

Lithium ion battery degradation mechanisms studied by on-line mass spectrometry, impedance, and *operando* optical emission spectroscopy

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To increase the energy density of lithium ion batteries, nickel-rich NCM ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ with $x+y+z=1$) and overlithiated so-called HE-NCM ($\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$; with $\text{M}=\text{Ni, Co, Mn}$) are being considered to be amongst the most promising cathode materials [1, 2]. However, at high states-of-charge (SOC), molecular oxygen is released from the surface of these materials, not only leading to a growth of the cathode impedance, but also to an enhancement of the oxidation of the electrolyte [3,4]. Based on these observations, we suggested that the overall oxidation of the electrolyte can be distinguished into a *chemical* oxidation mechanism triggered by the release of active oxygen at high SOC and into a purely *electrochemical* oxidation mechanism initiating at high potentials [5].

Using on-line electrochemical mass spectrometry (OEMS) [3-5] and impedance spectroscopy using a micro-reference electrode [6], we will deconvolute the mechanisms controlling the different electrolyte oxidation pathways on NCM and HE-NCM cathodes and quantify the associated impedance buildup at the cathode electrode. Furthermore, by means of *operando* emission spectroscopy we will show that the *chemical* electrolyte oxidation mechanism is triggered by the release of singlet oxygen from NCM and HE-NCM surfaces at high SOC. While the reason for the evolution of singlet oxygen is still unknown, it leads to electrolyte oxidation in a similar manner as was shown to occur when singlet oxygen is released during the charging of lithium-air cells [7,8].

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