Materials Failure Analysis of High-Power Li-Ion Batteries

PURDUE MATERIALS ENGINEERING

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The purpose of this project was to develop a materials failure analysis protocol to identify the root causes of failure in high power battery packs tested at the BIC under accelerated conditions. Plausible mechanisms were identified through examination of electrical measurements taken during charge/discharge cycling and post-test materials characterization. A combined analysis suggests that high charging rates can lead to degradation of the electrolyte which reduces battery lifetime.

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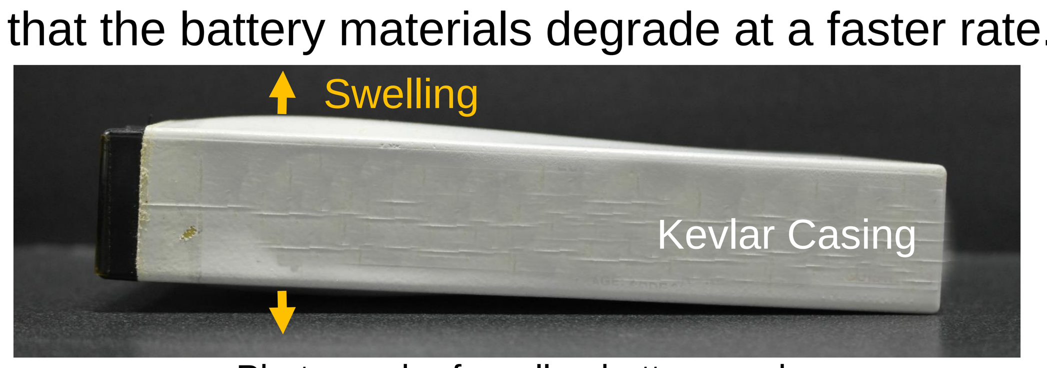
BIC BATTERY INNOVATION CENTER

Project Background

“High power” batteries, such as those used in electric vehicles, must be capable of achieving high rates of discharge. As a result of the high current that flows through the battery, various kinetic processes and chemical changes occurring in the battery components are accelerated. The net result is that the battery materials degrade at a faster rate.

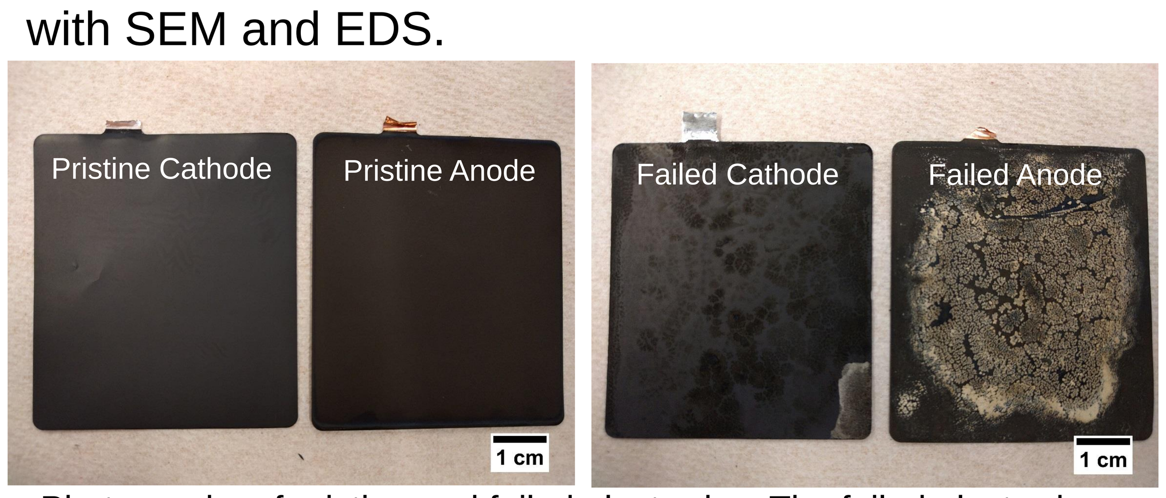


Photograph of swollen battery pack

A customer of the BIC reported swelling of their high-power battery packs during field use. Battery swelling presents considerable danger: the evolved gases inside the battery are often flammable and can be easily ignited.

Photograph of a battery pack after a “thermal event”, where it is expected that a spark caused by a short circuit ignited the battery electrolyte.

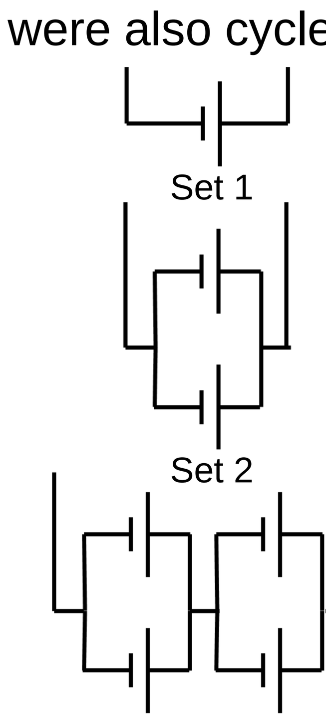
To identify root causes of materials failure (swelling or otherwise), additional batteries were cycled according to the customer’s specifications, and swollen packs were disassembled and characterized with SEM and EDS.

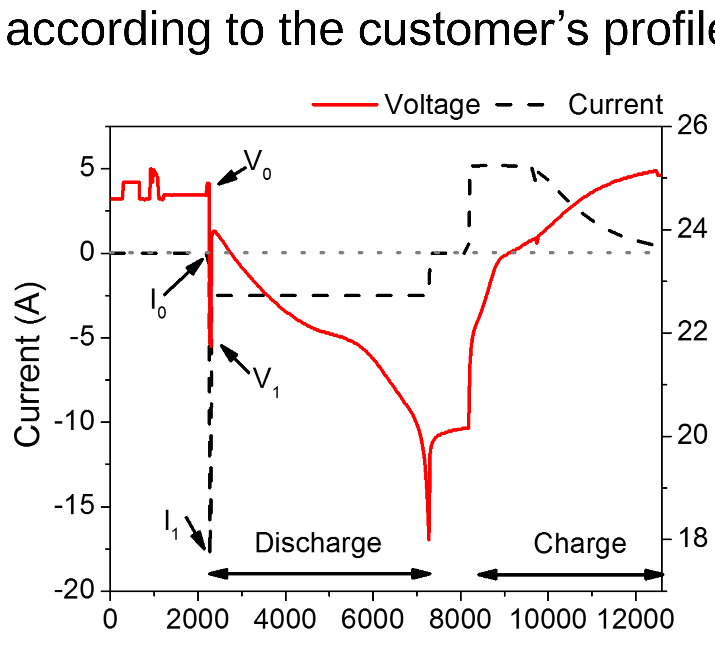


Photographs of pristine and failed electrodes. The failed electrodes were taken from a battery that was visibly swollen

Accelerated Test Protocol

The battery packs consisted of six pairs of pouch batteries wired in series, and the batteries within each pair were wired in parallel. The packs were cycled using a profile provided by the BIC’s customer. Individual pouch cells in different wiring configurations were also cycled according to the customer’s profile.





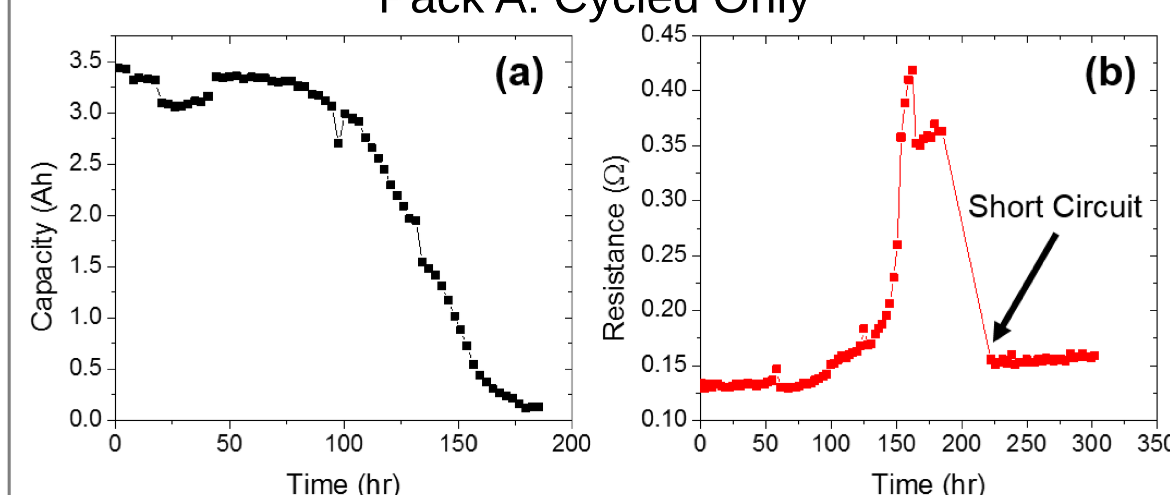
Battery charge/discharge cycle (~3.5 hrs)

Battery Pack Characterization

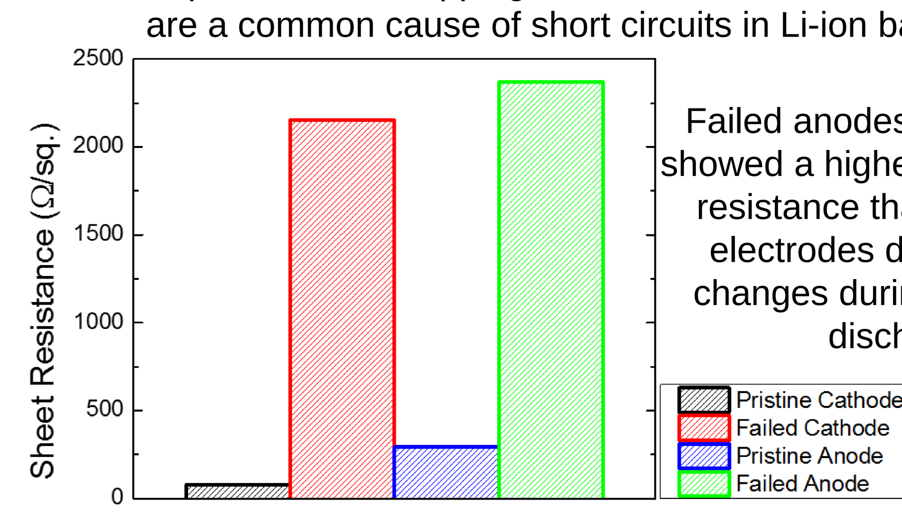
Resistance, voltage, temperature, and strain were monitored during cycling. Battery materials analysis included optical microscopy, SEM, EDS, XRD, and sheet resistance. ICP-MS is in progress.

Performance Degradation

Pack A: Cycled Only

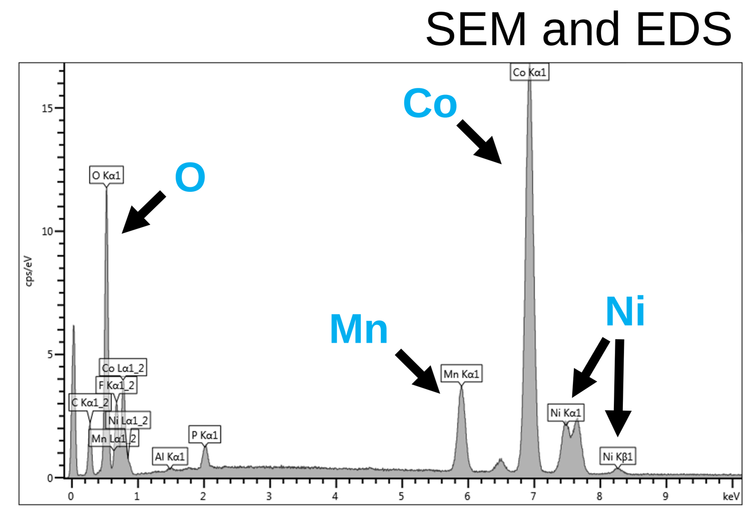


(a) Capacity fade and (b) corresponding resistance increase for a swollen battery pack. As the capacity decreased to zero, the resistance reached a peak before dropping due to a short circuit. Lithium dendrites are a common cause of short circuits in Li-ion batteries.

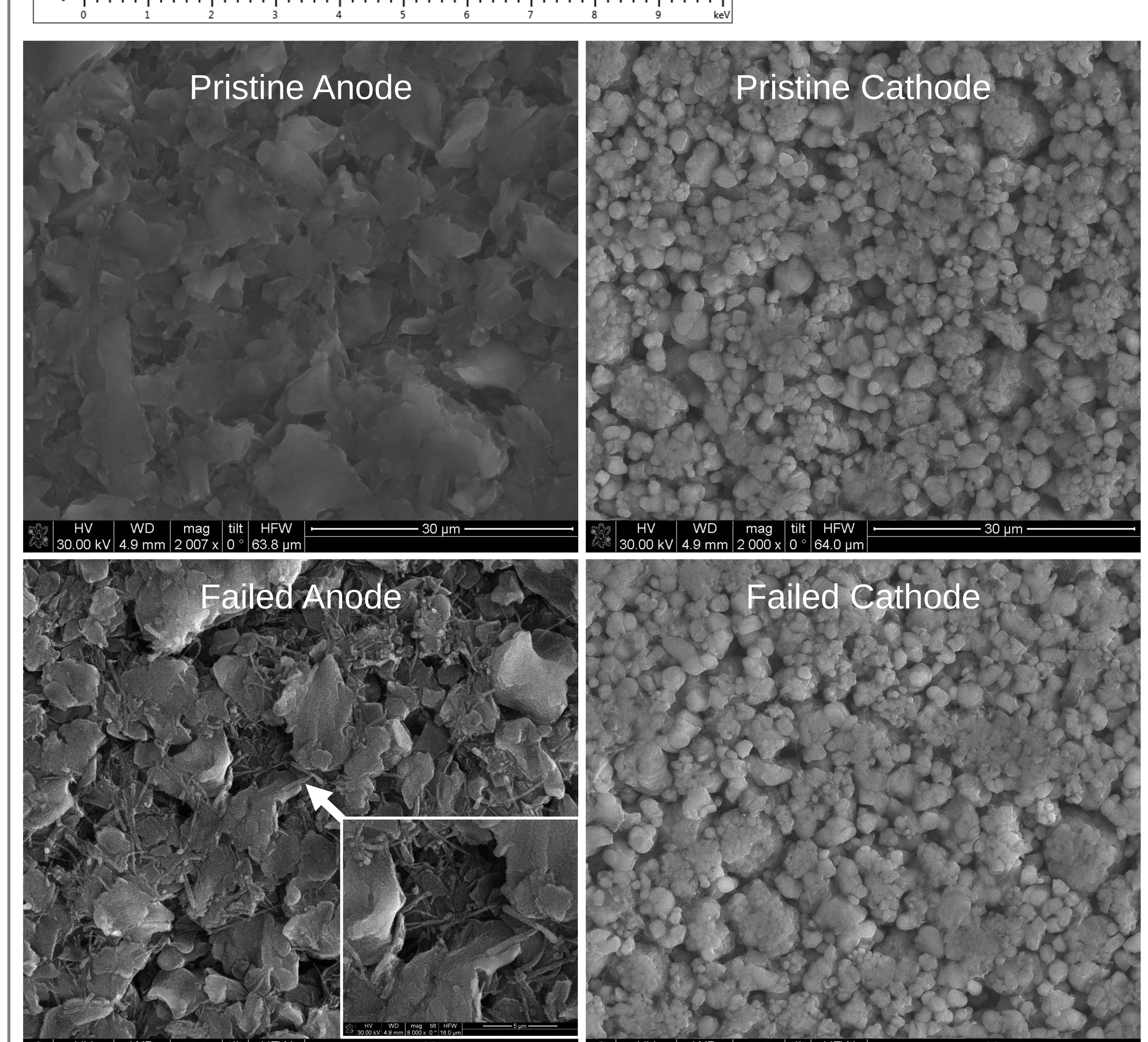


Failed anodes and cathodes showed a higher average sheet resistance than the pristine electrodes due to surface changes during charge and discharge.

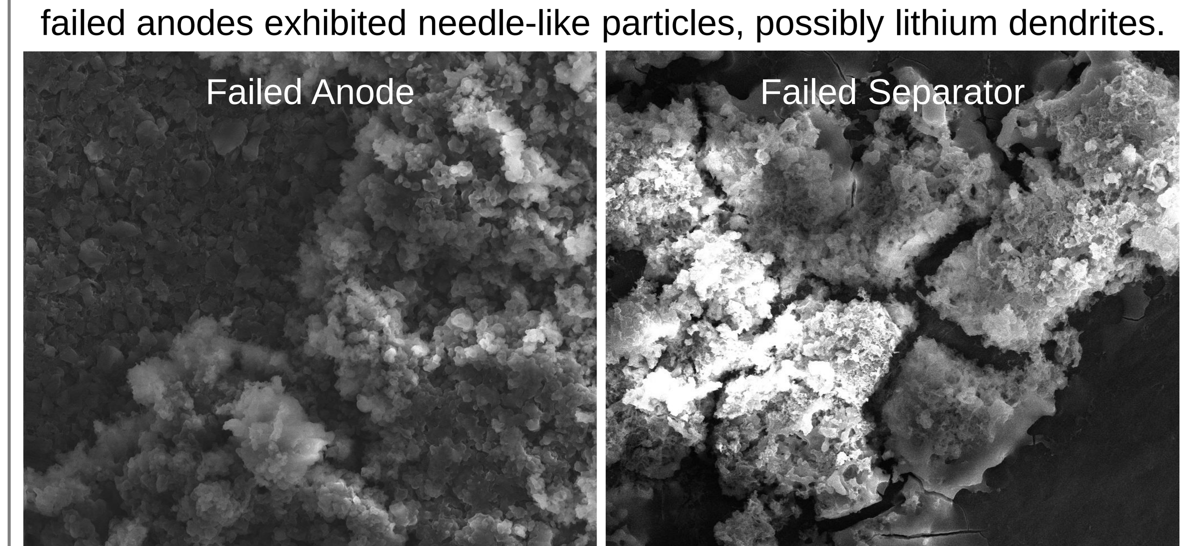
SEM and EDS



EDS suggests battery chemistry is **$LiNiMnCoO_2$**



Comparison of failed and pristine battery electrodes. No notable difference existed between the failed and pristine cathodes, but the failed anodes exhibited needle-like particles, possibly lithium dendrites.

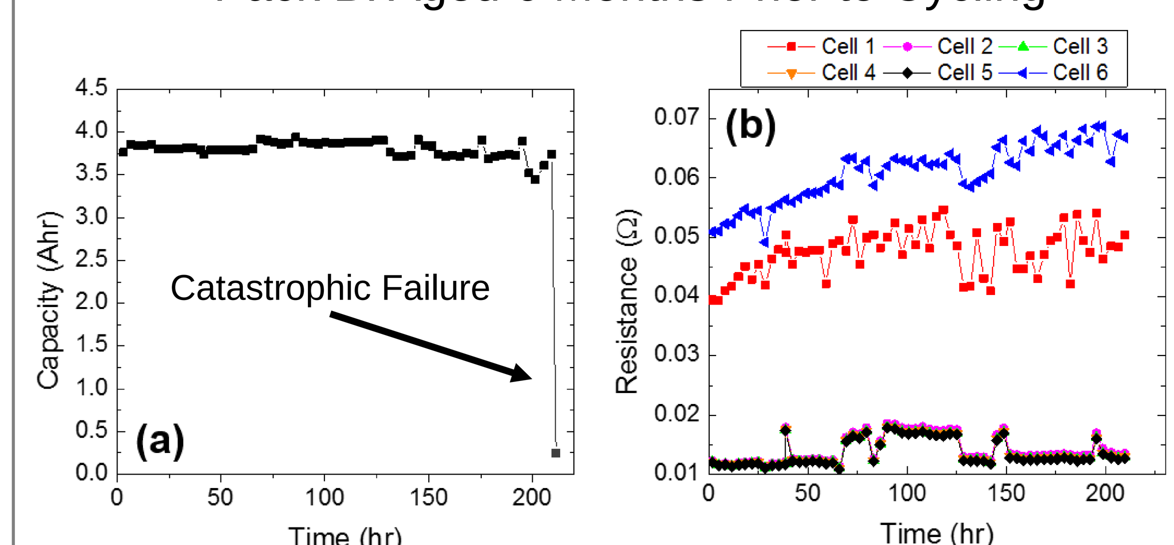


Failed anode and separator material contained clusters of oxide particles. EDS identified oxygen, fluorine, and phosphorous as the main components of these particles.

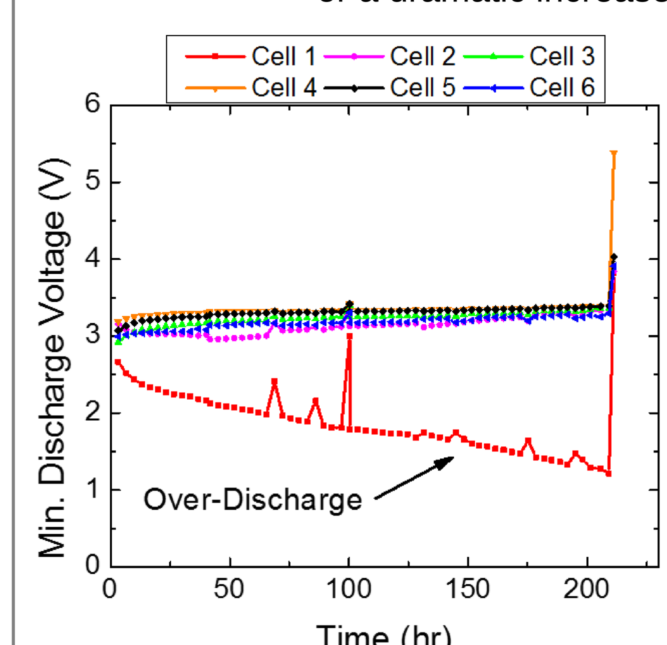
SEM and EDS results suggest that gradual battery failure is related to **electrolyte degradation** and/or **lithium dendrite growth** [1].

Catastrophic Failure

Pack B: Aged 6 Months Prior to Cycling



(a) Battery capacity and (b) corresponding resistance increase for a battery pack aged at 100% state of charge for six months before being cycled. Unlike the swollen pack, this battery did not show capacity fade or a dramatic increase in resistance.



Minimum discharge voltage for the six cell pairs on Pack B, which caught fire during testing. Cell 1 appeared to have been consistently over-discharged, likely contributing to the failure.

Over-discharge of a battery (discharge below 2.8 V) can cause **dissolution of the copper current collector** at the anode. As the battery is recharged, the dissolved copper can precipitate out of the electrolyte and aggregate into deposits, possibly **short-circuiting the battery** [2].

It is expected that a spark cause by a short circuit in Pack B caused the electrolyte to ignite.

Relationship of Failure to Charge/Discharge Profile

The charge profile imposes a current of 2.5 A on each pouch battery, which is about **30% higher than the maximum charge current recommended by the manufacturer.** Moreover, the charge takes place at an elevated temperature, which accelerates battery degradation. This was likely to be a factor in the failures of both Pack A and Pack B.

The duration and temperature at which Pack B was aged before being cycled also exceeded the manufacturer’s recommendation, possibly contributing to the sudden failure of the pack.

References

[1] Vetter, J. et al (2005). “Ageing Mechanisms in Lithium-Ion Batteries”, *J. Power Sources 147*
[2] Arora, P. et al. (1998). “Capacity Fade Mechanisms and Side Reactions in Lithium-Ion Batteries”. *J. Electrochem. Soc. 145* (10)

Recommendations

The charge rate for the battery packs should be decreased, and the minimum discharge voltages of each of the cell pairs should be periodically measured. Battery packs that consistently show discharge voltages below 2.8 V should be replaced. Finally, active cooling of the batteries during charging is recommended.