SAND2000-1734

4. Diagnostics

Abuse Tolerance

A. Development of an Abuse Tolerance Test Protocol with Continuous Gas Monitoring

Chris Crafts, Theodore Borek, Rudolph G. Jungst, Daniel H. Doughty, and Curtis Mowry
Mail Stop –0613, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185
Contact: Chris Crafts (505) 844-5610, fax: (505) 844-5924: email: cccraft@sandia.gov

Objective

- Develop comparative methods for studying the tolerance of lithium-ion cells to thermal abuse

Approach

- Develop techniques to expose 18650 cells to thermal extremes in a controlled manner and a safe environment. Do this in air while recording video as well as V, I, and T.
- Develop gas chromatographic and mass spectrographic methods to monitor emitted gases as 18650 cells are exposed to thermal extremes.
- Develop the above GC/TCD, GC/FID, and RGA/MS methods as supportive methods, paralleling the ARC, microcalorimetric, and DSC thermal tests done on 18650 cells and parts.

Accomplishments

- Thermal abuse tests done on Gen 1 cells in air showed a lower onset of thermal runaway and an increased severity of the event, with increased cell state-of-charge. At a 1°C/min heat rate, these events occurred near and above 200C.
- Gen 1 thermal abuse tests as a function of SOC were repeated in a safety bomb under a flow of He gas. CO_2, CO, CH_4, and residual DEC solvent were identified as the major emitted gases during thermal runaway.

Future Directions

- Thermal abuse tests on Gen 2 cells in air to look for improved abuse tolerance.
- Thermal abuse tests on Gen 2 cells under He to qualify and quantify by GC/TCD, GC/FID, and RGA/MS the continuously emitted gases.
- Identify hazardous gas products and recommend changes to further increase the thermal abuse tolerance of lithium-ion cells.

The primary objective of this project has been to develop and demonstrate experimental methods for studying the thermal abuse tolerance of Li-Ion, 18650 cells. This led in the first year of the program to the development of a thermal abuse method in which an 18650 cell was placed in a custom-made Cu block and observed while being heated at 1°C/minute in air to 200C. Both Sony and Gen 1 18650 cells have been tested this way (e.g. Figure 1). These remotely observed and recorded results, as visuals, support the other findings on the relative stabilities of Li-ion cells and their parts seen through Sandia microcalorimetry, Accelerating Rate Calorimetry (ARC), and Differential Scanning Calorimetry (DSC). In this, the second year of the program, DOE has directed the Sandia R&D Team to concentrate more on understanding the basic changes in Li-ion chemistry during thermal abuse.

To support this DOE redirection, an enhanced effort by Sandian Pete Roth is under way. This effort, employing microcalorimetry, ARC, and DSC on whole cells and prospective cell parts, is reported separately in this volume. The remainder of this passage explains the augmentation of the Cu block heating test with a test to continuously monitor the gases vented by the 18650 cell during thermal runaway.

Whole cell ARC testing has shown itself to be an excellent way to monitor self-heating in 18650 cells from room temperature to 200C. However, introducing a He gas flow through the ARC apparatus changes its heat flow parameters, and makes the results suspect. Using a helium gas flow around a cell is desirable as helium gas is non-reactive, and can be readily taken into a gas chromatograph (GC) or mass spectrometer (MS) to show the nature of vented gases, continuously, as they are evolved. By moving a cylindrical Cu block apparatus into a sealed Parr bomb, Sandia has been able to monitor an ARC-like heating event, and map the gases evolved.

The overall test setup is depicted in **Figure 2.** A helium flow of 610 cc/min was maintained around Gen 1 Li-ion cells which were heated at 1°C/min from room temperature to 200°C using a cylindrical, resistively-heated block isolated thermally from the bomb. Cell temperature and voltage were monitored as in air tests.

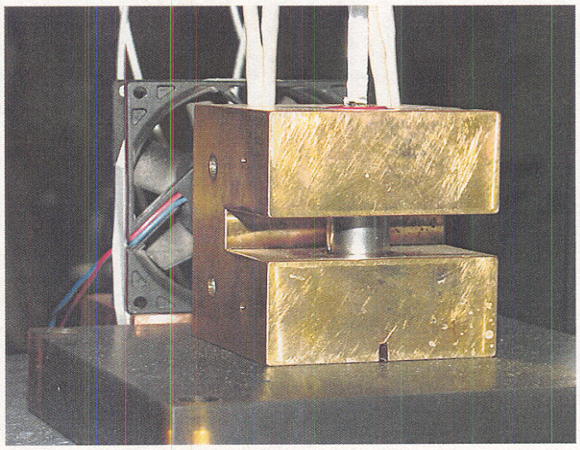

Figure 1: Cu block for heating 18650 cells in air.

Inert atmosphere thermal abuse tests were conducted in a 2 l Parr bomb (Parr Inst. Co., Moline, IL. MWP 1900). Evolved gases were sampled continuously out of the bomb exhaust loop with a Vacuum Technologies Inc. Aerovac residual gas analyzer (RGA) producing a full spectrum every 1.6 minutes, and every 10 minutes by a Varian 3400 dual column gas chromatograph (GC) equipped with thermal conductivity (TCD) and flame ionization detectors (FID). The TCD is useful for fixed gases and lightweight hydrocarbons while the FID is for general volatile organic species.

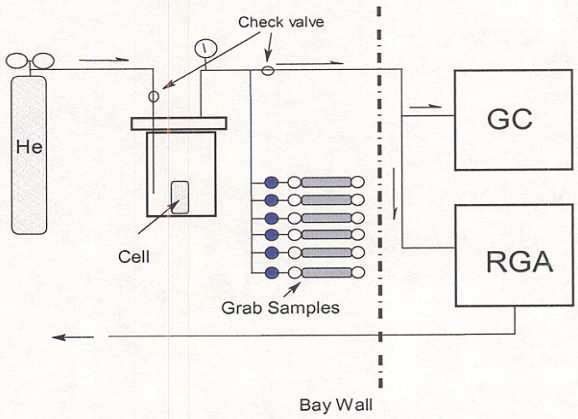

Figure 2: Parr Bomb Test Apparatus for Inert Atmosphere Thermal Abuse Tests.

Additionally, six remotely actuated, evacuated 150-cc cylinders were positioned in parallel to the bomb exhaust line to capture or "grab" gas samples at different moments in the test for further GC and GC/mass spectrometry analyses.

Results

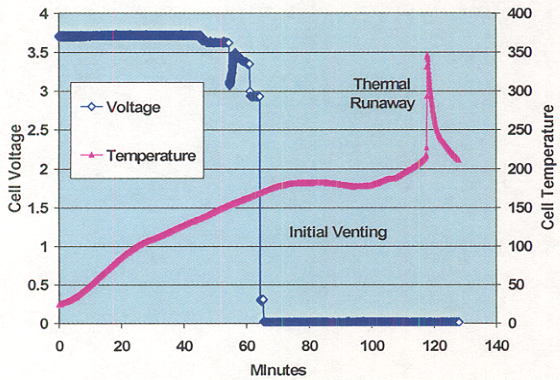

Figure 3: Heat Test on Gen I Cell at 20% SOC in air.

Thermal abuse tests in air

Thermal abuse testing as a function of SOC is reported here on Gen 1 cells where duplicate tests were run at 20, 50, and 80% SOC (example, see **Figure 3**). For Gen 1 cells, onset of thermal runaway occurred at a lower temperature and was more severe at higher cell SOC. Cells at lower SOC still fumed and were probably ignitable, but they did not autoignite, and they remained intact. Onset of thermal runaway by this method ranged between 190°C at 80% SOC and 225°C at 20% SOC.

Thermal abuse tests under inert atmosphere.

The GC and RGA instrument configuration permits the real-time observation of gases vented from the cell as a function of temperature. The short duty time of the RGA permits fast evaluation of evolved gases. The GC duty cycle is slower (12 minutes), but will separate and analyze products that have similar mass, e.g., mass 28 species CO, N_2, and C_2H_4. Using this apparatus, it was possible to observe different gas evolution events during heating. A cascade plot of the fixed gas GC(TCD) results on a Gen 1 cell is shown in **Figure 4.** There was an initial cell-venting event that may be observed, followed by a major cell venting when thermal runaway occurred. **Figure 5** shows a y-scale enlargement of the initial cell venting data. The organic GC(FID) results also showed the initial and major venting occurrences. One organic GC chromatogram is shown in **Figure 6**. There were many organic gas products, the principal species observed being methane, ethylene, ethane, and propylene. Higher organic C_4 and C_5 compounds were also observed.

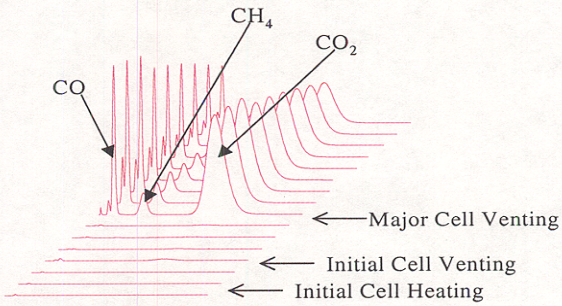

Figure 4: Fixed Gas GC Results. Gen 1 cell at 80% SOC.

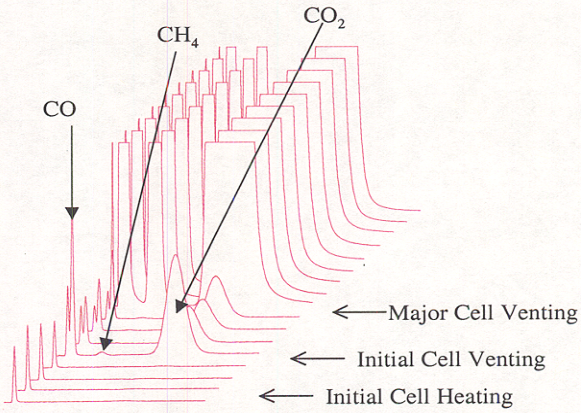

Figure 5: Enlargement of Initial Vent, Fixed Gas GC Results. Gen 1 cell at 80% SOC.

Several mass spectral traces collected during the initial and major vent occurrences are shown in **Figure 7**. Note the scaling factor for the y-axis of each plot. The increases in magnitude, during venting, of peaks attributable to hydrogen (mass 2), carbon monoxide (mass 28), and carbon dioxide (mass 44) were clearly observed. The grab

samples collected during the thermal abuse test were examined separately to complement the real-time gas data. Grab samples collected during the initial venting (Grab 1 through 3) and major venting (Grab 4 through 6) showed dramatically different amounts and inventory of gases, as seen **Figure 8**.

The grab sample analysis confirms the presence of hydrogen gas during the venting episodes for the cell. Mass spectrometry on the grab samples (not shown) re-affirmed the presence of 7.5% to 8.6% hydrogen in addition to indicating the reported product gases shown in **Figure 8**. The balance of the gas in the grab samples was helium from the bomb atmosphere. Fourier transform – mass spectrometry analysis of the grab samples shows a species of mass 39 (F_2H^-) in the negative ion mode; that datum, and the RGA signal at mass 20, suggest the presence of hydrogen fluoride. The presence of this species will be confirmed in later reactive-gas trapping experiments. **Figure 8** does not show hydrogen as He carrier GC with TCD detection does not work for that gas.

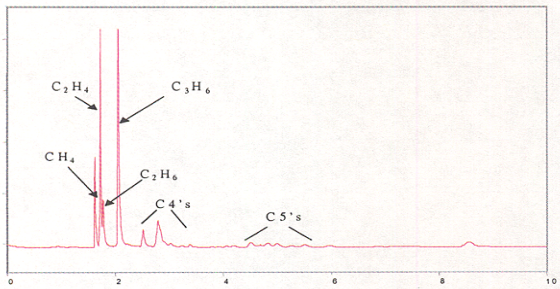

Figure 6: Thermal Abuse Organic Gas Chromatogram, mid-test. Gen 1 cell at 80% SOC. DEC elutes at 12 minutes.

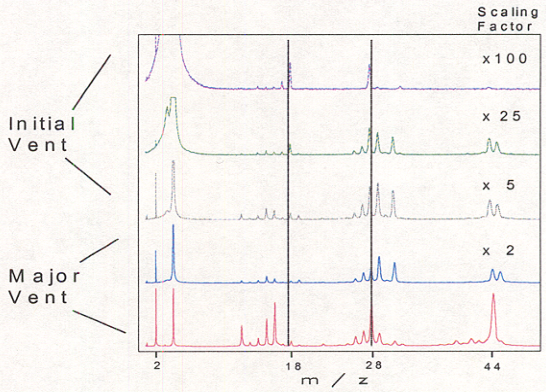

Figure 7: Thermal Abuse MS scans during venting of a Gen 1 cell at 80% SOC.

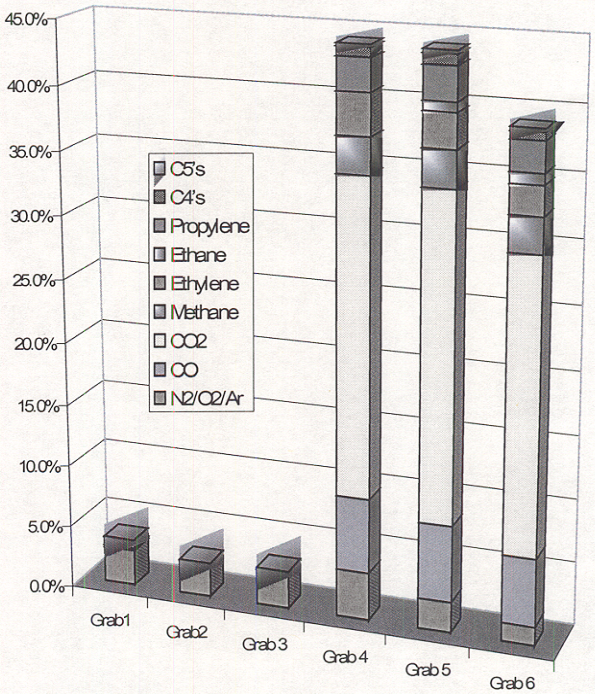

Figure 8: Grab Sample Gas Analysis.

Future Directions

The identification of evolved gases by the shown methods works well. Full quantification

of the identified gases will require the inclusion of mass flow controllers into the experimental set up, and is planned. It is not clear at this time which gases come from the destruction of the SEI layers at the electrodes and which come from additional reaction of the electrolyte solvents at the time of cell runaway. Joint studies with other ATD labs with solvents outside of built cells or in half cells will clarify some of these issues. Since the Gen 2 electrolyte composition is different, there is need for more activity in this area, in any case. The important role played by $LiPF_6$ in the maturation of SEI surfaces and in SEI breakup awaits exploration by LC/MS. Reactive gas trapping experiments will be carried out to further investigate the presence of HF.

Acknowledgment

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