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# The Influence of Cell Temperature on the Entropic Coefficient of a Lithium Iron Phosphate (LFP) Pouch Cell

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The reversible (entropic) heat source contributes to the thermal behavior of a lithium-ion battery in particular at the initial state of charge and discharge. One factor that affects the magnitude and direction of the reversible heat is called the entropic coefficient (EC). The objective of this research is to calculate the varying entropic coefficient values of the lithium-iron phosphate battery. A 14Ah lithium ion pouch cell, with a dimension of 220 mm  $\times$  130 mm  $\times$  7 mm, was studied in both charge and discharge. The SOC levels range from full charge to full discharge in 5% increments. The temperature levels vary from  $-20^{\circ}$ C to 55°C in 5°C increments. It reveals that there is a strong influence of cell temperature on the entropic coefficient when the cell is at its extreme upper or lower SOC level. A correlation was obtained to relate the EC to temperature and the SOC by curve fitting the experimental data. Calorimetric data and the EC measurement were combined to determine the irreversible heat generated in the cell. (© 2013 The Electrochemical Society. [DOI: 10.1149/2.082401jes] All rights reserved.

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The lithium iron phosphate (LFP) cell chemistry is gaining wide acceptance in battery electric vehicle (BEV) applications. Its inherent ability to tolerate abusive conditions and resist thermal runaway is especially attractive to battery pack designers. Battery manufacturers have responded by offering high capacity cells in a pouch format. This format provides excellent packaging efficiency and offers a very favorable area-to-volume ratio to facilitate thermal management. As a cell increases in its capacity, this ratio tends to decrease. Coupled with the higher current flows inherent with larger cells, a greater amount of heat generation (both reversible and irreversible) results.<sup>1</sup>

A unique characteristic of lithium batteries, as compared to other cell chemistries, is the thermal behavior exhibited during low rates (<1C) of charge or discharge. The contribution of the entropic (reversible) heat source is dominantly endothermic in nature during the charge cycle. However, it has also been found to be a source of exothermic heat if the state-of-charge (SOC) of the battery is at a specific level. Past researchers have attributed this to a phase change of the active material.<sup>1</sup> For either mode of behavior, the strength of the heat source itself is directly proportional to a factor called the entropic coefficient. The entropic coefficient quantifies the reversible change in the OCV that occurs in response to a temperature change of the cell. The entropic coefficient is not a constant factor and its value varies with different SOC levels and temperature.

The entropy change in the electrochemical reaction is also an important thermodynamic factor in cell thermal design and heat management.<sup>2</sup> The reversible heat generation rate has been found to be a significant portion of the total heat generation rate. Published research has found that the entropy change ( $\Delta$ S) can contribute a majority of the total generated heat at a 1C-rate discharge rate.<sup>3</sup> This is especially true in some cells with impedance values that are a fraction of a milliohm leading to suppressed levels of Joule heating. The appropriate combinations of cathode and anode materials have been investigated by some researchers to minimize reversible heat generation rate across the full SOC range.<sup>4</sup> However, it will be difficult to quantify the contributions of each electrode to measure entropy change. Data is usually not available on the exact composition and crystallographic phase transitions of the electrodes for commercially available test cells.

There are two main techniques used to determine the reversible heat generated in a cell. The first method is called potentiometric method where the entropy change can be estimated by calculating the relationship between the changes in open circuit voltage (OCV) of a cell versus the change in its temperature. The preferred approach would be to keep the SOC of the cell fixed while varying the temperature of the environmental chamber. In doing the opposite approach (varying the SOC level of the cell while keeping the chamber temperature constant), Thomas et al.<sup>5</sup> has found that a greater level of uncertainty is introduced into the entropic coefficient due to the difficulty of repeatedly tweaking a cell to a new SOC with any accuracy. Vetter et al. has found that low-temperature charging may lead to dendrite growth as well as lithium plating.<sup>6</sup> The implicit assumptions made with this method are that the electrochemical reaction distribution and temperature profile in the cell is uniform. Both assumptions should be valid due to the low C-rate cycling and the thin construction of the pouch cell. As a result, any errors are expected to be minimal.<sup>7,8</sup> Even so, cell inhomogeneity was generally ignored until recently for modeling at the pack level.<sup>9,10</sup>

The second method used to determine the reversible heat is called calorimetric method where the test cell is placed in a large foam block and cycled under low C-rates in order to approximate adiabatic conditions. Changes in the cell temperature are recorded through thermocouples mounted to the cell surface.<sup>11</sup> This method relies on measuring the heat difference that arises when a cell is charged as compared to that when it is being discharged. The contribution of the reversible heat in a cell is assumed to be responsible for half of this difference. The rationale is that it is a source of exothermic heat that combines with the irreversible heat during the first of a cycle and then it is an endothermic source to oppose the irreversible heat during the other half-cycle. Even though Onda et al.<sup>12</sup> and Thomas et al.<sup>5</sup> found that this method gave results similar to the potentiometric method, it tends to be less accurate due to several reasons. One is that impedance of the cell (as a function of SOC) can be slightly different when it is being charged as compared to being discharged. It also requires a large amount of impedance data to be collected. Additionally, as the amount of inactive thermal mass (pouch, tabs, etc.) in a cell's construction becomes larger, it can have an effect on data accuracy.<sup>10</sup> The inactive materials do not participate in heat generation but act to increase the heat capacity. For a given amount of heat, this results in a lowered reading from the thermocouple and a higher susceptibility to signal noise. Lastly, Hong et al.<sup>13</sup> found that this method produced entropic coefficients that were a function of the C-rate.

The application of entropic heat to thermal models has run the full gamut in simulation studies. It has either been assumed to be a nonlinear function of SOC, <sup>14–17</sup> a linear function between two SOC levels,<sup>3</sup> assumed constant,<sup>18–24</sup> not mentioned but included in the formulation,<sup>25–28</sup> or entirely neglected.<sup>29–32</sup> In summary, temperature has a strong influence on its performance characteristics regardless of the format or particular chemistry of the lithium-ion cell. Unfortunately, cell manufacturers rarely provide any details on the extent of this influence on battery behavior. A thorough understanding is critical for the researcher to construct accurate and realistic thermal models.

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Figure 1. Environmental chamber with edge-view of cell.

The objective of this research will be to reveal the entropic coefficient behavior of a LFP cell at its SOC and temperature extremes by using the potentiometric technique. The data collected will be mapped and curve-fitted to yield the equations necessary for future work in calculating cell heat capacity.

#### Experimental

*Experimental setup.*— This research investigated the entropic heat generation in a commercially available LFP pouch cell (F014) from EiG Corporation (South Korea). The cell uses a graphite anode and is encased in a laminated aluminum pouch. Rated for a nominal capacity of 14Ah, the nominal voltage is 3.2 V. Its dimensions are 220 mm × 130 mm × 7 mm and the cell weighs 381 grams. The in-plane thermal conductivity is 29 W/m K and the specific heat capacity is 1.39 J/g K. As done in past studies, it is assumed that thermal properties are isotropic and independent of temperature.<sup>3</sup> The Maccor environmental chamber is shown in Fig. 1 with its performance specifications listed in Table I. A 10-channel Maccor Model 4200 System with an accuracy of  $\pm$  2 mV was used to cycle the cells as well as collect the data. All 16 available t-type thermocouple channels were used to ensure that

Table I. Specifications of the Maccor environmental chamber.TEMPERATURE RANGE $-20^{\circ}$ C TO  $100^{\circ}$ CUNIFORMITY $\pm 0.8^{\circ}$ CACCURACY $\pm 0.8^{\circ}$ CPRECISION $\pm 0.05^{\circ}$ CINTERNAL DIMENSIONS $152 \text{ mm} \times 355 \text{ mm} \times 254 \text{ mm}$ 

the cell temperatures were at steady state before data collection at any temperature level as well as chamber temperature uniformity.

*Experimental technique.*— In this paper, the potentiometric technique was used mainly because it was the most straightforward and easiest to implement. The downside is that long time periods are required to allow the OCV to stabilize and accommodate low C-rates of charging.

Nine LFP cells were simultaneously placed inside the environmental chamber as the temperature was cycled between  $-20^{\circ}$ C and  $55^{\circ}$ C in 5°C increments. This approach greatly shortened the testing time needed to collect the huge amounts of data needed to perform a detailed analysis. Even so, three test runs were needed to collect data from every possible parameter combination.

The first task was to accurately determine the full capacity of each nearly-new cell. This was done by fully discharging each cell to 2 V at room temperature and then charging at a constant-current C/20 rate to 3.65 V. Then constant voltage was applied to 3.65 V with a charge current cutoff of 20 mA. Once the capacity was quantified, each cell could be accurately set to a pre-defined SOC level. The cells were then instrumented and placed in an environmental chamber at a set temperature. After a 4-hr soak time, the OCV of the cell is recorded. The chamber is then taken to a new temperature and, after soak time of four hours, the OCV is recorded again. It is known from prior research by the authors that the prismatic cell in natural convection reaches thermal equilibrium with its surroundings after only 30 minutes of elapsed time when there is initially a 5°C difference between the cell temperature and ambient temperature.<sup>33</sup> The excessive 4-hr soak time is for the benefit of the cell to reach potentiometric equilibrium. After charging/discharging, it is expected that the diffusion of lithium through the solid electrode phase will take longer to stabilize than the time needed for the cell to reach thermal equilibrium.<sup>34</sup>

Table II shows how the data collection work load was distributed among the 9 test cells in the chamber. Once the full cycle of temperature changes has been experienced by the cells, each was discharged by 45%. Discharge rate was C/10 and then a 4 hour soak before data collection started for the 2nd and 3rd rounds. Average temperature and OCV readings were collected over a 2 minutes period every 5 seconds at each temperature level. All voltage measurements collected on a particular cell was always segregated from the data of other cells during analysis. As was observed by researchers in other published articles, the response of the cell OCV to a change in the chamber temperature was nearly instantaneous.<sup>34</sup> The thin construction of this particular pouch cell (Biot number  $\approx 0.002$ ) helps keep thermal gradients to a minimum.

## **Results and Discussion**

Self-discharge in a cell has the effect of lowering the retained capacity and is accelerated by elevated temperatures and a high SOC. $^{35}$ 

Table II. Experimental procedure used to collect data on OCV changes vs. temperature.

COMMENTS RUN #1	Cell #1 SOC	Cell #2 SOC	Cell #3 SOC	Cell #4 SOC	Cell #5 SOC	Cell #6 SOC	Cell #7 SOC	Cell #8 SOC	Cell #9 SOC
Collect $\partial E_{OCV}$ / $\partial T$ across all temps from 55°C to $-20^{\circ}C$	100%	95%	90%	85%	80%	75%	70%	65%	60%
Discharge all cells by 45% SOC at room temperature at C/10 rate	₩	↓	↓	↓	↓	↓	↓	₩	₩
RUN #2									
Collect $\partial E_{OCV}$ / $\partial T$ across all temps from 55°C to $-20^{\circ}C$	55%	50%	45%	40%	35%	30%	25%	20%	15%
Discharge only the first 3 cells by 45% SOC at room temperature at C/10 rate	↓	↓	↓						
RUN #3									
Collect $\partial E_{OCV}$ / $\partial T$ across all temps from 55°C to $-20^{\circ}C$	10%	5%	0%	х	х	х	х	х	Х



Figure 2. (a) OCV changes of a 100% SOC cell in self-discharge while subjected to temperatures in the upper extremities of its operating temperature range. (b) OCV changes of a 100% SOC cell in self-discharge while subjected to the mid-range portion of its operating temperature.

According to Aurbach,<sup>36</sup> the graphite electrodes in a fully charged cell are strong reducing agents and the solid electrolyte interphase (SEI) that is formed on the surface cannot completely passivate them. As a result, electrons and ions can pass through this layer and increase the potential on the negative electrode in the process. Even though the cell itself is static and under no external load, there is a slight unavoidable loss in the open circuit voltage (OCV).

Accounting for self-discharge.— The raw entropic coefficient (i.e. not adjusted for self-discharge) was calculated by the ratio of OCV differences to the respective temperature differences. Since the changes in OCV values used in calculating the entropic coefficient are measured in fractions of a millivolt, the effect of self-discharge must be accounted. As compared to the LFP chemistries offered by other cell manufacturers, the EiG cell used in this work had a significant dropoff in OCV due to self-discharge at high SOC levels. As a result, the entropic coefficient was highly sensitive to the effects of selfdischarge. This was evident at the higher cell temperatures when the self-discharge rate was accelerated and the cell had an extensive soak time. Once the SOC of the cell falls below 95%, the slope of discharge curve is much more level making the effects of self-discharges on the OCV much less pronounced. As noted by other researchers, for cell temperatures below  $25^{\circ}$ C, the effects of self-discharge are almost non-existent and have been neglected during measurement time.<sup>12</sup> The reason for the lessened self-discharge is due to the fact that the electrochemical reaction has slowed considerably at low temperatures.

Figure 2a shows the effect of self-discharge on OCV readings at its most prominent state: a fully charged cell at high temperatures. The graph has been truncated to show a representation of the selfdischarge effects under these conditions. Note the level OCV readings in Figure 2b that shows self-discharge are nearly non-existent for the same cell when the cell temperature has been lowered to a moderate level.

The time span for the OCV to complete its response to a temperature change was approximately 26 minutes and was nearly the same for all of the test cells to complete their entropic transition. This very closely mirrors the time span needed for the cell to change its temperature to the new setting. In other words, the entropy change seems to be synchronized with the temperature change of the cell. Since the mass of the cell and the induced temperature change is constant throughout the trial, the 26 minute time span would apply to all of



Figure 3. (a) Close-up view of OCV readings before, during, and after a temperature change from  $55^{\circ}$ C to  $50^{\circ}$ C of a cell at 100% SOC. (b) Close-up view of OCV readings before, during, and after a temperature change from  $-15^{\circ}$ C to  $-20^{\circ}$ C of a cell at 100% SOC.

the different SOC levels. In Figure 3a, the change in the cell OCV that occurs before, during, and after a temperature change is shown in extreme close-up to reveal the behavior in detail at high temperature. Note that the negative slope of the OCV plot tends to progressively become level as the soak temperature decreases. Figure 3b shows the same 26 minute span needed for the transition to complete at very low temperatures. However, the decrease in OCV due to self-discharge is nearly zero at very low temperatures.

*Implementing the correction factor.*— The different linear rates of OCV decay due to self-discharge before and after each transformation change led to the decision that the overall correction factor would

be the average of the two rates. In this paper, transformation phase refers to the electrochemical process that the cell has undergone in response to the temperature change. The starting and ending point for this process at each temperature change is determined by the characteristic kinks that appear in the trend line of the OCV graph as shown in Figure 3b. The amount of OCV decay that occurred 26 minutes prior to and after the transformation phase were each calculated and then averaged together in order to yield a correction value. How this correction factor was applied to the OCV change depended on what was observed during the temperature change. The data points of a transformation phase. If the data showed that the



Figure 4. Surface map of entropic coefficients for the LFP test cell as a function of both SOC and cell temperature.

OCV change was a positive value (i.e.  $OCV_{end}$  minus  $OCV_{start}$ ), then self-discharge was suppressing the true OCV change. Therefore, the absolute value of the correction factor was added to it. Likewise, if the OCV change was negative during a decrease in temperature, then self-discharge was over-estimating this decline. As a result, the absolute value of the correction factor was subtracted from the OCV change.

The adjusted OCV values now reflect the change that occurs only as the result of a change in cell temperature. Although some scientific instruments allow for the auto-correction of self-discharge from the raw data, the correction of the data collected in this work was done manually. This was done for most of the 315 data points used to construct the surface map.

*Entropic coefficient map.*— Figure 4 shows a summary of all 315 data points (15 temperature levels at 21 different SOC values) calculated for the entropic coefficients across all temperatures and SOC levels. Note that the surface tends to stay relatively level as the temperature varies. This is in agreement with other studies performed on different lithium chemistries showing the change in cell entropy to be relatively independent of temperature.<sup>12</sup> This relationship is valid for most of the SOC range but not at its high or low extremities as shown in Figure 5. The largest magnitude occurs at a fully discharge cell at the high end of the temperature to the LiFePO<sub>4</sub> chemistry as discovered by other researchers.<sup>37,38</sup> According to Yazami and Reynier,<sup>39</sup>

these plateaus are indicative of a two-phase system during the phase transition.

Although the nearly-independent relationship between temperature and the entropic coefficient does not hold at extreme SOC values, as shown in Figure 6, it would be a negligible concern for all practical purposes. Designers of battery packs for electric vehicle applications typically avoid operating in the upper and lower extremities of the cell's capacity to maximize life. However, for the researcher, the entropic coefficient is an important parameter for a more accurate model of thermal behavior in a cell.

Degree of uncertainty in the entropic coefficient.— Every measurement involves some degree of error or uncertainty. The uncertainty in the entropic coefficient measurement is the result of two simple calculations: 1) the subtraction of the voltage and temperature measurements to yield the  $\Delta V$  and  $\Delta T$  values respectively and 2) the division of these two values. As a result, there is a propagation of the error as it is carried through these two steps. The error was estimated using the approach described by Coleman and Steele.<sup>43</sup>

The smallest incremental voltage reading available from the Maccor battery cycler is 0.15 mV. This means that the true OCV measurements must lie within  $\pm$  0.075 mV of the Maccor reading. The environment chamber is precise to within  $\pm$ 0.05°C. At some SOC levels, the error of the average entropic coefficient across the full temperature range is comparable to the  $\pm$ 4% presented in other studies.<sup>2</sup>



Figure 5. Entropic coefficient across the full temperature range for a LFP cell at 100% SOC and 0% SOC.



Figure 6. Cross-sectional profiles of entropic coefficient surface map across all SOC levels at a high, moderate, and low temperature settings.

 Table III. Step function polynomials of entropic coefficients (EC) as a function of SOC.

SOC%	Best-Fitting Polynomial of Entropic Coefficient (mV/°C)	R <sup>2</sup> value
5 to 35 35 to 75 75 to 95	$\begin{split} EC &= -2E \cdot 08(SOC)^6 + 3E \cdot 06(SOC)^5 - 0.0002(SOC)^4 + 0.0053(SOC)^3 - 0.0806(SOC)^2 + 0.6228(SOC) - 2.06\\ EC &= -1E \cdot 06(SOC)^4 + 0.0003(SOC)^3 - 0.0252(SOC)^2 + 0.9203(SOC) - 12.336\\ EC &= -1E \cdot 06(SOC)^4 + 0.0003(SOC)^3 - 0.0404(SOC)^2 + 2.1674(SOC) - 43.2 \end{split}$	0.9999 0.9901 0.9999

Curve-fitted equations.— An average profile of all of the entropic coefficient curves was constructed across nearly the full SOC range. As mentioned earlier, the entropic coefficients do not agree with each other very well with each other as the extremities of the SOC range. As a result, these portions were omitted from the average profile. The remaining profile represents 90% of the SOC range (between 5% and 95%) and was treated as a step function with a best-fitting polynomial to describe certain SOC ranges as shown in Table III. It should be noted that these equations pertain strictly for the particular test cell used in this study. Any other LFP chemistry would have to undergo its own dedicated testing to ascertain its unique entropic coefficient behavior. Furthermore, to take into account the SOC as well as the cell temperature, a Chebyshev series (10th order bivariate polynomial) was found to be the overall best-fitting equation to the measured data with a correlation coefficient of 98.53%. The equation format and its coefficient values found by Table Curve 3D software (v4.0) are located in the appendix. In other studies, it has been found that the average of absolute  $\Delta S$  value across the full SOC range for LiFePO<sub>4</sub> cells with graphite anodes tend to be lower than those of other chemistries.<sup>4</sup>

Once the entropic coefficient is determined, it can be used in the following equations to calculate the reversible heat generation in a cell.

$$\Delta S = -\partial G / \partial T_{cell} = nF \partial (E_{OCV}) / \partial T_{cell}$$
[1]

where G is the Gibbs free energy, n = 1 for an electrochemical chemical reaction involving lithium, F is Faraday's constant (96,485 C/mole), and  $\partial E_{OCV} / \partial T_{cell}$  is the entropic coefficient measured in volts per degree Celsius of temperature change of the cell. Being able to calculate the change in entropy of the cell,  $\Delta S$ , allows the determination of the rate of reversible heat.

$$Q_{\rm rev} = -T_{\rm cell} I \partial E_{\rm OCV} / \partial T_{\rm cell}$$
<sup>[2]</sup>

where  $Q_{rev}$  is the rate of reversible heat generation (W),  $T_{cell}$  is the absolute cell temperature (K), and I is the current (A). Here, the current is taken as positive during discharge.

*Comparisons to calorimetric data.*— The calorimeter used is an isothermal unit from Thermal Hazard Technology (THT). Here, each

face of the pouch cell is in contact with one side of a thin flat plate. The other side of each plate has a series of heat flow sensors mounted to it and, in turn, is connected to a heat exchanger. The heat exchangers are kept at a constant temperature via a recirculating water bath. The heat flow sensor generates an output voltage, U(V) that is proportional to the flow of heat, dQ/dt (W), which travels between the cell faces and heat exchangers during charge/discharge. This voltage signal is recorded as a function of time and is converted into a heat flow rate by multiplication with the calibration coefficient,  $\beta(W/V)$ . This coefficient is stored in the software settings of the calorimeter. In short, the equation used to calculate heat is:

$$dQ/dt = \beta U$$
 [3]

Since the cell is in intimate contact with the heat exchangers, it is held at a constant temperature (hence isothermal). As a result, there is no need to consider the heat capacity of the cell.

Calorimetric data has been collected and plotted on the total rate of heat generation for the 14Ah cell during a C/2 charge at  $28^{\circ}$ C. This C-rate ensures that the presence of reversible heat in the thermal behavior will be readily observed. Since Joule heat varies to the  $2^{nd}$ power of the current flow, the presence of endothermic reversible heat will be overwhelmed by the irreversible heat. For reference, the net amount of energy emitted by the cell over the full discharge cycle was 3.9 kJ and the average rate of heat generation was 0.54 W.

Figure 7 shows the total heat generation measured from the calorimeter and the reversible heat estimated from Eq. 2. Here, the influence of reversible heat on the overall heat generation of the cell is readily apparent for low current rates. The curve for the estimated reversible heat was calculated by using the entropic coefficient (variable Z) from the Chebyshev equation located in the appendix. The total heat rate profile shows the characteristic S-shape that has been attributed to entropic heating by Bang et al.<sup>41</sup> and Kim et al.<sup>42</sup>

This graph yields several noteworthy observations that give credence to its validity. At 10.5% SOC (see Zone A in the figure), the total heat generation in the cell is equal to zero. This is the point at which the endothermic heat of the reversible source cancels the exothermic heat of the irreversible sources. By making the two equal to each other, the irreversible heat at this point is 0.35 W. If this heat was to



Figure 7. Rate of heat generation as a function of SOC for a 14Ah LFP cell in full discharge at 28°C.

be attributed entirely to Joule heating, it would yield a cell resistance of 7 m $\Omega$  (0.35 W / (7A)<sup>2</sup>). This is an acceptable value since the ac impedance of the cell at 1 kHz routinely measures 6 m $\Omega$ –7 m $\Omega$ . At the 33% SOC point (see Zone B in the figure), the entropic heat is zero meaning that all of the total heat generated in the cell is irreversible in nature. This would equate to a comparable value of 0.39 W. Finally, at 84% SOC (see Zone C in the figure), if the minute contributions of the exothermic entropic heat were removed from the total heat being generated, it would leave 0.65 W of irreversible heat. This increase is to be expected as the cell impedance generally increases near the end of discharge.

The rate of reversible heat generation is zero at 33% SOC and nearly zero at 84% SOC. This means that the total heat generation at these two reference points can be almost entirely attributed to the contributions from irreversible heat sources.

#### Conclusions

Up to nine 14Ah LFP pouch cells were tested simultaneously in an environmental chamber to determine the change in OCV due to a change in temperature. In this study, the SOC settings of the cells were kept constant while the temperature in the chamber was varied. The large number of cells greatly accelerated the data collection process and minimized the amount of a drifting SOC level from excessive adjustments. The effect of self-discharge was removed in calculating the entropic coefficient. In contrast to the findings of other researchers, the entropic coefficient for this particular LFP chemistry exhibited a strong dependence on temperature when the cell is at its extreme upper or lower SOC level. At all other SOC levels, however, it was very nearly independent. A detailed knowledge of the entropic coefficient is needed to accurately calculate the amount of reversible heat generated in the cell during a charge or discharge cycle. The 315 data points collected at 21 different SOC values and at 15 different temperature ranges were plotted on a surface map. As shown in other studies, the entropic coefficient is strongly independent of temperature and dependent upon SOC levels. However, for this particular chemistry, it was found that the entropic coefficient was strongly influenced by cell temperature at 0% SOC and moderately influenced at 100% SOC.

Since the entropic coefficient is nearly independent of temperature for much of the SOC range, a step function was created that used polynomial equations derived from a best-fitting curve exercise. Furthermore, a Chebyshev series was found to fit the data very well in order to take into account the SOC as well as the cell temperature

Actual calorimetric data was collected to valid the curve-fitting model. It shows that the reversible heat calculated from the best-fit equations is in good agreement with the total measured heat generated during a 0.5C discharge under isothermal conditions.

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#### Appendix

The equation and coefficients are below, where:

x = Cell Temperature (K)

- y = Cell SOC (%)
- z = Entropic Coefficient (mV/K)
- x' = x scaled from -1 to 1 for the temperature range y' = y scaled from -1 to 1 for the SOC range of 0 to 100
- y = y scaled from -1 to 1 for the SOC range of 0 t  $T_n(x') = \cos(n^* \cos(x'))$
- $T_n(x') = \cos(n' \arccos(x'))$  $T_n(y') = \cos(n^* \alpha \cos(y'))$
- $\Gamma_n(y) = \cos(n a\cos(y))$

The Chebyshev equation format is shown below:

z = a + bT1(x') + cT1(y') + dT2(x') + eT1(x')T1(y') + fT2(y') + gT3(x')

+hT2(x')T1(y') + iT1(x')T2(y')

+jT3(y')+kT4(x')+lT3(x')T1(y')+mT2(x')T2(y')+nT1(x')T3(y')

+oT4(y') + pT5(x')

+qT4(x')T1(y')+rT3(x')T2(y')+sT2(x')T3(y')+tT1(x')T4(y')

+uT5(y') + vT6(x')

+aaT5(x')T1(y') + abT4(x')T2(y') + acT3(x')T3(y') + adT2(x')T4(y')

+aeT1(x') + T5(y')

+afT6(y') + agT7(x') + ahT6(x')T1(y') + aiT5(x')T2(y') + ajT4(x')T3(y') + akT3(x')T4(y')

+aIT2(x')T5(y') + amT1(x')T6(y') + anT7(y') + aoT8(x') + apT7(x')T1(y') + aqT6(x')T2(y')

+arT5(x')T3(y') + asT4(x')T4(y') + atT3(x')T5(y') + auT2(x')T6(y')+avT1(x')T7(y') + baT8(y')

+bbT9(x') + bcT8(x')T1(y') + bdT7(x')T2(y') + beT6(x')T3(y')

+bfT5(x')T4(y') + bgT4(x')T5(y')

+bhT3(x')T6(y') + biT2(x')T7(y') + bjT1(x')T8(y') + bkT9(y')

+b1T10(x') + bmT9(x')T1(y')

+bnT8(x')T2(y') + boT7(x')T3(y') + bpT6(x')T4(y')

 $+bqT5(x^{\prime})T5(y^{\prime})+brT4(x^{\prime})T6(y^{\prime})$ 

#### +bsT3(x')T7(y') + btT2(x')T8(y') + buT1(x')T9(y') + bvT10(y')

The coefficients for the above equation template are shown below:

a = -0.10189856	aa = -0.00387941	ba = -0.01261345
b = -0.03892254	ab = -0.00301971	bb = 0.002142093
c = 0.19695839	ac = 0.002150395	bc = 9.6497e-06
d = -0.00382405	ad = -0.00427044	bd = 0.005331322
e = 0.03012322	ae = 0.029611477	be = 0.001532663
f = -0.26307644	af = -0.07946056	bf = -0.00177502
g = 9.08559e-05	ag = 0.003886477	bg = 0.001413969
h = 0.021789868	ah = 0.001260506	bh = -0.00742182
i = -0.0636094	ai = -0.00180062	bi = 0.012389145
j = 0.039283551	aj = 0.000952563	bj = -0.02537289
k = -0.00409422	ak = -0.00470994	bk = -0.02546497
l = 0.004355865	al = 0.019622863	bl = 0.000963458
m = -0.00072045	am = -0.03051393	bm = 0.002385991
n = 0.036872116	an = -0.01763971	bn = 0.000992631
o = -0.07218337	ao = -0.00168422	bo = -0.00032674
p = -0.00131907	ap = -0.00103981	bp = -0.00200789
q = -0.00461314	aq = 0.000954728	bq = 0.002299676
r = -0.00478293	ar = -0.00197203	br = 0.000799174
s = 0.020490378	as = -0.00572634	bs = 0.004540313
t = -0.03688399	at = 0.007071596	bt = -0.0017611
u = 0.030410461	au = -0.00251404	bu = 0.02009112
v = -0.00141944	av = 0.023617117	bv = 0.005583818

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