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Investigating the Role of Energy Density in Thermal Runaway of Lithium-Ion Batteries with Accelerating Rate Calorimetry

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This work uses accelerating rate calorimetry to evaluate the impact of cell chemistry, state of charge, cell capacity, and ultimately cell energy density on the total energy release and peak heating rates observed during thermal runaway of Li-ion batteries. While the traditional focus has been on using calorimetry to compare different chemistries in cells of similar sizes, this work seeks to better understand how applicable small cell data is to understand the thermal runaway behavior of large cells as well as determine if thermal runaway behaviors can be more generally tied to aspects of lithium-ion cells such as total stored energy and specific energy. We have found a strong linear correlation between the total enthalpy of the thermal runaway process and the stored energy of the cell, apparently independent of cell size and state of charge. We have also shown that peak heating rates and peak temperatures reached during thermal runaway events are more closely tied to specific energy, increasing exponentially in the case of peak heating rates.

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Establishing a framework for understanding the hazards associated with thermal runaway reactions of lithium-ion batteries (LIBs) has become increasingly important in recent years as LIBs continue to capture new markets involving an array of abuse-prone applications such as electric vehicles, home energy storage systems, and utility storage. As these batteries are scaled up in size from Wh for consumer products to 2kWh for transportation or utility storage, the safety issues associated with these battery systems merit increasing concern. The maturity of the technology and the widespread public adoption is dependent on quantifying and mitigating the rising safety concerns related to thermal runaway.

LIB thermal runaway is caused by either an internal defect or an external source, often categorized as thermal (overheating), mechanical (crush/puncture), or electrical failure (short circuit, overcharge). Thermal runaway can potentially result from relatively normal operating conditions where the heat generation rate of the cells exceeds the heat removal from the battery system. The thermal runaway event could be extremely energetic with a high probability of generating smoke, fire, and particulate ejecta that could be critically dangerous for the user and/or the system. Traditionally, this is evaluated using battery abuse tests that perform qualitative or semi-quantitative measurements of the severity of a battery failure. Engineers and researchers rely on temperature measurements, voltage measurements, and visual observations to provide an overall evaluation of the severity of catastrophic battery failure. Abuse testing manuals and standard testing procedures are available from several organizations, with examples in Refs. 1–5. These typically rely on multiple tests to provide a broad, often qualitative understanding of thermal runaway in batteries. When a better understanding of material properties is desired, however, researchers typically turn to various calorimetry methods, such as accelerating rate calorimetry (ARC), to quantify the energy and kinetics of battery failure.

The use of ARC for evaluating lithium-ion batteries was pioneered in work by Dahn et al. studying the response of individual active materials6–8 and further developed for full cells by Roth et al.10–13 ARC closely simulates an overtemperature abusive test, yet it also provides reliable results at low internal heating rates, which is crucial to quantify the kinetics of the reaction. Furthermore, it provides essential information about the anatomy of catastrophic failure, which can be grouped into three major temperature regimes, as shown in Fig. 1; Stage 1: initial self-heating to thermal runaway onset, Stage 2: accelerating to thermal runaway, and Stage 3: high rate exothermic decomposition. Figure 1 illustrates this behavior for a typical layered metal oxide cell, but the temperatures observed and the magnitude of the peak heating rate can vary significantly depending on the cell chemistry, state of charge (SOC) and size of the cell.

The close study of ARC testing has allowed the deconvolution of the various stages of thermal runaway of a lithium-ion battery. Electrolyte degradation can begin as low as 50 °C–60 °C18–21 and has been previously shown to have an exothermic contribution even in the absence of active materials; this is likely responsible for the onset of the low rate self-heating in Fig. 1.22 As this heating progresses, the anode SEI can decompose allowing further reaction of the anode with the electrolyte.23–25 Early ARC studies by Dahn’s group9,11 and subsequent differential scanning calorimetry studies by Yamaki et al.25 showed that mild heating occurs when the anode is heated between 100 °C and 200 °C. This process also drives further decomposition of the electrolyte, leading to the venting that is typically observed in lithium-ion batteries at high temperatures.22,26–37 This combination of anode decomposition and electrolyte breakdown are the most likely causes of the accelerating heating observed in the transition to high rate runaway shown in Fig. 1.

When using layered metal oxide cathode materials such as LiCoO2 (LCO), LiNi1-x,MnCo2O6 (NMC), LiNi1-x,AiCo2O4 (NCA), and LiMnO2 (LMR) breakdown typically begins occurring at ~180 °C–200 °C and has strongly accelerating rates of exothermic heat release.12,38–45 This eventually leads to the high-rate thermal runaway event. When exploring cathode materials beyond layered metal oxides, similar transitions in behavior are often observed, but the mechanisms may change and the temperatures of various events can vary significantly. Cathode materials like LiFePO4 (LFP) and LiMn2O4 (LMO) in particular typically exhibit less energetic breakdown and/or breakdown at higher temperatures,13,46 but will still exhibit electrolyte breakdown as well as SEI and anode decomposition. Further, the decomposition products from common electrolytes are typically flammable and present a source of energy during thermal runaway unrelated to the active materials.22

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Most ARC investigations reported in the literature have considered relatively small cells (<3 Ah) and form factors that are useful for materials evaluation, but these designs are increasingly becoming less relevant for modern applications. Feng et al. performed the most comprehensive calorimetry studies of large-format cells by ARC. In particular, they studied a collection of large-format cells in multiple chemistries and were able to note some relationships with respect to cell SOC and energy density. Their data showed some exponential-like trends when plotting the peak heating rates in °C/min vs specific energy in Wh kg⁻¹. They also showed similar behavior with respect to SOC as well as a potential linear relationship between peak temperatures and state of charge. This presents some direct evidence that thermal runaway risk might be tied to the stored energy of cells. However, there are certain aspects of ARC testing that may complicate such conclusions from these data. Notably, testing is typically done with some level of restraint to limit expansion of the cell during thermal runaway. These constitute inactive masses that are in direct contact with the cell and effectively reduce the specific energy of the cell. Foreseeable impacts of this experimental approach include effectively reducing observed peak heating rates and temperatures.

The present work seeks commonality in the data that links the behavior across several different materials chemistries, sizes, and formats. This study analyzes and compares ARC results collected from cells ranging from 1 Ah 18650 cells to large-format cylindrical and prismatic cells up to 38 Ah. In addition to cells with layered metal-oxide cathodes, results are included from cells with LFP and LMO cathodes. The analysis also considers inactive masses of any cell holders or constraints in direct contact with the cell and effectively reduce the specific energy of the cell. Foreseeable impacts of this experimental approach include effectively reducing observed peak heating rates and temperatures.

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**Experimental**

This work tested cells of various cathode chemistries, sizes, and formats using ARC. Two primary test apparatuses were used for this work, both manufactured by Thermal Hazard Technologies. 18650 and smaller-format cylindrical cells were tested in the ES ARC while pouch-format and large-format cylindrical cells were tested in an Extended Volume ARC (EV ARC). In this study, the ES ARC has been considered only for comparisons between chemistries in 18650 cells. These cells were tested in cell holders sealed from air under an N₂ atmosphere. The cell holders used for the ES ARC are nominally 112 g, constructed from stainless steel and have a calculated heat capacity of 56 J K⁻¹. This mass is included in calculations of total heat capacity for the experiment to approximate the role this plays on the thermal environment, as well as the reduced energy density created by the cell holder.

For all tests, initial heating of the cells was performed up to 50 °C, after which the ARC commenced a heat-wait-seek mode. The cell would be heated by 5 °C followed by a 30-min wait. After the wait period, the ARC would repeat this process unless a self-heating >0.02 °C min⁻¹ was detected. Once this threshold was passed, the ARC maintained adiabatic conditions within the calorimeter and allowed exothermic self-heating of the cell to proceed. This period of self-heating constitutes the data collection period for the exothermic rate vs temperature plots shown in this paper. The heat-wait-seek profile continued until a maximum temperature of at least 400 °C. At this point the calorimeter would no longer search for any additional exothermic reactions, although thermal runaway events may continue to higher temperatures. Further details on ARC testing procedures are available in the Sandia Abuse Test Manual.

EV ARC testing was performed in open air inside the calorimeter due to the lack of standardization of battery sizes in larger formats. Constraints were used for pouch cells, which add mass and reduce the specific energy of the cell. The constraints are held in intimate contact with the cell and the masses are recorded to determine the total energy density of the fixture. ARC relies on maintaining an adiabatic environment during exothermic processes, but the heating rate that can be provided by the calorimeter is limited with respect to cell heating rates in full thermal runaway. The additional specific heat capacity of the cell holder helps reduce the cell heating rate during thermal runaway, which can thereby remain in the adiabatic region longer. Thermocouple placement was somewhat dependent upon the form factor of the cell being tested. In the case of pouch cells, thermocouples were attached to the negative tab of the cell. This provides good thermal conduction to the cell interior during adiabatic heating of the cell; however it may be slower to respond to the highest heating rates. This also prevented potential damage to the thermocouple when using physical constraints on pouch cells as damage to the sheath of the thermocouple may lead to erroneous readings. Thermocouples on cylindrical cells were attached to the side of the cell at approximately the half-height position of the cell cylinder. Schematics showing typical thermocouple placement are shown in Fig. 2. The rationale of this thermocouple selection is to best capture a representative temperature of the device under test and to capture the heat generated by materials decomposition within the cell.

**Figure 1.** Basic ARC data collected from an NMC-graphite cell showing various features of thermal runaway. Figure (a) shows the full exotherm event, in this case beginning at 95 °C and including a high-rate thermal runaway event at 225 °C. Figure (b) shows the onset processes from figure (a) on a logarithmic scale to better illustrate the low heating rate processes and the onset to thermal runaway.
pronounced effects and data here is differentiated by cathode and anode of NCA and LCO cathodes compared to an LFP cathode. While the array of the thermal runaway behavior of several widely used battery ARC in sealed sample holders is presented in Fig. 3. This shows a broad runaway event is typically determined by evaluating the change in heat capacity of the system under test. The enthalpy of the thermal contact with the cell were recorded and used to generate a calculated index. For heating rates normalized to cell capacity, the reported heat release is also multiplied by the cell capacity to get the heat release rate. For heating rates normalized to cell capacity, the reported heat release rate is also multiplied by the cell capacity to get the heat release rate.

Numeric results of the ARC tests were determined primarily from the dT/dt Rate vs Temperature plots, normalized to stored energy values. The masses of the cells and all fixturing materials in direct contact with the cell were recorded and used to calculate the heat capacity of the system under test. The enthalpy of the thermal runaway event is typically determined by evaluating the change in temperature for the full cell exotherm.

Results and Discussion

ARC results.—Sandia National Laboratories has long used ARC to compare the energetics of new chemistries. This has typically been done by constructing 18650-format cells of ~1 Ah with the materials in question for test. A collection of these data taken in the ES ARC in sealed sample holders is presented in Fig. 3. This shows a broad array of the thermal runaway behavior of several widely used battery chemistries. Even a cursory glance will note the high runaway kinetics of NCA and LCO cathodes compared to an LFP cathode. While the composition of the battery materials themselves likely have the most pronounced effects and data here is differentiated by cathode and anode material, other properties may impact thermal runaway behavior to a more limited degree. Material properties such as anode and cathode material specific surface areas may impact electrode-electrolyte interactions and may be worth exploring further.

Beyond chemistry, SOC is also well-understood to play a role in both the total energy and kinetics of thermal runaway. This was explored on a 16 Ah pouch-format LMO cell where the thermal runaway was evaluated at different states of charge. The summarized data are presented in Fig. 4 and the full ARC results and are provided in the supplemental information. The authors have also provided the raw data for this test at https://www.sandia.gov/ess-ssl/data-repository/. We ultimately identified two different trends in these data. First, the total enthalpy calculated for the cell thermal runaway event follows a linear pattern. It is worth noting that even at 20% SOC some exothermic activity was detectable. This observed linear trend with SOC is consistent with expected behavior for the major decomposition reactions in both the cathode and the anode. Meanwhile, the peak self-heating rates for this cell increase rapidly at high states of charge. The data in Fig. 4 fit an exponential pattern, with a rapid increase in peak heating rates observed above 60% SOC. The exponential pattern is consistent with expected kinetic behavior for the decomposition reactions at high states of charge; as more heat is released, it will cause more of the decomposition reactions to occur at higher temperatures, where the Arrhenius rates are exponentially higher.

Comparison of capacity and specific energy.—The above analysis considers only the as-charged capacity of cells as the normalizing factor. This provides a means to quickly and easily compare the relative thermal runaway risks posed by different lithium-ion chemistries and at different states of charge, provided the test cells have similar masses and total electrochemical capacities. However, analysis in terms of SOC alone does not provide good correlation to the reactions that drive thermal runaway processes. Developing a better understanding of the thermodynamics and kinetics of the reactions that drive thermal runaway requires a more relevant basis for normalizing data. Cell constraints and cell holders are often used, which present additional inactive mass to the system; when we move to higher capacity cells it requires performing tests in larger, non-standardized test fixtures. While for practical reasons these additional inactive masses cannot be fully avoided, we can evaluate their mass and heat capacity and include them in the total values for the cell being evaluated. As we assume the ARC is adiabatic, we assume here that any inactive mass in direct contact with the cell should be included in the overall mass for comparison to other formats and chemistries.

The data presented in Fig. 5 and Table I consider cells in an as-charged capacity range of 1.08–38 Ah (3.5–122 Wh) and chemistries including LFP, NMC, and NCA taken from historic data previously collected at Sandia as well as the LMO data shown in Fig. 4. These data were limited to results collected in open-air testing using the EV ARC, and the physical constraints used varied based on the cell construction and geometry. This variation in mass is accounted for in the overall energy density of the cells shown in Fig. 5b. The raw ARC data are provided in supplemental information. These data show the total enthalpy of thermal runaway as a function of the as-charged stored energy, and the peak thermal runaway temperatures as a function of the specific energy, calculated as described in Eq. 1 and accounting for the mass of any inactive material. This effectively corrects for the relatively high mass of the test apparatus when testing low capacity cells, as well as cells of similar chemistries with different specific energies.

Figure 5a tracks how the heat release during thermal runaway is impacted by the total energy storage of the cell. The enthalpy of the thermal runaway event tracks linearly with the total stored energy. This indicates safety implications for even low-specific energy cells or cells at lower states of charge. The stored energy is still available to potentially initiate events like cell venting and fire. If the cells in question are well insulated (similar to the adiabatic environment of the present study), even a low rate of energy release is able to drive

![Figure 2. Schematic showing typical thermocouple placements for primary sensors during testing.](image-url)
the cells to high temperatures. This is similar to results observed by Liu et al. that found increasing energy released during thermal runaway with increasing energy stored.50

More qualitatively, it can be useful to evaluate the ARC measurements in terms of the maximum thermal runaway temperature. These data are shown in Fig. 5b with the peak temperature as a function of specific energy. These data show in stark terms the increase in potential risk as specific energy increases. As higher energy density cells are fielded, it should be generally expected that peak temperatures observed in thermal runaway will increase. This becomes of particular concern if thermal runaway temperatures increase to a point where typical structural materials within battery
systems are affected (including aluminum, copper, and steel), increasing the likelihood of propagation to other cells.51

Meanwhile, peak heating rates follow an exponential curve (shown as linear on the log scale of Fig. 6) until very high specific energies, where the rate becomes roughly flat. This flattening at high peak heating rates may be a limitation of the equipment used, as at these high heating rates the ARC cannot match the high rates of self-heating. The exponential slope of the peak heat release rate as a function of the specific energy in Fig. 6, together with the related peak temperatures in Fig. 5b, suggest an Arrhenius approximation might be appropriate for analyzing the peak heating rates. This correlation between energy density and peak heating rates suggests that achieving a balance between high energy density and safety performance has limitations. While various precautions may reduce the likelihood of failure occurring (for example, a separator preventing the formation of internal short circuits), it may be difficult to fully avoid the potential consequences of thermal runaway without reducing the overall specific energy.

A more interesting question may be the implications of this work at the system level. Our own work on mitigating thermal runaway propagation has largely found the most success by increasing the inactive mass of the battery.51–53 In large multi-cell systems, the goal is to limit a single cell thermal runaway to only the immediate point of failure, or at least to delay any propagating failure long enough to allow the immediate vehicle or area to be evacuated. However, solutions that reduce the energy density of the system negate much of the advantage of advanced battery chemistries.

**Consideration of activation energies.**—The data from Fig. 6 are replotted in Fig. 7 with peak heating rate as a function of the temperature of peak heat release; the Arrhenius format with logarithmic rates and inverse temperatures is suitable for considering activation energies of processes with the fastest heat release. This is similar to approaches commonly used to derive kinetic parameters from other types of calorimetry.54,55 The effective activations energies observed for LFP and LMO are both about 190 kJ mole\(^{-1}\). The NMC data have more scatter, but the overall slope appears reasonably consistent with LFP and LMO cells. The slope of the high-temperature data from NCA cells is nearly flat, and the scatter between just four points precludes evaluating a meaningful activation energy (requires a negative slope and a correlation coefficient close to unity).

Other investigators have measured activation energies between 108 kJ mole\(^{-1}\) and 682 kJ mole\(^{-1}\), with most values occurring below 225 kJ mole\(^{-1}\) to 250 kJ mole\(^{-1}\), the activation energies at lower temperatures on the right side of Fig. 7 are reasonably consistent with the full-cell measurements from literature. These full-cell effective activation energies apply most directly to the event corresponding to the most rapid heat release, which may include the simultaneous decomposition of multiple components. An activation energy in the vicinity of 65 kJ mol\(^{-1}\)e\(^{-1}\) ha\(^{-1}\) s\(^{-1}\) has been proposed in some models for anode-electrolyte reaction heat release, though the same process can be fit by higher activation energies in the vicinity of 135 kJ mole\(^{-1}\).9,23,24 Cathode decomposition and electrolyte oxidation are often suggested to have activation energies in the 120 kJ mol\(^{-1}\)e\(^{-1}\) range.10,12,59

A recent simulation analysis in a cascading propagation scenario suggests that the high temperature heat-release rates transition to a lower activation energy at higher temperatures, perhaps an activation energy as low as 30 kJ mole\(^{-1}\) for temperatures around 600 °C to 700 °C.52 Such a shift is qualitatively consistent with the
high-temperature NCA data on the left side of Fig. 7 and implies a transition to a high-temperature regime where mass transport processes are limiting. Much of the variance of activation energies observed in literature is likely driven by the fact that most previous analyses require determination of activation energies at the component level. This work presents a potential means to evaluate the activation energies of thermal runaway at the full cell level, experimentally accounting for the multitude of reactions that can occur during a full-cell thermal runaway process.

Comparison to thermodynamics of major decomposition reactions.—Some of the trends discussed in the preceding sections can be explained in terms of the thermodynamics of the thermal runaway reactions. The quantity of reactive materials available for the major decomposition reactions in both electrodes is proportional to SOC (the number of transferred lithium atoms). This does not include thermal contributions from SEI and self-decomposition of electrolyte, but these are expected to be small compared to other sources. The enthalpy of decomposition for lithiated graphite with electrolyte has been calculated from thermodynamics and should be similar for the negative electrodes in all these cells.

Figure 8a compares the ARC measurements to estimates of anode heat release, assuming exothermic heat of 281.4 kJ mol$^{-1}$ lithium in the charged graphite anode. The calculated anode heat release corresponds surprisingly well to the ARC heat release measurements; some possible explanations are presented below in connection with Fig. 9. The two lowest NMC points in Fig. 8a and subsequent plots correspond to the two NMC cells with lowest capacity in Fig. 5a, which depart farthest from the linear trend in both plots. If these particular NMC enthalpy measurements are overstated with respect to the rest of the data (possibly due to an overestimated heat capacity for pouch cells of the smallest size), then the corresponding points in Fig. 8a and subsequent plots would shift to the left, which would improve the trends in all cases.

Layered metal oxides decompose to rock salts when heated sufficiently, releasing 1 oxygen atom per delithiated site. When the enthalpy of this cathode decomposition reaction is lumped with the heat from oxidation of the solvent, thermodynamic calculations have shown that the heat generated per mole of delithiated metal oxide only varies by $\sim$10% for LCO, NMC, and NCA. Therefore, cells with graphite anodes and layered metal oxide cathodes and liquid organic electrolytes should yield similar quantities of heat via thermal runaway reactions for a given quantity of stored energy. Figure 8b shows the heat release predicted for layered metal oxide decomposition with electrolytes, which is on the same order of magnitude as the anode heat release, but usually lower than the ARC measurements. A recently published thermodynamic database and calculation method was used for these estimates with the assumption that NCA = $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ and NMC = $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$. The predictions in Fig. 8 also assume that a discharged cathode is fully lithiated ($x = 1$ at SOC = 0).

In contrast, release of 0.5 oxygen atom per delithiated site has been estimated for decomposition of LFP and release of either 2 oxygen atoms or 1 oxygen atom per delithiated site has been proposed for decomposition of LMO. Because the number of oxygen atoms released per vacant lithium site is distinct for different types of decomposing cathode materials, oxidation of solvent with oxygen from the cathode cannot explain why the enthalpies of decomposition for different types of cathode materials would be similar on a
vacant lithium site basis. Figure 8b does not include LFP or LMO because a thermodynamic database for the applicable reactants and products (similar to Ref. 49) has not yet been evaluated and published. Calorimetry of charged LFP cathodes\textsuperscript{40} exhibits lower heat release than layered metal oxides, which is most likely due to the lower oxygen release per delithiated site in LFP.

Figure 9a considers NMC and NCA cathode materials and is a summation of the predicted anode heat release from Fig. 8a and layered metal oxide cathode heat release from Fig. 8b with respect to the ARC measurements. Since the predicted heat release from both electrodes is similar, the sum of heat release from both electrodes shown in Fig. 9a exceeds the ARC measurements by a factor of ~2 for both large and small NCA cells at different SOCs, and a smaller margin for most of the NMC points. The excess predicted heat release for NCA cells may be explained in the same manner as recent simulations of full cells, where it was assumed that the individual electrode decomposition reactions illustrated in Fig. 8 were limited by venting electrolyte in order to limit cell temperature rise to a level consistent with experimental data.\textsuperscript{52}

Figure 9b compares the NMC and NCA ARC measurements to a competing reaction that has been proposed by several authors,\textsuperscript{57,65–68} wherein oxygen from cathode decomposition reacts with lithium from the anode, producing Li$_2$O as a product.\textsuperscript{66} This path is expected to compete for the same reactants consumed by the decomposition reactions assumed in Fig. 8, and it could feasibly become dominant, especially after the electrolyte vents and the separator melts. Given that oxygen from the cathode is generally produced in excess of the amount needed to consume all the lithium in the anode, Fig. 9b provides a plausible explanation for why these decomposing full cells generate similar amounts of heat per unit of stored energy with different cathode materials. In reality, the anode decomposition reaction begins at a low rate near 100 °C.\textsuperscript{8,9,23} but the similar trends in Figs. 8a and 9b demonstrate nearly equivalent heats of reaction for the anode reaction with electrolyte (281.4 kJ mol$^{-1}$ lithium in anode) and the reaction between anode lithium and cathode oxygen (306.6 kJ mol$^{-1}$ lithium in anode for NMC-532 and 271.4 kJ mol$^{-1}$ lithium in anode for NCA). The similar activation energies with different cathode materials in Fig. 7 also lends credibility to the idea that a common reaction process whereby oxygen from the cathode reacts with lithium from the anode is responsible for the observed high-rate behavior for cells with different cathode chemistries. This may have implications as well when anode materials with varying levels of reactivity with oxygen are used.

The thermodynamics and residual species associated with decomposition of electrode materials (including cells utilizing LFP and LMO cathodes) should be investigated further in future works to see whether one of the two paradigms represented by Fig. 9, becomes more compelling. These paradigms are summarized as follows: Fig. 9a shows that the measured heat release is less than the calculated heat release from decomposition of individual electrodes; previous simulations have shown that this excess heat production may be prevented if decomposition is limited by electrolyte (which vents from cells during thermal runaway).\textsuperscript{52} Figure 9b shows that a reaction between the two electrodes via an oxygen intermediate is thermally consistent with the ARC heat release measurements, and this proposed reaction happens to be energetically comparable to the decomposition of lithiated graphite with electrolyte.

Ultimately, this analysis suggests that the severity of thermal runaway reactions may be heavily tied to the energy density of the materials used for electrochemical storage and may be difficult to fully engineer out of a system. However, there are impacts from the inactive portions of the battery that are only briefly touched upon here and present important areas for improvement. The flammability of the electrolyte in lithium metal cells and lithium-ion cells presents a source of stored chemical energy in addition to that available from the stored electrochemical energy. It has been previously estimated that accounting for chemical combustion can significantly increase the released energy from a cell.\textsuperscript{51,55,69,70} In addition to the electrolyte, flammable plastic components have been reported to contribute significantly to the heat release in fire scenarios. While high energy density of the active materials is a desired feature of a battery, the flammability of the electrolytes and cell packaging materials is not. This makes the pursuit of chemically inactive electrolytes and cell packaging a very promising path to improve single-cell battery safety even as active material chemistry advances.

**Conclusions**

An evaluation of ARC data presented here, when normalizing for energy density, indicates that peak runaway temperatures in adiabatic environments tend to be linearly proportional to the cell specific energy. These data cover four cathode chemistries, multiple form factors, and stored energy ranging from 3.5 to 122 Wh. This follows from ARC measurements that show the heat released is also linearly proportional to the stored energy. More importantly, perhaps, ARC measurements of the heat-release rate suggest that the kinetics of cell failure display an exponential relationship with increasing energy density. This compares well to a materials-level analysis of oxygen release observed for layered metal oxide cathodes.

In a practical scenario, thermal runaway occurs when the self-heating rate of a battery failure event exceeds the heat loss rate in its current environment or installation. The logical next step is that increasing energy density will lead to increased consequences of thermal runaway occurring. With exponentially faster heat release at higher energy density it will be easier for the thermal runaway to
Table I. Tabulated data for results shown in Figs. 5–7.

| Material | Peak rate (W) | Peak runaway temperature (°C) | Enthalpy of runaway (kJ) |
|----------|---------------|-----------------------------|---------------------------|
| LFP      | 2.20E + 00    | 271                         | 13.9                      |
| LFP      | 4.33E + 01    | 321                         | 15.0                      |
| LFP      | 1.63E + 02    | 348                         | 25.4                      |
| LFP      | 7.51E + 01    | 331                         | 23.7                      |
| LFP      | 2.62E + 03    | 353                         | 150                       |
| LFP      | 7.11E + 03    | 414                         | 271                       |
| LFP      | 6.27E + 03    | 414                         | 272                       |
| LFP      | 3.02E + 03    | 366                         | 303                       |
| LFP      | 5.82E + 03    | 365                         | 275                       |
| LFP      | 1.48E + 04    | 682                         | 20.1                      |
| NCA      | 7.43E + 03    | 651                         | 16.7                      |
| NCA      | 1.11E + 04    | 765                         | 22.2                      |
| NCA      | 3.15E + 04    | 476                         | 254                       |
| NMC      | 4.20E + 01    | 318                         | 155                       |
| NMC      | 1.40E + 01    | 277                         | 128                       |
| NMC      | 9.70E + 01    | 300                         | 117                       |
| NMC      | 8.65E + 03    | 299                         | 148                       |
| NMC      | 3.42E + 01    | 295                         | 165                       |
| NMC      | 3.35E + 03    | 338                         | 189                       |
| NMC      | 3.28E + 03    | 328                         | 194                       |
| NMC      | 3.77E + 00    | 238                         | 40.5                      |
| LMO      | 2.72E + 00    | 237                         | 38.7                      |
| LMO      | 3.92E + 00    | 239                         | 79.7                      |
| LMO      | 4.25E + 00    | 248                         | 117                       |
| LMO      | 2.21E + 01    | 262                         | 127                       |
| LMO      | 2.43E + 01    | 267                         | 117                       |
| LMO      | 8.80E + 01    | 285                         | 140                       |
| LMO      | 7.33E + 01    | 283                         | 154                       |
| LMO      | 6.07E + 02    | 300                         | 164                       |
| LMO      | 4.09E + 02    | 297                         | 168                       |

exceed any heat dissipation to the environment, likely leading to more severe consequences in terms of further damage or cascading failure. This would be considered intuitive if discussing chemical energy storage but is a concept often avoided when considering electrochemical energy. As new technologies are developed with increased energy in mind, increasing attention will need to be paid to designing mitigation into systems that minimize consequences.

The overall energy released during thermal runaway in this work scales quite well with the stored energy; however, during a practical thermal runaway there will also be other concerns not evaluated here, including the significant energy available from inactive materials. The combustion of the electrolyte and its decomposition products can be a significant contributor if the thermal runaway process is energetic enough to provide an ignition source. Plastic packaging may play a role as well. Faster rates of heat release and higher peak runaway temperatures associated with higher energy densities observed here will be more likely to ignite these inactive materials. The potential for fire and the heat it generates may be of particular importance when considering system-level safety, as it provides a means beyond the exothermic failure of the active materials to initiate runaway in other cells, driving a propagating battery failure.

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