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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 $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes were measured for thermal reactivity in the open circuit cell condition. Accelerating rate calorimetry (ARC) was used to measure cell thermal runaway as a function of state of charge (SOC). Microcalorimetry was used to measure the time dependence of heat generating side reactions also as a function of SOC. Components of cells were measured using differential scanning calorimetry (DSC) to study the thermal reactivity of the individual electrodes to determine the temperature regimes and conditions of the major thermal reactions. Thermal decomposition of the SEI layer at the anodes was identified as the initiating source for thermal runaway. The cells with Li_xCoO_2 cathodes showed greater sensitivity to SOC and higher accelerating heating rates than seen for the cells with $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes. Lower temperature reactions starting as low as 40°C were also observed that were SOC dependent but not accelerating. These reactions were also measured in the microcalorimeter and observed to decay over time with a power-law dependence and are believed to result in irreversible capacity loss in the cells.

INTRODUCTION

Lithium ion batteries have become increasingly important in high-power applications for both the commercial and military markets. 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. 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. Previous work has shown that Li-ion cells can become thermally unstable at relatively low temperatures with increasing state of charge (1,2).

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

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charge states (1). This intrinsic cell property is critical in the design of safe battery systems. Isothermal microcalorimetry measures the temperature and time dependence of heat generating side reactions that contribute to the onset of thermal runaway and determine the lifetime of the cell. 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 $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes. Individual cells were measured as well as electrode material from disassembled cells. Electrodes were also prepared from sheets of starting material and cycled in half cells to obtain electrodes with set states of charge.

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 as the active anode using PVDF as the binder material (3). The electrolyte is a mixture of carbonate-based solvents with LiPF_6 as the ionic salt. These cells were cycled using an Arbin battery tester (Arbin Corp., College Station, Texas) and the charge states set based on an initial calibration of these cells that determined cell voltage as a function of SOC.

The cells with $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes were prepared in the 18650 configuration and had a nominal capacity of 0.9 Ah (1C rate). The cathodes and MCMB carbon anodes were prepared using PVDF binder and the cell electrolyte was LiPF_6 /ethylene carbonate (EC): diethylcarbonate (DEC) (1:1). These cells were cycled and calibrated in the same manner as the SONY cells.

The SONY-type half cells were prepared from starting materials consisting of Li_xCoO_2 as the active cathode material and Li_xC_6 (MCMB 2528 carbon) as the active anode material with 5 wt% PVDF as binder. The electrolyte (EM Industries, Inc.) consisted of ethylene carbonate (EC): propylene carbonate (PC): diethyl carbonate (DEC) (1:1:2 by weight) with 1.0 M LiPF_6 as the salt. These half cells were cycled using a Li metal working electrode and reference. An Arbin battery tester was used to set the charge state set based on the measured reversible coulombic capacity of each anode or cathode.

The open circuit thermal output of the cells was measured using a CSC 4400 isothermal microcalorimeter (Calorimetry Sciences Corp., Provo, UT) at 25°C and 60°C. The cells were measured from 0-100% SOC for periods of up to 800 hours. 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 160°C for the initial ARC runs and later limited to 140°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

ARC:

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 1, 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 occurred as low as 115°C for the fully charged cell and as high as 132°C for the 50% SOC cell. 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 $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells are shown in Figure 2. 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 132°C independent of the SOC. However, greater weight loss due to electrolyte expulsion was observed with increasing SOC. The corresponding cell voltages also decreased at the vent temperature. 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 SEI layer and subsequent reaction of the Li_xC_6 (4,5). Our results are consistent with this interpretation for both types of cells. However, the low temperature reactions in the 40°C - 70°C range are due to an unidentified source, although electrochemical oxidation of the solvent at the positive cathode may be occurring (6). The behavior of the $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells where similar thermal response was seen with increasing electrolyte ejection for increasing SOC suggests that gas generation was more severe in these cells. Since these cells had different cathode material and solvent than the SONY cells, enhanced solvent decomposition may have occurred.

Microcalorimetry:

Isothermal microcalorimetry was performed at 25°C and 60°C for each set of cells. Both types of cells showed an initial peak in heat output followed by a decreasing thermal output modeled by a power law function. SONY cells were measured for 0%, 20%, 50%, 80% and 100% SOC at 25°C and for 50% and 90% SOC at 60°C . The 25°C data (Figure 3) show that the greatest initial heat output occurred for the 100% and 0% SOC cells while the 50% SOC cells showed the minimum heat output. The cells with the

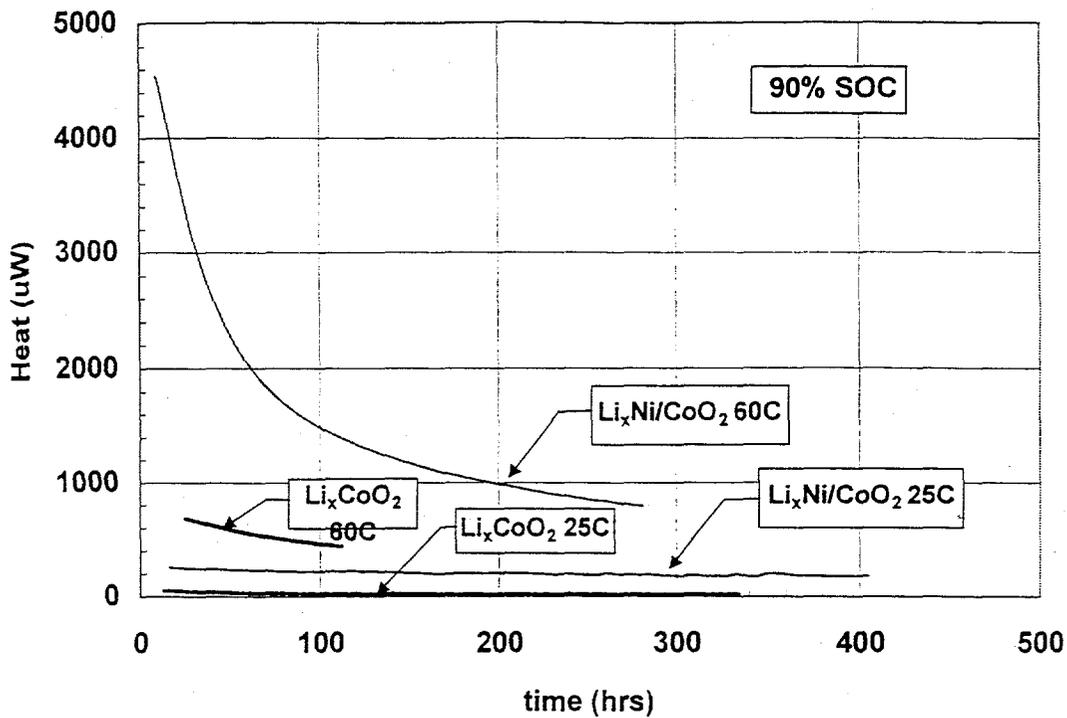


Figure 1. ARC data and cell voltages for Li_xCoO_2 (SONY) cells as a function of state of charge (each ARC data set offset by $0.025^\circ\text{C}/\text{min}$ for clarity).

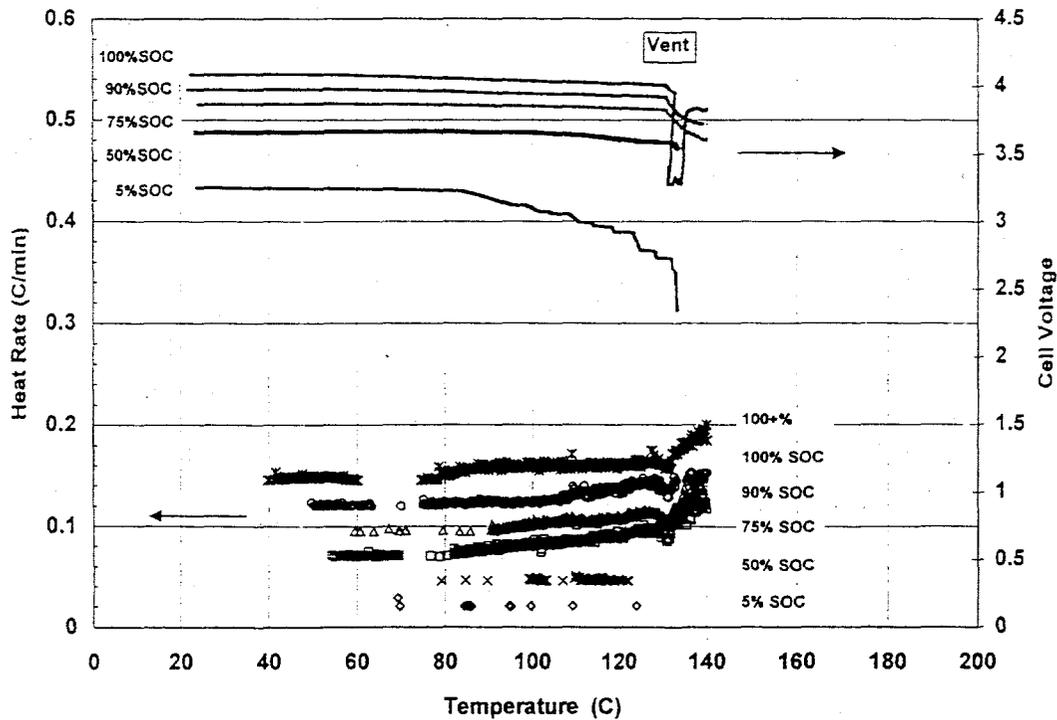


Figure 2. ARC data and cell voltages for $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells as a function of state of charge (each ARC data set offset by $0.025^\circ\text{C}/\text{min}$ for clarity).

lower SOC decayed more rapidly to a level of only 10-20 μW after long times while the higher SOC cells remained a factor of 2-3 times higher in output. Figure 4 shows the average thermal output as a function of SOC for these cells at 100 hr and 350 hr measured from the end of the charge/discharge preparation step. This clearly shows the relative region of thermal stability at the intermediate charge states and the more rapid equilibration at the lower states of charge.

The $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells were measured at 50% and 90% SOC and showed higher thermal output compared to the SONY cells both at 25°C and 60°C. Figure 5 shows a comparison of these cells at 90% SOC. The $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells showed a much greater sensitivity to SOC at 60°C than was seen for the SONY cells, with an initial heat output of almost 5000 μW compared to 700 μW for the SONY cells.

The microcalorimetry data show the time dependence of the reactions observed initially in the ARC measurements at the lower temperature range. As mentioned earlier, these reactions may involve solvent oxidation at the cathodes. SEI decomposition and formation reactions may also be taking place. These side reactions are decaying with time and are not "reset" by subsequent charge/discharge cycling, suggesting that the reaction has a fixed amount of reactants. The peaks in thermal output at either end of the SOC may be due to two separate reactions.

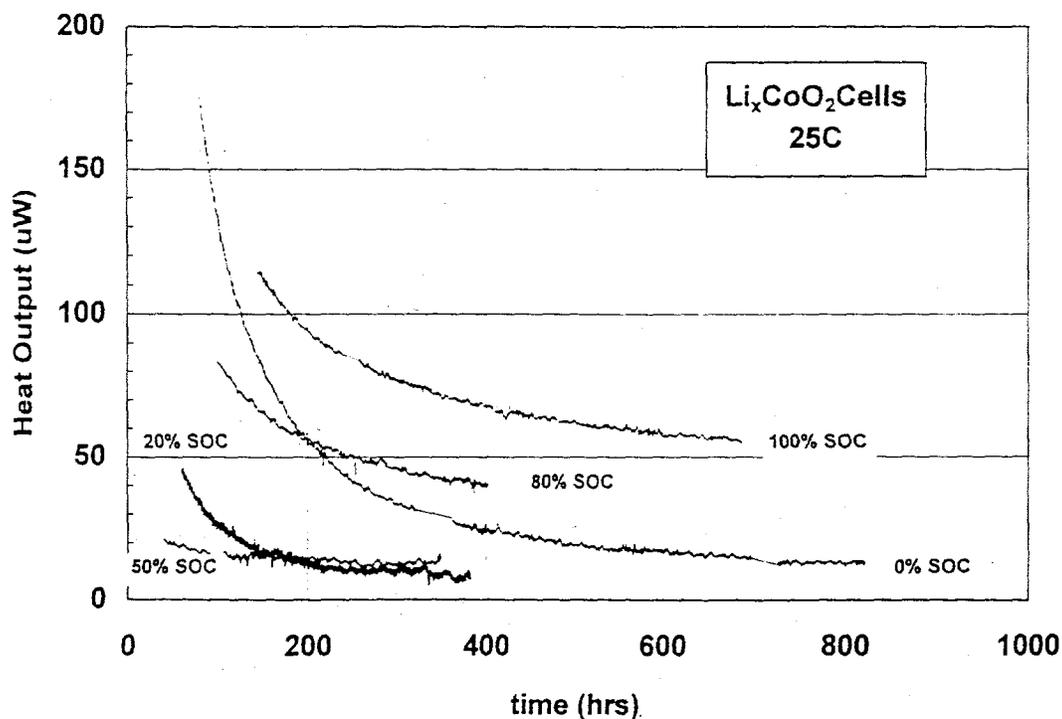


Figure 3. Microcalorimetry data for Li_xCoO_2 (SONY) cells as a function of SOC.

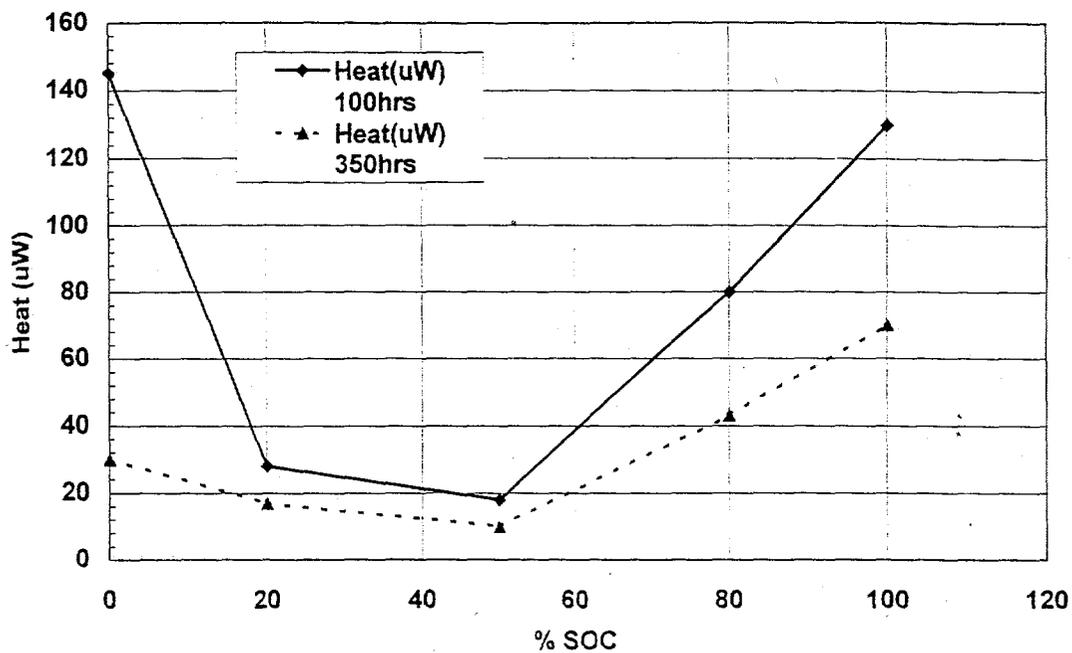


Figure 4. Microcal data for Li_xCoO_2 (SONY) cells as a function of SOC at 25°C.

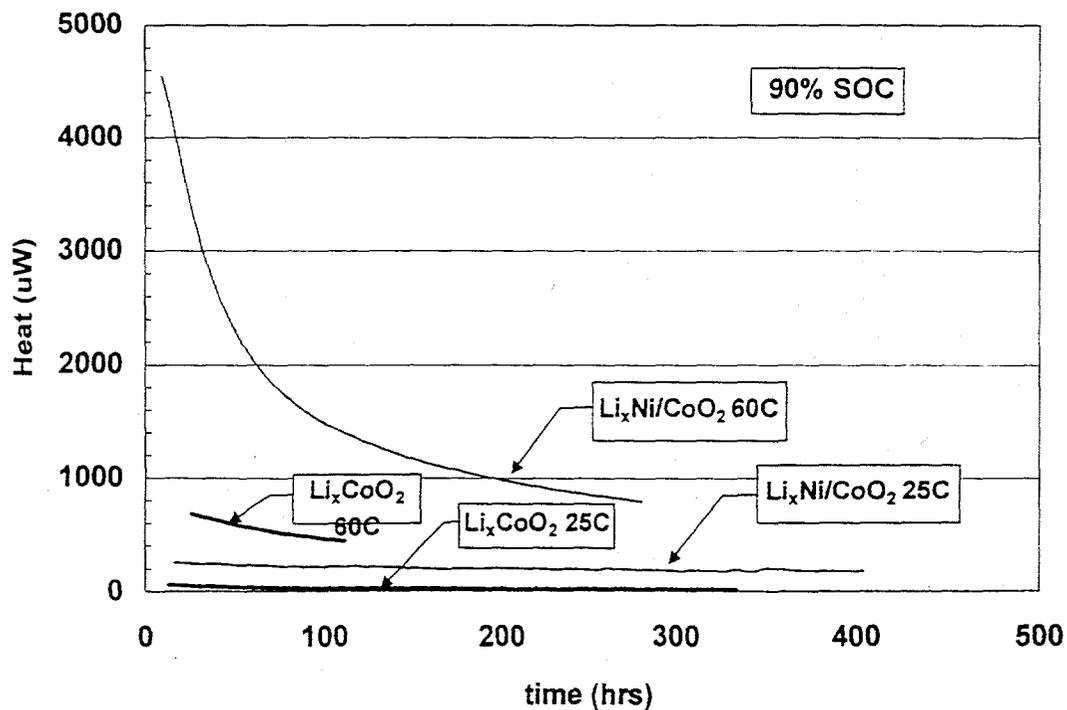


Figure 5. Comparison of microcalorimetry data for Li_xCoO_2 and $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cells at 90% SOC for 25°C and 60°C.

DSC:

DSC analysis was performed on anode and cathode material with SONY-type composition as well as on anodes and cathodes from disassembled SONY cells. The carbon anode material was cycled several times in a half cell apparatus until a stable charge/discharge capacity was obtained. This cycling allowed irreversible Li reactions with the anode to stabilize and the SEI layer to form (7). The reversible charge/discharge capacity was determined and used to set the Li level in the anodes. A fully charged anode is designated as $Li_x=1.0$ and a discharged anode as $Li_x=0.0$. The actual Li levels were not measured but are believed to be close to these values (8). Figure 6 shows the DSC data for anodes with $Li_x=0.1, 0.7$ and 0.9 . These measurements were performed in sealed Al pans in the presence of electrolyte. These measurements and others at intermediate Li levels showed that an exothermic reaction took place with peak reactivity between 85°C and 105°C . However, the magnitude and temperature of this reaction showed no correlation with Li level.

Measurements were also made of anode material removed from cycled SONY cells in the fully charged and discharged state. These measurements showed similar exothermic behavior as seen for the half cells but occurred at higher temperature near 125°C . Measurements of cathode material from the half cells and the SONY cells showed no significant thermal activity in the temperature range below 200°C . The electrodes from the $Li_xNi_{0.8}Co_{0.2}O_2$ cells have not yet been measured.

The DSC data support the observations made during the ARC runs of an exothermic reaction in the 80°C to 130°C temperature range. The reaction observed in the anode and not in the cathode further supports the model of anode initiated thermal runaway. The SOC dependence of the reaction seen in the ARC and not by DSC suggests that the exothermic cell behavior is driven by cell potential and not just by the unbiased contribution of the cell components.

CONCLUSIONS

Li-ion cells of the 18650 design with Li_xCoO_2 cathodes (commercial SONY cells) and $Li_xNi_{0.8}Co_{0.2}O_2$ cathodes were measured for thermal reactivity in the open circuit cell condition using several thermal analytical techniques. Low temperature reactions in the 40°C - 70°C temperature range were measured by microcalorimetry and ARC and were seen to be very temperature and state of charge dependent. The $Li_xNi_{0.8}Co_{0.2}O_2$ cells were more reactive than the Li_xCoO_2 cells, especially at the higher temperatures. Thermal runaway reactions were measured by ARC for several states of charge and were observed to occur at lower temperature with increasing SOC. The Li_xCoO_2 cells were more reactive and showed more SOC dependence than the $Li_xNi_{0.8}Co_{0.2}O_2$ cells while the $Li_xNi_{0.8}Co_{0.2}O_2$ cells seemed to generate more gas products. DSC analysis of the Li_xCoO_2 cells showed the anode exothermic reactions believed to initiate thermal runaway while indicating no intrinsic contribution from the cathode material.

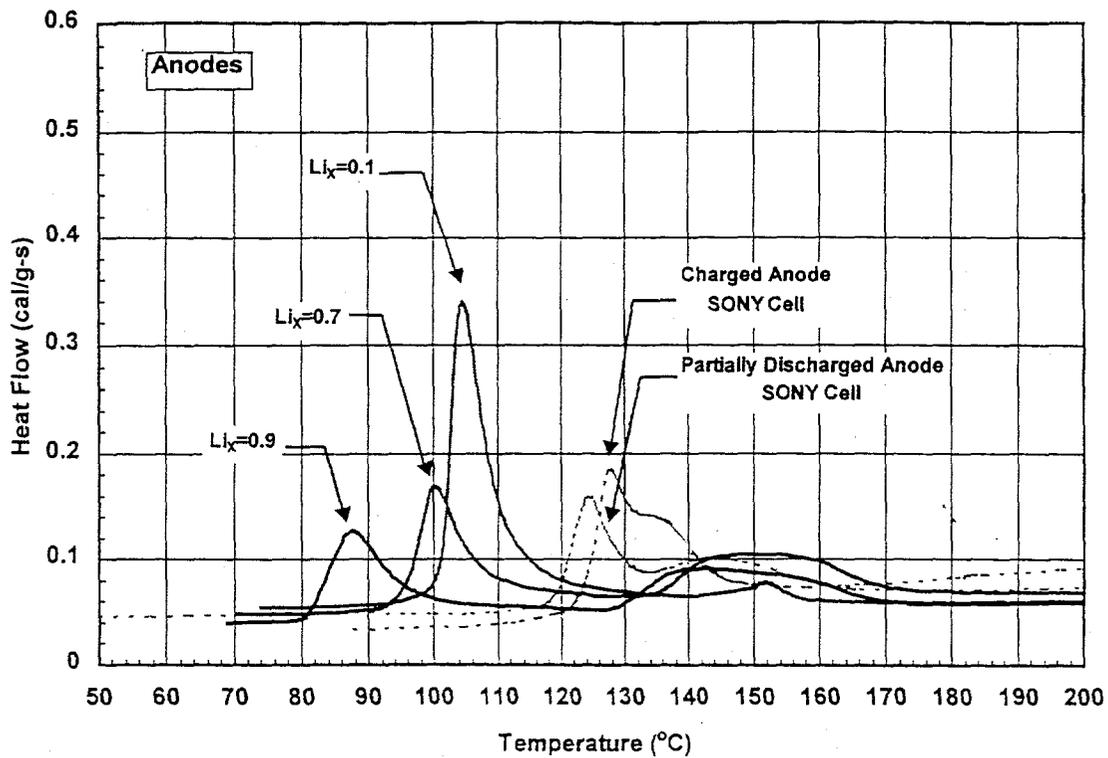


Figure 6. DSC data for $\text{Li}_x\text{Co}_{0.2}\text{O}_2$ (SONY type) anodes prepared from half cells and disassembled 18650 cells.

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