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Diagnostic examination of thermally abused high-power lithium-ion cells

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Abstract

The inherent thermal instability of lithium-ion cells is a significant impediment to their widespread commercialization for hybrid-electric vehicle applications. Cells containing conventional organic electrolyte-based chemistries are prone to thermal runaway at temperatures around 180 °C. We conducted accelerating rate calorimetry measurements on high-power 18650-type lithium-ion cells in an effort to decipher the sequence of events leading to thermal runaway. In addition, electrode and separator samples harvested from a cell that was heated to 150 °C then air-quenched to room temperature were examined by microscopy, spectroscopy, and diffraction techniques. Self-heating of the cell began at 84 °C. The gases generated in the cell included CO_2 and CO, and smaller quantities of H_2, C_2H_4, CH_4, and C_2H_6. The main changes on cell heating to 150 °C were observed on the anode surface, which was covered by a thick layer of surface deposits that included LiF and inorganic and organo-phosphate compounds. The sources of gas generation and the mechanisms leading to the formation of compounds observed on the electrode surfaces are discussed.

Keywords: Accelerating rate calorimetry; X-ray photoelectron spectroscopy; Raman spectroscopy; Gas analysis; $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$

1. Introduction

Cells based on Li-ion chemistries offer significant improvements in specific energy and specific power density over standard nickel metal-hydride and lead-acid cells. Li-ion rechargeable cells are now the standard for mobile communication and computing applications. However, these chemistries have not yet penetrated the commercial market for large-scale uses such as in hybrid-electric vehicles. The most significant impediment to the use of these chemistries is the inherent thermal instability of cell components and the flammability of the organic-based electrolytes. The poor abuse tolerance behavior of these cells becomes even more critical for modules based on large numbers of relatively high-capacity cells. The US Department of Energy (DOE) is addressing this problem through the Advanced Technology Development (ATD) effort as part of the FreedomCAR and Vehicle Technologies Program [1]. The ATD program is a cooperative research effort of several US National Laboratories to advance development and characterization of materials in support of battery manufacturers and the automotive industry.

The thermal abuse response of Li-ion cells has been studied at both the component and cell levels using the calorimetric techniques of accelerating rate calorimetry (ARC) and differential rate calorimetry (DSC) [2–6]. These data have shown that the thermal runaway process can be described as occurring in three stages. In Stage 1, low-rate reactions are initiated at the anode around 90 °C (see Fig. 1a and b) followed by a steadily increasing reaction rate. Significant solid electrolyte interphase (SEI) layer breakdown occurs by 120 °C, which leads to electrolyte reduction at the exposed lithiated graphite anode. In Stage 2, reactions are initiated at the cathode around 140–160 °C, depending on the composition of the active (oxide) material. Stage 3 reactions are characterized by high-rate runaway (peak rates >100 °C min^{-1}) and usually occur at or above 180 °C. Stage 3 reactions are primarily the result of oxygen generation from cathode decomposition and subsequent oxidation of the electrolyte [7,8].

In this article, in an effort to decipher the sequence of events leading to thermal runaway, we present ARC measurements conducted on high-power 18650-type lithium-ion cells. The gases generated during these experiments were analyzed by gas

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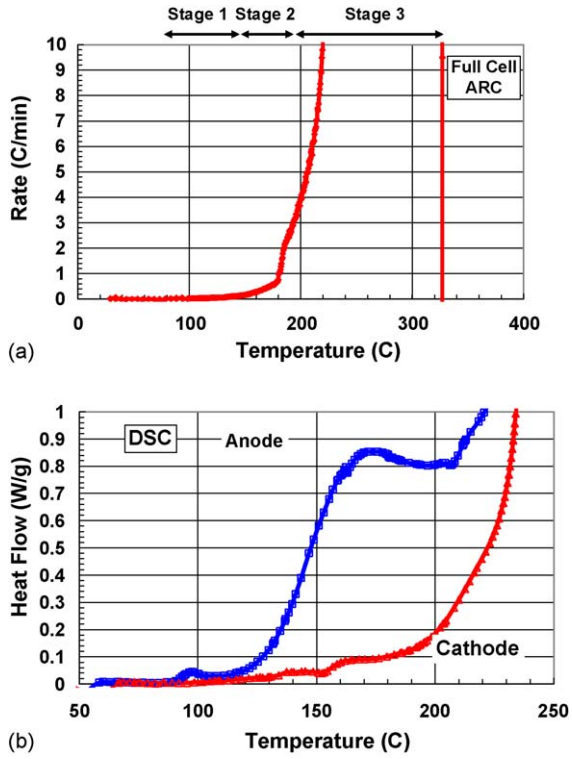

Fig. 1. Calorimetry profiles (at 100% SOC) for an 18650 cell with Mag-10 graphite anode and a $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode in 1.2 M EC:EMC (3:7 by wt.) electrolyte. (a) ARC profile showing the three stages of thermal runaway and (b) DSC profile showing the anode/cathode onset reactions.

chromatography/mass spectroscopy (GC/MS). These data are complemented by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) results obtained on electrodes and separators harvested from a cell that was heated to 150 °C then air-quenched to room temperature (RT) to preserve its thermal history. We discuss the sources of gas generation and possible mechanisms leading to the formation of compounds observed on the electrode surfaces.

2. Experimental

2.1. Cell chemistry and initial conditioning

The ∼1 Ah 18650-type cells used in this study (henceforth referred to as Gen2 cells) were manufactured by Quallion LLC (Quallion LLC, P.O. Box 923127, Sylmar, CA 91392-3127, USA). The positive electrode (cathode) contained a 35 μm coating of 84 wt.% $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, 4 wt.% SFG-6 graphite, 4 wt.% acetylene black, and 8 wt.% polyvinylidene fluoride (PVDF) binder on a 30-μm-thick Al foil; the active material (oxide) loading density was 8 mg $(cm^2)^{-1}$. The negative electrode (anode) contained a 35 μm coating of 92 wt.% MAG-10 carbon and 8 wt.% PVDF binder on an 18-μm-thick Cu foil; the active material (graphite) loading density was 4.9 mg $(cm^2)^{-1}$. The electrolyte contained 1.2 M $LiPF_6$ in an ethylene carbonate:ethyl methyl carbonate (EC:EMC, 3:7 by wt.) solvent. A 25-μm-thick Celgard 2325 separator provided electronic isolation between the electrodes, while allowing the conduction of lithium ions. Initial characterization tests on the cells included five C/1 cycles between 3.0 and 4.1 V and a C/25 cycle, which confirmed that the cell capacity was ∼1 Ah. The cells were then charged to 100% state of charge (SOC) or 4.1 V for subsequent experiments. This voltage is used in the ATD program as the maximum state of charge limit in order to enhance lifetime of the cells during the extended periods of use required for hybrid electric vehicles.

2.2. ARC measurements and cell disassembly

ARC was used to measure the initial thermal response of the cells and to take the cells to a maximum reaction temperature under controlled conditions. The ARC apparatus (Arthur D. Little Model 2000) used a specially designed holder for the 18650 cell that allowed full containment of all generated gases while maintaining good thermal contact with the cell. Monitoring the gas pressure allowed calculation of the evolved gas volume; gas samples were obtained after the run for later GC/MS study. Some of the cells were heated to a maximum temperature of 150 or 160 °C, then cooled rapidly with high flow-rate compressed air. These quenched cells were transferred to an argon glove box and disassembled in the still-charged state. Most of the cathode coating peeled off the Al current collector and adhered to the separator during disassembly, whereas the anode coating remained on the Cu current collector. The cell components were then stored in Ar-bearing hermetic containers until further diagnostic examination.

2.3. Materials examination

Several tools were used to determine the structural, morphological, and compositional changes of the cell components that resulted from heating to elevated temperatures. Most samples were examined "as-harvested," i.e., without prior solvent washing. SEM was conducted on a high-resolution Hitachi S-4700 microscope with a field emission electron source. The samples were briefly exposed to air before insertion into the analysis chamber. X-ray diffraction (XRD) data were collected on a Philips powder diffractometer using Cu-Kα radiation for two-theta values of 20–80°. The samples were examined in a specially designed, hermetically sealed container to avoid any incidental exposure to air.

A LabRam (ISA Groupe Horiba) Raman microscope system was used to analyze the surface structure and composition of the cathode and anode. The excitation source was an internal He–Ne (632 nm) 10 mW laser. The power of the laser beam was adjusted to 0.1 mW. The diameter of the laser beam at the sample was ∼1.2 μm. Electrode samples were examined in an airtight optical cell that was assembled in a He-filled glove box prior to the transfer to the Raman microscope. Individual Raman spectra were processed and deconvoluted using the PeakFit 4.0 commercial software package.

XPS spectra were obtained on a Kratos AXIS Ultra spectrometer under ultrahigh vacuum (10^{-9} Torr) conditions. To avoid air exposure, the electrode pieces were mounted on the XPS sample holder in an Ar glove box (<1 ppm H_2O, <5 ppm O_2) and