

Thermal Abuse Studies on Lithium Ion Rechargeable Batteries

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ABSTRACT

The thermal stability of Li-ion cells with intercalating carbon anodes and metal oxide cathodes was measured as a function of state of charge and temperature for two advanced cell chemistries. Cells of the 18650 design with Li_xCoO_2 cathodes (commercial SONY cells) and $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathodes were measured for thermal reactivity in the open circuit cell condition. Calorimetric techniques of differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC) were used to characterize these cells in both full cell configuration and as individual electrode components. The effects of thermal aging on cell thermal response were also investigated.

Introduction

Lithium-ion batteries (organic liquid electrolyte) have an advanced battery chemistry that exhibits superior performance characteristics to virtually all other rechargeable battery systems at room temperature. Consequently, this system is experiencing unparalleled growth and growth potential. These batteries demonstrate enhanced safety over the lithium metal systems that are subject to internal short circuits due to dendrite formation at the lithium metal surface after repeated cycling. The Li-ion cells use a carbon matrix for the intercalation of the Li ions at the anode in the charged state and use a metal oxide for Li ion intercalation at the cathode in the discharged state. This interchange of Li ions is referred to as a "rocking chair" cell. The formation of the active layers of each electrode material requires the use of polymeric binder material and conductivity enhancing additives. The electrolytes usually consist of a mixture of carbonate-based solvents and a Li salt. The lifetime and safety of these cells depends on the thermal stability of these active layer mixtures in the presence of electrolyte solution.

Calorimetric techniques are useful in measuring the thermal performance of actual cells under operating conditions and for determining the reactivity of the cell components which contribute to this performance. Accelerating rate calorimetry (ARC) can determine the thermal self heating rate of cells under adiabatic

conditions for different charge states. This intrinsic cell property is critical in the design of safe battery systems. Examination of cell components and cell starting materials by differential scanning calorimetry (DSC) determines the thermal contributions of each cell element as a function of temperature and electrochemical state.

We have used these techniques to characterize two Li-ion cell chemistries using Li_xCoO_2 and $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathodes. In this study, we measured the thermal stability of these cells as a function of state of charge (SOC) and after aging/cycling. We identified the source of the primary thermal reactions.

Experimental

We measured commercial SONY cells (US18650S STG) which had nominal 1.2 Ah capacity at 1C rate. The SONY-type cells consist of Li_xCoO_2 as the active cathode and Li_xC_6 intercalating carbon (coke) as the active anode using PVDF as the binder material (1). The electrolyte is a mixture of the carbonate-based solvents propylene carbonate (PC):dimethyl carbonate (DMC) with LiPF_6 as the ionic salt.

The cells with $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathodes were prepared in the 18650 configuration and had a nominal capacity of 0.9 Ah (1C rate). These cells are referred to as GEN1 Cells. The cathodes and MCMB carbon anodes were prepared using

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PVDF binder and the cell electrolyte was (1M) $\text{LiPF}_6/\text{ethylene carbonate (EC):diethylcarbonate (DEC) (1:1)}$.

The ARC measurements were performed using an ARC-2000 accelerating rate calorimeter (Columbia Scientific Industries, Austin, TX) using a specially designed holder for the 18650 cells which allowed simultaneous monitoring of cell voltage. The maximum cell temperature was limited to 140°C for the initial ARC runs and later limited to 160°C for the remainder of the cells, which was above the vent temperature of the cells. DSC analysis of cell components was performed using a DSC 2920 (TA Instr., New Castle, DE) up to a temperature of 400°C in sealed aluminum pans.

Results and Discussion

Initial safety thermal ramps were performed on the cells to determine the temperature ranges of the major thermal events. Figure 1 shows sequential pictures of a cell (GEN1) at 80% SOC ramped in a thermal block up to 200°C . The flammable electrolyte is seen to freely flow from the cell at about 150°C followed by explosive decomposition at 200°C . In order to characterize this behavior under more controlled conditions, the cells were measured in the ARC apparatus.

SONY cells were measured at states of charge of 0%, 50%, 75%, 90% and 100%. The ARC data for these cells, shown offset in Figure 2, show how the onset temperature of accelerating heat rate decreases with increasing SOC. A threshold of $0.02^\circ\text{C}/\text{min}$ is used to define sustained self heating. Accelerating self heating began as high as 130°C for the 0% SOC cell and decreased to about 80°C for the 100% SOC cell. Drops in cell voltage were associated with sudden decreases in the heating rate, suggesting that cell venting occurred at those temperatures. Venting did not stop the accelerating self heating of these cells and thus did not provide a thermal safety mechanism.

The ARC data for the $\text{Li}_x\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ cells are shown in Figure 3. The data sets are offset by $0.025^\circ\text{C}/\text{min}$ for clarity. These cells were measured at 5%, 50%, 75%, 90% and 100% SOC. In addition, a cell (100+% SOC) was overcharged by 0.1V to 4.2V to measure sensitivity of the cells under abnormal conditions. It is clear that these cells are more

thermally stable than the SONY cells. Continuous self generated heating only occurred for a SOC of 75% or greater and began around 80°C , independent of SOC. Venting in these cells occurred at 130°C independent of the SOC. A region of thermal output was observed at lower temperatures (40°C - 70°C) which was sensitive to the cell potential, occurring at lower temperatures with increasing potential (SOC). A source of heat for the initiation of accelerating self heating (thermal runaway) has been identified in the anode material as the decomposition of the solid electrolyte interphase (SEI) layer and subsequent reaction of the Li_xC_6 with the solvent (2-4). Our results are consistent with this interpretation for both types of cells.

It has been shown that the SEI layer formed during initial lithiation transforms over time, reacting with HF in the electrolyte (5,6). This layer changes from a primarily organic layer to a more stable inorganic layer composed mostly of LiF. This new layer can affect the rate of thermal decomposition of the remaining SEI layer. We measured the effect of aging in the SONY and GEN1 cells by holding them for increasing periods at elevated temperatures. Figure 4 shows the ARC data for the SONY aged cells (25°C - 70°C). Aging is seen to result in a loss of the low-temperature reactions. With increased aging temperature and time the onset of thermal runaway shifts to higher temperature but all cells showed a sharp rise in heating rate around 115°C followed by accelerating heating rate due to continued electrolyte reduction.

Figure 5 show ARC data for GEN1 cells aged/cycled at increasing temperatures (25°C - 60°C). These cells initially showed a reduction in thermal output as a result of aging at 40°C . However, with aging at the higher temperatures of 50°C - 60°C the cells behaved similarly to fresh cells. These results suggest that the LiF layer that has been seen to form on the anodes may be very delicate. Although LiF will not dissolve at these temperatures, the morphology of the layer may depend on aging/cycling temperature and the surface characteristics of the carbon particles. If the inorganic layer is discontinuous and cracked, the electrolyte can penetrate near to the carbon particle and intercalated Li can continue to form new SEI with the associated heat generation.

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Conclusions

Calorimetric analysis has identified cell and component reactions in Li-ion cells that contribute to the complex thermal response of these cells. Initial low-temperature reactions result from conversion of the anode SEI layer to more stable phases. This reaction can lead to thermal runaway in cells in the fully charged state. Aging results in partial completion of these reactions, which change the composition and morphology of the SEI layer. Aging does not result in increased thermal reactivity and may result in passivation of the SEI layer under certain conditions.

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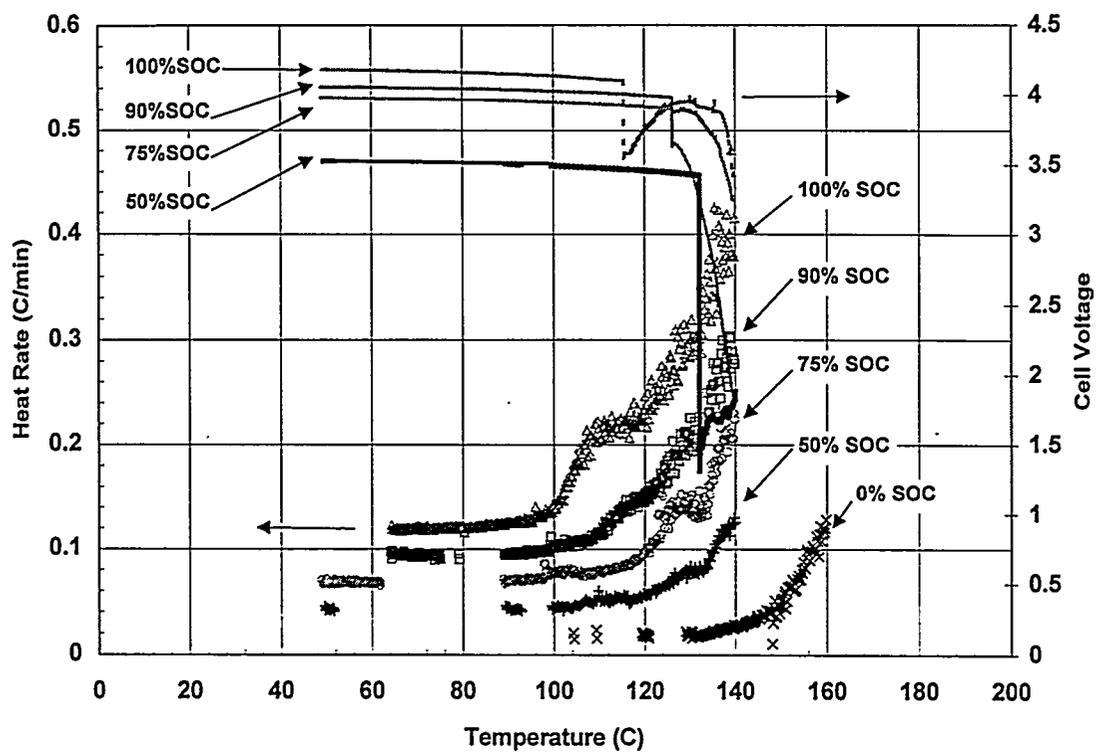


Figure 2. ARC data for SONY Li-ion cells as function of state of charge.

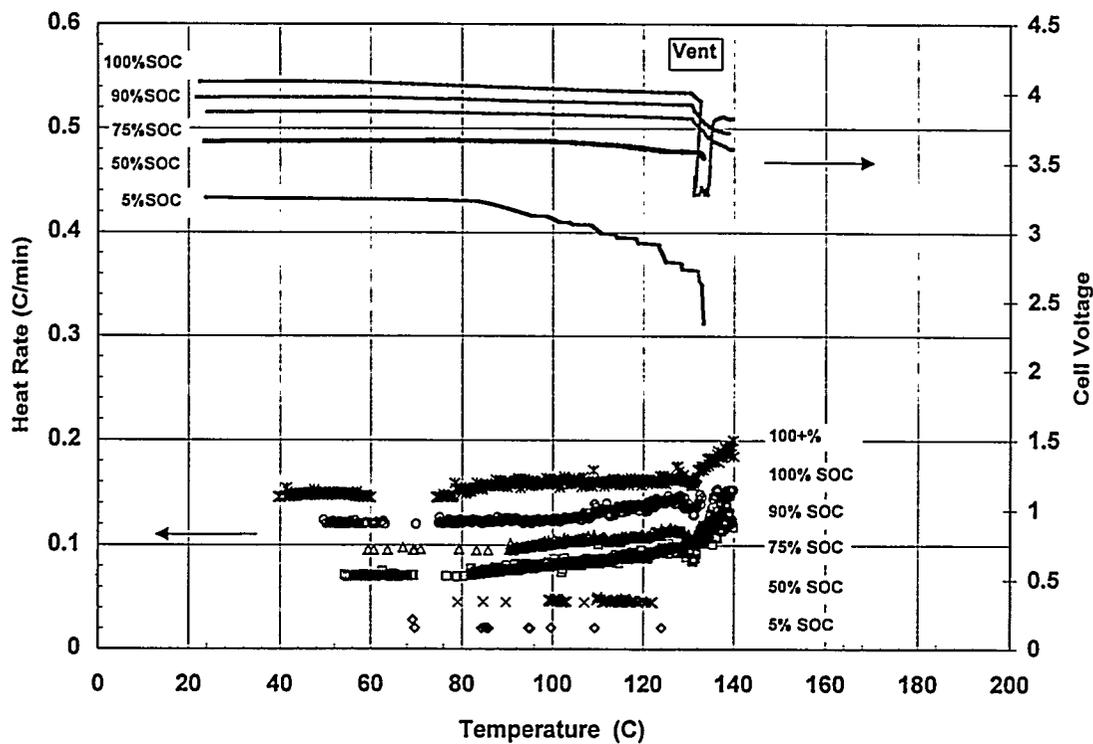


Figure 3. ARC data for GEN1 Li-ion cells as function of state of charge.

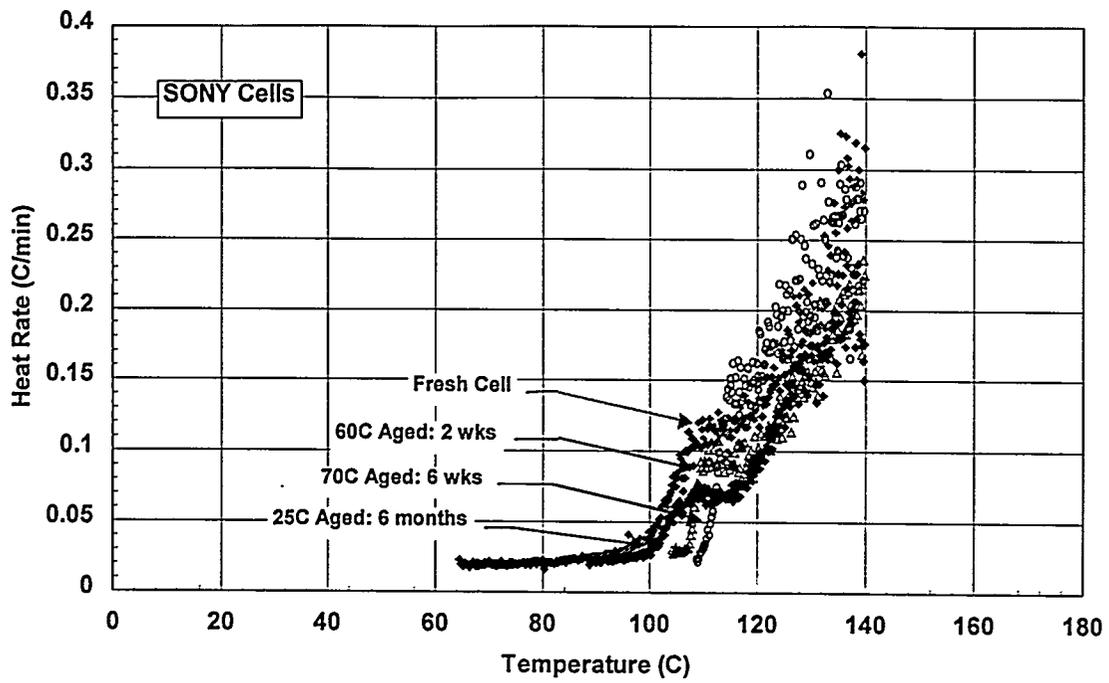


Figure 4. ARC data for aged SONY cells.

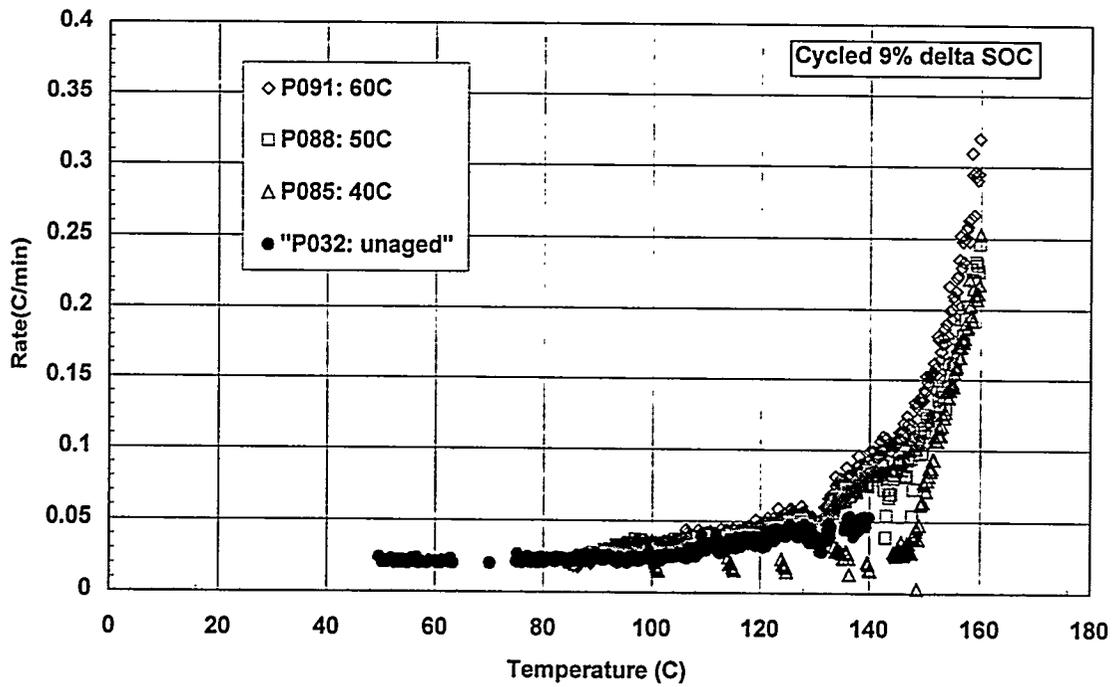


Figure 5. ARC data for age GEN1 cells.