Potential Dependence of Gas Evolution in 18650 Cylindrical Lithium-Ion Batteries Using In-Situ Raman Spectroscopy

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Low-cost, high-performance lithium-ion batteries (LIBs) are one of the main driving forces of industrial innovation in electric vehicles (EVs), mobile devices, and fixed energy storage systems (ESSs). The demand for high energy density has increased the electrode density and increased the cutoff voltage of LIBs above 4.3 V, which has raised serious concerns about their safety. In general, such evolved gases raise critical safety concerns because many of these gases are toxic, explosive, or highly flammable. Our study showed that the newly developed gas analysis setup was non-disruptive and highly reliable [1-2]. Along this line, herein, commercially available 18650 cylindrical cells were subjected to gas analysis using our specially-designed Raman analysis setup. To accelerate gas evolution, the staying potential was changed from 4.2 to 4.8 V up to 2000 h. During this measurement, an electrochemical analysis is conducted to evaluate cell performance. Gas evolution rates were determined by the aging time and the staying potential, resulting in a nonlinear partial-pressure-dependence as a function of the aging time. Initially, the evolution of carbon dioxide and carbon monoxide was significant. After potential-dependent onset times, hydrogen and methane generation increased suddenly. At low potential ranges of 4.2–4.4 V, mostly hydrogen gas was generated, whereas at high potential ranges (>4.6 V), methane becames dominant. Even at 4.4 V, importantly, the absolute accumulative H_2 gas pressure was >3 atm, raising the requirement to monitor such gas for better safety even under nominal operating conditions. Moreover, cumulative partial pressures of the detected gases exceeded the range 5–10 atm, which was associated with the staying potential. The electrochemical analysis of the aged LIBs showed that the capacity fade was accelerated by the increase in the staying potential while the resistances remained similar.

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