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Calorimetric Study of Thermal Performance and Abuse Tolerance in Li-Ion Cells

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Objectives

- Identify chemical mechanisms leading to cell thermal instability and thermal runaway.
- Develop and demonstrate calorimetric methods useable in the identification of construction factors or chemical constituents leading to reduced thermal tolerance, reduced thermal stability, or reduced operational lifetime in Li-ion cells.
- Determine the effects of aging on cell thermal stability.
- Develop a knowledge base of cell thermal properties leading to improved cell designs.

Approach

- Test whole 18650 size cells by the method of Accelerating Rate Calorimetry (ARC) to determine cell properties leading to cell thermal runaway.
- Test whole 18650 size cells under low to moderate temperature by Isothermal Microcalorimetry to measure long-term thermal reaction rates.
- Measure the thermal inter-reactivity of fresh cell solvents, conductive salts, and fresh/aged cell electrodes recovered from disassembled test cells by using Differential Scanning Calorimetry (DSC).
- Determine thermal response of whole cells from measurements of the reactivity and interactions between cell components leading to improved cell designs.

Accomplishments

- Completed ARC measurements of fresh GEN1 cells from 0% to 100% state-of-charge (SOC) showing that accelerated self-heating only occurs for SOC greater than 50%. Demonstrated the presence of two reaction temperature regimes: a non-accelerating region below 70°C and an accelerating region above 80°C. Both regimes show increased activity with increasing SOC.
- Demonstrated by ARC measurements of aged/cycled GEN1 cells that aging/cycling completes low-temperature reactions seen in fresh cells, thus raising the onset temperature for thermal runaway. Showed that reactions that do occur start above 100°C and are abrupt followed by repassivation.
- Demonstrated by isothermal microcalorimetry that the low-temperature heat generating reactions do not depend on electrical charge/discharge

cycling but are dependent only on temperature, SOC and time at temperature.

- Performed extensive DSC thermal characterization of GEN1 cell anodes, cathodes and electrolyte for disassembled cells that had undergone various aging/cycling tests at different SOC. Determined reaction and decomposition regions for SEI layers, electrolyte, binder and active materials.

Future Directions

- Perform gas analysis of decomposition products of individual cell components using simultaneous TGA/FTIR.
- Perform ARC pressurized cell (bomb) tests of individual cell components.
- Perform calorimetric characterization of GEN2 cells and cell components.

The use of high-power Li-ion cells in hybrid electric vehicles is determined not only by the electrical performance of the cells, but by the inherent safety and stability of the cells under normal and abusive conditions. The thermal response of the cells is determined by the intrinsic thermal reactivity of the cell components and the thermal interactions in the full cell configuration. The purpose of this study is to identify the thermal response of these constituent cell materials, their contribution to the overall cell thermal performance and the effects of aging on this behavior. Calorimetric techniques were used as a sensitive measure of these thermophysical properties.

ARC Analysis:

ARC allows determination of adiabatic cell response to increasing temperature and thus measures the onset and development of thermal runaway under controlled conditions. ARC runs were performed on GEN1 cells at several SOCs while monitoring the cell voltages, as shown in Figure 1. The heating rate of the cells showed a strong SOC dependence. The cells with 50% or lower SOC showed no accelerating heating, only transient heating spikes, while the cells with higher SOC showed accelerating heating above 75°C. A low-temperature constant heating rate region was observed whose onset temperature decreased with increasing SOC. This region was separated from the accelerating heat region by about 10°C. Cell voltages dropped abruptly near 130°C with a corresponding dip in the cell heating rate. These results are due to cell venting and also due to separator melt. These GEN1 cells show greater thermal stability than the commercial Sony cells. This stability may result from differences in mechanical construction rather than intrinsic thermal behavior since the GEN1 anodes have been shown by DSC to behave similarly to the Sony anodes and the anodes are the initial heat source for thermal runaway.

Microcalorimetry Analysis:

The low temperature reactions observed during the ARC runs were monitored under more controlled conditions in the isothermal microcalorimeter. Cells were measured at several SOCs at 25°C and 60°C. Previously, we have shown that the cells exhibit strongly increased heat output with increasing temperature consistent with the behavior observed during both DSC and ARC measurements. However, at these lower temperatures GEN1 cells showed much greater heat output compared to the Sony cells. The heat output decayed following a power-law dependence. Interruption of the microcalorimetry measurements for charge/discharge cycling did not change the thermal output for a given SOC as shown in Figure 2. The cells were removed, electrically cycled and set to a different SOC. After measurement at the new SOC, the cells were returned to the original value. The cells resumed their thermal decay profile from the time of the interruption. This behavior shows that the heat output measured in the microcalorimeter is not the result of internal equilibration or residual heat decay from cycling. This heat output most likely results from low-rate decomposition and reformation of the SEI layer that has been previously measured by DSC. Heat output will also result from oxidation and reduction reactions of the electrolyte, which can impact the cell lifetime and capacity. The differences in reactivity between the Sony and GEN1 cells may result from the different solvents, differences in the morphology of the intercalating carbons and different reactivity of the different metal oxide cathodes. It has been shown that the GEN1 $LiNi_{0.8}Co_{0.2}O_2$ cathodes are more thermally active than the Sony $LiCoO_2$ cathodes, especially at higher SOC.

DSC Analysis:

Full cells that had been electrically cycled were disassembled and the electrodes measured up to 400°C in sealed Al pans. The data for the anodes from both Sony and GEN1 cells (50% SOC), shown in Figure 3, exhibited very similar behavior as expected since they have similar intercalating carbon compositions. A low-temperature region from about 100°C-200°C shows an exothermic reaction that has been found to involve SEI decomposition from a metastable species formed during initial cycling to more stable inorganic reaction products followed by further electrolyte reduction. This reaction has been seen to start as low as 80°C. The exact temperature range of these reactions depends on the particular solvent and salt species used for the electrolyte. The exothermic SEI reactions dominated the low-temperature response and were somewhat higher for the material from the GEN1 cells.

The DSC data for the GEN1 cathodes (50% SOC) are shown in Figure 4 along with data for the Sony cathodes. The $Li_xNi_{0.8}Co_{0.2}O_2$ cathodes from the GEN1 cells were markedly more exothermic than the Li_xCoO_2 Sony cathodes at similar SOC and the reactions initiated at slightly lower temperature. Some low-level exothermic reactions were observed in the 100°C-200°C range. These thermal signatures are similar to those seen for the anode SEI but much lower in magnitude. These reactions can possibly result from the reaction of a cathode SEI layer that has been observed by other techniques.

Cell Aging Effects:

The effects of aging at elevated temperatures were measured by performing ARC runs of thermally aged Sony and GEN1 cells. Figure 5 shows the results for the Sony cells which had been aged for 6 months/25°C, 11 days/60°C and 6 weeks/70°C. The cells showed less low-temperature reactivity with increased aging. All cells were measured at 100% SOC. The data show that aging resulted in loss of the low-temperature heat output with increasing time and temperature. The onset temperature of sustained heat output increased with increased time/temperature aging. These measurements suggest that the SEI layer is undergoing partial conversion from the metastable species to the stable inorganic species even at these low temperatures. The majority of this conversion takes place relatively quickly (less than two weeks) at 60°C since little further change was noticed for the 70°C/6 week cell. The sudden increase in self-heating in the 100°C-110°C range suggests that the remaining SEI layer undergoes rapid conversion followed by further reaction of the lithiated anode with the electrolyte with increasing temperature. This rapid increase corresponds closely with the onset of the exothermic peak observed by DSC for charged anodes removed from full cells.

A GEN1 cell was aged for 4 weeks at 60°C. The ARC run (Figure 6) showed no thermal output below 125°C. Two abrupt increases in heating that quickly decayed below the ARC low-limit threshold were observed above 125°C. These GEN1 cells apparently form a converted SEI layer at low temperatures which acts like a brittle passivation layer. This layer can break down, exposing the Li-intercalated carbon followed by a rapid reaction process probably involving reduction of the electrolyte to form a new layer. The aged GEN1 cells thus show greater thermal stability at low temperatures but may exhibit abrupt heating if forced to higher temperatures above 125°C, which can occur under abusive conditions.

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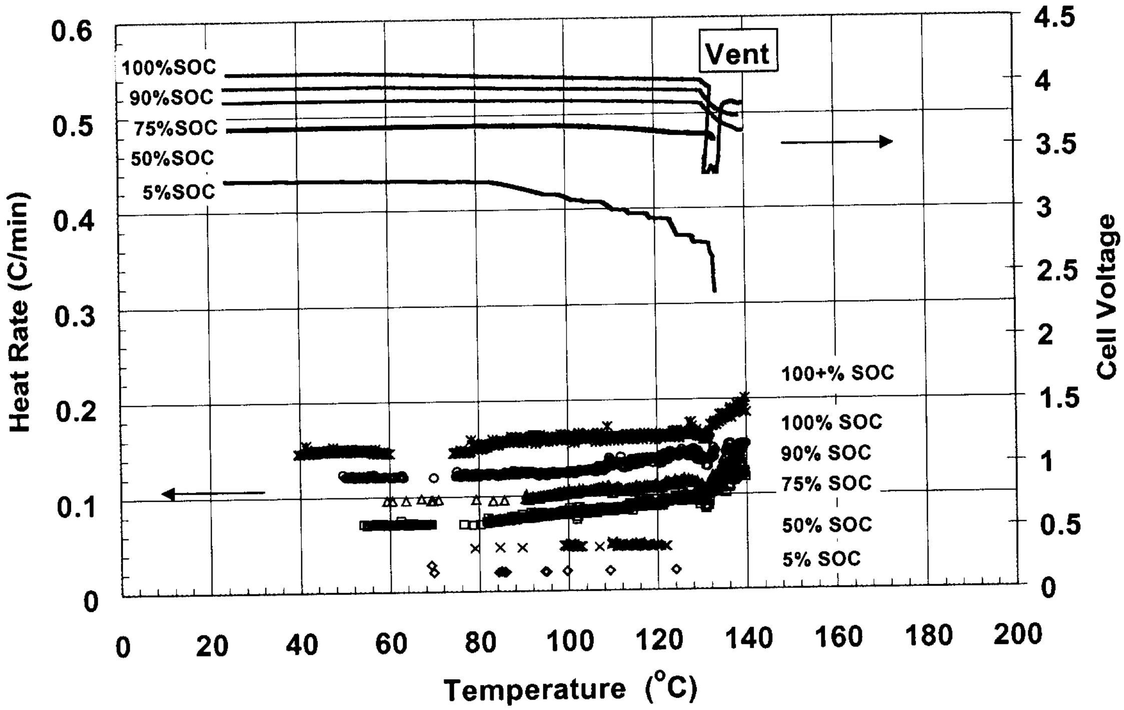

Figure 1. ARC runs of GEN1 cells at increasing SOC (vertically offset).

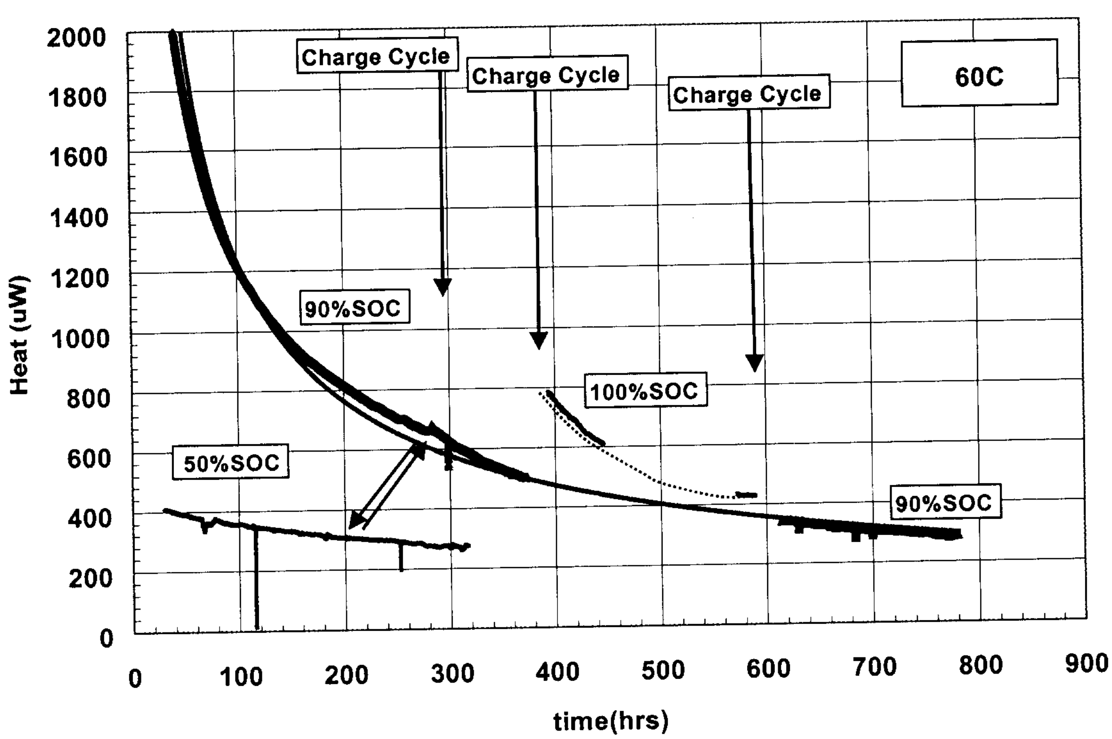

Figure 2. Microcalorimetry of GEN1 cell at 60C showing effect of changing SOC.

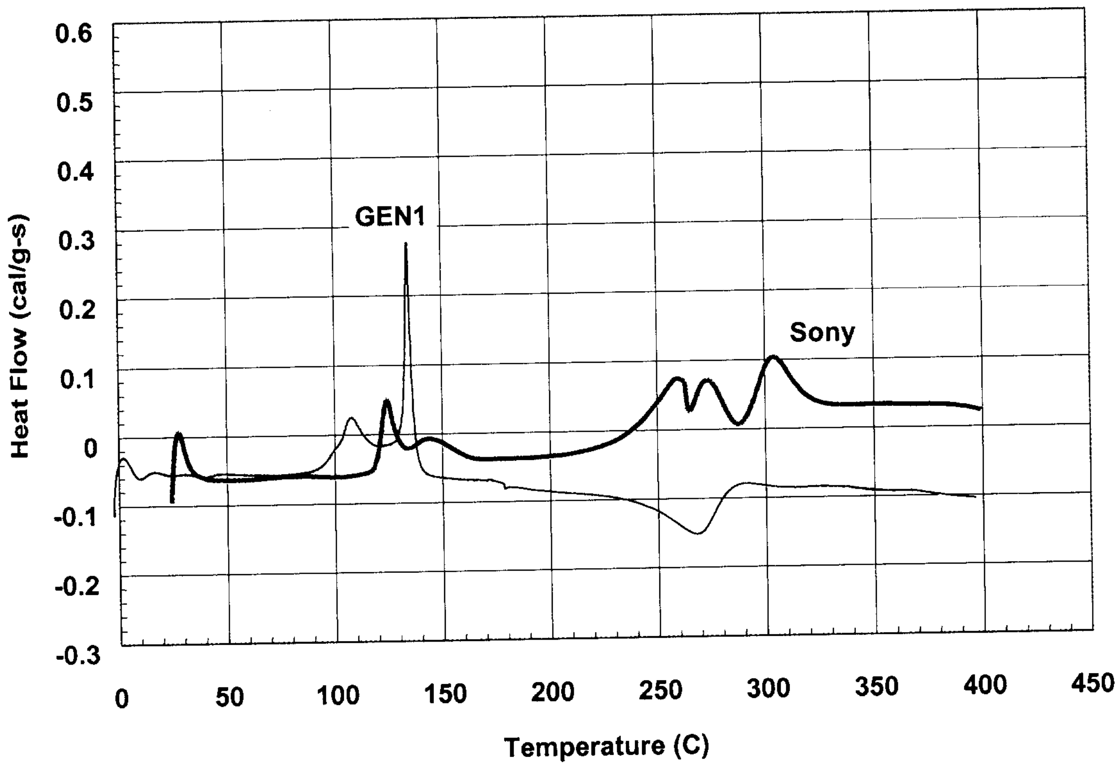

Figure 3. DSC data of GEN1 and Sony anodes at 50% SOC.

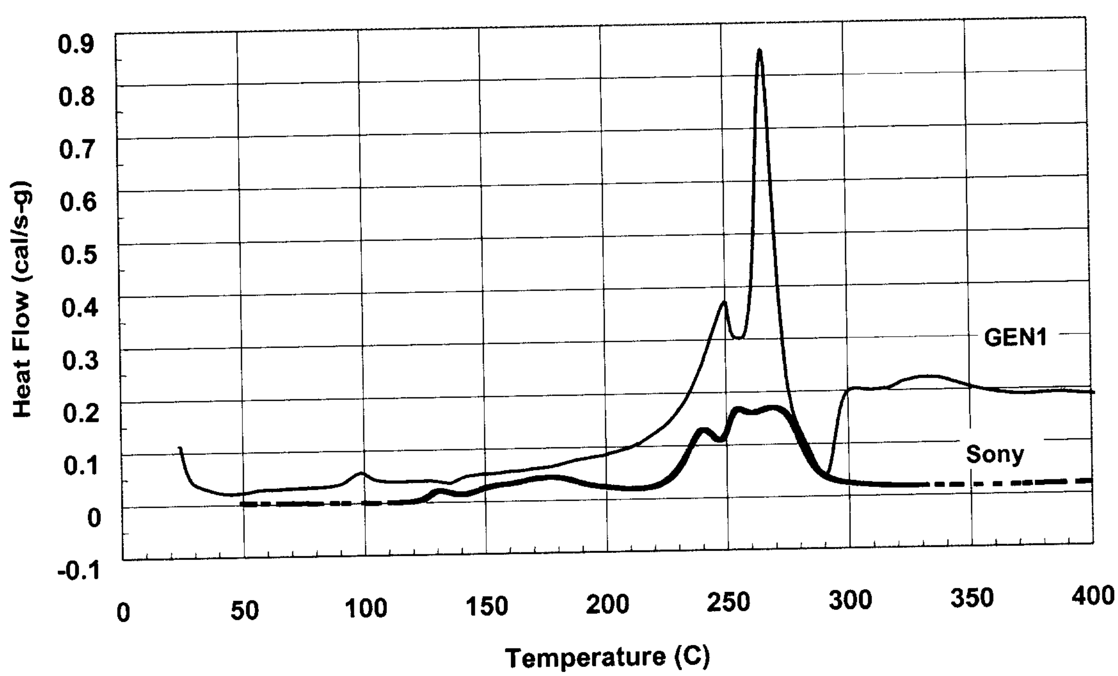

Figure 4. DSC data for GEN1 and Sony cathodes at 50% SOC.

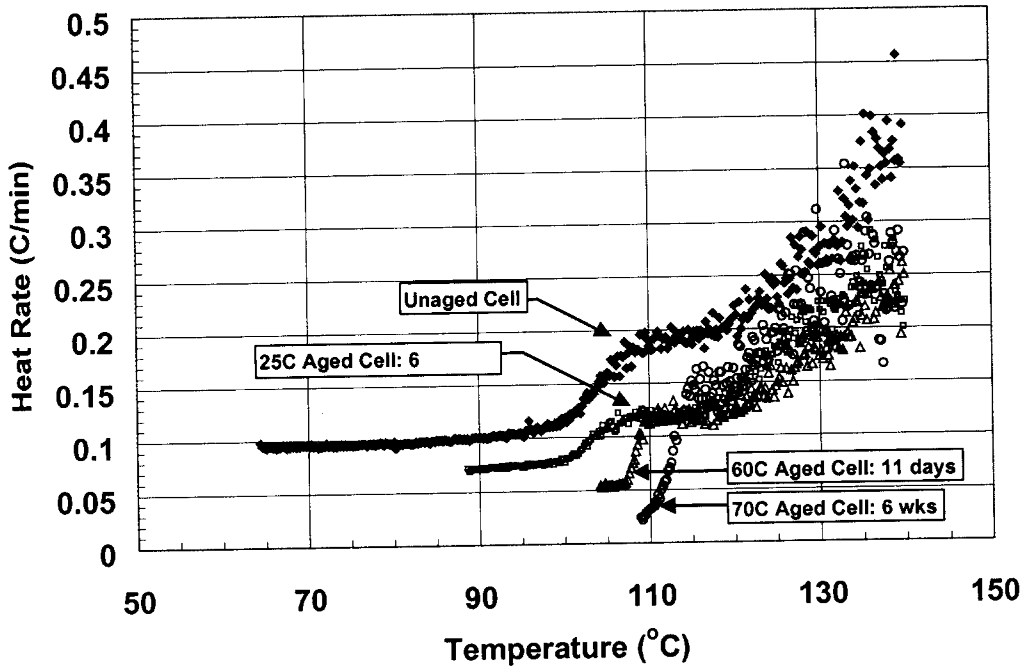

Figure 5. ARC results for aged Sony cells at 100% SOC (vertically offset).

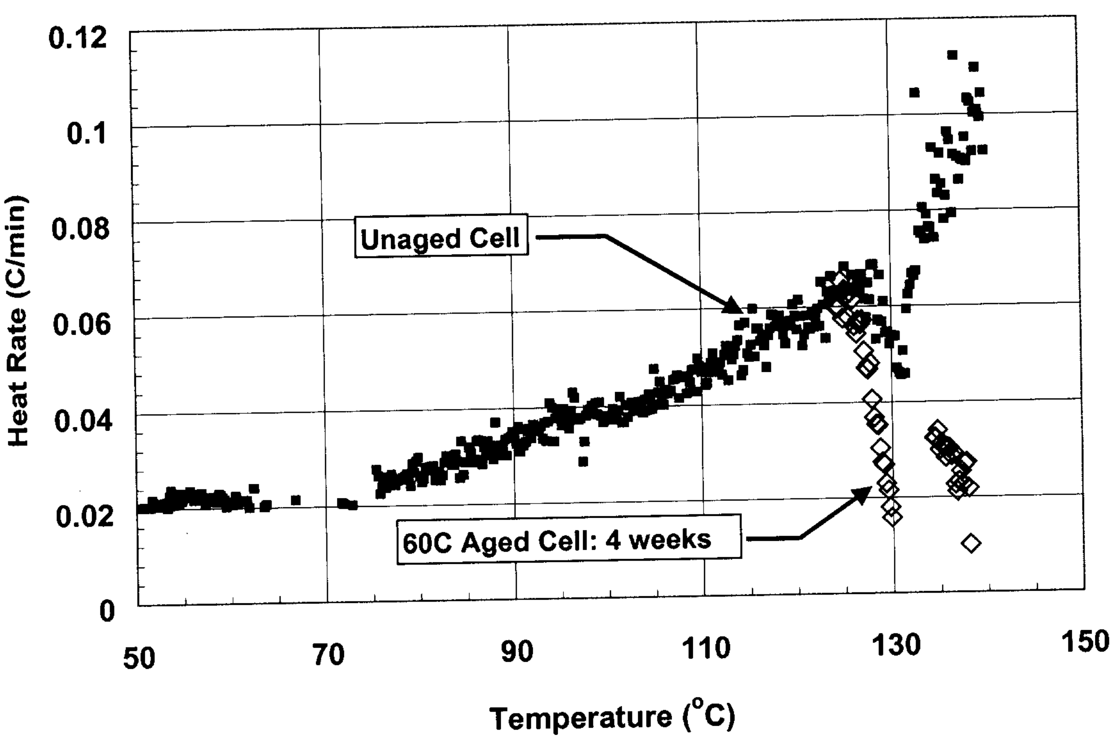

Figure 6. ARC results for aged GEN1 cell at 100% SOC.