Thermal Properties of Lithium-Ion Battery and Components

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Experimental thermal property data of the Sony US-18650 lithium-ion battery and components are presented, as well as thermal property measuring techniques. The properties in question are specific heat capacity ($C_p$), thermal diffusivity ($\alpha$), and thermal conductivity ($k$), in the presence and absence of electrolyte [1 M LiPF$_6$ in ethylene carbonate-dimethyl carbonate (EC:DMC, 1:1 wt %)]. The heat capacity of the battery, $C_p$, is 0.96 ± 0.02 J g$^{-1}$ K$^{-1}$ at an open-circuit voltage (OCV) of 2.75 V, and 1.04 ± 0.02 J g$^{-1}$ K$^{-1}$ at 3.75 V. The thermal conductivity, $k$, was calculated from $k = \alpha C_p$, where $\alpha$ was measured by a xenon-flash technique. In the absence of electrolyte, $k$ increases with OCV, for both the negative electrode (NE) and the positive electrode (PE). For the NE, the increase is 26% as the OCV increases from 2.75 to 3.75 V, whereas for the PE the increase is only 5 to 6%. The dependence of both $C_p$ and $k$ on OCV is explained qualitatively by considering the effect of lithiation and delithiation on the carbon carrier density, which leads to n-type semiconduction in the graphitic NE material, but a change from semiconducting to metallic character in Li$_x$CoO$_2$ PE material. The overall effect is an increase of $C_p$ and $k$ with OCV. For $k$ this dependence is eliminated by electrolyte addition, which, however, greatly increases the effective $k$ of the layered battery components by lowering the thermal contact resistance. For both NE and PE, the in-plane $k$ value (measured along layers) is nearly one order of magnitude higher than the cross-plane $k$. This is ascribed mostly to the high thermal conductivity of the current collectors and to a lesser extent to the orientation of particles in the layers of electrodes.

A successful rechargeable lithium battery of high energy density has been developed based on shuttling of lithium ions between two intercalation electrodes (“rocking chair cell”). Commercially available lithium-ion cells have a negative electrode (NE) consisting of a copper foil coated with a mixture of carbon-based material, binder, and carbon black, an electrolyte consisting of lithium salts in organic solvent, and a positive electrode (PE) consisting of a mixture of lithium transition metal oxides, binder, and carbon black coated over aluminum foil. The separator (Sp) is a microporous polymer having good ionic and sufficiently low electronic conductivity, such as polypropylene. During charge, lithium ions deintercalate from the PE and intercalate into the NE, and the reverse takes place during discharge.

The operation of most lithium-ion cells is limited to a temperature range of 20 to 55°C, in which heat generation due to internal resistance and polarization is easily controllable by working within the voltage window (upper/lower cutoff voltage) and range of charge/discharge rates recommended by the manufacturers. Abuse conditions (high discharge/charge rates, short circuits, and operation at high ambient temperature) steeply accelerate the net accumulation of thermal energy in lithium-ion cells. The rate of heat generation increases exponentially with cell temperature, while the rate of heat transfer to a cool environment (ambient cooling) increases only linearly. Ultimately, the cell may experience “thermal runaway” accompanied by pressure buildup, which may lead to bursting of the cell, or fire. To guarantee a safe operation under any conditions, commercial lithium-ion cells are therefore of relatively small size.

For portable and mobile power applications, however, scaled-up batteries are desirable. For example, systems of 100 W/kg power transfer to a cool environment (ambient cooling) increases only linearly. For both NE and PE, the in-plane $k$ value (measured along layers) is nearly one order of magnitude higher than the cross-plane $k$. This is ascribed mostly to the high thermal conductivity of the current collectors and to a lesser extent to the orientation of particles in the layers of electrodes. For portable and mobile power applications, however, scaled-up batteries are desirable. For example, systems of 100 W/kg power transfer to a cool environment (ambient cooling) increases only linearly.

However, for a more accurate check on the validity of the one-dimensional assumption, one must know the thermal conductivities of cell components in the direction of the electrode surface (in-plane $k$) as well as perpendicular to it (cross-plane $k$). Experimental values for these properties are not widely available in the literature; therefore, this work aims to present some methods of measurement and provides relevant data. The experiments are illustrated by application to the commercially available Sony US-18650 cylindrical lithium-ion cell, which has a nominal capacity of 1.35 Ah. The cell was retrieved from a double-battery pack used in Sony Camcorders, purchased in September, 1996, from the Sony Products Store in Chicago, IL 60616. This cell contains a NE which consists of specially tailored micrographic carbon flakes as NE material and a highly layered structure LiCoO$_2$ as PE material. Based on the masses of active PE and NE materials, recovered from current collectors coated on both sides, a loading ratio of about 1.89 was estimated for this cell. The exact amount of binder material and other additives included in both electrodes is unknown. The individual cell components were measured and weighted, with results shown in Table I.

Two different methods of measuring $C_p$ were used: (i) transient temperature measurement and (ii) adiabatic calorimetry. Similarly, two methods were used to obtain $k$ values for cell components. In the first method, the cross-plane $k$ was determined by applying a known heat flux across the surface of PE/Sp/NE layers, and sampling the temperature difference at known locations between the stacked layers. In the second method, both cross-sectional and in-plane $k$ values were calculated from cross-plane and in-plane thermal diffusivity ($\alpha$) values. $k$ was measured by a xenon flash technique (XFT), with and without electrolyte [1 M LiPF$_6$ in EC:DMC (1:1 wt%)].

**Experimental**

Specific heat capacity, method 1 (cooling transient).—Figure 1 shows a schematic diagram of the heating assembly used to measure $C_p$ of a Sony battery at OCV = 2.74 V. The core of this assembly was formed by an insulating cylindrical block of polystyrene foam (120 mm od, 150 mm long) with a closed-end cylindrical cavity (19 mm id, 100 mm deep). A high-resistance Ni/Cr heater (AWG 24, from Omega), electrically insulated by high-thermal-conductivity tape, spirally wound, was fitted close to the cavity wall. An Arbin battery cycler (Arbin Instrument Corporation, College Station, TX, model BT-2042) supplied direct current to the heater.

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Table I. Physical parameters of the Sony 18650 lithium-ion battery components.

<table>
<thead>
<tr>
<th>Components</th>
<th>Positive electrode</th>
<th>Negative electrode</th>
<th>Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total electrode mass, g</td>
<td>15.2</td>
<td>9.10</td>
<td>1.28</td>
</tr>
<tr>
<td>Total length, mm</td>
<td>521.1</td>
<td>534.0</td>
<td>1192.0</td>
</tr>
<tr>
<td>Total width, mm</td>
<td>52.9</td>
<td>56.0</td>
<td>59.2</td>
</tr>
<tr>
<td>Total thickness, mm</td>
<td>0.185</td>
<td>0.198</td>
<td>0.025</td>
</tr>
<tr>
<td>Foil thickness, mm</td>
<td>0.02</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>Mass of active material, g</td>
<td>13.9</td>
<td>7.35</td>
<td></td>
</tr>
</tbody>
</table>

The external heat-transfer coefficient ($h$, W m$^{-2}$ K$^{-1}$), determining heat loss from the assembly, was measured using a type 416 stainless steel reference sample ($C_p = 0.56$ J g$^{-1}$ K$^{-1}$), shaped to the geometry of the Sony battery (18 mm diam, 65 mm long). The reference sample was placed inside the heater cavity and heated to 60°C, slowly enough for the sample temperature to remain uniform. The power to the heater was then cut off, and the temperature ($T$) was sampled at 1 s intervals by two type E (Ni-Cr vs. Cu-Ni) thermocouples attached at opposite sides of the reference sample, at a location midway along its length. The ambient temperature ($T_a$) was sampled independently with a type E thermocouple positioned at a location 300 mm from the outside wall of the insulating block. Data sampling continued until the temperature difference (sample/ambient) was less than 1 K. Convection cooling was prevented by making the cavity fit the reference sample or cell closely.

An energy balance

$$\dot{Q}/hA = mC_p\left[(T - T_a) + mC_p/dTdt\right]$$

was used to calculate the external heat-transfer coefficient ($h$) of the assembly. Here, $\dot{Q}$ is the heat supplied by the heater, and the other symbols (see List of Symbols) refer to the sample. The solution to this equation is

$$T - T_a \over T_{ss} - T_a = 1 - \exp(-\tau)$$

where

$$\tau = t \over mC_p/hA$$

and

$$T_{ss} = T_a + \dot{Q}/hA$$

Here $t$ is the time elapsed since the start of heating, and $T_{ss}$ the temperature when the steady state is reached.

Since $Q = 0$ during cooling, the solution to Eq. 1 becomes simply $\theta = \exp(-\tau)$, where $\tau$ is defined as above with $t$ being the time elapsed since the start of cooling. Therefore, if the value of $C_p$ is known, $h$ can be obtained from $mC_p/h$ times the negative slope of a plot of $\ln[(T - T_a)/(T_{ss} - T_a)]$ vs. time

$$h = -mC_p/A \left(\ln[(T - T_a)/(T_{ss} - T_a)]\right)$$

Figure 2a shows a plot of $\ln[(T - T_a)/(T_{ss} - T_a)]$ vs. cooling time for the reference sample, whose slope ($-0.0008$ s$^{-1}$), with $m = 152.7$ g, $C_p = 4.65$ J g$^{-1}$ K$^{-1}$, and $A = 4.18 \times 10^{-3}$ m$^2$, yields $h = 13.45 \pm 0.1$ W m$^{-2}$ K$^{-1}$. The same procedure applied to the Sony cell at OCV = 2.75 V (Fig. 2b), yields a slope ($-0.00175$ s$^{-1}$) from which, with the value $h = 13.43 \pm 0.1$ W m$^{-2}$ K$^{-1}$, $m = 49$ g, and $A = 4.18 \times 10^{-3}$ m$^2$, as determined previously, the $C_p$ of the Sony cell would be 0.800 J g$^{-1}$ K$^{-1}$. To check this result, the value of $C_p$ was determined directly, using adiabatic calorimetry.

Specific heat capacity, method two (adiabatic calorimetry).—Figure 3 shows a schematic diagram of the two-part adiabatic calorimeter used for measuring $C_p$. The lower part consists of a thin-walled cylindrical aluminum container (ca. 0.3 mm thick, 25 mm id, 100 mm long) partially filled with transformer oil and a heating coil. The container is surrounded by a Styrofoam and Dewar insulation assembly. The upper part of the calorimeter is used to preheat the reference sample or cell to be immersed, or to stabilize its temperature. It also contains a heater coil and is insulated by styrofoam. In the lower chamber, high thermal conductivity transformer oil (Midtown Petroleum Co., IL, L no. T-1026) is used for rapid dissipation of temperature differences in the calorimeter. Heating is provided by a Hewlett Packard-6632A dc power supply. A microvoltmeter

![Figure 1](image1.png)

**Figure 1.** Detail of heat-flux calorimeter setup for measuring the specific heat capacity of the Sony US-18650 lithium-ion battery. Inset: typical plot of cooling profile for battery or reference sample.

![Figure 2](image2.png)

**Figure 2.** Cooling profiles of (a, top) stainless steel reference sample; (b, bottom) Sony US-18650 lithium-ion battery. Both are initially heated to 50°C.
Keithley 2000, 10 channel multimeter) measures the temperatures of sample and oil bath simultaneously. The upper and lower chambers are separated by a sliding trap door made of Styrofoam. To immerse the reference sample or battery into the transformer oil of the lower chamber, the trap door is pulled out. A wire restrains the fall of the sample so as to avoid splashing.

The calorimeter constant, i.e., total heat capacity ($K$, J K$^{-1}$), was determined using a reference sample of aluminum or type 416 stainless steel, sized to the geometry of the Sony lithium-ion cell. The sample was placed in the upper insulation compartment of the calorimeter, but not heated, while the bath oil was heated to a temperature of 310 to 315 K. After the bath oil reached a stationary temperature (typically after 1 to 2 h), the reference sample or cell (still at room temperature) was immersed slowly. The final temperature of the lower chamber was measured after about 10 min. Figures 4a and b show typical temperature profiles for the aluminum reference sample and the Sony cell.

The calorimeter constant ($K$) was calculated from

$$K = (mC_p\Delta T)_{\text{bath}} = (mC_p\Delta T)_{\text{sample or battery}}$$

The results are given in Table II, in chronological order. Apparently, changes (probably physical) occurred after the first three measurements. Since the time needed for heat conduction in aluminum is much shorter than in stainless steel, equilibrium is reached more rapidly, and the graphs (Fig. 4) are easier to read accurately. Hence the values based on the aluminum reference sample are probably more reliable. The last two of the values based on stainless steel agree with these. Therefore, the average over five independent aluminum standard measurements, conducted at 24 h apart, was used to calculate $K$.

To determine $C_p$ of the Sony cell ($C_p_{\text{battery}}$), the hot bath oil/room-temperature sample procedure was adopted. The temperature difference cell/bath oil was monitored from the initial difference to thermal equilibrium, at 1/2 min intervals. $C_p_{\text{battery}}$ was then calculated from Eq. 4.

Table III shows $C_p_{\text{battery}}$ values measured in the range of room temperature to ca. 315 K. These values are higher than those obtained by the first method by about 20%. They also are closer to the values estimated$^{1-8}$ or measured by others.9

**Table II. Specific heat capacity of reference samples.** $C_p_{\text{Al}}$: specific heat capacity of aluminum reference sample from experimental measurements evaluated by using the averaged value of the calorimeter constant, $K_{\text{Al}}$, derived from measurements using a type 416 stainless steel sample. $C_p_{\text{SS}}$: specific heat capacity of type 416 stainless steel reference sample similarly evaluated using the averaged value of the calorimeter constant, $K_{\text{Al}}$, derived from measurements using an aluminum reference sample.

<table>
<thead>
<tr>
<th>Calibration constant</th>
<th>$K_{\text{SS}}$</th>
<th>$K_{\text{Al}}$</th>
<th>$C_p_{\text{Al}}$ vs. $K_{\text{SS}}$ (J g$^{-1}$ K$^{-1}$)</th>
<th>Relative deviation</th>
<th>$C_p_{\text{SS}}$ vs. $K_{\text{Al}}$ (J g$^{-1}$ K$^{-1}$)</th>
<th>Relative deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>112.30</td>
<td>96.71</td>
<td>0.898</td>
<td>&lt;1%</td>
<td>0.462</td>
<td>&lt;1%</td>
<td></td>
</tr>
<tr>
<td>107.35</td>
<td>97.15</td>
<td>0.947</td>
<td>5.2%</td>
<td>0.461</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>106.90</td>
<td>95.88</td>
<td>0.877</td>
<td>2.5%</td>
<td>0.461</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>98.52</td>
<td>92.90</td>
<td>0.968</td>
<td>7.5%</td>
<td>0.462</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>94.51</td>
<td>98.50</td>
<td>0.92</td>
<td>4%</td>
<td>$C_p_{\text{av}} = 0.92$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>103.91 ± 7%</td>
<td>96.20 ± 2%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CRC Handbook: $C_p_{\text{Al}}$ = 0.900 J/g°C and $C_p_{\text{SS}}$ = 416 = 0.460 J/g°C.
directly the thermal conductivity of composite stacked layers of the battery component PE, NE, or PE/Sp/NE layers stacked, using a heat flux perpendicular to the plane of the layers. Prior to thermal-conductivity measurements, conducted in open air with no electrolyte present, samples were washed in ethanol and dried at 60°C under argon atmosphere in a dry box. The heating assembly was a form of terminal resistor composed of high resistance Ni/Cr wire (AWG 28, from Omega) with a nickel strip spot-welded to each end. Each nickel strip was soldered to two stranded copper wires; one for current application and the other for potential measurement. Current was measured by a Keithley model 2000 microvoltmeter. The thermal conductivity \( k \) was then calculated using Eq. 5

\[
 k = \frac{(L_o/A)(I/V\Delta T_x)}{[5]}
\]

where \( \Delta T_x \) is the temperature difference between the heater plate (read by thermocouple no. 1 in intimate contact with the copper plate) and the \( x \)th layer above the copper plate. \( V \) is the potential difference across the heater wire; \( I \), the supplied current; \( L_o \), the distance over which \( \Delta T_x \) is measured; and \( A \), the surface area of each of the sample layers.

The choice of insulation materials is important, \(^1^1\) as well as the location of the thermocouples. The thickness of a single PE/Sp/NE assembly was ca. 0.42 mm. Thermocouple no. 1 was located at zero distance from the heater plate, thermocouples no. 2 to no. 5 at distances \( L_1 \) to \( L_4 \) from the surface of the heater plate, which closely corresponds to the accumulated thickness of successive layers. Thermocouples were flat tip (0.18 mm thick) type E (Omega Corp, Stamford, CT 06907).

The measured values of \( k \) range from 0.66 to 0.33 W m\(^{-1}\) K\(^{-1}\) depending on the current level and location where \( \Delta T_x \) was measured. However, all values were lower than those calculated from data for lithium-ion battery components (PE, NE, and separator) given by Chen and Evans \(^3\) and Kanari. \(^9\) Because we felt that our direct thermal conductivity measurements at steady state might be affected by inevitable heat losses, we used a second dynamic method to check these \( k \) values.

**Thermal conductivity, method 2, from thermal diffusivity measurement.**—If the thermal diffusivity (\( \alpha \)) of a stack of components is

<table>
<thead>
<tr>
<th>Experiments</th>
<th>( \Delta T ) (Oil) (K)</th>
<th>( \Delta T ) (Batt.) (K)</th>
<th>( K_{ad} ) (J g(^{-1}) K(^{-1}))</th>
<th>( C_p ) based on ( K_{ad} ) (J g(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( OCV = 3.75 \text{ V} )</td>
<td>4.07</td>
<td>8.94</td>
<td>96.2</td>
<td>1.012</td>
</tr>
<tr>
<td></td>
<td>3.39</td>
<td>6.38</td>
<td>96.2</td>
<td>1.088</td>
</tr>
<tr>
<td></td>
<td>2.47</td>
<td>5.41</td>
<td>96.2</td>
<td>1.020</td>
</tr>
<tr>
<td></td>
<td>2.63</td>
<td>5.70</td>
<td>96.2</td>
<td>1.036</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>1.04 ± 0.034</td>
</tr>
<tr>
<td>( OCV = 2.75 \text{ V} )</td>
<td>2.41</td>
<td>5.18</td>
<td>96.2</td>
<td>1.010</td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>6.25</td>
<td>96.2</td>
<td>0.909</td>
</tr>
<tr>
<td></td>
<td>1.72</td>
<td>4.11</td>
<td>96.2</td>
<td>0.936</td>
</tr>
<tr>
<td></td>
<td>2.02</td>
<td>4.67</td>
<td>96.2</td>
<td>0.967</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
<td>6.25</td>
<td>96.2</td>
<td>1.000</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td>0.96 ± 0.018</td>
</tr>
</tbody>
</table>

### Table III. Specific heat capacity of the Sony US-18650 lithium-ion battery at \( OCV = 3.75 \text{ V} \) and \( OCV = 2.75 \text{ V} \). All experiments carried out using (hot bath/room-temperature cell) procedure.

<table>
<thead>
<tr>
<th>( K ) (Oil) (K)</th>
<th>( K ) (Batt.) (K)</th>
<th>( K_{ad} ) (J g(^{-1}) K(^{-1}))</th>
<th>( C_p ) based on ( K_{ad} ) (J g(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.63</td>
<td>5.70</td>
<td>96.2</td>
<td>1.036</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>1.04 ± 0.034</td>
</tr>
<tr>
<td>2.41</td>
<td>5.18</td>
<td>96.2</td>
<td>1.010</td>
</tr>
<tr>
<td>2.54</td>
<td>6.25</td>
<td>96.2</td>
<td>0.909</td>
</tr>
<tr>
<td>1.72</td>
<td>4.11</td>
<td>96.2</td>
<td>0.936</td>
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<tr>
<td>2.02</td>
<td>4.67</td>
<td>96.2</td>
<td>0.967</td>
</tr>
<tr>
<td>2.81</td>
<td>6.25</td>
<td>96.2</td>
<td>1.000</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>0.96 ± 0.018</td>
</tr>
</tbody>
</table>

### Figure 5. Schematic diagram of an experimental setup used for thermal conductivity measurement of lithium-ion battery components.
known, then the thermal conductivity can be calculated from the product of α with the effective density ρ and the effective $C_p$, as shown in Eq. 6:

$$C_p = \frac{\Sigma (\rho V C_p)_{1}}{\Sigma (\rho V)_{1}}$$

where $V_i$, $\rho_i$, and $C_p_i$ are the volume fraction, density, and specific heat capacity of the $i$th component, respectively.

The xenon flash facilities at the High Temperature Materials Laboratory (HTML) of Oak Ridge National Laboratory, Oak Ridge, TN, were used to measure the α of a stack of dissected Sony-cell components. In the XFT technique (see schematic diagram, Fig. 6a), the front face of the stack of disk-shaped samples is subjected to a short pulse of a xenon flash lamp, and the temperature rise at the rear face of the sample is measured as a function of time by a photopyrometer. Given the sample thickness ($L$) and half-time of the maximum temperature rise at the rear face of the sample ($t_{1/2}$), thermal diffusivity is calculated from Eq. 7:

$$\alpha = 1.37 L^2 t_{1/2}$$

This equation is an approximation of the unsteady-state heat conduction solution based on classical theory (see Appendix, which also has a discussion of errors associated with the method).

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**Figure 6.** (a) Schematic diagram of xenon flash experimental setup; (b) arrangement of Sony 18650 cell component layers for in-plane thermal diffusivity measurement; (c) arrangement of layers for cross-plane thermal diffusivity measurement; (d) schematic diagram of the xenon flash technique sample holders XFT arrangement designed to maintain uniform compression of stacked component layers with electrolyte.

The α of Sony-battery components PE, NE, or assemblies PE/Sp/NE were measured with and without electrolyte [1 M LiPF$_6$ in EC-DMC (1:1 wt %)], at room temperature. Two sets of α measurements were conducted: (i) the heat pulse was directed perpendicularly to the planar surface of disk-shaped (16 mm diam) samples of the layered components or assemblies; and (ii) the heat pulse was directed parallel to the planar surface of the rectangular sample layers ($10 \times 7$ mm), stacked to form a parallelepiped of 100 mm$^3$ × 7 mm. The NE and PE were each 0.19 ± 0.01 mm thick, and the separator 0.020 ± 0.002 mm. Figures 6b and c show a schematic diagram of the assemblies used for cross-plane and in-plane α measurements. Both sample holders (Fig. 6d) were designed to contain electrolyte material, and the compression force was controlled such that the PE, NE, or PE/Sp/NE layers could be compressed with equal force for each individual set of measurements. This ensured the accuracy and reproducibility of the results, which requires controlled and uniform pressure over the stacked layers. Controlled compression was ensured by screwing down the two halves of the sample holder assembly until a dial gauge registered a thickness equivalent to the sum of the individually measured values of the layer and the sample holder thickness. All sample preparations for α measurements of PE, NE, or PE/Sp/NE were prepared in a glove bag filled with argon. A Sony battery, previously charged to the desired OCV, was dissected, and each component washed with ethanol and dried for 24 h at 65°C. Samples were cut to rectangular and disk shapes of dimensions given above and then placed in the specially designed airtight sample holders. Experiments on samples without electrolyte were conducted at first, and then they were transferred back into a glove bag for adding electrolyte. The electrolyte was injected through a small hole on the side of the sample holders, after which the hole was plugged with thermostep epoxy.

Cross-plane α measurements could be made only for a three-layer stack consisting of PE or NE, or for one PE/Sp/NE assembly. If stacks of less than three layers were used, the rear face temperature rise was too rapid and saturated the detector even when the minimum gain was used. When more than three layers were used, the signal intensity did not rise to the level needed for a reasonably accurate value.

In our experiments, the pulse time was less than 1% of the characteristic diffusion time $t_c$, and the energy was uniformly absorbed at the front face of the sample. Effects of finite pulse time, nonuniform heating, and heat loss, and methods of correction for them, are discussed elsewhere. 12-16 (See also Appendix.)

**Results and Discussion**

**Composition of electrode materials.—** To determine the composition of NE and PE materials retrieved from cells at various OCVs (2.45 and 3.75 V), powder X-ray diffraction profiles were obtained using a diffractometer equipped with a copper target X-ray tube (Rigaku-MiniFlex-CN2005C111, Rigaku Corporation, Danvers, MA). Scanning electron microscopy was used to determine the particle shape and geometry of the samples. The NE material was found to be carbon-flakes with distinct basal plane, in the size range from, 20 to 45 μm. For NE material, the intensity ratio of the (002) plane to background is $R = 1.71$ for OCV $= 2.45$ V, and $R = 1.69$ for OCV $= 3.75$ V. Based on these XRD data, it appears that the NE material is a moderate-range graphite hard carbon, with graphene layers of lower stacking order than typical graphite. The ratio $R$ represents the extent of the stacking of graphene layers: the stacking sequence is ABAB in the virtual absence of lithium ($OCV = 2.45$ V), and a combination of ABAB and AAAAA at $OCV = 3.75$ V, corresponding to nearly complete stage 2 intercalation.

The PE material (Li$_2$Co$_{2}$O$_4$) at the desired OCV (10 to 20 μm) was found to have a pronounced layer structure. The XRD profile showed a (003) to (104) plane ratio equal to 4.92.

**Specific heat capacity.—** Table III reports values of $C_p$ for the Sony US-18650 lithium-ion cell. These values were measured by method 2, which, as discussed, yields more reliable results than method 1. The $C_p$ values are $1.04 ± 0.03 J g^{-1} K^{-1}$ at $OCV = 3.75$ V, and $0.96 ± 0.03 J g^{-1} K^{-1}$ at $OCV = 2.45$ V.
0.02 J g⁻¹ K⁻¹ at OCV = 2.75 V. The Cₚ at OCV = 2.75 V agrees well with the calorimetric results reported by Haas et al.⁹ (Cₚ = 0.925 J g⁻¹ K⁻¹). These authors provide no experimental details or information about state-of-charge of the battery.

Our results indicate that Cₚ increases with increase in OCV. In graphite, stage one lithiation causes an increase in the graphene interlayer spacing and graphene layer readjustment from ABAB to AAAA arrangement. In LiₓCoO₂, delithiation causes structural changes, which may include a phase change toward the end of charge.¹⁸ This hexagonal-to-monoclinic phase change was first identified by Reimers and Dahn,¹⁸ who detected a first-order phase transition occurring during delithiation of LiₓCoO₂. This transition involves a significant expansion of the c lattice parameter of the hexagonal unit cell of LiₓCoO₂. Near x = 0.5 this is accompanied by lattice disordering leading to a monoclinic unit cell phase transformation.¹⁸ Tsutomo and Ueda¹⁹ reported that delithiation of LiₓCoO₂ in the regions 0.75 < x < 1.0 and 0 < x < 0.25 takes place by two successive two-phase reactions, whereas in the region 0.75 < x < 0.25 it proceeds by a single-phase reaction plus a phase change due to the formation of a monoclinic phase near x = 0.55. In any case, these changes are accompanied by changes of interatomic forces and distances, which are likely to affect both the phonon modes of vibrations and the electronic states near the Fermi level. These structural changes in LiₓCoO₂, caused by delithiation, may be responsible for the slight increase of Cₚ of the cell with OCV.

To analyze the behavior of Cₚ with OCV further, we note the following. The Debye temperatures (T₀) of all elemental constituents of NE and PE [Cu (340 K), C (1850 K), Al (375 K), Li (460 K), and Co (385 K)],¹⁶ are higher than the temperature range of the present measurements (310 to 315 K). Hence, the heat capacity values are affected by the sum of contributions from electrons and phonons. An exact determination of the electron and phonon contribution to Cₚ and the effect of OCV on this, requires knowledge of lattice vibrations and the coupling constant with the electrons, which is beyond the scope of this work. However, noting that T₀ of elemental constituents of LiₓCoO₂ are much closer to the experimental temperature than that of graphite, we may at least expect that the electronic contribution to Cₚ of LiₓCoO₂ is smaller than that of phonons. In contrast to this, for the NE a larger electron contribution to Cₚ may be expected, since graphite has a high T₀ (1850 K) and Cₚ is proportional (ITₐ)³ (see Ref. 20).

The interpretation of trends in Cₚ values is made more difficult in the case of the NE, due to the complex nature of intercalation in graphite. When lithium ions intercalate into graphite, they share electrons with carbon-carbon rings of graphene layers in a semi-ionic bonding.²¹ Thus, intercalated lithium does not exhibit a clearly ionic or clearly metallic behavior. The exact balance may depend on the type of graphitic carbon host. X-ray photoelectron spectroscopy (XPS) results by Yata et al.²² show that lithium intercalated in hard carbon has a bond energy between 56.1 and 55.9 eV. This (1s) bond energy (ca. 56 eV) is higher by about 1 eV than that of metallic lithium (~55.2 eV), but lower than that of ionic lithium in, e.g., LiBF₄ (ca. 58.0 eV). Sato et al.²² show by nuclear magnetic resonance (NMR) the presence of both ionic carbon-lithium and covalent lithium-lithium bonding in heat-treated polyphenylene. However, delithiation makes carbonaceous material an n-type host with an upshift in the Fermi level, which changes the electron energy density at the Fermi surface. This facilitates electron transfer to the conduction band in intercalated graphite and causes it to have a different electronic thermal energy than that of pure graphite. Such a condition would make the electronic contribution to heat capacity or diffusivity in the host graphite increase as the lithiation increases.

Thus, a detailed explanation of the dependence of Cₚ on OCV requires consideration of the effect of intercalation/delintercalation on the density of the vibrational modes of phonons and the electronic density of states, for both graphite and LiₓCoO₂. The data available in the literature are too scarce to allow such an analysis. However, in view of the accuracy of our measurements and based on the qualitative arguments presented above, it is implausible that structural changes in PE and NE materials associated with the change of OCV = 2.75 V to OCV = 3.75 V cause Cₚ to increase from 0.96 to 1.1 J g⁻¹ K⁻¹.

### Table IVa. Cross-plane thermal properties of Sony US-18650 lithium-ion battery components with and without electrolyte [EC-DMC (1:1 wt %)/1 M LiPF₆].

<table>
<thead>
<tr>
<th>Materials</th>
<th>ρ (g cm⁻³)</th>
<th>Cₚ (J g⁻¹ K⁻¹)</th>
<th>α (cm² s⁻¹); sd 4 × 10⁻⁴</th>
<th>k (W m⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>OCV = 2.45 V</td>
<td>OCV = 3.75 V</td>
</tr>
<tr>
<td>PE</td>
<td>3.115</td>
<td>0.601</td>
<td>0.0124</td>
<td>2.33</td>
</tr>
<tr>
<td>NE</td>
<td>1.622</td>
<td>0.623</td>
<td>0.0088</td>
<td>0.89</td>
</tr>
<tr>
<td>PE/Sp/NE</td>
<td>2.290</td>
<td>1.089</td>
<td>0.0076</td>
<td>1.90</td>
</tr>
<tr>
<td>PE/Sp/NE + electrolyte</td>
<td>2.680</td>
<td>1.280</td>
<td>0.0099</td>
<td>3.39</td>
</tr>
</tbody>
</table>

### Table IVb. In-plane thermal properties of Sony US-18650 lithium-ion battery components with and without electrolyte [EC-DMC (1:1 wt %)/1 M LiPF₆].

<table>
<thead>
<tr>
<th>Materials</th>
<th>ρ (g cm⁻³)</th>
<th>Cₚ (J g⁻¹ K⁻¹)</th>
<th>α (cm² s⁻¹)</th>
<th>k (W m⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>OCV = 2.45 V</td>
<td>OCV = 3.75 V</td>
</tr>
<tr>
<td>PE</td>
<td>3.121</td>
<td>0.602</td>
<td>0.115 ± 0.0040</td>
<td>0.116 ± 0.0010</td>
</tr>
<tr>
<td>NE</td>
<td>1.620</td>
<td>0.598</td>
<td>0.090 ± 0.00017</td>
<td>0.156 ± 0.0030</td>
</tr>
<tr>
<td>PE/Sp/NE</td>
<td>2.291</td>
<td>1.088</td>
<td>0.0071 ± 0.0040</td>
<td>0.099 ± 0.00150</td>
</tr>
<tr>
<td>PE/Sp/NE + electrolyte</td>
<td>2.78</td>
<td>1.278</td>
<td>0.058 ± 0.0010</td>
<td>0.079 ± 0.0004</td>
</tr>
</tbody>
</table>

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showed that the room-temperature electrical conductivity of LiCoO₂ is \( \sim 10^{-3} \, \text{S m}^{-1} \), increasing to \( \sim 1 \times 10^2 \, \text{S m}^{-1} \) for Li₀.₁₇CoO₂. They stated that removing lithium ions from LiCoO₂ decreases the Co-Co distance. Calculations by Goodenough²⁸ indicate that when the Co-Co distance is less than 0.283 nm, LiCoO₂ has metallic character, and that it is a semiconductor when the Co-Co distance is greater than 0.283 nm. The metallic behavior is due to delocalized electrons formed when the Co-Co distance falls below the critical value. Molemda et al. point out that the Co-Co distance shrinks to about 0.281 nm as \( x \) decreases from 0.8 to 0.17. LiCoO₂ with 0.17 < \( x \) < 0.8 is metallic: electrical conductivity is temperature independent.

Effect of particle size and orientation.—According to our experience, most of the battery-grade carbon materials, except meso-carbon microbeads (MCMB) or carbon fibers, consist of flakes with a distinct basal plane. The flat planes probably become attached to each other and to the current collector during NE fabrication, in which a slurry of carbon particles in a suspension of binder and solvent is dispersed over the copper foil. The cross-plane thermal conductivity is low because the copper layers are in series with the carbon layers, and the carbon layers are deposited from the slurry such that the \( c \) axes of the flakes are oriented in the cross-plane direction. This gives the carbon layers a high thermal resistance in this direction. Electrical resistance in that direction is high as well.

Figure 7 depicts the highest heat-transfer paths in the NE, in agreement with the thermal conductivities measured in this work. The same heat-conduction paths appear to exist in the PE. There, in contrast to the NE, the in-plane thermal conductivity is expected to be only slightly higher than the cross-plane one.

**Conclusions**

Thermal properties of the Sony US-18650 lithium-ion battery and stacked layers of components (PE, NE, or PE/Sp/NE) have been measured. The heat capacity of this battery depends on its state of charge and increases by 8% as OCV changes from 2.75 to 3.75 V. The thermal conductivity of the NE material depends more strongly on the state of charge than that of the PE material. These findings can be explained qualitatively by consideration of electronic and phonon contributions to heat capacity and thermal conductivity.

The cross-plane thermal conductivity of an electrolyte filled PE/Sp/NE assembly is 3.4 W m\(^{-1}\) K\(^{-1}\). The in-plane thermal conductivity of stacked layers of battery components is higher than the cross-plane conductivity by nearly a factor of 10. This difference may be attributed (especially for the NE) to the orientation of particles or flakes during the formation of thin electrode layers and to the presence of the metallic current collectors.

The presence of electrolyte [1 M LiPF₆ in EC-DMC (1:1 wt %)] increases the thermal conductivity of the stacked layers of PE/Sp/NE by nearly 55 to 70% and eliminates the OCV dependence.

**Acknowledgment**

This work was supported by the Army Research Office, under grant no. DAAH04-94-G-0055. The XFT facilities at Oak Ridge National Laboratory (Metals and Ceramics Division, HTML) were made available for this work with support of the University Users Program, contract DE-AC05-96OR22464 by Lockheed Martin Ener-

**Table V.** Thermal property values of Sony US-18650 lithium-ion battery components from this work and from the literature.

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \rho ) (g cm(^{-3}))</th>
<th>( C_p ) (J g(^{-1}) K(^{-1}))</th>
<th>( k ) (W m(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>2.920</td>
<td>1.134</td>
<td>2.18</td>
</tr>
<tr>
<td>NE</td>
<td>1.410</td>
<td>1.184</td>
<td>1.40</td>
</tr>
</tbody>
</table>
gy Research Corporation. The cooperation of Luis Revera (Merck Co. USA) in supplying electrolyte is gratefully acknowledged. The authors would like to thank Robert Zeckman (IIT Mechanical Aerospace and Materials Engineering) for technical assistance.

Appendix A

The basic theory underlying the XFT is as follows: the three-dimension-

equation

\[ \alpha \nabla^2 T = \frac{\partial T}{\partial t} \]  

[A-1]

governs heat diffusion in the sample, with temperature \( T \) as a function of time \( t \) and position \( x \). Assuming a finite slab of thickness \( L \) and a large area, uniformly illuminated, without heat losses at the side and back surfaces, conduction of heat becomes one-dimensional and the transient temperature is \( T(x,t) \). If the input energy pulse duration is much shorter than the characteristic time of the sample thickness from the front to the back of the sample, the exact solution of Eq. A-1 may be replaced by the analytic solution for an instantaneous pulse. Parker et al.\(^{17} \) have shown that the temperature rise at the rear face of the sample \( (x = L) \) is

\[ T(L, t) = \frac{Q}{C_p L} \left[ 1 + 2 \sum_{n=1}^{\infty} \left(-1\right)^n \exp \left(-\frac{\alpha n^2 \pi^2}{L^2} t\right) \right] \]  

[A-2]

Here, \( Q \) is the pulse energy density \((J/m^2)\) impinged on the front face of the sample; \( C_p \) the specific heat; and \( \rho \) the density of the sample. For samples less than 3 mm thick and of moderate thermal diffusivity, the pulse duration should be less than 10% of the characteristic diffusion time, which from Eq. A-2 is \( t_c = L^2/\alpha \). From Eq. A-2, the maximum temperature rise at the rear face of the sample is

\[ T_{\text{max}} = \frac{Q}{C_p \rho L} \]  

[A-3]

At any time \( t > 0 \), the temperature rise at the rear face of the sample as a fraction of its maximum temperature rise is

\[ V = 1 + 2 \sum_{n=1}^{\infty} \left(-1\right)^n \exp \left(-\frac{n^2 \pi^2}{L^2} t_c \right) \]  

or

\[ V = 1 + 2 \sum_{n=1}^{\infty} \left(-1\right)^n \exp (-\pi^2 n^2 B_1) \]  

[A-4]

Here \( V \), the normalized temperature rise, is defined as \( T(L,t)/T_{\text{max}} \), and \( B_1 = \alpha t_c L^2 \). From Eq. A-4 it follows that if \( V_c = 1/2 \), then \( B_1 = \alpha t_c L^2 = 1.37 \). Thus the half-time of the temperature rise, \( t_{1/2} \), can be used to determine \( \alpha \)

\[ \alpha = 1.37 L^2/\tau_{1/2} \]  

[A-5]

Thermal diffusivity measurements by light-flash methods require accurate measurement of the effective sample thickness and the rear-face temperature rise as a function of time, at any given fraction \( x \) of the maximum temperature rise. Since \( \alpha \) varies with the square of the sample thickness \( L \), extra attention is needed to measure the sample thickness. The uncertainties in temperature rise time on the rear face of the sample are related to deviations of the actual experimental conditions from those assumed in the mathematical models. The assumed conditions are (i) energy pulse time much shorter than characteristic diffusion time, (ii) uniform energy distribution on the front face of the sample, and (iii) no heat loss from the sample to the sample holder. A detailed discussion on the effects of finite pulse time, nonuniform heating, and heat-loss, as well as corrections for these, is available elsewhere.\(^{12-17} \) A major source of error is heat loss due to scattering of input light, or due to a highly reflective sample with a low aspect ratio (diameter/thickness). The method of obtaining values used in this work is the Clark and Taylor ratio method,\(^{13} \) which is independent of the heat losses. This method is based upon the difference between the theoretical no-loss curve and the normalized curve of temperature rise vs. time. Nevertheless, in this work the heat-loss effects were minimized by selecting a high-aspect-ratio design for sample geometry, using sapphire windows of high transparency to xenon light. To minimize light scattering, the sample holder and rim of the window were painted black. The opaqueness of battery components also helped minimized light scattering.

**List of Symbols**

- \( A \): surface area of battery or reference sample, \( m^2 \)
- \( B_i \): dimensionless number for transient diffusion, Eq. A-4
- \( C_p \): heat capacity, J g\(^{-1}\) K\(^{-1}\)
- \( h \): convective heat-transfer coefficient, W m\(^{-2}\) K\(^{-1}\)
- \( k \): thermal conductivity, W m\(^{-1}\) K\(^{-1}\)
- \( m \): mass of cell or reference sample, kg
- \( Q \): light energy pulse density, J m\(^{-2}\)
- \( Q \): heat generation rate, W
- \( T \): temperature of calorimeter or sample, K
- \( T_a \): ambient temperature, K
- \( T_s \): steady-state temperature, K
- \( t \): characteristic time for diffusion, s
- \( V \): dimensionless temperature rise, Eq. A-4
- \( V_c \): volume fraction
- \( \alpha \): thermal diffusivity, m\(^2\) s\(^{-1}\)
- \( \rho \): effective density, kg m\(^{-3}\)
- \( \tau \): dimensionless time

**References**