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Accelerated Rate Calorimetry and Complementary Techniques to Characterize Battery Safety Hazards

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Corresponding Author:	Corey T Love, Ph.D. U.S. Naval Research Laboratory Washington, District of Columbia UNITED STATES
Corresponding Author's Institution:	U.S. Naval Research Laboratory
Corresponding Author E-Mail:	corey.love@nrl.navy.mil
Order of Authors:	Corey T Love, Ph.D.
	Emily J Klein
	Rachel Carter
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TITLE:
Accelerating Rate Calorimetry and Complementary Techniques to Characterize Battery Safety Hazards

AUTHORS AND AFFILIATIONS:
Emily J. Klein[1*], Rachel Carter[1,2*], Corey T. Love[1*]

[1]Chemistry Division, U.S. Naval Research Laboratory, Washington, D.C., USA
[2]NRL/NRC Post-doctoral Research Associate, Washington, D.C., USA

*These authors contributed equally.

Corresponding Author:
Corey T. Love (corey.love@nrl.navy.mil)

Email Addresses of Co-authors:
Emily J. Klein (emily.klein@nrl.navy.mil)
Rachel Carter (rachel.carter.ctr@nrl.navy.mil)

KEYWORDS:
lithium-ion battery, battery safety, accelerated rate calorimetry, ARC, thermal runaway, 18650 cell

SUMMARY:
A method to characterize the potential failure hazards of lithium batteries is achieved with accelerating rate calorimetry. Heat and pressure release, visual observation of the failure event, and the capture of evolved gases are collected in this experiment to identify the worst credible threats of batteries taken to failure.

ABSTRACT:
The hazards associated with lithium-based battery chemistries are well-documented in the press and social media due to their catastrophic nature. Risk is typically qualitatively assessed through an engineering risk matrix. Within the matrix, potentially hazardous events are categorized and ranked in terms of severity and probability to provide situational awareness to decision makers and stakeholders. The stochastic nature of battery failures, particularly the lithium-ion chemistry, makes the probability axis of a matrix difficult to properly assess. Fortunately, characterization tools exist, such as accelerated rate calorimetry (ARC), that characterize degrees of battery failure severity. ARC has been used extensively to characterize reactive chemicals but can provide a new application to induce battery failures under safe, controlled experimental conditions and quantify critical safety parameters. Due to the robust nature of the extended volume calorimeter, cells may be safely taken to failure due to a variety of abuses: thermal (simple heating of cell), electrochemical (overcharge), electrical (external short circuit), or physical (crush or nail penetration). This article describes the procedures to prepare and instrument a commercial lithium-ion battery cell for failure in an ARC to collect valuable safety data: onset of thermal

runaway, endotherm associated with polymer separator melting, pressure release during thermal runaway, gaseous collection for analytical characterization, maximum temperature of complete reaction, and visual observation of decomposition processes using a high temperature borescope (venting and cell can breach). A thermal "heat-wait-seek" method is used to induce cell failure, in which the battery is heated incrementally to a set point, then the instrument identifies heat generation from the battery. As heat generates a temperature rise in the battery, the calorimeter temperature follows this temperature rise, maintaining an adiabatic condition. Therefore, the cell does not exchange heat with the external environment, so all heat generation from the battery under failure is captured.

INTRODUCTION:

Rechargeable batteries, specifically lithium-ion chemistry, have allowed functioning of an all-electric society encompassing all aspects of daily life such as transportation, communication, and entertainment. For these energy storage applications, charge capacity equates to range or runtime. Maximizing these parameters leads to aggressively high energy lithium-ion cells. Unfortunately, as electrical energy increases within lithium-ion cells, so does detrimental energy release when a failure occurs[1]. A number of regulatory agencies, professional societies, and independent laboratories have developed standards to better characterize the safety of rechargeable batteries. One method used to quantify the thermal intensity of a battery safety event is accelerated rate calorimetry (ARC)[2,3]. This type of calorimetry is performed near-adiabatically to capture explicit heat generation from a material or battery cell at the onset of an exothermic reaction, then through thermal runaway and combustion type reaction processes. The ARC instrument provides an opportunity to characterize the worst-case heat, pressure, and gas generation from an exothermic material reaction in a safe and controlled laboratory environment.

The ARC instrument was first developed in the 1970s to simulate exothermic runaway reactions from hazardous and reactive chemicals at safe scales and evaluate the hazards of reactive chemicals to devise safety procedures for handling, usage, storage, and transportation[4]. In the early 1980s, ARC was first used for the purpose of studying thermal runaway reactions in lithium cells. The ARC operates through "adaptive adiabatic control", which means the calorimeter temperature tries to match the cell temperature while a reaction is occurring. There is also no heat exchange between the sample being tested and the surrounding environment. In doing so, as the cell self-heats and its temperature rises, heat transfer between the cell and its surroundings is minimized. A schematic of the ARC chamber with heating elements and locations for lithium-ion cell testing is shown in **Figure 1**.

The ARC instrument is available in several sizes to accommodate a wide range of battery materials, cell components, cells, batteries, and battery modules, as shown in **Table 1**. The ARC also offers a range of thermal analysis testing protocols, including the most prevalent for lithium-ion battery safety characterization known as heat-wait-seek (HWS). ARC measurements can be performed in an "open" or "closed" testing configuration. The main difference between these two testing configurations is the ability to perform pressure and gas sampling measurements in the closed system. The open configuration lends itself to visual observation through use of a high temperature camera or borescope[4,5]. The use of a small spherical pressure vessel or "bomb" has been utilized in the ARC to measure reaction heat release from battery electrode materials[6]. Typically, heat release is governed by the lithium concentration in the materials and intensifies in the presence of organic electrolyte solvents and lithium salts[7,8]. At the cellular level, an extended volume ARC is required to safely retain the heat, pressure, and gas release from the thermal runaway process. Additionally, features can be incorporated into the ARC instrument to induce battery failures via nail penetration, electrochemical overcharge, or external short circuit.

Sandia National Laboratory has historically been a leader in ARC characterization of batteries in support of the U.S. Departments of Energy and Transportation. Sandia has published many reports highlighting its importance in generating critical safety data, which has influenced federal policy and safety standards[9,10]. In the report, they provide optimal test parameters, data collection, and reporting criteria[9]. Most of the recommended practices are adopted in this article to characterize the thermal hazard of a single cylindrical lithium-ion cell under thermal runaway utilizing the HWS protocol. Specifically, the ARC can provide objective quantitative evidence of factors affecting the safety of lithium-ion batteries and battery materials (i.e., maximum temperature, heating rate as function of time/temperature, vent gas as a function of time/temperature, and chemical analysis of hazardous substances from vented gas and smoke) during a battery failure.

The most commonly used ARC testing protocol for battery safety testing is HWS. The HWS protocol offers accurate detection of exothermic reactions occurring within lithium-ion cells and is more accurate than a simple ramped heating mode. This is the standard method for battery thermal runaway characterization. The chamber is heated to an initial start temperature, then a wait time is applied that depends upon the sample mass and heat transfer properties. After this step, the calorimeter seeks for an exotherm greater than the set sensitivity (e.g., 0.02 °C/min). If no exotherm is observed in the allotted time period, the chamber again heats by a defined temperature step (e.g., 5 °C), and the process is repeated. **Figure 2** shows the process flowchart for HWS (**Figure 2A**) and experimental data illustrating the various stages of HWS through the first several iterations (**Figure 2B**).

Complete definitions of each of the testing steps in the HWS protocol are as follows. Heat mode is the power given to chamber heaters to elevate chamber and device under test (DUT) temperature. Wait mode occurs when thermal equilibrium is established between the calorimeter and bomb or test article. Seek mode occurs when calculations of change in temperature are determined, and the time relates to the change in sensitivity, typically 0.02 °C/min. Cool mode is initiated at the end of a test, when a maximum temperature or pressure has been achieved. The traditional cooling mechanism involves flowing an inert gas such as nitrogen into the chamber. Alternatively, liquid nitrogen may be introduced into the chamber to expedite cooling. Exotherm mode refers to an increase in temperature observed after a seek step is termed exotherm. This describes an environment in which self-heating of the test article is greater than the selected sensitivity, typically 0.02 °C/min. Exotherm mode continues until the rate of self-heating falls below the desired sensitivity, at which point another heat mode is triggered, and the heat-wait-seek sequence continues until a maximum temperature or pressure limit is reached.

PROTOCOL:

1. Calibration of calorimeter

NOTE: It is important to calibrate the calorimeter to accommodate any changes in heat transfer conditions to/from the same cell (e.g., connecting large diameter electrical cables to the cell) or replacement of the main measurement thermocouple. The instrument should be recalibrated after a period of 2–3 months, as thermocouple responses can change with prolonged use.

1.1. Use a small spherical vessel or “bomb” for calibration of the calorimeter.

1.2. Attach an empty spherical bomb of known material (i.e., titanium, stainless steel, aluminum, etc.) to the underside of the calorimeter lid.

1.3. Ensure that the calorimeter is clean and free of debris.

1.4. Match the calibration conditions to the anticipated testing conditions. Any special fixtures must be present within the chamber in the anticipated location for proper calibration.

1.5. Connect the tip of the bomb thermocouple wire to the surface of the spherical bomb vessel. The tip must be in contact with the bomb in order for the calibration to work correctly. Secure the thermocouple wire and leads with high temperature tape, if necessary.

1.6. Ensure that the calorimeter lid is completely closed, with the lid and base showing good contact.

1.7. Close the blast box to eliminate air currents blowing across the calorimeter, which can affect the measurement.

1.8. Use the following parameters for a calibration test: temperature step = 25 °C; start temperature = 50 °C; end temperature = 405 °C; temperature rate sensitivity = 0.01 °C/min; and wait time = 30 min.

1.9. Ensure that the previous calibration offsets are cleared from the software.

1.10. Begin the calibration procedure.

2. Phi factor test

NOTE: Even the highest performing ARC cannot achieve full adiabicity. Therefore, some heat is lost during the test and must be accounted for to provide accurate calorimetry data.

2.1. Account for thermal loss by calculating an offset factor, ϕ, using the following equation:

$$\phi = 1 + \frac{c_b m_b}{c_s m_s}$$

Apply the known heat capacity and mass (*c* and *m)* for the bomb and sample. Complete a drift test after calibration of the chamber. Ensure that the resulting phi factor is within ±0.02 °C/min.

3. Heat mass and heat capacity of commercial battery cells for destructive testing

3.1. Calculate the heat capacity during a short, mild, nondestructive heating of the cell. Perform this operation in a temperature range of 25–55 °C (ambient temperature to the maximum recommended operating temperature of the cell). Use liquid nitrogen to evaluate heat capacity from sub-ambient temperatures.

3.2. Collect the single cell mass for three identical cells.

3.3. Affix a heater mat along the axis of a single 18650 cell with high temperature tape.

NOTE: The physical test set-up can vary with cell geometry, and a heater mat of suitable size is required for different cell sizes.

3.4. For extended volume calorimeters, bundle three cells, including the cell with heater mat, into a triangle shape. Tape the cells together with aluminum tape.

3.5. Attach a control thermocouple at the mid-length of a cell adjacent to the cell with the heater mat.

3.6. Suspend the three-cell triangle from the top of the calorimeter using metal wire.

3.7. Securely replace the calorimeter lid.

3.8. Ensure wires from heater exit the calorimeter and are connected to the variable power supply.

3.9. Initiate the heat capacity test by activating the power supply to ramp from 30–60 °C over a period of ~2 h.

NOTE: Typical temperature *vs.* time data (converted to K/s) used to calculate c_p is provided in **Figure 3**. The power supplied to the heater is calculated by multiplying the power supply voltage and current to provide the power in units of W or J/s. The heater power is divided by the slope of the temp *vs*. time plot to provide the thermal mass in units of J/K. Finally, the thermal mass is divided by the sample mass to provide the cell heat capacity in units of J/g·K. An example of the heat capacity measurement is shown below, according to data in **Figure 3**:

Slope of temperature *vs*. time, from raw data: 0.3738 °C/min = 0.00623 K/s
Power from heater: (8.53 V x 0.639 A) @ 30% = 1.635 W = 1.635 J/s
Thermal mass (power/slope) = 262.472 J/K
Heat capacity (thermal mass/mass) = 262.472 J/K divided by 244 g = 1.075 J/g·K

4. Destructive failure testing a commercial 18650 lithium-ion battery cell

4.1. Standard “heat-wait-seek” for battery cell

4.1.1. Ensure that the commercial battery/cell test article or “device under test” (DUT) is at the desired state of charge (SOC) for testing; ideally, the SOC is 100% to represent the “worst credible threat” of a battery failure.

4.1.2. Open the lid of the outer chamber.

4.1.3. Remove the top lid of the calorimeter to arrange for placement of the battery test article. The chamber should be clear of debris using a standard vacuum and light solvent wipe of the calorimeter walls.

4.1.4. Mount the cylindrical cell into a cell holder in the vertical direction and place it slightly off-center of the calorimeter’s interior. Off-center placement ensures maximum video capture during the thermal runaway event when the high temperature borescope camera is not obstructed by ejected electrolyte vapors, smoke, and cell ejecta from the cell’s top vent.

NOTE: Alternatively, the cell may be fixed in a horizontal direction using a standard ring-stand. Anytime that additional items such as ring stands are entered into the calorimeter, another calibration should be performed.

4.1.5. Affix the thermocouple designated “bomb thermocouple” to the cylindrical cell at the wall mid-length and secured with high temperature nickel wire. This is done to 1) keep the thermocouple in place during mechanical straining of the cell can and 2) avoid melting of alternative high temperature tape, which sometimes cannot withstand the degree of heat release from the cell.

NOTE: It is important to maintain good contact between the thermocouple and cell wall to ensure the accurate temperature reading required to control adiabatic heating of the calorimeter chamber.

4.1.6. Secure the DUT with appropriate alligator style clips for cell charge, discharge, open circuit voltage monitoring, or electrochemical impedance measurements. Run the electrical leads through the grooves on the top surface of the calorimeter chamber.

4.1.7. Replace the calorimeter lid careful not to pinch any thermocouples or electrical leads.

4.1.8. Use the manual focus features on the high temperature borescope to maximize picture quality prior to testing. Often the borescope is focused on the bottom plate of the cell holder to account for fluctuations in optical focus during heating of the calorimeter.

4.1.9. Initiate a thermal HWS testing protocol. The testing parameters and representative values are as follows:
Start temperature: 35 °C
End temperature: 305 °C
Temperature step: 5 °C
Temperature rate sensitivity: 0.02 °C/min
Wait time: 30 min
Calculation temperature step: 0.2 °C
Cool temperature: 35 °C
Release temperature: 50 °C
Safety pressure: 200 Bar
Maximum temperature drop: 25 °C
Maximum pressure drop: 20 Bar
Max exotherm rate: 1000.00 °C/min
Maximum pressure rate: 100000 Bar/min
Data log temperature step: 1.00 °C
Data log time step: 0.5 min
Exotherm log temperature step: 1.00 °C

4.1.10. If gas collection is desired, set the collection temperature (e.g., 120 °C) and collection time period (e.g., 0.5 min).

4.1.11. Initiate the HWS test and allow the cell to enter thermal runaway.

NOTE: Once a maximum temperature of the calorimeter is reached, an exhaust fan is automatically initiated to remove any smoke from the calorimeter.

4.1.12. Allow the chamber to completely cool to near ambient temperature before opening the ARC and removing the calorimeter lid. Cooling time for the chamber may be expedited using liquid or gaseous nitrogen injection into the bottom of the chamber. Without nitrogen-assist, cooling may take up to 24 h.

4.1.13. The ARC HWS process results in the decomposition/combustion of the battery cell, leaving combusted electrode materials and debris inside the chamber. Clean the calorimeter using a shop vacuum and wipe the walls of the calorimeter with a mild solvent.

5. Ensuring successful ARC test of lithium-ion cell

5.1. Ensure that the cell is at the appropriate SOC. Fully charged cells typically provide the greatest heat release and earliest onset temperature, indicating the worst credible safety threat.

5.2. Ensure that the bomb thermocouple is secured to cell with metal wire. Failure to adhere the thermocouple tip to the battery sidewall will not capture the effects of self-heating.

5.3. Double-check the thermocouple designations: bomb is attached to cell, sample is free floating within the calorimeter chamber, and (if using multiple auxiliary thermocouples) their locations are known and verified.

5.4. If performing open circuit voltage monitoring or performing electrochemistry in the ARC, make sure that the cell registers an expected voltage value. Unexpected voltage or negative voltage suggests that the electrical leads within the ARC canister may have lost connection or the leads have been reversed. Be careful not to short the cell during set-up, as the whole chamber is metallic.

6. Interpreting ARC data and calculating heat of reaction

6.1. Calculate the hotel heat of reaction in units of heat per mass (J/g or J/kg).

6.2. Use temperature *vs.* time data to obtain basic thermal properties of the reaction, such as the onset of exotherm, T_{onset}, and maximum temperature of the reaction, T_{max}, using the equation:
$\Delta T = T_{max} - T_{onset}$.

6.3. Use the heat capacity measured in the previous procedure and calculation of ΔT to calculate the total heat of reaction. Use the ϕ offset factor to account for lack of perfect adiabicity.

$$\Delta H = \Delta T \cdot c_s \cdot \phi$$

6.4. Calculate the pressure rise during reaction using the following equation:

$$\Delta P = P_{max} - P_{min}$$

6.5. Plot the logarithmic temperature rate *vs*. temperature to show how the reaction develops across the temperature range (**Figure 4B**). Convert the temperature rate (°C/min) into units of J/s using the heat capacity.

REPRESENTATIVE RESULTS:

Representative data from the HWS experiment of a fully charged 18650 commercial lithium-ion battery cell is provided in **Figure 4A,B**. The figure shows cell temperature as a function of time during a “closed” ARC testing set-up. Basic thermal features (T_{onset}, $T_{max,}$ and ΔT) are highlighted in the figure. The location of T_{onset} is the beginning of the exothermic step, which continues until T_{max} is reached. Cell voltage along with the maximum pressure and change in pressure (P_{max} and ΔP, respectively) may also be collected during this experiment. Gas analysis can be performed on the vent and/or combustion products of the ARC experiment in the “closed” test set-up. Representative gas chromatography for gaseous products collected during the thermal runaway reaction typically show the presence of combustion products (CO, CO_2, and CH_2), along with electrolyte solvents diethyl carbonate and electrolyte decomposition products (H_2 and HF).

As mentioned above, the ARC test may also be carried out in the “open” testing set-up. In this configuration, temperature and voltage data can be collected in unison with visual observation using a high temperature borescope. **Figure 5** shows representative snapshot images taken during the onset of cell self-heating through thermal runaway. Short video clips of the thermal runaway process captured in the ARC “open” test set-up are provided in the supplemental information.

Unsuccessful ARC experiments can originate from several sources. First, failure to fully charge the battery cell will result in heat release at a lesser scale than the “worst case scenario”, which is often the best indicator of ultimate safety. **Figure 6** shows the result of ARC testing a cell charged to only 30% SOC. Clearly, the thermal energy released from the cell is subdued when the SOC is decreased. Additionally, failure to secure the thermocouple to the cell under test will yield false thermal readings and will not capture the DUT’s self-heating. When the DUT thermocouple becomes detached from the battery cell, it measures the inside chamber temperature, which will never self-heat. Therefore, the HWS protocol will never reach an exotherm condition.

At a sufficiently high thermal condition, the battery cell will enter thermal runaway, but no self-heating data will be collected. **Figure 7** shows the HWS seek behavior for a cell in which the bomb thermocouple becomes detached from the DUT. When carrying out a “closed” test, a leak in the pressure vessel indicates no build-up of pressure; thus, gas release cannot be quantified. O-ring seals on the pressure vessel should be changed between tests, and pressure-holding of the vessel should be checked if leaks continue, as the integrity of the vessel may be compromised.

FIGURES AND TABLE LEGENDS:

Figure 1: Schematic of calorimeter. Schematic illustration of interior chamber of the accelerated rate calorimeter (ARC) with heating elements on the top, bottom, and sides of the chamber. Under adiabatic control, the chamber temperature matches the sample temperature to solely monitor heat release from reactions occurring within the sample.

Figure 2: Heat-wait-seek methodology. (**A**) Flowchart of HWS methodology and notional temperature, time, and sensitivity conditions, as well as (**B**) experimental data of the first several HWS sequence iterations demonstrating the experimental approach.

Figure 3: Heat capacity plot. Time *vs*. temperature plot used to calculate heat capacity of an

18650 cylindrical lithium-ion cell (blue curve). The red trend line shows a high R^2 value, indicating a high degree of linearity in the data.

Figure 4: Temperature *vs*. time data. Typical data collection **vs**. temperature: DUT temperature, cell voltage, and pressure for HWS of fully charged 18650 lithium-ion battery cell.

Figure 5: Photographs of lithium-ion cell under thermal runaway. Screenshot images taken by high temperature borescope of commercial 18650 cell entering thermal runaway during HWS. The duration from initial condition to complete combustion occurs within 1 s.

Figure 6: Insufficiently charged cell. Example of an unsuccessful ARC measurement, in which the cell was not charged to 100%. Clearly, there is a difference in the failure behavior of representative lithium-ion 18650 cells charged to 100% and 30% SOC. The desired SOC should be 100%, which provides the highest credible safety hazard.

Figure 7: Failure to secure thermocouple. An additional example of an unsuccessful ARC measurement in which the bomb thermocouple has become detached from the DUT. Since the cell temperature is no longer being measured, the chamber continually ramps until the maximum temperature set point (in this case, 300 °C).

Table 1: Experimental capabilities offered by modular ARC instrument.

Supplementary Files: Short video clips of destructive battery testing in the ARC using HWS is provided as supplementary information.

DISCUSSION:

The HWS testing procedure accomplished with the ARC instrument is critical to determining the worst credible safety threat posed by a lithium-ion battery. The measurements of self-heat onset temperature and maximum temperature during thermal runaway provide the necessary objective data to accurately assess the safety of lithium-ion cells. Through the use of ARC-based experiments, battery safety metrics can be measured in a controlled and reproducible manner.

One limitation of the ARC instrument is that the calorimeter volume must scale with the material or battery cell under test. Therefore, the researcher is limited by the size of the calorimeter, which dictates how much cumulative energy is introduced into the chamber for testing. For most academic researchers, a smaller calorimeter is adequate to measure thermal properties of battery materials and cell components. Industrial and applied research laboratories are likely to require larger calorimeters capable of accommodating high energy cells and collections of cells or battery modules. Future testing capabilities should be developed to measure the thermal heat release of lithium-ion batteries subjected to safety testing procedures. The ARC maintains a fairly open architecture, which lends itself to the addition of complementary characterization equipment, such as spectrometers and thermal imaging cameras.

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DISCLOSURES:

The authors have nothing to disclose.

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Figure 1

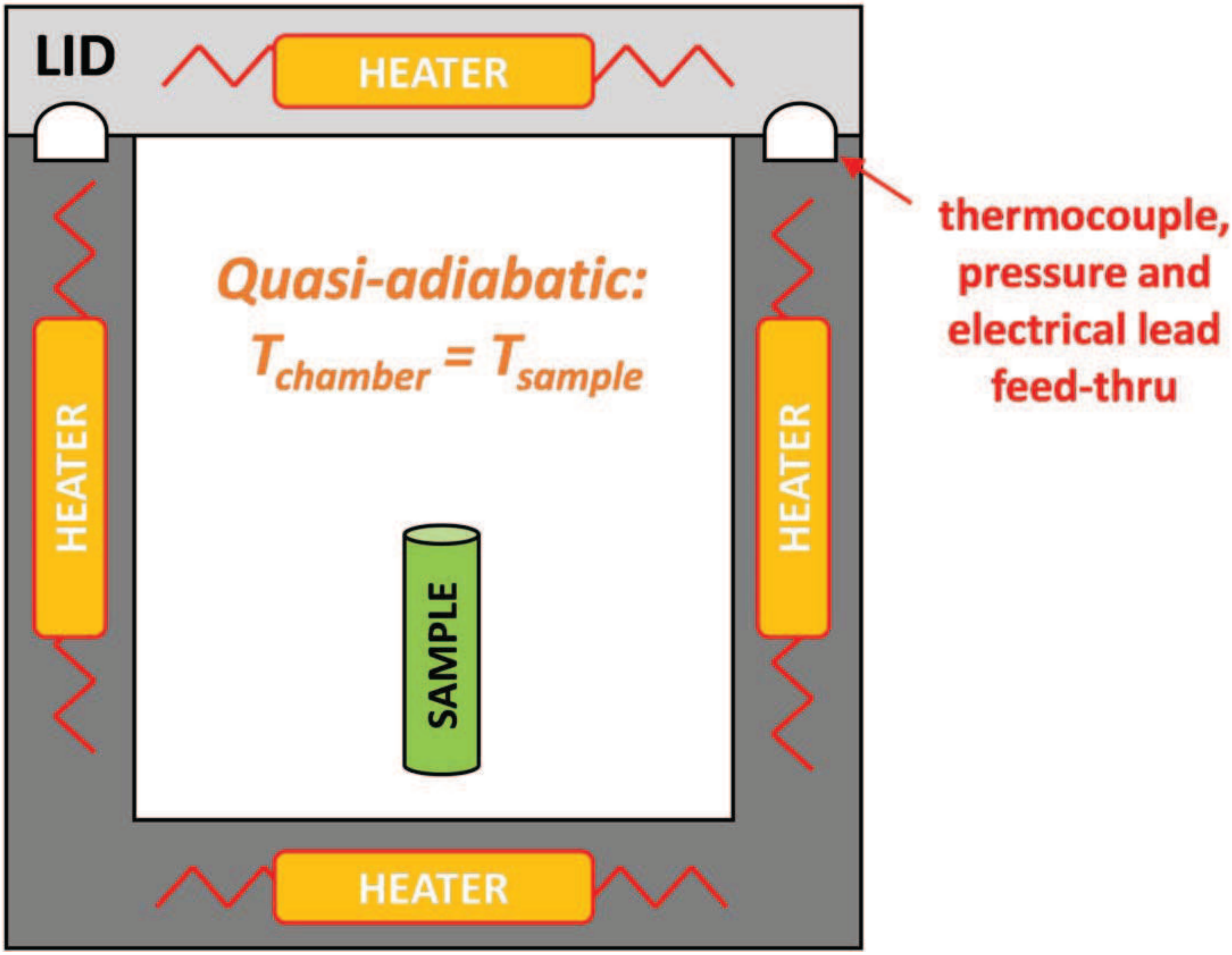
LID
HEATER
HEATER
HEATER
HEATER
Quasi-adiabatic:
$T_{chamber} = T_{sample}$
SAMPLE
thermocouple, pressure and electrical lead feed-thru

Figure 2

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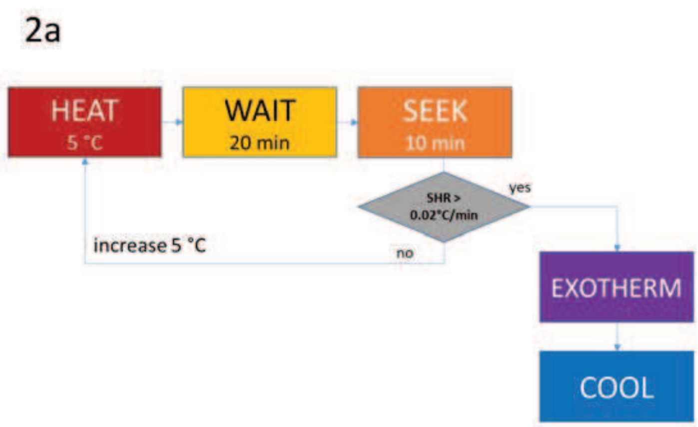

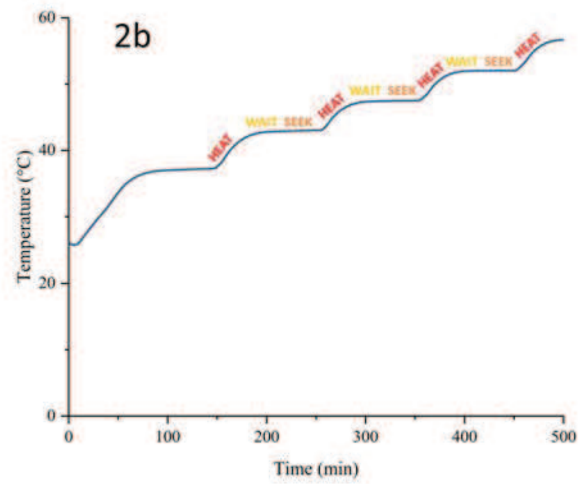

Figure 3

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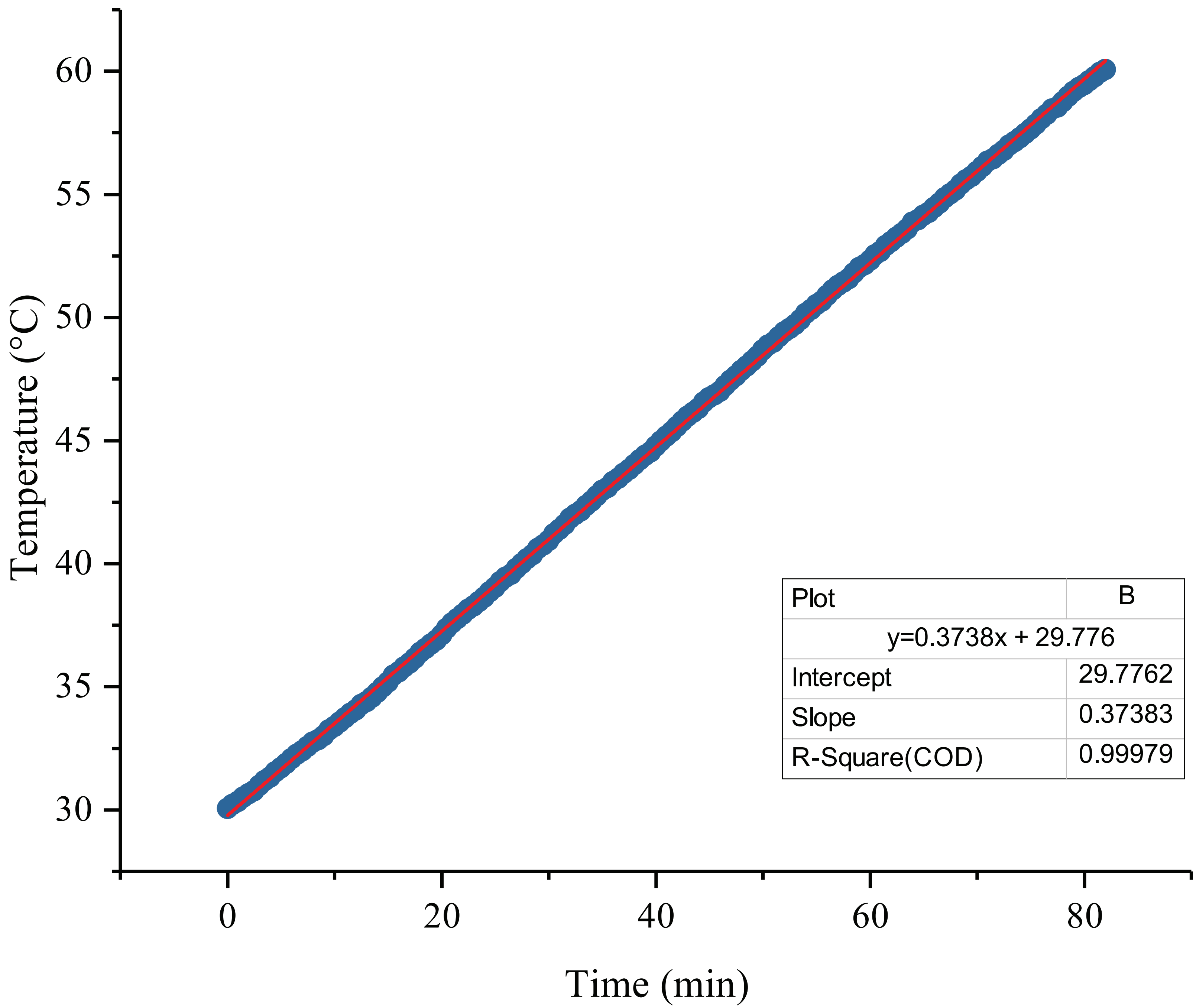

Figure 4

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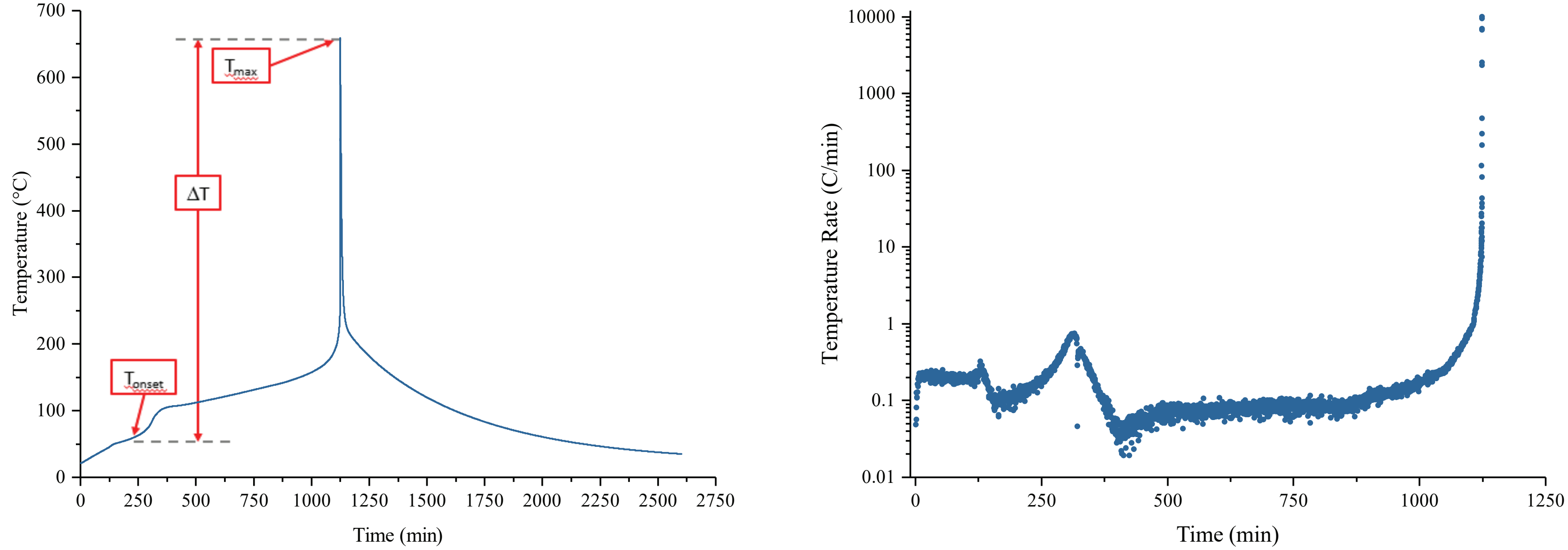

Figure 5

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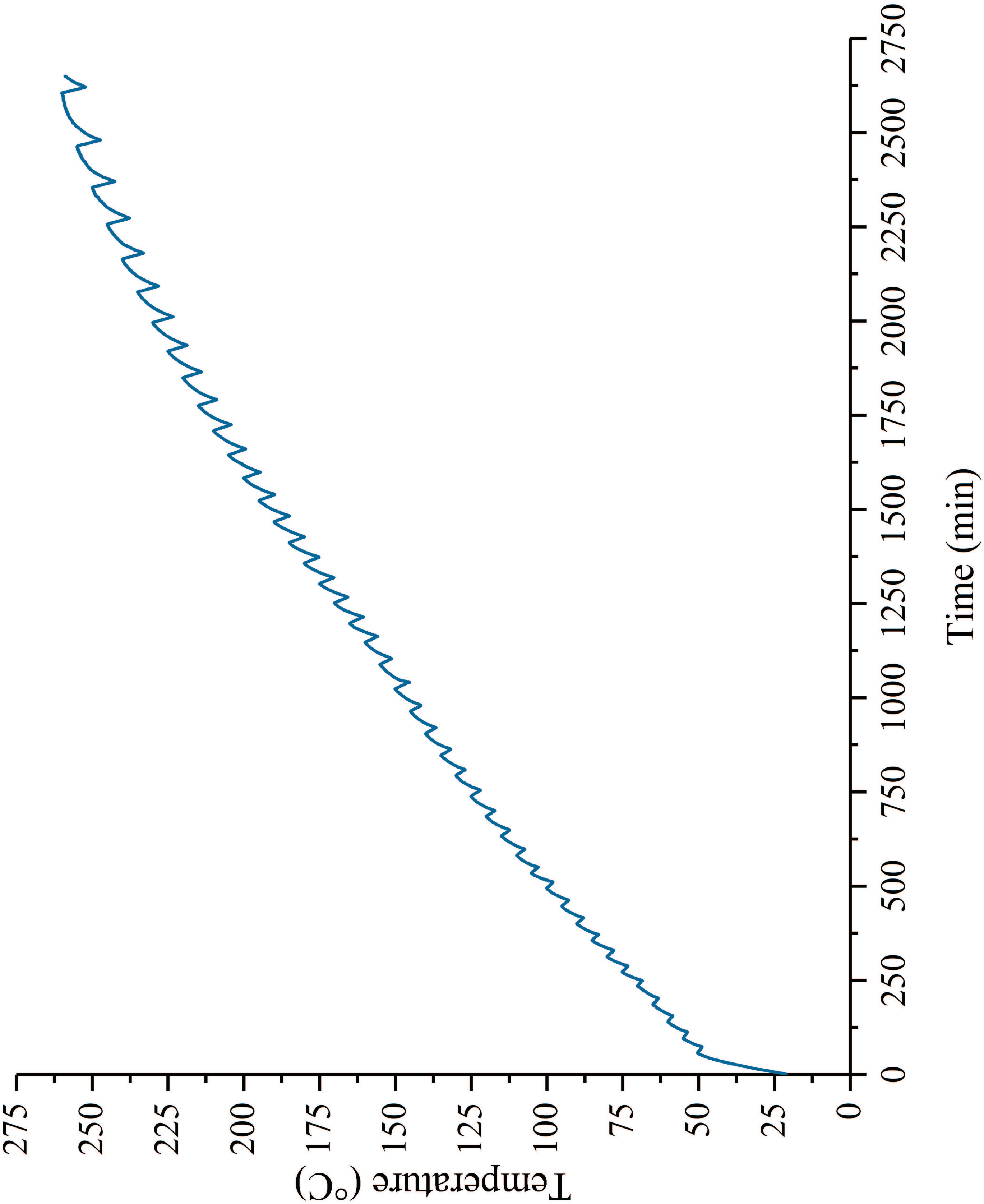
Figure 6



Temperature (°C)
0
25
50
75
100
125
150
175
200
225
250
275
Time (min)
0
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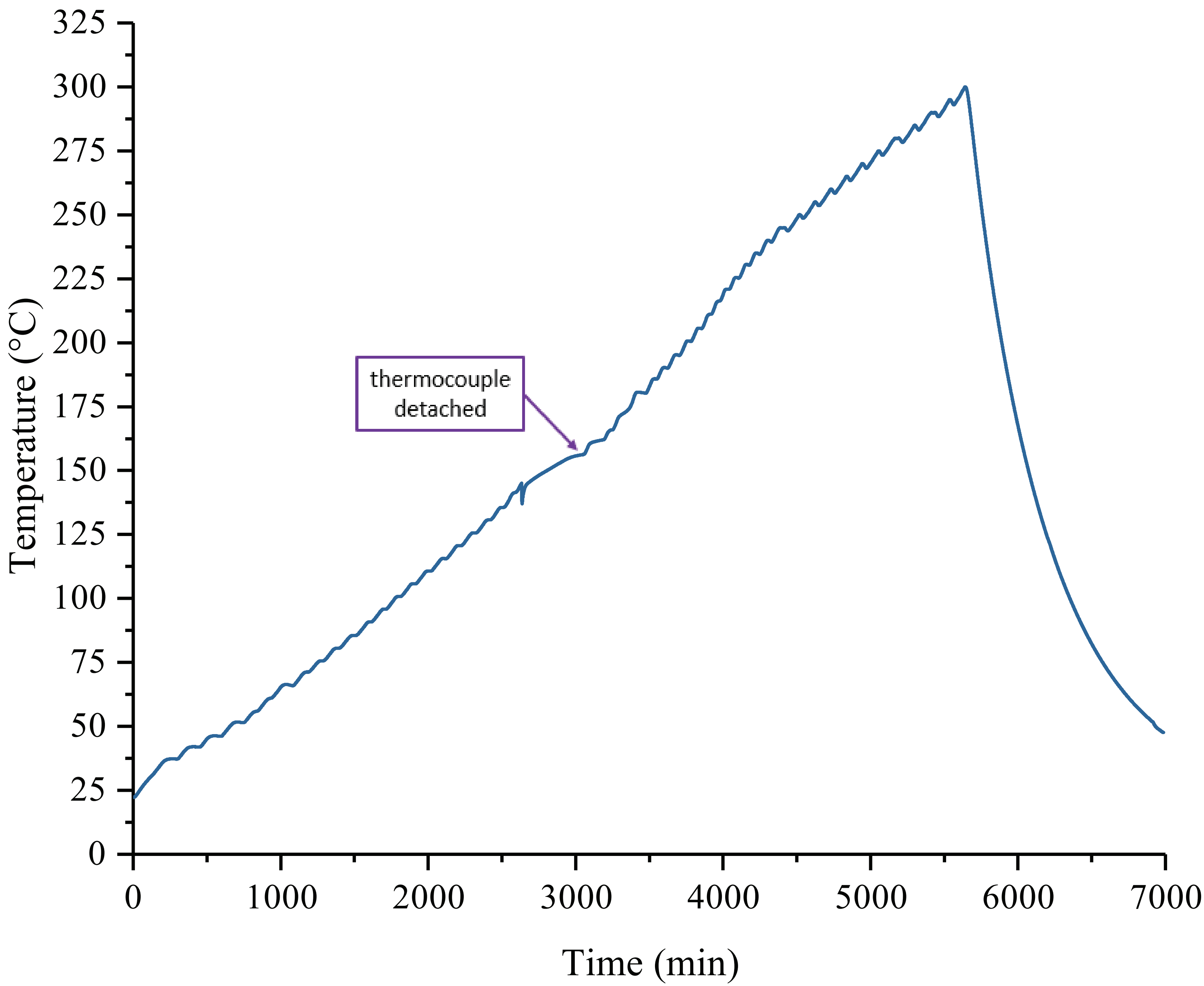
500
750
1000
1250
1500
1750
2000
2250
2500
2750

Figure 7



Temperature (°C)
Time (min)
thermocouple detached
0
25
50
75
100
125
150
175
200
225
250
275
300
325
0
1000
2000
3000
4000
5000
6000
7000

Video or Animated Figure

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cell components	cell testing		add'l features
	“<u>open</u>”	“<u>closed</u>”	
active materials	cylindrical cells	coin cells	nail penetration/crush
electrolyte solvents	pouch cells	pressure sensing	spark generation
electrolyte salts	prismatic cells	gas collection	short circuit
electrode foils	small packs	voltage	overcharge
separators	video monitoring	measurement	

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
borescope	Optronics		Rigid, high temperature borescope
Energy Lab Potentiostat	Princeton Applied Research / Ametek		potentiostat capable of collecting open circuit voltage, galvanostic/pc
Extended Volume Accelerating Rate Calorimeter	Thermal Hazard Technologies		Mid-sized system, sample range: components to batteries. Working
high temperature tape	non specific		
lithium-ion battery cell	various		rechargeable mixed metal oxide versus graphite lithium-ion cell in 18(
mat heater	Omega		form factor and size dependent upon battery cell for heat capacity m(
spherical bomb	Thermal Hazard Technologies		small volume bomb for calibration of ARC

tentiostatic battery cycling and electrochemical impedance spectroscopy

volume: 0.57 m^3

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1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

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Title of Article: Accelerated Rate Calorimetry and Complimentary Techniques to Characterize Battery Safety Hazards

Author(s): Emily Klein, Rachel Carter, Corey T. Love

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CORRESPONDING AUTHOR

Name:	Corey T. Love
Department:	Chemistry Division
Institution:	U.S. Naval Research Laboratory
Title:	Materials Engineer
Signature:	[signature]
Date:	30 MAY 2019

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Dear Dr. Wu,

The authors thank you, the editorial staff and the reviewers for their careful review of our manuscript. We are excited our contribution will be in included in an upcoming edition of JoVE. The revised manuscript captures all of the suggested and required changes made by the editors and reviewers with one exception. I have given an explanation below for why we feel one change is not needed, Reviewer #2, General Comment #4. Thank you again for your hard work and dedication to improving the quality of our contribution.

Regards,
Corey T Love

Editorial comments:
1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.
Completed.

2. Please obtain explicit copyright permission to reuse any figures from a previous publication. Explicit permission can be expressed in the form of a letter from the editor or a link to the editorial policy that allows re-prints. Please upload this information as a .doc or .docx file to your Editorial Manager account. The Figure must be cited appropriately in the Figure Legend, i.e. "This figure has been modified from [citation]."
After careful review it was determined Figure 1 is sufficiently different than others in the literature therefore the text "adapted from" was eliminated.

3. JoVE cannot publish manuscripts containing commercial language. This includes company names of an instrument or reagent. Please remove all commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents.
Corrections made.

4. Please adjust the numbering of the Protocol to follow the JoVE Instructions for Authors. For example, 1 should be followed by 1.1 and then 1.1.1 and 1.1.2 if necessary. Please refrain from using bullets or dashes.
Completed.

5. Please add a one-line space between each of your protocol steps.
Completed.

6. Please ensure that all text in the protocol section is written in the imperative tense as if telling someone how to do the technique (e.g., "Do this," "Ensure that," etc.). Any text that cannot be written in the imperative tense may be added as a "Note."
Completed.

7. There is a 2.75 page limit for filmable content. Please highlight 2.75 pages or less of the Protocol steps (including headings and spacing) in yellow that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.
Completed.

8. Each figure must be accompanied by a title and a description after the Representative Results of the manuscript text.
Completed.

9. All figures should be uploaded separately to your Editorial Manager account.
Completed.

10. Please combine all panels of one figure into a single image file.
Completed.

Reviewer #1:
Manuscript Summary:
Manuscript details the operation and procedure for accelerated rate calorimetry. This manuscript could be useful for someone who wants to do safety tests on batteries.

Major Concerns:
None.

Minor Concerns:
Some grammatical errors in the manuscript, but nothing major.

line 2: Title is correct in page 1, but on page 2, "Complimentary" should be "Complementary"
line 30: Change "hazard" to "hazardous"
line 54: remove hypen in "daily-life"
line 58: comma needed after "societies"
line 71: comma needed after "storage", comma needed after "1980s"
line 81: comma needed after "batteries"
line 90: comma after "Typically"
line 92: "safety" -> "safely", comma after "pressure"
line 93: comma after "Additionally"
line 94: "nail penetration or electrochemical overcharge or external short circuit" -> "nail penetration, electrochemical overcharge, or external short circuit"
line 99: "which then influences" -> "which has then influenced"
line 100: comma should be after "report" not "entitled"
line 101: comma after "Systems"
line 102: comma after "collection"
line 105: i think "quality" would be better as "quantitative"
line 107: "and" needed before "chemical"
line 115: "for" -> "for whether"
line 124: comma after "stage"
line 127: space needed between value and units line 144: comma after "gloves"
line 147: period needed at end of sentence line 151: to/from the same what? cell?
line 184: italicize "c" and "m"
line 185: "of the ARC but is" -> "of the ARC, it is"

line 206: "ramps from 30 C to 30 °C" are you sure temperature range is correct? also °C only needs to be stated once e.g., "ramps from 25 - 55 °C"
line 212: "unit" -> "units"
line 223: ";" -> ":"
line 224: "Power" -> "power"
line 230: "(SOC)" needed after "state of charge"
line 281: comma after "desired"
line 284: comma after "reached"
line 302: "Double check" -> "Double-check", "is" required between "bomb" and "attached"
line 303: comma after "chamber", comma after "thermocouples"
line 316: what do you mean by "calculation of DT"? "DT" has not been introduced in the manuscript line 327: "charges" -> "charged"
line 329: "Tmax & ⍰T" -> "Tmax, and ⍰T"
line 339: comma after "above"
line 340: comma after "configuration"
line 352: comma after "cell"
line 364: "measurement" -> "measurements"
line 366: "Through use" -> "Through the use"
line 377: This paragraph seems a little out of place. You state that no other equipment exists to collect this data. But the previous paragraph as not about collecting data, but about the limitation of the ARC due to size. I think the third paragraph should be put in the first paragraph after the second sentence and before the last sentence.
line 378: The second sentence seems a little out of place. I think it would be best just to remove it because if it is an ARC, the sentence is unnecessary because you have already stated that ARCs can measure conditions of thermal runaway; if it is not an ARC, then why is it even in the manuscript besides filling up the requisite number of references?
line 381: "will do doubt" -> "will no doubt"
line 383: "complimentary" -> "complementary"
line 394: comma after "bottom"
line 395: comma after "control"
line 297: comma after "time"
line 403: comma after "voltage"
line 409: comma after "Clearly"
line 410: you have "state of charge" without hyphens in line 230, either use hyphens in both or none line 414: comma after "measured"
line 415: "point, in this case it is 300 °C." -> "point; in this case, it is 300 °C." or "point; in this case, 300 °C."
Figure 2a: You are missing °C in the SHR. Also, put a space between unit and value for "HEAT 5 °C" and "increase 5 °C".
Figures 4a, 4b, 6, 7: Put a space in the x-axis and y-axis titles between title and units.
Table of Materials: uncapitalize all the materials/equipment names as well as in comments/descriptions
All corrections listed above have been completed.

Reviewer #2:
In the present work, the authors presented a protocol to instrument, conduct and characterize thermal abuse on commercial lithium ion batteries in an accelerated rate calorimeter system. The methodology allows studying safety abuse scenarios under safe and controlled conditions. The data collected ranges from thermal properties determination, onset of thermal runaway to collection of byproduct gases from

the failure mechanisms. System preparation and calibration parameters will be helpful for new users of this type of systems.

General Comments:
*Page 2. Line 38. "Abusive insults?"
“Insults” has been removed.

*Page 2. Line 39. Overcharge is considered an electrochemical abuse.
Corrected.

*Page 6. Line 180. Typo: Adiabaticity
Corrected.

*Page 6. Line 180. Mention the average mass for the cell used in this test.
The mass we are referring to is the empty bomb required for the calibration. This will change from instrument to instrument and is specific to any battery-related experiment. For this reason we believe adding the typical mass may be misleading and confusing.

*Page 6. Line 180. Check step 3.i
Corrected.

Format Comments:
1. Follow the manuscript format.
Link: https://www.jove.com/files/Instructions_for_Authors.docx
Protocol must be numbered as 1, 2, 3,…; 1.1, 1.2, 1.3,…; 1.1.1, 1.1.2, 1.1.3,… 2. Check the Latin abbreviations. Incorrect eg. ; Correct: e.g., 3. Use the active/imperative voice and complete sentences throughout the protocol.

Each of these items have been corrected in the revised manuscript.