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 (LiNiₓCoᵧMnₓO₂ with x+y+z=1) and overlithiated so-called HE-NCM (Li₁+xM₁-xO₂; with M=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].

References: