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THERMAL PERFORMANCE AND CHARACTERIZATION OF Li-ION CELLS AFTER AGING/CYCLING

E. Peter Roth
Lithium Battery R&D Dept. 2521
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0613

ABSTRACT

The effects of aging on the thermal stability of Li-ion cells was measured as a function of aging temperature and electrical cycling for two advanced cell chemistries. 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. Accelerating rate calorimetry (ARC) was used to measure cell thermal runaway at 100% state of charge (SOC). Components of cells were measured using differential scanning calorimetry (DSC) to study the thermal reactivity of the individual electrodes. Cells were exposed to aging/cycling routines from 25°C to 60°C at 80% SOC. Aging and cycling resulted in a loss of low-temperature reactions below 80°C. Although cells aged/cycled at 40°C showed a reduction in thermal output, cells aged/cycled at 50°C and 60°C behaved much like the unaged/uncycled cells. Changes in the SEI passivation layer on the anode can account for these observed behaviors.

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 depend on the thermal stability of these active layer mixtures in the presence of electrolyte solution.

Earlier work by Dahn et. al. has shown that a solid electrolyte interphase (SEI) layer forms on the anode upon initial charging (1-3). This layer is composed of reduction products of the Li intercalated carbon and the alkyl carbonate based electrolyte. This initial SEI layer formed with the $LiPF_6$ salt is metastable and transforms as a function of time and temperature to a more stable inorganic layer including LiF and possibly other salt reduction products (4). However, Li diffusion continues through this layer and

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additional metastable SEI products can continue to form. The metastable SEI layer transforms exothermically beginning at temperatures below 100°C and is the source of initial heat generation in the cell. The initial thermal output of an aged cell is a complicated function of the anode SEI layer composition and morphology.

Determination of the thermal performance of aged cells is important in setting safety limits on cell use in extended use applications. This paper presents data on the thermal performance of Li-ion cells aged and electrically cycled at increasing temperatures and cycle depth. This study was part of the thermal abuse characterization effort for the Advanced Technology Development (ATD) program, which is funded by the US DOE and is chartered with the development of advanced high-power Li-ion cells for hybrid electric vehicle applications.

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) is used to 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 $Li_xNi_{0.8}Co_{0.2}O_2$ cathodes. Individual cells were measured as well as electrode material from disassembled cells.

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 intercalating carbon (coke) as the active anode using PVDF as the binder material (5). The electrolyte from these cells was determined to be PC:DMC/$LiPF_6$. 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 $Li_xNi_{0.8}Co_{0.2}O_2$ 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 1M $LiPF_6$ in ethylene carbonate (EC): diethylcarbonate (DEC) (1:1). These cells were cycled and calibrated in the same manner as the SONY cells. These cells are the first in series of ATD prototype cells and are referred to as GEN1 cells.

ARC measurements were performed using an ARC-2000 accelerating rate calorimeter (Colombia 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

The effects of aging at elevated temperatures were measured by performing ARC runs of thermally aged Sony and GEN1 cells. Figure 1 shows the results for the Sony cells both unaged (as-received) and which had been additionally aged without cycling for 6 months/25°C, 11 days/60°C and 6 weeks/70°C. All cells were measured at 100% SOC. The unaged cell shows a plateau in the heating rate at 110C consistent with the depletion of the metastable SEI layer followed by further electrolyte reduction (2). The cells showed a loss of low-temperature reactivity with increasing time and temperature. The onset of sustained heat output did not begin until 90°C for the 6 month/25°C cells compared to reactions starting below 70°C for unaged/25°C cells. The onset temperature increased to 105°C for the 11 day/60°C cell and to 110°C for the 6 week/70°C cell. The cell heating rate responses showed the plateau behavior in the 110°C-115°C range seen for the unaged cells, although the onset of heating was much sharper for the cells aged at elevated temperature. These measurements suggest that the SEI layer is changing, undergoing partial conversion from the metastable species to a more stable species even as low as room temperature. Work by others has shown that a partial substitution process takes place whereby the original alkyl carbonates of the SEI layer are partially replaced by LiF. This reaction results from HF in the electrolyte, which is a product of trace water that is always present (4,6). As expected, this reaction proceeds more quickly with increasing temperature. The majority of this conversion takes place in 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 either the remaining SEI layer undergoes rapid conversion followed by further reaction of the lithiated anode with the electrolyte or that the new stable SEI layer losses coverage of the carbon allowing renewed electrolyte reduction.

The GEN1 cells were aged/cycled in a constant temperature thermal chamber at 80% state of charge for a period of 4 weeks. In addition, cells were kept at room temperature for approximately 8 months after initial receipt. The cycled cells were given a series of discharge (12s)/charge (2s) pulses at 8C that depleted the charge state by either 3%, 6% or 9%, depending on the number of pulses. The cells were then returned to 80% SOC and the cycle repeated. The period of the discharge/charge profile was from 80s to 240s and was repeated continuously for the entire aging period. After cycling, the cells were placed in cold (10°C) storage until ready for measurement in the ARC.

Figure 2 shows the ARC data for the cells aged/cycled at 40°C for each of the three delta SOCs. Also shown is the thermal response for a fresh cell measured shortly after initial receipt. This initial ARC run was terminated at 140°C since the cell thermal stability and reaction rates initially were not known. First, note that the GEN1 cell thermal output is much less than that observed for the SONY cells. It is not clear whether this difference is due to differences in the cell electrolytes and anode carbon compositions or whether due to differences in the cell assembly. Initial cell self-heating began as low as 50°C although the heat rate did not start to accelerate until above 100°C. The most notable change due to the aging/cycling profile is the complete loss of the low-temperature reactions below 80°C that were seen in the fresh cell. This shift is explained by a reduction of available metastable SEI material in the aged cell. Heat output did not start until 95C and was intermittent and not self-sustaining until 145°C when the heating rate increased sharply. In these GEN1 cells the reacted SEI layer acts as if it were a brittle layer which breaks down followed by a rapid healing process probably involving reduction of the electrolyte to form a new layer. This brittle layer could result from a continuous LiF film formed during aging. Work by Sato et. al. has shown that a LiF layer grows on the surface of the carbon SEI layer (6). This layer becomes sharper, more defined with increasing HF. These cells thus show greater thermal stability at low temperatures than the fresh cell. No difference was seen as a function of increasing delta SOC during cycling.

The next cells measured were the 50°C aged/cycled cells. Figure 3 shows the data for these ARC runs. Interestingly, the cells thermal outputs were very similar to that of the fresh cell. The cells did not show the intermittent thermal output seen for the 40°C aged/cycled cells. Heat output began at 85°C and increased continuously up to the run limit of 160°C. Cell venting was observed at 130°C for all cells, which resulted in a dip in the heating rate. The 60°C aged/cycled cells showed behavior similar to the 50°C cells. Figure 4 shows a comparison of the runs for cells cycled at 9% SOC from each aging temperature. The data from the 50°C and 60°C cells suggest that the SEI layer formed during aging is 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.

The thermal output of the full cell is a sum of the thermal outputs from the anodes, cathodes and electrolyte. In order to determine the source of the initial cell heating, the individual electrode materials were measured by DSC. The cells were disassembled in an Ar glove box and sealed in Al pans with the electrolyte. Figure 5 shows the data for the anodes removed from charged and discharged 25°C aged cells. An exothermic peak was observed for all cells in the 100°C-150°C temperature range. This peak has been identified as resulting from decomposition of the metastable SEI layer and is independent of the state of the degree of lithiation of the carbon (2). At higher temperatures, the lithiated carbon (charged) continues to react exothermically with the electrolyte, forming new SEI, while the delithiated (discharged) carbon showed no further reactivity. Figure 6 shows the DSC data for the corresponding cathodes. The cathode reactions are highly charge dependent but do not begin until temperatures greater than 200°C, thus do not contribute to the initial cell heating. Figure 7 shows data for aged and aged/cycled anodes in the charged state. No significant change is seen in thermal output, suggesting that the SEI conversion reactions taking place at low temperatures during aging/cycling do not result in bulk transformation of the metastable SEI. These reactions may result in changes more to the SEI electrolyte interface.

CONCLUSIONS

Thermal aging of Li-ion cells has been shown to result in a loss of low-temperature reactions as measured by ARC. Cells aged/cycled at 40°C showed very low, intermittent thermal outputs below 140°C while cells aged/cycled at 50°C and 60°C behaved much like initial fresh cells. These results, along with DSC data, suggest that the bulk of the initial metastable SEI layer remains intact at these temperatures but that reactions are occurring which may affect the SEI/electrolyte interface. Overall, aging does not result in any increased safety concerns for these Li-ion cells.

ACKNOWLEDGEMENTS

The author thanks GiGi Gonzales for sample preparation, Bob Patton for the ARC measurements and Jennifer Dobbs for the DSC measurements. We acknowledge the support of DOE Office of Advanced Automotive Technology through the PNGV Advanced Technology Development (ATD) High Power Battery Development Program. Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

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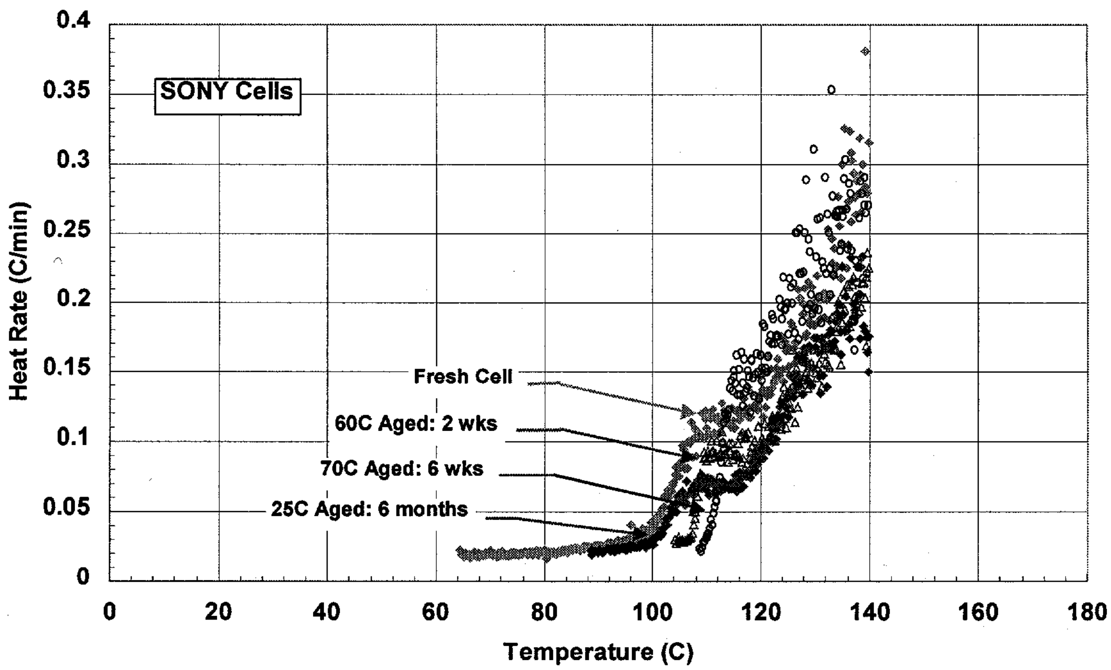

Figure 1. ARC runs for aged SONY cells at increasing temperature/time.

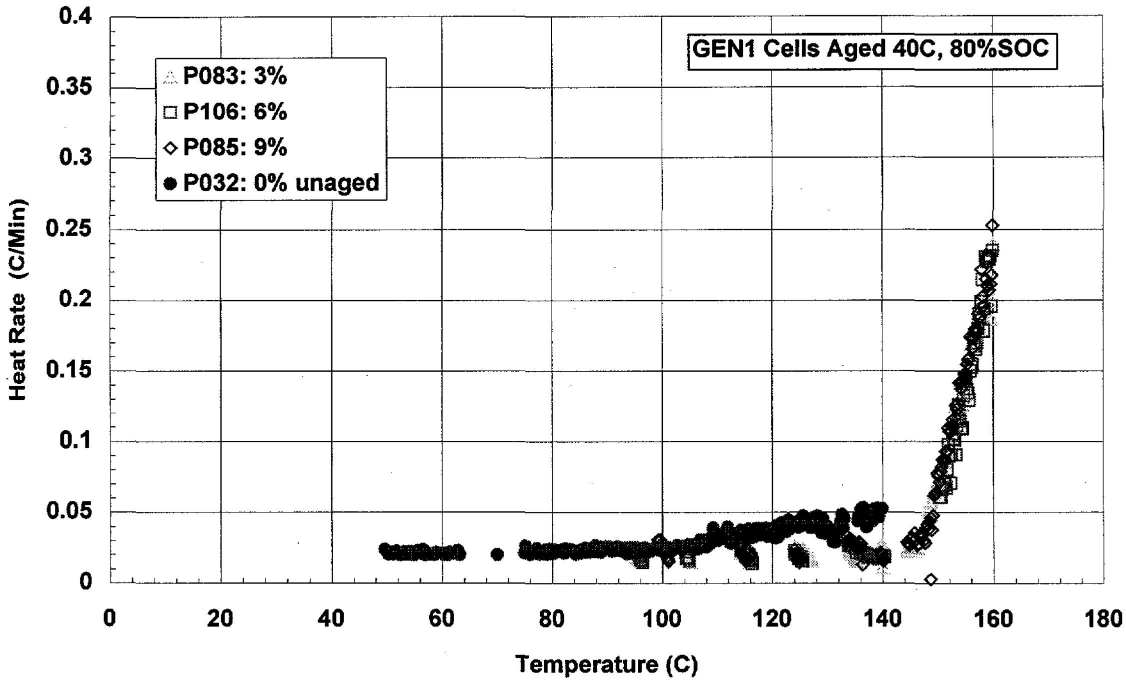

Figure 2. ARC runs for GEN1 cells aged at 40°C, 80% SOC for increasing delta SOC.

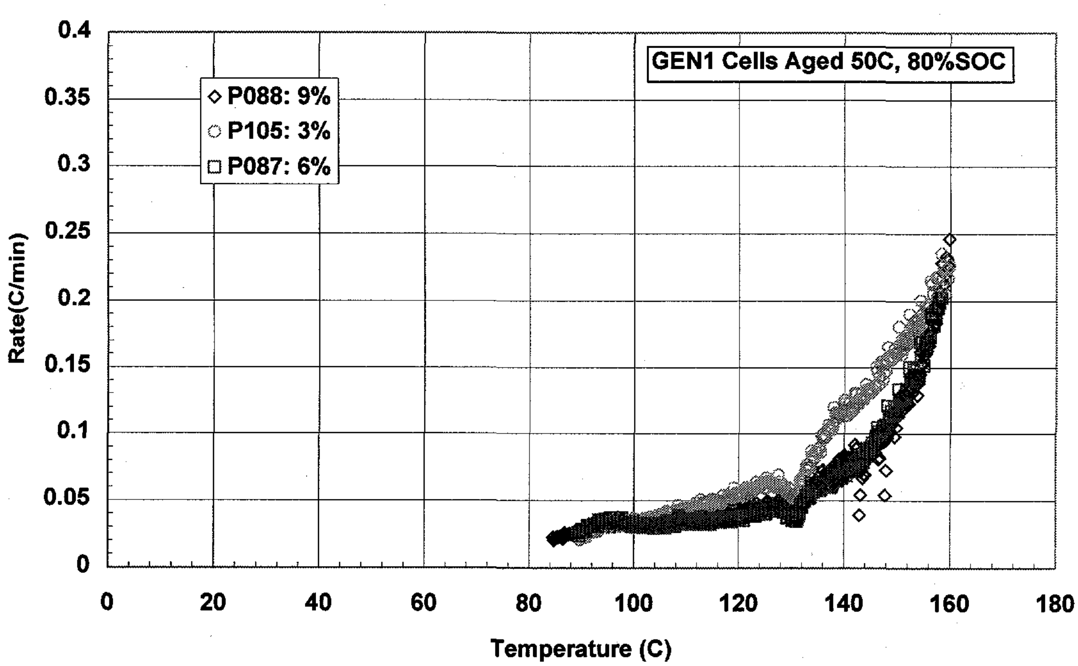

Figure 3. ARC runs for GEN1 cells aged at 50°C, 80% SOC for increasing delta SOC.

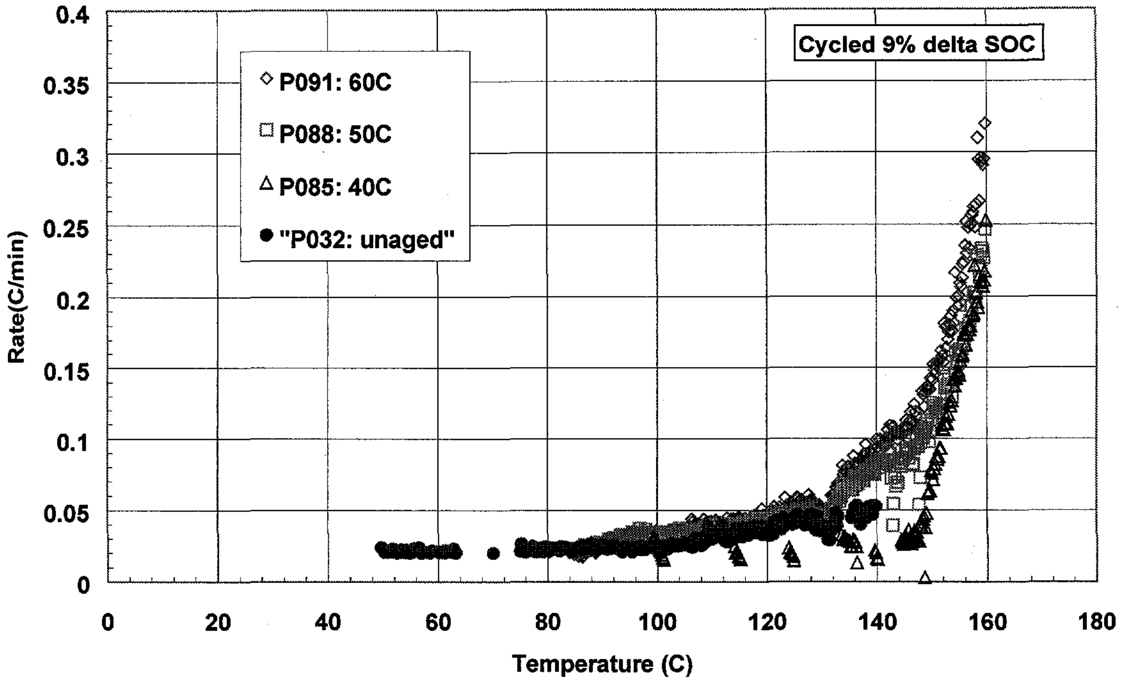

Figure 4. ARC runs for GEN1 cells cycled at 9% delta SOC for increasing temperature.

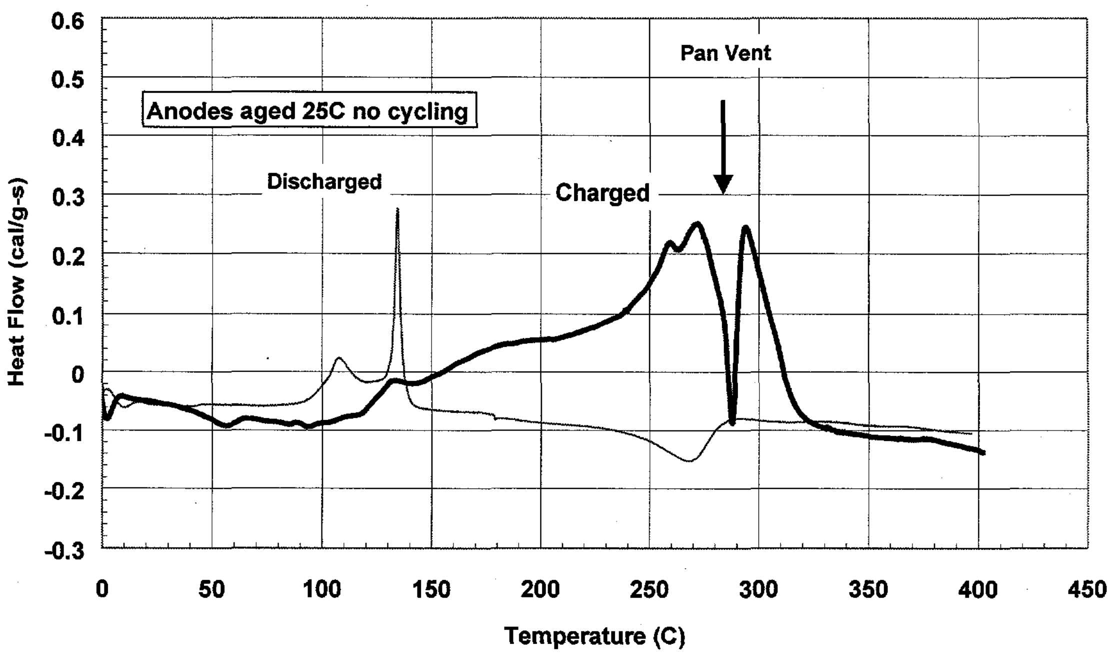

Figure 5. DSC data for 25°C aged GEN1 anodes both charged and discharged.

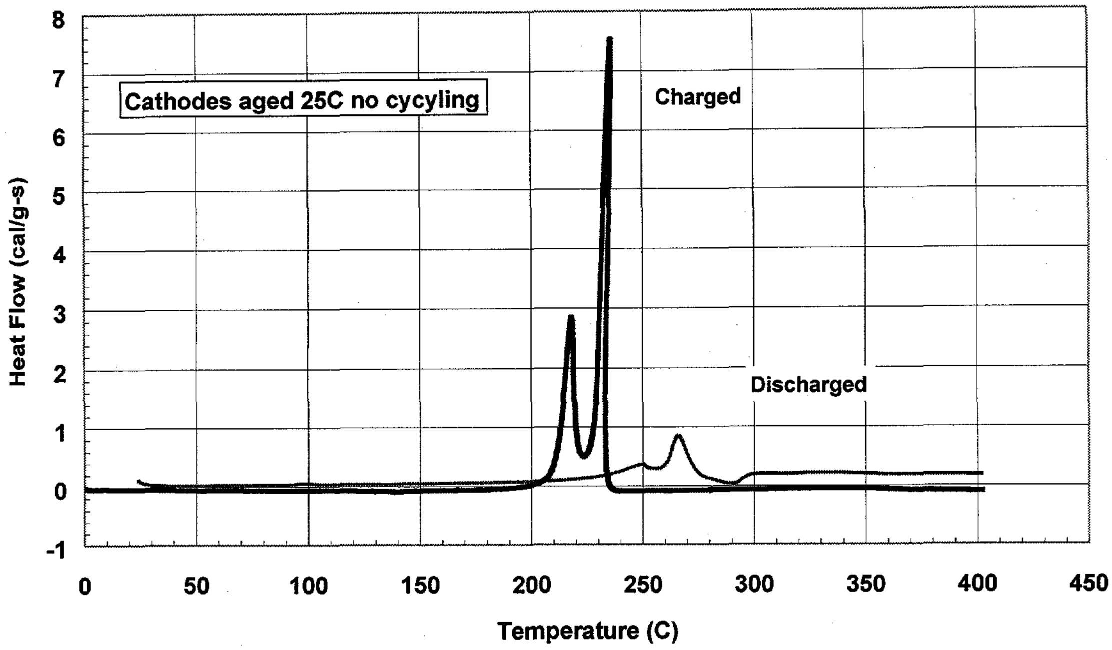

Figure 6. DSC data for 25°**C** aged GEN1 cathodes both charged and discharged.

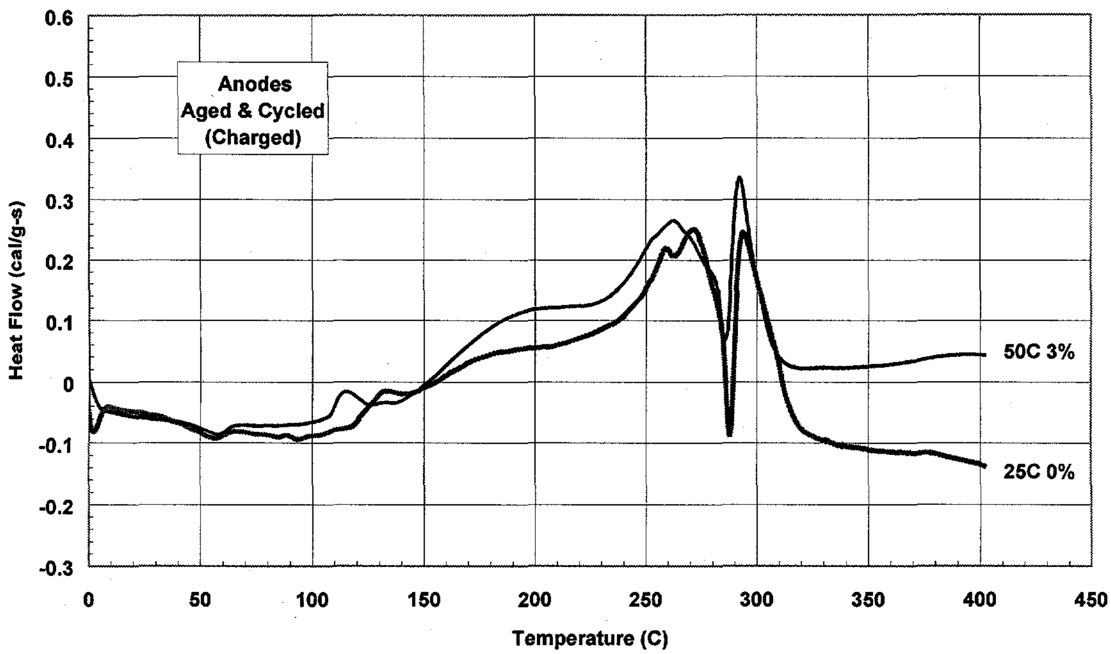

Figure 7. DSC data for GEN1 anodes (charged) aged and aged/cycled at 50°**C** 3% delta SOC.