

Mechanistic observations from the aging of lithium-ion cells with layered-oxide positive electrodes

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High energy density lithium-ion batteries are needed for transportation applications in order to increase the driving range of vehicles on a single charge. Towards this end, electrochemical cells, containing lithium-bearing layered oxides in the positive electrode, are being cycled to increasingly higher voltages to increase energy density. Cell lifetimes are, however, affected by this cycling with performance degradation, which includes cell capacity fade and impedance rise, being greater at the higher voltages.

Our experiments, in cells with reference electrodes, indicate that the positive electrode is the main contributor to cell impedance rise, whereas the negative electrode is the main contributor to capacity fade.¹ *Cross-talk* between the electrodes contributes to these changes in performance during electrochemical cycling. For example, the dissolution of transition metals into the electrolyte from the positive (oxide) electrode and their subsequent deposition at the negative (graphite) electrode increases cell capacity fade; we have proposed mechanisms to explain the role of transition metals in accelerating capacity fade.²

In contrast, *cross-talk* appears to have a beneficial effect on cell impedance rise. Our experiments show that during cycling at elevated voltages, the impedance rise is lower for cells containing graphite-based negative electrode than for cells containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based negative electrodes cycled under comparable conditions.³ We postulate that gases (such as CO_2 , H_2 , etc.), generated during electrolyte oxidation at the high voltages of the positive electrode, play an important role. These gases are gradually depleted by reactions at the graphite electrode, but such reactions do not occur at the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode. The build-up of these reductive gases inside the cell affects the integrity of the positive electrode coating and also leads to structural modifications in the oxide particles, causing the observed impedance rise.

Various diagnostic techniques to determine and quantitate cell performance degradation will be highlighted during the presentation. Approaches to mitigate this performance degradation, including the use of electrode coatings and electrolyte additives, will be also be discussed.

References:

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- [2] J.A. Gilbert, I.A. Shkrob, D.P. Abraham, J. Electrochem. Soc. 164 (2017) A389-399.
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