Journal of Power Sources 293 (2015) 283-291

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Experimental study on the influence of temperature and state-ofcharge on the thermophysical properties of an LFP pouch cell



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HIGHLIGHTS

• The specific heat capacity of the LFP battery increases slightly with temperature.

• The specific heat capacity of the LFP battery is independent of SOC.

• The cross-plane thermal conductivity of the battery is independent of temperature.

• Increasing SOC decreases the cross-plane thermal conductivity of the LFP battery.

• The LFP battery has nearly twice the thermal conductivity of the dry cell.

ARTICLE INFO

Article history: Received 7 March 2015 Received in revised form 26 April 2015 Accepted 20 May 2015 Available online 26 May 2015

Keywords: Thermal conductivity Specific heat capacity Isothermal calorimetry lithium ion phosphate pouch cell

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Past research has shown that the specific heat capacity and thermal conductivity may be influenced by the battery's temperature and/or its state-of-charge (SOC). However, there has not been any clear relationship uncovered between these test parameters and the thermophysical properties of the battery. Therefore the objective of this research is to measure the thermophysical properties of a Lithium Iron Phosphate (LFP) pouch cell at different surface temperatures and SOC levels. An isothermal calorimeter is used to measure the specific heat capacity at various temperature points and SOC levels. This same instrument is then reconfigured to perform as a heat flow meter apparatus and yield cross-plane thermal conductivity measurements. A commercially available 14 A h pouch cell was used as the test specimen. On average, the specific heat capacity of the cell increases slightly with temperature but remains independent of SOC. The behavior of the cross-plane thermal conductivity is opposite in nature. Its value increases with decreasing SOC but is largely unaffected by temperature. A lithium-ion battery with electrolyte has nearly twice the thermal conductivity of the dry cell version without electrolyte.

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1. Introduction

A thorough understanding of the thermophysical properties for a lithium ion battery plays an important role in the proper design of its thermal management system. These properties directly influence the magnitude of temperature gradients within the cell during operation. Ideally, these gradients are kept to a minimum by the thermal management system [1]. Studies on temperature uniformity of the cell are relatively sparse. Yang et al. [2] developed a thermal management method that quantifies the effects of temperature gradients on cell lifetime uniformity and is based on the

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Arrhenius equation to assess cell health. According to Rugh et al. [3], pack temperature gradients should be no more than 3 °C–4 °C and the operating temperature range should be 15 °C–35 °C for the pack. There are several penalties to the battery pack for failing to meet this criteria; a decrease in the battery pack life and lower performance. It has been found that the lifespan for a lithium-ion cell is reduced by approximately 2 months for every degree of temperature rise while operating in a temperature range of 30 °C-40 °C [4]. In addition, capacity and power degradation is also accelerated at elevated cell temperatures [5–10]. For example, Thomas et al. [5] conducted a statistically designed accelerated aging experiment that investigated the effects of aging time, temperature, and state-of-charge (SOC) on the performance of lithiumion cells and found the power fade involved two concurrent degradation processes. Broussely et al. [6] discussed the detrimental effects on cell performance due to high temperatures and





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the possibility of initiating violent reactions. Arora et al. [7] reviewed the current literature on capacity fade mechanisms and attempts to describe the information needed and the directions that may be taken to include these mechanisms in advanced lithium-ion battery models. Aurbach et al. [8] also presented a review of some critical aspects related to interactions between cathode materials and electrolyte solutions in lithium-ion batteries that occur at elevated cell core temperatures. Additionally Broussely et al. [9] found that at elevated cell temperatures, a high SOC level induces side reactions at the positive interface and leads to oxidation of the electrolyte components. This results in an increase of the cell's impedance and possibly the slow evolution of carbon dioxide gas. Finally Vetter et al. [10] did a comprehensive review and evaluation of the mechanisms of lithium-ion battery aging. They found that capacity and power fade are enhanced at elevated cell temperatures due to an increase in the decomposition of the electrolyte and binder as well as in the SEI growth.

In trying to accurately predict the thermal behavior of Li-ion cells, researchers have relied on various models that incorporate a wide range of operating conditions and thermophysical properties [11–18]. Chen et al. [11] developed a model which demonstrated that thermal management may not be an issue for batteries under low discharge rates. However, under high discharge rates, the temperature of a battery may increase remarkably if the thickness of a cell stack exceeds a certain value. In addition Chen et al. [12] developed a three-dimensional model to simulate and compare heat generation and transport within a lithium polymer electrolyte battery under galvanostatic discharges and a dynamic power profile. The results indicate that the anisotropic thermal conductivity within the battery is an important factor influencing thermal performance and should be taken into consideration in battery design. Furthermore, a thermal analysis of lithium-ion batteries during charge/discharge and thermal runaway has been carried out with a mathematical model created by Chen et al. [13]. Bernardi et al. [14] developed a general energy balance for battery systems that is useful in estimating thermal characteristics of the cell. The temperature changes of a cell as a result of electrochemical reactions, phase changes, mixing effects, and joule heating are incorporated into the model. Pals and Newman [15] present a model to predict the thermal behavior of the lithium/polymer battery with physical properties that are allowed to vary with temperature. Building on this one-dimensional model, Pals and Newman [16] create another model to predict the temperature profile in a cell stack. The accuracy of using heat-generation rates from these isothermal discharges to estimate heat-generation rates during non-isothermal discharge is assessed. A model developed by Newman and Tiedemann [17] treats a three-dimensional battery module as a block which generates heat uniformly throughout. The temperature rise as a function of time is worked out based on equations for heat conduction in solids. Saito et al. [18] uses calorimetry to measure the heat of discharge and to create an empirical model. They found that the heat is due mainly to two factors; the battery reaction and the electrochemical polarization. Accuracy of the thermal parameters that are inputted into a model has a direct effect on the validity of the simulation results. Fleckenstein et al. have shown that a nearly one order of magnitude difference in the thermal parameters inputted into a computer model would result in a nearly one-order of magnitude discrepancy in the predicted cell temperature gradient [19].

Specific heat capacity is one of the most important thermophysical properties in the proper modeling of a thermal management design for a battery [20–23]. Both computational and experimental methods have been used to determine the specific heat capacity of a battery. Of the two, computational methods [24] are the most straightforward approach but it requires accurate values for both the mass and specific heat capacity for all of the individual cell constituents in the cell. This usually involves either having to dissect the test cell or gaining access to proprietary data from the manufacturer [25-27]. To overcome this hurdle, some researchers use surrogate data cited in existing references and publications and some of the cited parameters were used without consideration for differences in the batteries [28,29]. There have been a myriad of different experimental approaches used in finding the specific heat capacity of a full cell. One technique measures the transient cooling of a heated cell quickly immersed in an insulated chamber filled with a known mass of dielectric oil [30,31]. Once steady-state has been achieved, the resulting temperature change of the oil/cell system is noted. Hence, the overall specific heat capacity of the system can be found. Another method similar in concept to transient cooling is adiabatic calorimetry. It also uses an insulated test chamber but is typically not filled with any liquid medium and may use heat flux gauges [32]. No calorimeter design is truly adiabatic and the challenge is to quantify parasitic heat loss to the surroundings. Sakoda et al. [33] mounted Kapton® film heaters in a rather complicated thermal-vacuum chamber with circulating liquid nitrogen. In this setup, the core temperature is varied but the state-of-charge (SOC) of a cylindrical cell is kept constant. Villano et al. [34] used a differential scan calorimeter (DSC) to find the specific heat capacity of the cathode and electrolyte in a lithium cell. Lastly, a technique used by several researchers to find thermophysical properties of a battery is thermal impedance spectroscopy (TIS) [19,35,36]. The specific heat capacity is estimated from a Nyquist plot of the cell's surface temperature response to current pulses at various frequencies.

The influence of bulk temperature and SOC on the specific heat capacity of lithium cells has been previously researched. Some have found that the specific heat capacity of a cell is not only weakly dependent on its core temperature but also on its SOC [37]. The explanation given is that during cycling, a cell experiences phase transitions of the active materials on its electrodes. This involves significant expansion and contraction of its crystalline lattice [38]. These changes are accompanied by changes in interatomic forces and distances, which are likely to affect both the phonon modes of vibrations. Maleki et al. [39] found that the specific heat capacity of the 18650 LiCoO2 cell to increase with open circuit voltage $(1.04 \text{ Jg}^{-1} \text{ K}^{-1} @ 3.75 \text{ V vs.} 0.96 \text{ Jg}^{-1} \text{ K}^{-1} @ 2.75 \text{ V})$. Murashko et al. [40] found that the specific heat capacity for a large format pouch cell using a lithium titanate anode to be statistically independent of SOC. Neither of these studies delved into the influence of cell temperature on specific heat capacity. The one study that did investigate this aspect of was done by Kalu et al. [41]. They studied Li/BCX and Li/SOCl₂ cylindrical cells at the extreme SOC values of 0% and 100% and at cell temperatures that ranged from 0 °C to 60 °C. They found that there was a cell bulk temperature dependence of the specific heat capacity at 100% SOC but a poor dependence at 0% SOC. Kubow et al. [42] and Takeuchi et al. [43] also studied the heat capacities of different sizes of Li/BCX cells by calorimetry and adiabatic discharge respectively. Their experiments were conducted at a single cell temperature and the average specific heat capacity ranged from 0.85 to 1.05 J g⁻¹ K⁻¹.

Besides specific heat capacity, another thermophysical parameter, thermal conductivity, also affect the thermal performance of a Li-ion battery. Thermal conductivity, k, is the intrinsic property of a material to conduct heat. The ability to do so depends on the availability of free electrons within the material and the degree to which it possesses a crystalline structure. Due to the layered construction of a pouch cell, the thermal conductivity is highly orthotropic. The cross-plane thermal conductivity, k_z , (along the cell thickness) is usually found to be an order of magnitude less than the in-plane conductivity (k_x and k_y). Vertiz et al. studied the relationship between SOC and the cross-plane thermal conductivity of a 14 A h LFP pouch cell [44]. They found that it reached a maximum value of 0.284 W m⁻¹ K⁻¹ at the 50% SOC level. This maximum was 16%–17% higher than what was measured at the SOC extremes of 100% SOC and 0% SOC respectively.

Techniques for precisely measuring thermal conductivity are much more complex than they may initially appear. Care must be taken to ensure that heat flow is one-dimensional and that it be accurately measured. The guarded hot plate technique (GHPT), represented by ASTM C177-04 [45] and ISO 8302:1991 [46], is probably the most commonly one used in thermal conductivity measurement because the required materials are relatively inexpensive and does not require the need of a calibrated reference. However, this setup requires two test samples to be used. Another technique, represented by ASTM C518-10 [47] and ISO 8301:1991 [48], is a variant of the guarded hot plate and is commonly referred to as the heat flow meter. This research will modify an isothermal battery calorimeter as a heat flow meter to measure cross-plane thermal conductivity of Li-ion pouch cell.

In summary, both specific heat capacity and thermal conductivity play an important role in battery performance. A detailed experimental procedure and analysis will be presented to measure the value of these two parameters and to study how they will vary with the cell operating conditions.

The remainder of this paper is organized in three sections. Section 2 discusses the methodology used in measuring the specific heat capacity and cross-plane thermal conductivity of the pouch cell. In Section 3, the data is analyzed and the results are discussed for each thermophysical property. Finally, in Section 4, conclusions are drawn from the findings with potential areas of work that may warrant future study.

2. Methodology

This research investigates the thermophysical properties of a lithium iron-phosphate (LFP) pouch cell as a function of its temperature and state of charge (SOC). There are several different robust algorithms to accurately estimate the SOC of a lithium-ion battery [49,50]. In this study, the SOC level is set by first finding the full capacity of the test cell. This is done by fully discharging it at the 0.5C rate at room temperature, waiting 10 min, and then charging it to the upper voltage limit. The same is done for the discharge half-cycle. The average of the capacity values measured for the two half cycles is deemed to be the cell's rated capacity. The SOC level is established by coulomb counting to the desired fraction of the full capacity. This is also done at the 0.5C rate and room temperature.

For this study, new test cells were procured directly from the manufacturer and were all from the same production run. This commercially available cell has a nameplate capacity of 14.5 A h and uses a graphite coated anode. Encased in a laminated aluminum pouch, it has an operating temperature range of -30 °C to 50 °C and a specific energy of 100 Wh/kg. The specifications of the cell are listed in Table 1.

2.1. Measurement of specific heat capacity

Isothermal calorimeters are designed to maintain the battery at a constant preset temperature. Fig. 1 shows a schematic diagram of the commercial isothermal calorimeter used in this research that is specifically designed for large format pouch cells. The heat transfer is detected by highly sensitive thermopiles which are placed between the pouch cell and heat exchangers. Beads of sealant between the platen periphery and the heat exchangers isolate the sensors from interacting with the surrounding air of the calorimeter interior.

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Test cel	l specifications.	
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Height	220 mm
Width	140 mm
Thickness	7 mm
Mass	385 g
Nominal capacity	14 A h
Maximum charge voltage	3.65 V
Nominal voltage	3.2 V
Minimum discharge voltage	2.0 V
Maximum charge current	1C
Maximum discharge current	10C
Specific heat capacity (per manufacturer)	1.39 J g ^{−1} °C ^{−1}

During testing, all cells are placed in the middle area of the lower platen. The possibility exists that the tabs of the live cells may short when upper platen is lowered. As a result, all live test cells have the tabs wrapped in electrical tape prior to insertion in the instrument.

Several precautions are taken in the setup to ensure that the heat exchanger temperatures were as stable as possible since the accuracy of the results depend on prolonged states of equilibrium. The insulated heat exchangers are connected in parallel to a water bath held at a constant temperature. This allowed both heat exchangers to directly receive flow from the same supply. The base surfaces of both heat exchangers were insulated with pads to minimize heat loss with the surrounding air of the calorimeter interior. The water in the bath has a minimum amount of ethylene glycol in the mixture to prevent freezing at low temperatures and suppress bacteria growth. The intent here I to minimize fluid viscosity and maximize its ability to absorb heat. In addition, the hoses that make the connection between the instrument and water bath are kept as short as possible and wrapped in polyethylene foam insulation.

Determining the heat capacity of the pouch cell involves measuring the total energy transferred between it and the heat exchangers as a result of a change to the water bath temperature. The amount of energy, Q_{cell}, absorbed or lost, is related to the specific heat capacity, C_p, by the following equation:

$$Q_{cell} = \int_{t_1}^{t_2} \dot{Q} \, dt = \int_{T_1}^{T_2} m C_p \, dT \tag{1}$$

where \dot{Q} is the heat transfer rate (W), t_1 and t_2 is the time span in which the cell temperature transition commences and finishes respectively (sec), m is mass of the pouch cell (grams), C^p is specific heat capacity of the cell (J g⁻¹ °C⁻¹), and T₁ and T₂ are the initial and final temperatures of the cell (°C). Since the temperature change of the cell core occurs in small increments (2 °C), it is assumed that the specific heat capacity of the cell remains constant in its temperature range. By integrating the area under the heat rate vs. time curve, the total heat transfer can be found and thus the specific heat capacity can be determined by Eq. (2):

$$C_p = Q_{cell} / [m(T_2 - T_1)]$$
(2)

2.2. Measurement of cross-plane heat conductivity

The isothermal calorimeter is reconfigured as a heat flow meter to perform cross-plane thermal conductivity measurements of the cell. It incorporates a layer of heat flux transducers which are typically thermopiles that produce a voltage output proportional to the heat flux. These sensors are placed between a heat exchanger plate (which is kept at a controlled surface temperature) and the



Fig. 1. Schematic of the isothermal calorimeter.

test sample. A heat exchanger on the other side of the test sample is kept at a different surface temperature. A temperature gradient between the cell faces is established and heat flows across its thickness. These thermopiles have been calibrated against a reference sample in which the thermal conductivity is documented. An advantage of this technique over the guarded hot plate is that it requires only one test sample (i.e. pouch cell). The assembly is also generally smaller in size which reduces the amount of time needed for the stack to achieve steady state. The upper platen/heat exchanger subassembly has a drive screw connected to an electric motor. This allows the application of a precise compressive load on the test specimen. In order to ensure one-directional heat flow, side guard heaters are applied to the periphery of the cell core. Side guard heaters are typically electrically resistive elements in the form of either a flexible polyimide film sheet or wire. When a steady current flow is applied, a set temperature can be maintained on the surface where the heater is mounted.

Normally active in calorimeter mode, the upper thermopiles have been deactivated by altering a software setting. This allows the system to recognize only heat flow through the bottom platen and not be "double counted" by the upper thermopiles. As shown in Fig. 2a, each heat exchanger plate was connected to its own water bath supply to create a controlled temperature gradient across the cell thickness.

An assumption used in the calculation of thermal conductivity with the reconfigured calorimeter is that the convective heat flux is uniform across the exposed surface of the platens. In reality, edge effects can make the heat flux higher along a platen's perimeter. This is due to the fact that, depending on the water bath temperatures, there may be a greater temperature gradient with the surrounding air than between the two platens. To rectify this, a wall of aerogel insulation surrounds the lower platen as shown in Fig. 2b. This wall of aerogel strips is high enough so that when the upper platen is electrically lowered onto the test cell, it creates an enclosure in which it has almost no thermal interaction with the surrounding air. As a result, the convective heat flux is more uniform across the exposed surface of the platen.

Measurements are taken at three different cell surface temperature levels (-5 °C, 25 °C, and 55 °C) as well as three different SOC levels (0%, 50%, and 100%) to determine if these parameters had any effect on the cross-plane thermal conductivity.

Thermal contact resistance (TCR) can be an issue but it can be "calibrated out" if the same loading is applied from one test run to the next. Thermal pastes can also be used to reduce TCR but it can never be completely eliminated.

2.2.1. In-plane thermal conductivity

This study does not investigate in-plane thermal conductivity because the design of the reconfigured calorimeter does not lend itself to this type of measurement. The two heat exchanger platens cannot be spaced apart enough to accommodate the height or width of the pouch cell. Needless to say, in-plane thermal





Fig. 2. a. Rear view of calorimeter (right) with insulated hosing to two water baths for thermal conductivity measurements. b. View of calorimeter interior with strips of aerogel insulation forming a wall around the lower platen.

conductivity is still an important route for the heating and cooling of a wound or prismatic cell and, as such, is important for model simulations.

Performing this type of measurement is similar in concept to that done for measuring cross-plane thermal conductivity. Here, a temperature gradient is established across the cell length or width by a known heat output created by a source on one edge of the pouch and a heat sink attached on the opposite edge. The exposed surface area of the pouch should also have side guard heaters applied to it to ensure one-dimensional heat flow between the source and sink. This setup is made somewhat complicated by the small surface area offered by the thinness of the pouch cell side to mount any heaters.

2.3. Accommodating baseline shift

The calorimeter itself takes part in the storing and releasing of heat when a change in temperature occurs within the heat exchangers. As a result, it becomes necessary to quantify this contribution and make adjustments accordingly using Eq. (3).

$$Q_{cell} = Q_{cell \& calorimeter} - Q_{calorimeter}$$
(3)

It is assumed that the heat capacity of the instrument itself remains constant over the narrow temperature change for each data point. Depending on the temperature setting of the instrument, it is found through experimental testing that the value for $Q_{calorimeter}$ typically varies between 1.7 kJ °C⁻¹ to 2.1 kJ °C⁻¹ across the full range of test temperatures.

When plotted, the cell's absorption of heat due to an increase in the water bath temperature will be similar to that seen in Fig. 3a. In this plot, the heat profile responds to a change in the water bath temperature from 23 °C to 25 °C. The negative reading indicates endothermic heat flow into the test cell due to a rise in the water bath temperature. Integrating the area within this curve will yield the total amount of energy transferred (Joules) during the transient period. However, this integration is somewhat complicated by an unavoidable phenomenon. The heat curve does not return to zero even though it has reached steady state regardless of how much time has elapsed. It instead stabilizes at some other value (in this case, approximately -0.25 W). This offset is referred to as a baseline shift. It is due to an increase in the convective heat transfer from the surfaces of the two platens during the increase in its surface temperature. Heat loss from the platens to its surroundings is directly proportional to the difference between the platen surface temperature and the environmental temperature.

Knowing the rate at which the baseline shifts and when it occurs during the transient period is crucial to calculating an accurate value for amount of energy absorbed or released by the cell. Fortunately, there is a procedure to construct the baseline profile by coupling it to the profile of the surface temperature change of the platens. Several t-type thermocouples attached to both platens measure the changing surface temperatures as the water bath makes the transition to its new temperature setting. This change in platen surface temperature is shown in Fig. 3b. Due to the direct relationship between the two, the platen surface temperature profile dictates the profile of the shifting baseline. In Fig. 3c, the true total heat transfer is the area encompassed between the dotted line of the shifted baseline and the solid line of the heat profile.

2.4. Calorimeter calibration

A copper plate of 99.99% purity (C10100 alloy) is used as a reference to validate the procedure. The relationship of the specific heat capacity to its temperature is taken into account and is

expressed as the best-fit polynomial shown below [51]:

$$Cp(T) = 6.1206 \times 10^{-4} + (3.6943 x 10^{-3})T - (1.4043 \times 10^{-5})T^{2} + (2.7381 \times 10^{-8})T^{3} - (2.8352 \times 10^{-11})T^{4} + (1.4895 \times 10^{-14})T^{5} - (3.1225 \times 10^{-18})T^{6}$$
(4)

where Cp(T) is the temperature-dependent specific heat capacity of copper (J $g^{-1} \circ C^{-1}$) and T is the temperature (°C). The test procedure is able to determine the specific heat capacity of the copper plate to be 2.5% below its theoretical value.

2.5. Measurement uncertainty analysis

Finding the values for the cell's specific heat capacity and thermal conductivity involves mathematical operations on data collected from several different types of measurements: time, mass, cell and ambient temperatures, and heat energy. Each type of instrument used has a certain degree of precision in its measurement and is summarized in Table 2.

The propagation of error that occurs in the calculations is found using the principle quadrature formulas as prescribed by Taylor [52]. It is found that the systematic uncertainty in the specific heat capacity of the cell due to measurement error to be ± 0.0058 Jg⁻¹ °C⁻¹. This represents $\pm 0.42\%$ of the specific heat capacity cited by the manufacturer in Table 1 (1.39 J g⁻¹ °C⁻¹). The uncertainty is kept low by the fact that the incremental temperature change is always 2 °C. This improved the signal-to-noise ratio of all of the measurements. The measurement error inherent in the cross-plane thermal conductivity measurements is $\pm 1.9\%$. In this series of tests, 1500 N of compressive loading is always applied to the test cells and represents the upper design limit of the calorimeter. Calibration of the thermopiles is also done under this same load to ensure the same degree of sensor sensitivity.

3. Results and discussion

3.1. Specific heat capacity as a function of SOC

As shown in Fig. 4, there is a weak positive correlation of the cell specific heat capacity for the LFP cell with its SOC. Over the full temperature range subjected to the cell core, the average slope of the specific heat capacity is 0.00043 J g⁻¹ °C⁻¹ for each percent increase of SOC. Even then, the average coefficient of determination (R^2) across all SOC levels is only 75%. This means that 75% of the total variation seen in the specific heat capacity values at any set temperature can be attributed to a varying SOC.

3.2. Specific heat capacity as a function of cell surface temperature

For the LFP test cell, specific heat capacity is positively affected by cell core temperature across all SOC levels. Fig. 5 shows this relationship for a variety of different SOC levels. The average coefficient of determination (R^2) is 99% meaning that nearly all of the variation in the specific heat capacity values is explained by the varying temperature. On average, the slope of the best-fitted line for the specific heat capacity as a function of temperature of the LFP cell is 0.0074 J g⁻¹ °C⁻².

3.3. Cross-plane thermal conductivity as a function of SOC

The thermal conductivity of two different Li-ion chemistries is



Fig. 3. a. Heat absorption of the 14 A h cell undergoing a temperature change of 23 °C–25 °C. b. Surface temperature profile of the calorimeter platens during a change in water bath temperature from 23 °C to 25 °C. c. Heat profile with a properly shifted baseline due to increased heat transfer from the platens as the 14 A h cell temperature increases from 23 °C to 25 °C.

tested under abusive and normal operating conditions as shown in Fig. 6. The 14 A h LFP cell shows a tendency to have its crossplane thermal conductivity increase nearly 6% as its SOC decreases from 100% to 0%. As shown in Fig. 6, there is a $\pm 1.9\%$ measurement error in each data point so this property is statistically independent of cell temperature when in its operating range of 3.65 V–2 V. However, when the cell is discharged to 0 V,

Table 2Measurement error in instrument readings.

Measurement	Precision
Temperature	±0.005 °C
Mass	±0.0005 g
Time	±0.05 s
Heat rate	±0.5 mW

this measurement declines nearly 18% from its value at 0% SOC (2 V).

A supplemental study of cross-plane thermal conductivity was performed on a commercially-available 75 A h NMC pouch cell. As shown in Fig. 7, measurements taken under the same conditions as the LFP cell shows the same general behavior exhibited by NMC pouch cell.

3.4. Cross-plane thermal conductivity as a function of cell surface temperature

Fig. 8 shows the cross-plane thermal conductivity of the 14 A h cell as a function of cell surface temperature for three values of SOC (0%, 50% and 100%). The cross-plane thermal conductivity is independent of cell temperature ($-5 \circ C-55 \circ C$) across its full SOC range.



Fig. 4. Specific heat capacity of the 14 A h LFP cell as a function of SOC at several different temperatures.



Fig. 5. Specific heat capacity as a function of temperature for different SOC levels.

3.5. Effect of electrolyte on cross-plane thermal conductivity

A unique opportunity is put to use concerning the effect of

electrolyte on the TCR of a pouch cell. This effect would make itself

evident in the cross-plane thermal conductivity. An inert (without electrolyte) version of the 75 A h cell is measured and compared to a production cell depleted to 0 V. For the 75 A h pouch cell, the electrolyte accounts for 16.5% of the mass and consists of lithium



Fig. 6. Cross plane thermal conductivity of 14 A h cell as a function of OCV at room temperature.



Fig. 7. Cross plane thermal conductivity of 75 A h cell as a function of OCV at room temperature.

hexafluorophosphate (LiPF $_6$) in a mixture of an organic solvent containing ethylene carbonate (EC) and ethyl methyl carbonate (EMC).

Both the dry inert cell and live cell are tested under identical test conditions to remove the influence of any extraneous variables. The upper and lower water bath temperatures are set at 23 °C and 25 °C respectively. The upper platen pressure is also set at 1500 N for both cells. It is found that the presence of electrolyte in the cell core increases the thermal conductivity by 92% (0.21916 W/mK vs. 0.42131 W/mK). This is significantly higher than the 55%–70% cited for the Sony 18650 cells studied by Maleki et al. [39]. This may be due to the fact that other researchers simply punctured the cell container and allowed the electrolyte to drain/evaporate. It is possible that a residue film remained on the mating surfaces of the electrodes and helped lower the TCR.

4. Conclusions

The specific heat capacity and cross-plane thermal conductivity is measured using an isothermal calorimeter for an LFP pouch cell. The influence of SOC on the specific heat capacity of the LFP cell is very weak. Hence this relationship can be considered to be negligible enough to be omitted from any cell modeling. However, the influence of temperature on specific heat capacity warrants consideration in modeling and calculations. Over the full temperature range from -5 °C to 55 °C, this property can vary 38%. The rate of charge or discharge will most likely affect the specific heat capacity of the cell to the extent that the resulting rate of heat generation will alter the temperature. Besides a temperature difference between the platen surface and environment, the shifting baseline of the heat profile is also dependent on the spacing between the platens. As a result, when a cell of a different thickness is to be tested, it necessitates a new surface temperature profile of the platens to be compiled.

The cross-plane thermal conductivity is independent of temperature across its full SOC range. The cross-plane thermal conductivity shows a weak inverse relationship with the cell SOC while in its operating voltage range. However, as the cell is discharged to 0 V, the trend reverses and the property shows a marked decline. This behavior was seen for both the LFP and NMC electrochemistries. The cross-plane thermal conductivity of a dry LFP cell is also measured. The dry cell was manufactured using the same materials and processes as the production cells. The only difference is the absence of electrolyte. As compared to other studies that investigated dry cells, the results in this work shows that the effect of electrolyte on thermal conductivity is much more pronounced.



Fig. 8. Cross plane thermal conductivity of 14 A h cell as a function of temperature for different SOC levels.

Based on the data presented in the graphs, there appears to be no interactive effects between cell temperature and SOC on neither the specific heat capacity nor the cross-plane thermal conductivity. The two variables appear to be largely independent of each other in regards to influencing the thermophysical properties of the cell.

Due to safety concerns, no testing is performed at voltages that exceeded the upper limit of the cell's operating range. During abusive operation, products of irreversible side reactions are formed. It is assumed that the presence of these products in the pouch cell are so thermally insulating in nature that it counteracts the thermal conductivity behavior seen in normal operation. It also tends to explain the marked increase in the cell's electrical resistivity. No empirical data is available in published literature that details the thermophysical properties of pouch cells under abusive conditions. This insight may prove useful for researchers creating computer models of cells undergoing abusive treatment.

There are several areas of potentially continuing work. One would be the effect of aging and cycle life on the thermophysical properties of a cell. Another topic of interest would be the effect, if any, of increasingly higher external pressures on the thermal contact resistance of the cell. A much smaller pouch cell would have to be a test specimen since the upper plate of the calorimeter used in this research is limited in the amount of force it can apply.

Acknowledgments

This research was supported by the Michigan Space Grant Consortium (MSGC). The MSGC creates, develops, and promotes programs that reflect NASA strategic interests in space-related science and technology in Michigan.

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