Thermal Reactions in Li-Ion Cells

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Abstract: The thermal stability and gas-generating reactions of Li-ion cells with intercalating carbon anodes and metal oxide cathodes were measured as a function of state-of-charge and temperature for two advanced cell chemistries. Two custom-designed 18650 cells (GEN1 and GEN2) were constructed for the Department of Energy (DOE) Advanced Technology Development (ATD) program, which aims to understand and mitigate the thermal runaway mechanisms in high-power cells for the hybrid electric vehicle program. The thermal reactivity of the cells and the cell components were measured along with the generated gas species.

Accelerating rate calorimetry (ARC) was used to measure cell thermal runaway of full cells as a function of state-of-charge (SOC) up to and beyond the cell vent temperature. Cell gases were collected from the vented cells or by puncturing the unvented cells and analyzed using gas chromatography (GC). Differential scanning calorimetry (DSC) was used to study the thermal reactivity of the individual components from disassembled cells. In addition, anode and cathode materials from post-mortem cells were obtained for measurement in sealed (bomb) capsules in the ARC. These measurements were performed to determine the individual material thermal decomposition profiles and the pressure profile from the gas generating reactions. Gases were collected for comparison with the full cell gases and analyzed by GC.

Thermal decomposition of the anode solid electrolyte interphase (SEI) layer initiated at temperatures below 80°C and contributed to the start of thermal runaway (Figure 1). The different anode carbon particle morphology used in the cell designs resulted in significant variations in the onset of thermal runaway in the GEN1 and GEN2 cells (Figure 2). The GEN2 MAG10 anode particles showed a flake morphology that was more difficult to passivate with SEI than was seen for the spherical GEN1 MCMB particles. ARC measurements of the individual electrode components in electrolyte indicated that strong exothermic reactions result from anode and cathode reactions with the electrolyte in the temperature range of 180°C to 220°C. This corresponds with the explosive decomposition seen for full cells during thermal ramps to these temperatures. Gas evolution in the cells began around 125°C and increased with increasing temperature. The major evolved gases were CO2, CO, H2, and C2H4 as shown in Figure 3. These gas species were very similar to those determined just from the thermal decomposition of the electrolyte. Gas evolution from the cells and individual cell components indicated that gas evolution of the EC:EMC(3:7)/LiPF6 electrolyte was the major source of the gas species.

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