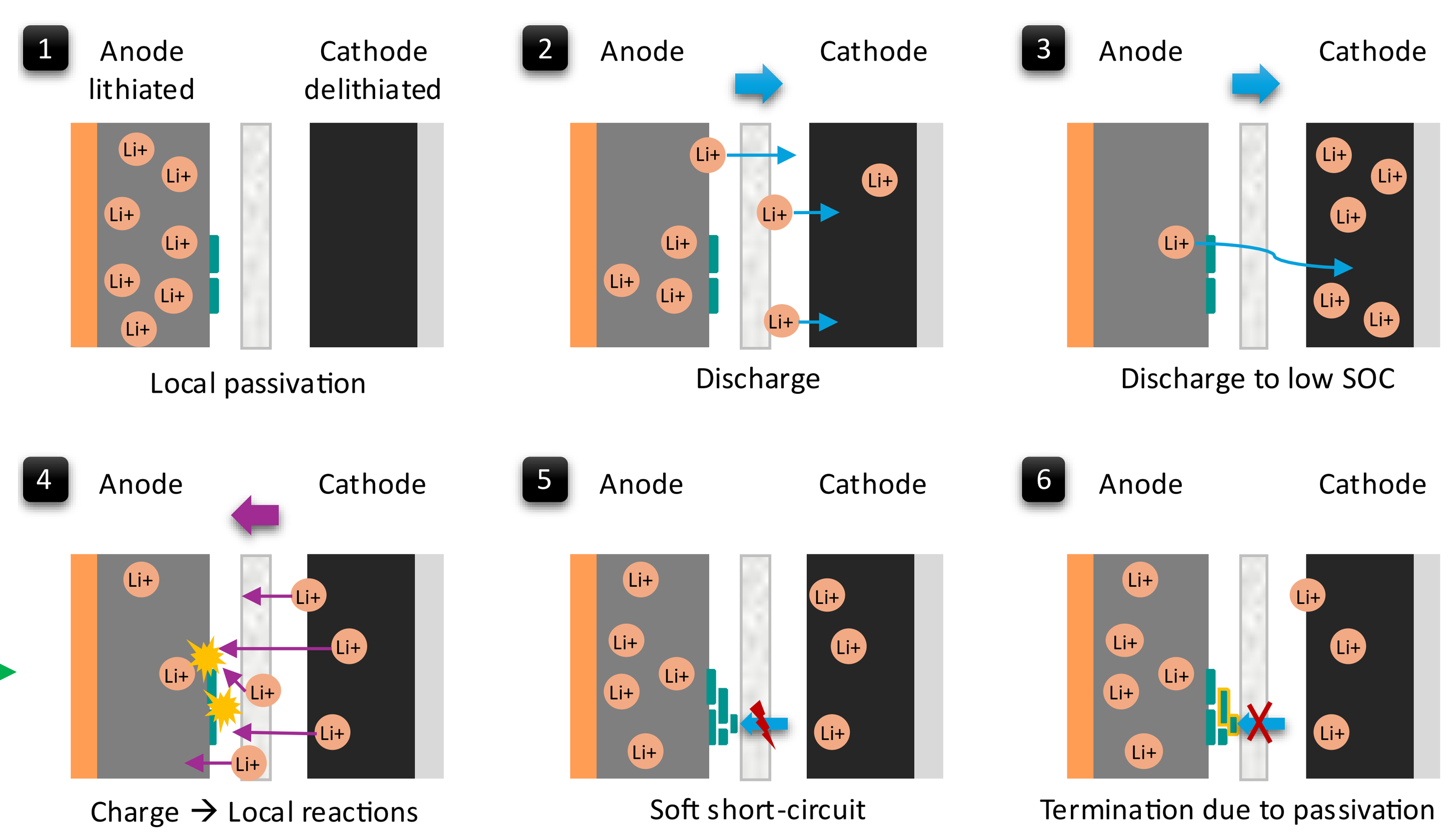


- Inhomogenous lithation states during anomaly.
- Surface patterns on anode mirrored on separators, appear to be pressure-related (e.g. current collector tab imprinted)
- Signs of elevated heat found
- Localized lithium plating found

Discussion

Potential explanations for root-cause

1. **Lithium plating** ✗
   Can cause anomalies, but cannot explain high cumulative charging surplus
   - Reversible plating would be observable as "stripping"
   - Irreversible plating would lead to rapid capacity loss
2. **Redox-shuttle mechanism** ✗
   Could explain high cumulative charging surplus, but does not account for current-rate dependency and self-resolving behavior
   - RS are potential-driven and facilitated by high temperatures
3. **Pressure- & degradation-induced soft shorts** →
   Mechanism aligns with all observations in this study
   → **Most plausible explanation**



Implications

- **Safety & Reliability:** Anomaly occurs within valid operational range → potential safety issues without single-cell temperature monitoring
- **Diagnostics:** Need for anomaly detection algorithms, based on identified precursors (e.g. charge balance) or data-driven
- **Mitigation**: Findings suggest inhomogeneities on anode side as main drivers (local plating, pressure distributions), evolving during high-SOC aging. Highly cell specific → further research required.

Further information can be found in our publication in the Journal of Energy Storage:

Available online soon (01/26).

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