

Heterogeneous degradation of mechanically constrained lithium-ion cells

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Here we investigate the mechanisms by which the compressive mechanical stress that arises during operation of constrained lithium-ion cells affects long term capacity retention. The long term performance of constrained lithium-ion cells is important since lithium-ion cells typically operate in mechanically constrained environments. Examples of mechanical constraints are the containers of cylindrical and prismatic cells as well as the stack pressures applied to pouch cells during operation. In the absence of external constraints, lithium-ion cells are often constrained by their own geometry. For example, the wound structure of an electrode jelly roll acts as a constraint to electrode expansion.

Previously we constrained commercial pouch cells (LCO/C) with different initial stack pressures and monitored stress state and capacity during cycling. We found that the compressive stress within the cell generally increased with cycling such that the compressive stress after long term cycling is significantly higher than the initially applied stack pressure. Figure 1 shows the capacity of the cycled cells as a function of cycle number. Higher stress levels generally led to higher rates of capacity fade, although a slight constraint was found to be beneficial to long term performance compared with an unconstrained pouch cell. Here we present the results of a post mortem analysis in which the cells are disassembled and characterized.

We find that the capacity fade occurs as a result of cycleable lithium loss through irreversible lithium consumption by side reactions. This lithium loss is aggravated by mechanical stress, revealing a coupling between mechanical stress and chemical degradation. We observe the formation of solid surface films on the cycled cell anodes as seen in Figure 2. Cells cycled under higher levels of stress show higher amounts of film coverage. As seen in Figure 2, the solid films form in a periodic pattern along the face of the anodes such that they are aligned when the electrodes are in the wound configuration, further supporting the notion of a coupling between mechanics and chemistry. The capacity fade in the unconstrained cells is attributed to loss of contact between the electrodes and separator as a result of rippling of the originally flat electrode faces [1].

In general, the observed degradation is spatially non-uniform, suggesting the importance of non-uniformities in cell degradation. In addition to the spatially heterogeneous distributions of the observed surface films, we find localized pore closure in the separator [2-3]. The lithium content within the cycled anodes, seen in Figure 2, is also distributed in a spatially non-uniform manner after cycling, which we can observe visually by exploiting the color changes that occur with graphite staging [4]. We will discuss the origins of the observed mechanically mediated chemical degradation as well as the effects of mechanical stress on non-uniform cell operation.

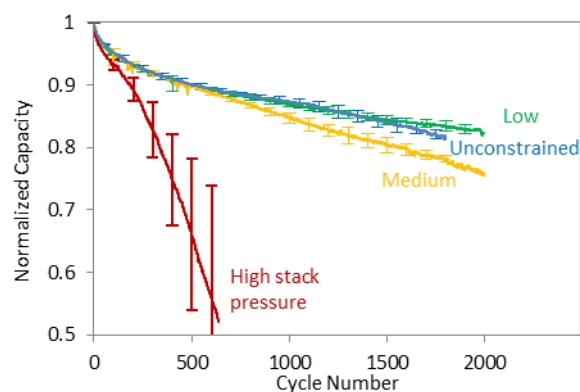


Figure 1. Capacity of constrained pouch cells during cycling. The cells are initially constrained with different initial stack pressures: low is 0.05 MPa, medium is 0.1 MPa, and high is 1.5 MPa. Higher stack pressures lead to higher rates of capacity fade.



Figure 2. Photographs of a pristine cell (left) and a cell cycled under an initial stack pressure of 0.1 MPa. Spatially non-uniform lithium content in the anode can be seen based on graphite coloration as well as the presence of localized surface films.

References

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