

Thermal Stability Studies of Li-Ion Cells and Components

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Thermal stability of fully charged 550 mAh prismatic Li-ion cells (Sn-doped LiCoO_2 /graphitic carbon) and their components are investigated. Accelerating rate calorimetry (ARC) is used to determine the onset temperature of exothermic chemical reactions that force the cell into thermal runaway. Differential scanning calorimetry (DSC) and thermogravimetry analysis are used to determine the thermal stability of the cell's positive electrode (PE) and negative electrode (NE) materials from 35 to 400°C. The cell self-heating exothermic reactions start at 123°C, and thermal runaway occurs near 167°C. The total exothermic heat generation of the NE and PE materials are 697 and 407 J/g, respectively. Heat generations of the NE and PE materials, washed in diethyl carbonate (DEC) and dried at $\approx 65^\circ\text{C}$ under vacuum, are significantly lower than unwashed samples. Lithium plating increases the heat generation of the NE material at temperatures near the lithium melting point. Comparison of the heat generation profiles from DSC and ARC tests indicates that thermal runaway of this cell is close to the decomposition temperature range of the unwashed PE material. We conclude that the heat generation from the decomposition of PE material and reaction of that with electrolyte initiates thermal runaway in a Li-ion cell, under thermally or abusive conditions.

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A Li-ion cell consists of a carbon-based negative electrode (NE); a porous polymer membrane separator (high density polypropylene and/or polyethylene); and positive electrode (PE) containing lithium transition metal oxides (LiMO_2 , $\text{M}=\text{Co}$, Ni , or Mn); and a mixture of lithium salt and organic solvents provides an electrolytic medium for Li-ions to shuttle between the PE and NE. Electrodes are produced by coating slurries of active PE or NE material, polymer binder (most commonly polyvinylidene difluoride (PVDF), and small amounts of high-surface area carbon onto a metallic current collectors. The separator (Sp) electrically isolates the PE and NE but allows Li-ion transfer between them. During charge, Li-ions deintercalate from the PE and intercalate into the NE, while the reverse takes place during discharge. Passivating solid electrolyte interface (SEI) layers that form on the NE during charge/discharge of the cell inhibit extensive reaction of the electrolyte and the NE.¹ Aurbach *et al.*² also noted the formation of passivation films on the PE as well, although this effect is less well studied. The SEI-layers improves cell cycle life, *i.e.*, charge/discharge, between upper and lower electrochemical potentials associated with the PE and NE of Li-ion cells.³

Abuse conditions (over charge/discharge, short circuits, and operation at high temperatures) accelerate the rate of heat generation in a Li-ion cell. Heat generation increases exponentially with temperature while heat dissipation only increases linearly.⁴ Insufficient heat dissipation can cause thermal runaway, *i.e.*, a self-sustaining increase in cell heating as various components react exothermically. Thermal runaway can lead to catastrophic failure of the cell including violent venting or rupture along with ignition of the contents. Details of thermal runaway in Li-ion batteries are available elsewhere.⁴⁻¹⁶ Therefore, Li-ion batteries have limited operation temperature range, charge/discharge rate, and upper/lower voltage.

In order to improve the safety of Li-ion batteries, it is necessary to understand the thermal stability and heat generation from decomposition and/or exothermic reaction of the materials within the cell. While some prior studies are reported in the literature,¹⁷⁻²⁴ there is insufficient information available to draw solid conclusions about the role of the PE and NE materials on the initiation of thermal runaway and the relative heat generation of these components during runaway.

Dahn *et al.*¹⁷ showed that, at or above some critical temperature, the PE material Li_xNiO_2 , Li_xCoO_2 , or $\text{Li}_x\text{Mn}_2\text{O}_4$ is unstable and liberates oxygen into the electrolyte which, when heated above its flash point, reacts violently. The amount of oxygen released on heating increases with decrease in the x value. The structural reversibility of Li_xNiO_2 is good for $0.3 < x < 1$, but it degrades rapidly for $x < 0.3$.

For Li_xCoO_2 , the lower critical value of x is near 0.5. Zhang *et al.*¹⁸ have noted the sensitivity of these PE materials to heating. Their DSC results show an exothermic heating with onset temperatures around 200 and 230°C for $\text{Li}_{0.25}\text{NiO}_2$ and $\text{Li}_{0.25}\text{CoO}_2$, respectively. They too attributed these heat generations to the decrease in thermal stability of their sample materials, due to oxygen loss on heating. Wainwright investigated the behavior of Li_xNiO_2 /graphite and Li_xCoO_2 /graphite coin cells exposed to spot welder pulses on the positive electrode of the cell case.¹⁹ He showed that the welder power needed to initiate cell venting decreases significantly as the value of x decreases in Li_xMO_2 ($\text{M}=\text{Ni}$ and Co). He attributed this to a decrease in the thermal stability of his sample materials, due to oxygen loss on heating.

The oxygen liberation rate can be dependent on crystal structure and particle size of the delithiated PE materials. For example, our differential scanning calorimetry (DSC) results indicate that the heat generation of 5 μm particles of Li_xCoO_2 (delithiated to capacity = 116 mAh/g) is 492 J/g and that of 20 μm particles is 298 J/g. Li *et al.*²⁰ showed that the thermal stability of LiNiO_2 increases with the fundamental particle size of the material rather than the size of agglomerates.

Pasquier *et al.*²¹ studied the thermal stability of a NE made of mesocarbon microbeads (MCMB) and PVDF binder. They suggested that at first, between 120 and 140°C, there is a reaction due to the transformation of the SEI-layer products into lithium carbonate. On further heating, lithiated carbon reacts with molten PVDF via dehydrofluorination at temperatures near 200°C. Both reactions depend strongly on the specific surface area of the NE material, which in itself depends on particle size, and the degree of lithiation. They stated that reducing the specific surface area clearly improves thermal stability when PVDF is utilized as binder in the NE. Our DSC results show that the heat generation of a PVDF-free NE is nearly independent of lithium content and is significantly lower than that of the same NEs utilizing 8 wt % PVDF as binder.²² DSC results of Menachem *et al.*²³ show that heat generation of oxidized samples of lithiated graphite is significantly lower than that of unoxidized samples. This was attributed to the high reactivity of surface species at the unoxidized graphite. The authors demonstrated that the reaction of the mixed solvent EC:DEC (1:2 v/v) or the electrolyte EC:DEC (1:2 v/v): 1 M LiAsF_6 with graphite is endothermic, but exothermic with lithiated graphite. The presence of lithium salt lowers the endothermic heat of the reaction and increases its onset temperature from 185 to near 205°C. Tran *et al.*²² demonstrated a strong dependence of electrochemical lithium intercalation properties with respect to particle size and surface characteristics for both natural and synthetic graphite of various types.

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Page 1 of 6

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It is, however, evident that the heat generation of the NE depends on the type and amount of binder material, the particle size of the active carbon, its microporosity, and the lithiation stage. PE thermal stability and heat generation also depend on particle size and the crystal structure of the specific active material used. The SEI-layer that forms by the reaction of electrolyte with NE material also plays a part in determining thermal stability of the Li-ion battery.

While the studies discussed above provide some understanding of the thermal stability of Li-ion battery components, there is little information available which correlates materials thermal stability studies with full Li-ion cell behavior.

We have used accelerating rate calorimetry (ARC) to evaluate the thermal stability of commercial 550 mAh prismatic Li-ion cells in the charged state (open-circuit voltage, OCV = 4.15 V). Thermal stability of the NE and PE materials were evaluated independently and as stacked layers of PE/Sp/NE via DSC and thermogravimetry analysis (TGA). The focus here is primarily on the onset temperature of the exothermic heat generation of the charged cell, and thermal stability of its component materials "as is" vs. samples washed with solvent and dried under vacuum prior to testing. Dramatic differences in heat generation are observed for electrode materials tested "as is" vs. those of washed samples. A fully charged cell was selected since this state poses greater safety concerns relative to the discharged states.

Experimental

The commercial cell chosen for this study is a prismatic Li-ion cell with 550 mAh nominal capacity. X-ray diffraction patterns indicate that the PE and NE materials of the cells are LiCoO_2 and moderately graphitite carbons. Scanning electron microscopy/energy dispersive X-ray analyses (SEM/EDX) show the PE material is doped with Sn and has particle sizes of about 10 to 15 μm . SEM micrographs show various shapes for the NE active material that are not consistent with graphite flake or spherical MCMB. Fourier transform infrared (FTIR) spectroscopy indicates that both electrodes contain polyvinylidene difluoride (PVDF) binder. Manufacturer Safety Data Sheets for this cell show the electrolyte to contain ethylene carbonate (EC), methylethyl carbonate (MEC), and LiPF_6 .

Cell conditioning.—Five cells from the same batch were preconditioned by cycling five times between 4.2 and 3.0 V and finishing in the charged state. The charge step consisted of a constant-current step of 250 mA followed by a constant-voltage step at 4.2 V until the current dropped to 25 mA. Discharge steps were at 250 mA. At the time of the experiment, all cells were at OCV = 4.15 V and charge capacity of 550 mAh. An Arbin battery cycler (Arbin Instruments Corporation, College Station, TX) was used for cell conditioning and monitoring cell potential.

Cell thermal behavior (ARC).—An accelerating rate calorimeter (ARC, model 2000, Arthur D. Little Co., Cambridge, MA) was used to determine exothermic heating in the cell at OCV = 4.15 V from 35 to 300°C. The ARC was operated under heat-wait-search mode, 5°C/min heating rate, 10°C temperature steps, and 15 min wait-time for the cell/cell holder assembly and ARC heating jacket to reach equilibrium. Time-temperature data on the thermal behavior of the cell under adiabatic conditions were collected. Adiabatic conditions in the ARC are achieved by equalizing the heating jacket and cell/cell holder assembly temperatures once the self-heating reactions of the cell are initiated. Details on calibration procedures and the importance of sample/sample holder size and geometry are given in the ARC manual. In our case, the cell holder was an aluminum container that was shaped tightly to the cell geometry. Special efforts were made to design a cell holder of the lowest thermal mass, which has good thermal contact with the cell and has a fixed thermocouple position during experiments. Such precautions are required since battery geometry can change as internal pressure increases in the cell, because of electrolyte and electrode materials decomposition and subsequent reactions.

Cell components thermal stability (DSC/TGA).—The preconditioned cells were disassembled in a helium-filled dry box. The active electrode materials were then recovered from the surfaces of the current collectors. A sample of ≈ 15 mg PE material or ≈ 7.5 mg NE material was immediately sealed in an aluminum container specially designed for thermal stability analysis using DSC/TGA (Rheometric Scientific, Piscataway NJ). Samples of nearly similar amounts were separately soaked in DEC solvent for 36 h and then dried under vacuum at $\approx 65^\circ\text{C}$ for 12 to 14 h. Samples were thoroughly rinsed in DEC before and after soaking. After drying, each sample was sealed in an aluminum container as described above. Comparison of washed and unwashed samples allowed determination of the effects of the electrolyte and SEI-layers on heat generation and thermal stabilities of PE and NE materials. DSC/TGA scans of unwashed Sp/PE/Sp/NE layers stacked together in the same sample container were also conducted. The separator diameter in the Sp/PE/Sp/NE stacks was larger than PE and NE, and it thus prevented short-circuiting inside the sample holder. This procedure allowed study of the full cell condition synergistic effects of cell components. Active materials ratios of 2:1 were chosen to simulate the loading ratio used in most LiCoO_2 /graphite Li-ion cells.

DSC scans of lithium foil, PVDF, aluminum chips, and electrolyte (1 M LiPF_6 in EC:DMC:DEC) were performed in aluminum containers, in the range from 30 to 300°C. No artifact reactions were detected. This insured the chemical stability of the aluminum container used as a sample holder. DSC scans of a charged cell electrolyte (5 mg) and the residue of that electrolyte were also conducted. The electrolyte was obtained by puncturing a hole in the upper left corner of the cell and holding it upside down until the electrolyte leaked out. The electrolyte residue was prepared by placing an aluminum container filled with electrolyte in an oven between 45 and 50°C overnight, in a dry box. This allowed components of the electrolyte to vaporize, leaving EC and LiPF_6 . DSC scans of stock electrolyte [1 M LiPF_6 in EC:DMC:DEC (40:30:33 v/v)] from Grant Chemical, exposed to the same drying condition, were also performed. These DSC scans were conducted in order to assign some of the peaks observed for unwashed samples.

Simultaneous thermal analysis (STA, model 410, a DSC/TGA by Rheometric Scientific) was used to evaluate the thermal stability of samples. The heating rate was 10°C/min, and the temperature ranged from 35 to 400°C. DSC and TGA profiles, differentiated with respect to temperature (dW/dT or dM/dT), were used for accurate determination of onset temperatures for heat generation and mass loss. The area under the heat flow profile from DSC, located above the horizontal baseline, was used to calculate heat generation (J/g). Superimposition of mass loss and heat generation profiles helped determine whether reactions occurring in samples during heating were oxidation or reduction processes: heat generation accompanied with mass loss is an "oxidation" process, and heat generation that leads to near zero mass loss is considered a "reduction." The background peak effect was handled by subtracting the DSC profile of the preheated samples (PE and NE materials and Sp/PE/Sp/NE) from the actual heat-generation data presented here.

Results and Discussion

ARC test on charged cell.—Figure 1A shows thermal behavior of a cell at OCV = 4.15 V, in the range from 25 to 300°C. The cell self-heating rate (SHR) is determined by differentiation of temperature with respect to time (dT/dt , °C/min). A small self-heating exothermic reaction starts near 112°C but is not self-sustaining. The next heating step increased cell temperature to 123°C, above which the cell slowly self-heats to 167°C, at which point thermal runaway occurs. Figure 1b shows the temperature ranges where cell self-heating occurs prior to thermal runaway.

DSC/TGA of cell components analysis.—**NE material.**—Figure 2A to C depicts the DSC/TGA profiles of NE material recovered from a cell at OCV = 4.15 V: (A) sample washed in DEC and dried at $\approx 65^\circ\text{C}$ under vacuum; (B) sample with SEI-layer in the presence of electrolyte; and (C) sample with SEI-layer and some lithium plat-

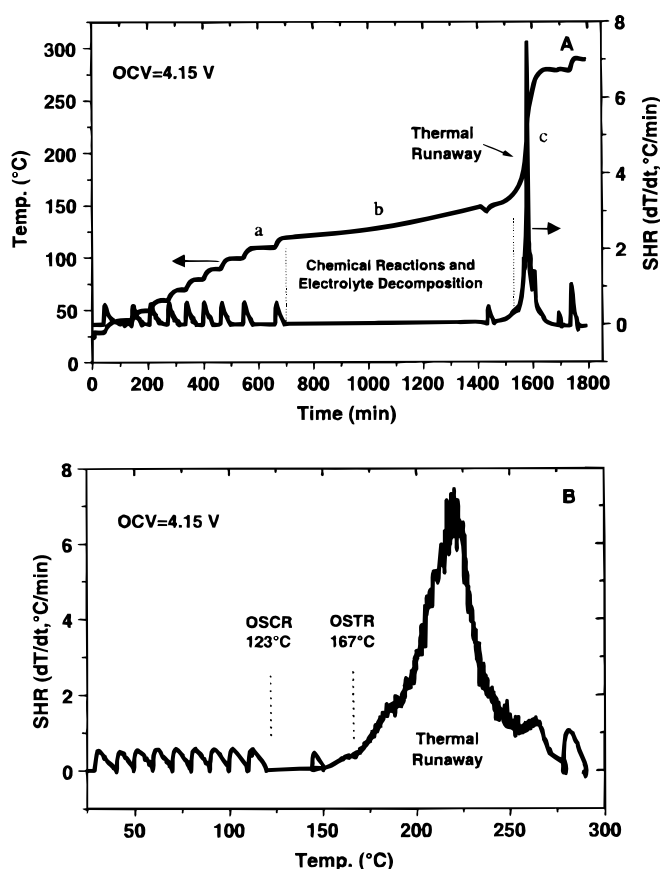


Figure 1. (A) ARC of a 550 mAh commercial Li-ion cell, with open-circuit potential at 4.15 V, under adiabatic conditions: (a) small exothermic chemical reaction, (b) self-heating reaction prior to thermal runaway, and (c) cell thermal runaway region. (B) Cell SHR vs. temperature. The onset of chemical reaction preceding thermal runaway starts $\approx 123^\circ\text{C}$, onset of thermal runaway starts $\approx 167^\circ\text{C}$.

ing, in the presence of electrolyte. Sample A shows a near-zero mass loss. For sample A, the heat generation (317 J/g) is mostly attributed to the reaction of Li_xC_6 with PVDF. The reaction begins at $\approx 200^\circ\text{C}$ and reaches a maximum at 287°C . This appears to be a reduction reaction, since no mass loss occurs. The sample shows little evidence of heat generation due to electrolyte decomposition or reaction with the NE material. This indicates that our procedure for removing the SEI layer or electrolyte from NE has been effective.

For sample B, the larger heat generation (697 J/g) is attributed to SEI-layer breakdown and electrolyte decomposition, and possible reactions of products with Li_xC_6 and PVDF. Thermal decomposition of the SEI-layer occurred at $\approx 100^\circ\text{C}$. The main heat generation, which is due to the reaction of Li_xC_6 with PVDF started at $\approx 210^\circ\text{C}$ and reached a maximum at 300°C . The sample experiences $\approx 8\%$ mass loss, which mostly occurs between 125 and 260°C . The heat generation of fresh electrolyte, or electrolyte without volatile components, is endothermic upon heating, from room temperature to 300°C . Therefore, the main difference between heat generation in washed and unwashed NE materials can be attributed to the decomposition reaction of electrolyte with NE material.

Sample C, heat generation (827 J/g) is attributed to thermal decomposition of the SEI-layer, electrolyte decomposition, reaction of electrolyte with lithium-metal, and reaction of Li_xC_6 and PVDF. The SEI-layer breakdown occurred near $\approx 100^\circ\text{C}$. The main heat generation (reactions of plated lithium-metal, Li_xC_6 , and PVDF) began near the melting point of lithium (180°C) and reached a maximum at $\approx 310^\circ\text{C}$. The sample experienced a mass loss of about 9.5%, which occurred mostly between 125 and 260°C . The difference between mass loss and heat generation of samples B and sample C is related

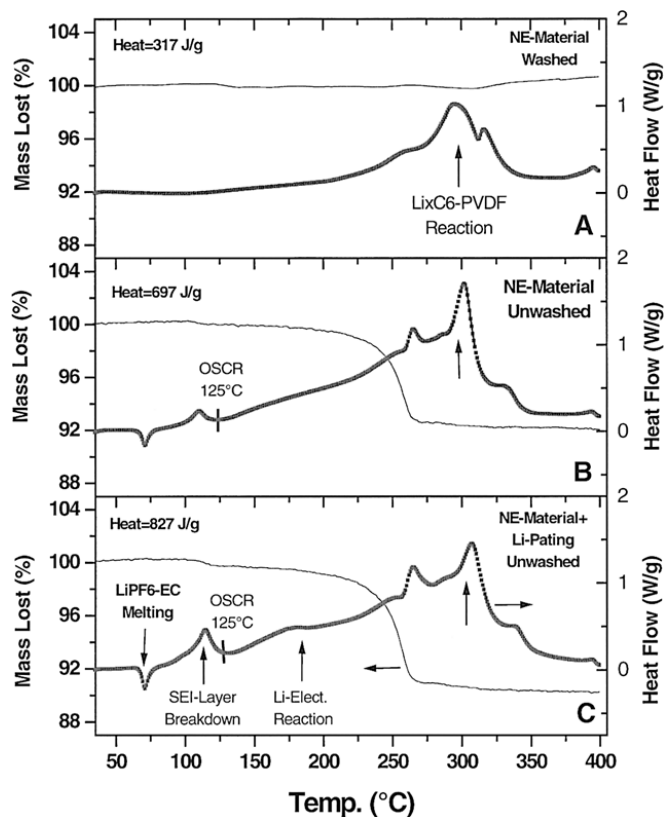


Figure 2. DSC and TG profiles of NE material from the 550 mAh commercial Li-ion cell, with open-circuit potential at 4.15 V: (A) washed sample, (B) unwashed sample, and (C) unwashed sample with lithium plating.

to lithium plating on sample C. Small mass losses from both unwashed samples B and sample C, at temperatures above 260°C , indicate that the reaction of Li_xC_6 and PVDF is mostly a reduction process. In summary, reactions below 260°C are related to SEI-layer breakdown and electrolyte decomposition. Above 260°C , the major reaction is between Li_xC_6 and PVDF. These results are consistent with previous studies of MCMB NE materials.¹⁷

PE material.—Figure 3A and B depict the DSC/TGA scans of washed and unwashed PE materials (Sn-doped Li_xCoO_2), recovered from a cell at OCV = 4.15 V. The washed sample results are similar to prior studies¹⁵⁻¹⁷ and show no evidence of heat-generation peaks for electrolyte or passivation layers (Fig. 3A). Again, this indicates that our procedure for removing the electrolyte and possible passivation layers is effective.

Heat generation from the washed sample (146 J/g) occurs between 178 and 250°C with a mass loss of $<1\%$; and between 250 and 400°C , with a mass loss of about 4.5%. These exothermic heat generations are attributed to sample decomposition, accompanied by oxygen liberation.¹⁵⁻¹⁷ Detailed thermal decomposition steps of the washed PE material, based on the X-ray diffraction analysis, are discussed below.

Heat generation (407 J/g) of the unwashed sample begins near 167°C and rises sharply to a maximum at 214°C (Fig. 3B). The total mass loss is 11%. The lower onset temperature of thermal decomposition and higher heat generation and mass loss of the unwashed sample are attributed to decomposition of the electrolyte and any passivation layer along with possible subsequent reaction of oxygen liberated from the PE material with the electrolyte.

Through independent DSC experiments, under open atmosphere, we observed that the thermal response of EC-based electrolyte is endothermic. This suggests that the high heat generation of the unwashed sample, upon heating, is not simply due to reaction of liberated oxygen from the decomposition of PE material with electrolyte.

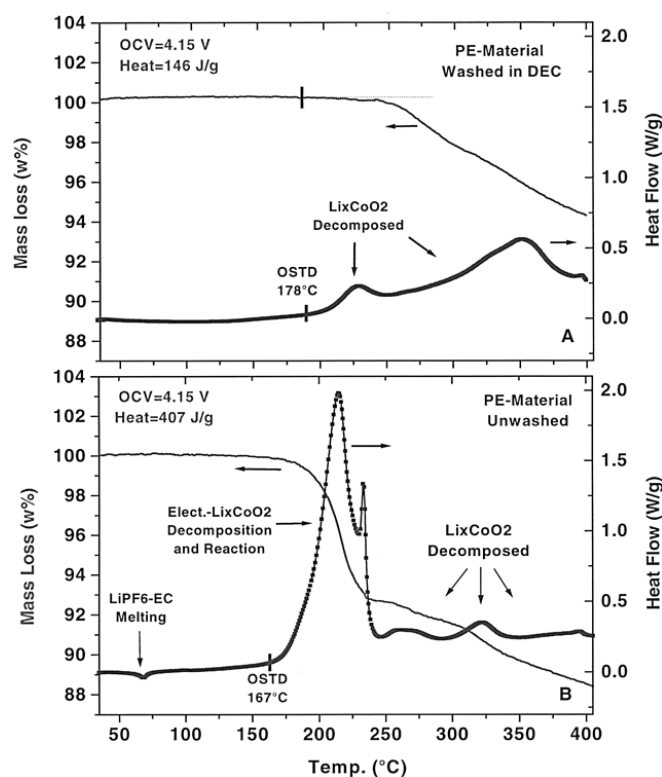


Figure 3. DSC and TG of PE material from 550 mAh commercial Li-ion cell, with open-circuit potential at 4.15 V: (A) washed sample and (B) unwashed sample.

If this were the case, an exothermic reaction would be expected from the DSC results of the electrolyte sample in air (oxygen environment). It appears that there is a complex synergistic relationship among the electrolyte and delithiated Li_xCoO_2 and/or its decomposition products that creates this large exothermic reaction. The combination of these materials may catalyze the electrolyte/oxygen reaction. In any case this reaction coincides with the onset of thermal runaway in the Li-ion cell. Further heat is generated with PE material decomposition upon heating.

Sp/PE/Sp/NE.—Figure 4 is superimposition of DSC/TGA scans of stacked Sp/PE/Sp/NE layers vs. DSC of PE and NE materials alone. For Sp/PE/Sp/NE, the total heat generation (931 J/g) contains two distinct exothermic peaks, one between 167 and 225°C, and the other between 240 and 275°C. The former matches the exothermic heat generation from PE material decomposition closely, while the latter falls in the range where the reaction of Li_xC_6 and PVDF binder occurs in the NE material. The main mass loss from Sp/PE/Sp/NE falls in the range where decomposition of electrolyte and PE material occurs. The overall differences between the heat-generation profiles perhaps is due to differences in the chemistry of the PE and NE material taken together in the presence of a separator, as Sp/PE/Sp/NE. Through some independent studies, it was found that the exothermic heat profiles of PE and NE materials often change when contacted on both sides with separator.

Thermal runaway event leading to thermal runaway.—The self-heating onset of the full cell near 112 and 123°C observed in accelerating rate calorimeter (ARC) experiments correlate with SEI-layer breakdown and electrolyte reactions on the unwashed NE observed in the DSC/TGA experiments. The onset of thermal runaway in the full cell ($\approx 167^\circ\text{C}$, ARC data) matches the onset of unwashed PE thermal decomposition ($\approx 167^\circ\text{C}$, DSC/TGA), and reaction of that electrolyte. The total heat evolved by the cell was not measured, to avoid possible damage to the ARC. However, the heat evolved certainly includes decomposition of both the PE and NE materials.

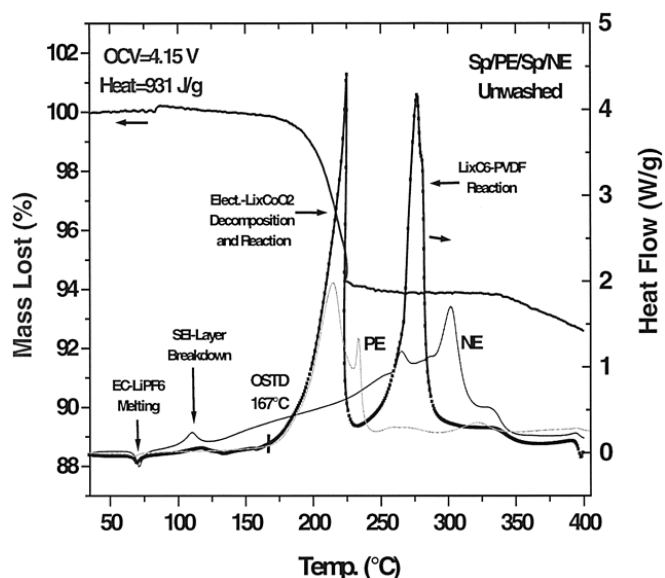


Figure 4. DSC and TG of unwashed Sp/PE/Sp/NE composite vs. PE and NE materials.

The full cell ARC data and component DSC/TGA data are consistent with the following thermal reaction scheme for this cell: (i) thermal breakdown of the SEI-layer on the NE material, (ii) thermal decomposition/reaction of electrolyte with the NE material, (iii) thermal decomposition of the PE material and reaction of electrolyte, and (iv) reaction of PVDF binder with lithiated NE material (Li_xC_6). Among these steps, the reaction of lithium intercalated carbon with PVDF binder (item iv), delivers a considerable amount of heat. Prior studies showed MCMB-25 28/PVDF (12.5 wt %) NE can deliver 1200 J/g when lithiated to 85% of its full capacity at C/5 rate.¹⁷ DSC results of the present study show that a similar NE material of the same MCMB as Ref. 17 (with 8 wt % PVDF) delivers nearly 1100 J/g when the sample lithiated to OCV = 0.01 V at C/5 rate. The differences can be attributed to capacity and binder differences. Note that the NE samples recovered from the full cell are not lithiated to their full capacity. To avoid lithium plating, lithium-ion cells typically contain excess anode capacity. Thus, when the cell is fully charged, the anode is only about 80 to 90% lithiated.

Several practical consequences for Li-ion cell safety can be inferred from these data. The onset of exothermic reaction of the NE occurs at relatively low temperatures ($\approx 120^\circ\text{C}$) in this cell. However, the heat generated by these reactions is fairly small. As long as the cell is able to dissipate this heat, the cell temperature will not reach the onset temperature for thermal runaway. Therefore, careful cell design and applications engineering are essential to ensure cell safety in this temperature region. Otherwise the heat generated by these NE reactions may be sufficient to raise the cell temperature above the thermal runaway onset temperature.

Thermal runaway onset appears to be associated with PE decomposition in this cell. The importance of the PE thermal stability is well known¹⁴⁻¹⁶ and has prompted efforts to find alternatives to LiCoO_2 , notably LiMn_2O_4 .

While the thermal decomposition onset of the NE and binder material occurs at relatively high temperatures, the substantial heat generated by this reaction certainly contributes to the ultimate consequences of a thermal runaway event. Therefore, the safety of a given cell can be directly affected by both PE and NE materials.

X-ray diffraction analysis.—**NE material.**—Figure 5 shows XRD patterns of the NE material of a fully discharged test cell, synthetic graphite (SFG-44, Lonza), and mesocarbon microbeads (MCMB-25 28, Osaka Gas Co.). The figure inset is a magnification of the (002) plane, which appears between 25 and 27° depending on the interlayer spacing (d) of the graphene sheets. Note that the diffracted X-ray

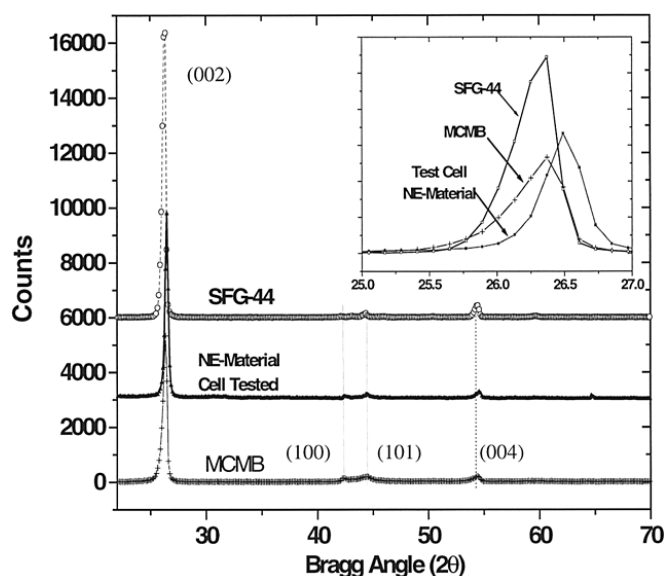


Figure 5. XRD patterns of a fully discharged commercial 550 mAh cell NE material and that for the synthetic graphite (SFG-44) and MCMB: inset is magnification of patterns for plane (002) that represent the degree of graphitization.

counts for the test cell NE material (6643 , $2\theta = 26.48^\circ$) is slightly higher than MCMB (5543 , $2\theta = 26.37^\circ$) and much lower than SFG-44 (10813 , $2\theta = 26.36^\circ$); all samples' fwhm are similar. This indicates that the test cell NE material is a graphitic carbon with structural characteristic similar to MCMB than to highly graphitic SFG-44 carbon.

PE material.—Figure 6A shows mass loss and dM/dT vs. temperature profiles of washed PE sample recovered from T-cell at OCV = 4.15 V. This indicates that the sample experiences a near zero mass loss between 30 and 185°C and 1% mass loss from 185 to 235°C . Figure 6B is a superimposition of X-ray diffraction profiles of washed PE samples (OCV = 4.15 V) preheated to 30, 235, 310, or and 580°C , respectively. The figure inset is a magnification of changes in the diffraction angle (2θ) of the (003) crystallographic plane. Note that although little heat generation occurs in these ranges, the peak intensity of the (003) plane (Fig. 6B) was lowered by 4000 counts. This suggests that the PE material of the cell (OCV = 4.15 V) restructures before initiating the major decomposition/heat generation step above 235°C . Restructuring induces the appearance of the (006) plane and probably occurs in the range from 180 to 235°C where the mass loss is about 1%. Heating to 310°C causes further loss of structure, evidenced by the up-shift in 2θ , the lowering of peak intensity counts for the (003) and (104) planes, and the broadening of peaks for the (101) and (107) planes. Further heating to 580°C causes further lowering of peak intensity of the (003) plane and formation of additional new phases. Note that the lowering of peak intensity of the (003) plane indicates deterioration in the degree of layered structure in Li_xCoO_2 . The increase in 2θ shows that the interlayer distance (d_{003}) of the (003) plane decreases. This shows that the oxygen layers of the frame structure are collapsing as more and more oxygen is removed from the sample by heating to higher temperatures. Unlike Li_xNiO_2 , which on heating transforms from a layered structure to the spinel, the delithiated Li_xCoO_2 does not undergo such a phase transformation.²¹ On heating to temperatures above 245°C , delithiated Li_xCoO_2 decomposes to form a layered structured LiCoO_2 and stable Co_3O_4 .^{17,18} In this case other phases (marked as "*" in Fig. 6B) appear near $2\theta = 32$, 38, 45, and 62° .

Conclusion

The objective of this work was to correlate the thermal stability of cell components with the thermal behavior of a complete cell

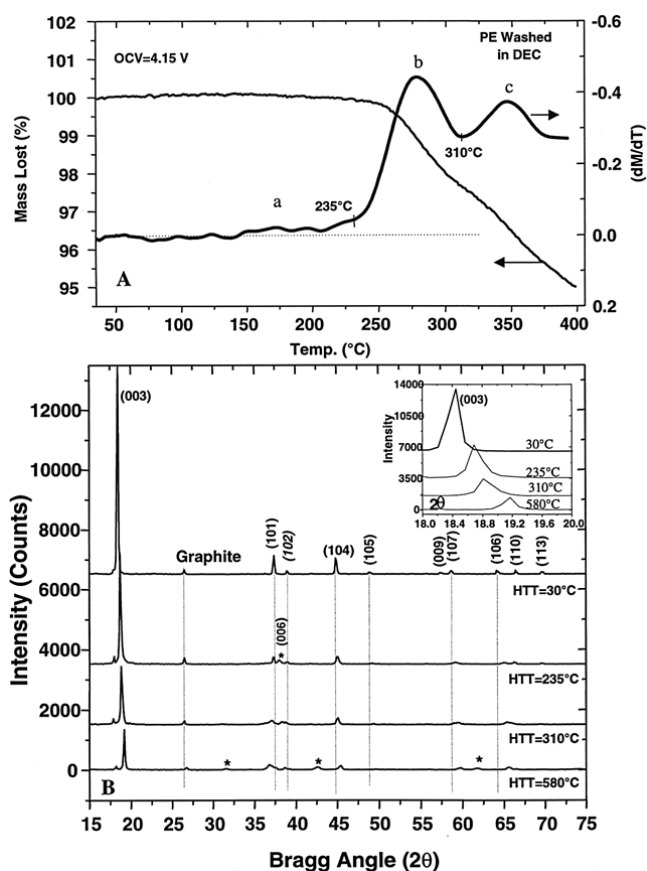


Figure 6. (A) Mass loss and dM/dT vs. T . for washed PE material of OCV = 4.15 V. Three regions of different loss rates are marked a, b, and c. (B) X-ray diffraction profiles of PE material preheated to 30, 235, 310, and 580°C . Inset shows detail of (003) crystal plane: (*) indicates new phases appearing with increasing sample heating temperature.

under thermally abusive condition. An accelerating rate calorimeter was used to determine the temperature ranges where a commercial cell starts self-heating and goes into thermal runaway, while differential scanning calorimetry and thermogravimetric analysis provided data on the thermal stability of this cell's PE and NE materials along with composite samples of Sp/PE/Sp/NE. ARC data show that the cell begins self-heating slowly from ≈ 123 to $\approx 167^\circ\text{C}$, and then goes into thermal runaway. The onset of cell self-heating matches the temperature range of SEI-layer breakdown and decomposition of electrolyte and reaction of that with PE and NE materials. The thermal runaway temperature of the cell matches the temperature at which thermal decomposition of unwashed PE material occurs. The following steps characterize the mechanism for thermal runaway in this cell. First, there is a slow thermal decomposition of the SEI-layers and electrolyte reaction on the NE. Second, the PE decomposes and reacts with electrolyte. The heat from this reaction is sufficient to raise the internal cell temperature to 250°C , the range where reaction of Li_xC_6 and PVDF occurs.

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