Aging mechanisms of C_6/NCM Li-ion batteries unraveled by non-destructive and postmortem methods

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The growing demand for sustainable energy storage devices intensively requires rechargeable lithium-ion batteries (LIBs) with higher specific capacity and stricter safety standards.[1] The layered ternary transition metal oxide (NMC) electrode system outperforms others and attracted much attention in both academia and industry.[2] Despite many merits, the NCM electrode system suffers from potential safety hazards, posing severe challenges to large-scale commercialization.[3] Thus, a profound understanding of the aging mechanisms of the NCM electrode system is vital for performance improvement.

In the present work, as an effective non-destructive method, the extrapolated electromotive force (EMF) curve is employed for determining the irreversible capacity losses (ΔQ_{ir}) of NCM LIBs under different aging conditions.[4, 5] Furthermore, the componence of solid-electrolyte-interphase (SEI) film on cycled cathode and anode surfaces is confirmed *via* X-ray photoelectron spectroscopy (XPS).

On the basis of EMF curves simulations, the ΔQ_{ir} of C_6/NMC532 batteries as the function of cycle time and cycle number is determined under three different aging temperatures (30°C, 45°C, 60°C). Two degradation regions, a logarithmic region (L-region) and an exponential region (E-region), have been identified for 30°C cycled battery, while E-region is absent for 45°C and 60°C cycled batteries. The results show that under 30°C aging temperature, the degradation of batteries is attributed to two mechanisms (Mechanism I, Mechanism II). Noteworthy, the effect of Mechanism II on battery degradation under lower temperature is significant, owing to the kinetic retardation and polarization increases. In addition, the different evolutions of ΔQ_{ir} with cycle number and time imply that these two parameters are independently influencing the development of ΔQ_{ir}, and both are crucial for degradation diagnosis. EMF derivative analyses are proposed as a non-destructive method to identify the degradation mechanism on individual electrodes elegantly. The evolutions of dV_{EMF}/dQ *vs* Q and dV_{EMF}/dQ *vs* V plots unravel the graphite aging mechanism under different temperatures.

The components of SEI and CEI on cycled anode and cathode are further analyzed *via* XPS measurements. On the anode surface, Ni, Mn species can be detected in SEI film, indicating the cathode dissolution induced by the detrimental effect of HF in the electrolyte. While on the cathode surface, chemical components, including LiF. LiCOOR, and transition metal fluoride (MeF_2) are found in CEI film. Therefore, combing the non-destructive and post-mortem analyses, the detailed aging mechanisms can be described systematically for C_6/NMC Li-ion batteries.

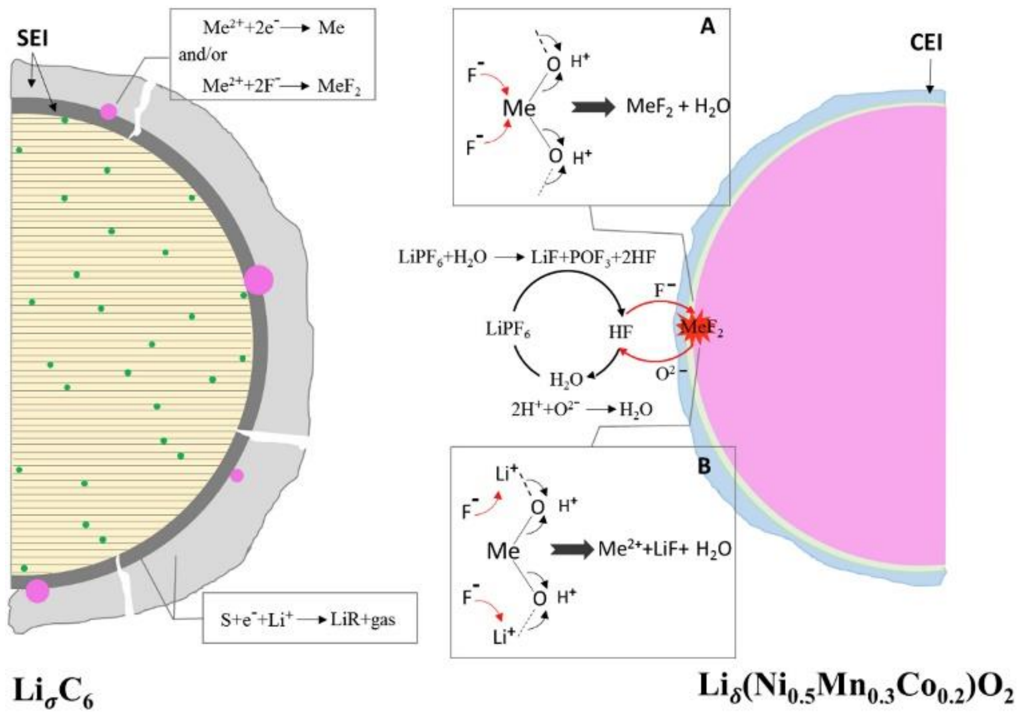

Figure 1. Schematic representation of the various ageing mechanisms of C_6/NMC Li-ion batteries.

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