



Energetics of lithium ion battery failure



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HIGHLIGHTS

- First measure of anaerobic failure energy of lithium ion batteries.
- Novel and simple bomb calorimeter method developed and demonstrated.
- Four different cathode chemistries examined.
- Full range of charged capacity used as independent variable.
- Failure energy identified as primary safety hazard.

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ABSTRACT

The energy released by failure of rechargeable 18-mm diameter by 65-mm long cylindrical (18650) lithium ion cells/batteries was measured in a bomb calorimeter for 4 different commercial cathode chemistries over the full range of charge using a method developed for this purpose. Thermal runaway was induced by electrical resistance (Joule) heating of the cell in the nitrogen-filled pressure vessel (bomb) to preclude combustion. The total energy released by cell failure, ΔH_f , was assumed to be comprised of the stored electrical energy E (cell potential \times charge) and the chemical energy of mixing, reaction and thermal decomposition of the cell components, ΔU_{rxn} . The contribution of E and ΔU_{rxn} to ΔH_f was determined and the mass of volatile, combustible thermal decomposition products was measured in an effort to characterize the fire safety hazard of rechargeable lithium ion cells.

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1. Background

Rechargeable lithium ion batteries (LIB) are being used at an increasing rate because of their high energy density and the ability to be used repeatedly with little degradation in performance [1,2], and research to produce higher capacity lithium ion batteries [3,4] with better safety systems [5] is ongoing. Greater capacity means more stored energy to do electrical work, but can also mean greater thermal hazard if this energy is released suddenly due to an internal short circuit caused by a contaminant, manufacturing defect, mechanical insult, overcharging or the heat of a fire [6,7]. An internal short circuit results in a rapid discharge of electrical energy inside the cell that raises its temperature and causes mixing, chemical reactions and thermal decomposition of the cell components in an auto-acceleratory, exothermic process called thermal

runaway that generates combustible gases and results in expulsion of the cell components [6–9]. Thermal runaway propagates by heating of adjacent cells in closely spaced bulk shipments, and the combustible volatiles released at failure can accumulate in the compartment and cause a conflagration or explosion if ignited [6–9]. The driving force for propagation of thermal runaway to adjacent cells is the release of thermal energy during cell failure [10,11]. Until recently, experiments to measure failure energy were limited to differential scanning calorimeter measurements of the individual cell component reactions [7,12] or accelerating rate calorimeter (ARC) measurements of the entire cell at early stages of cell failure [12,13].

Recent attempts to measure the total energy released by cylindrical 18-mm diameter by 65-mm long (18650) lithium-ion cells/batteries (LIB) during thermal runaway have used adiabatic calorimeters with a closed pressure vessel [12] or purpose-built thermal capacitance (slug) calorimeters [9,14]. The slug calorimeter measurements rely on an energy balance computed from the temperature history of the LIB in an open system to deduce the energy

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release at failure. Consequently, the total energy released during thermal runaway could not be measured because the cell contents were ejected into the room at failure and a significant portion of the energy released by mixing, reaction, and thermal decomposition of the cell components occurred outside of the cell/calorimeter. The combustion energy released when the contents of lithium metal (non-chargeable) and lithium ion (rechargeable) cells discharged at failure and burned in air was measured separately in a fire calorimeter, and found to be comparable in magnitude to the thermal energy released by cell failure at higher states of charge [14].

The present study is an attempt to measure the total energy of the chemical processes responsible for failure and thermal runaway of 18650 LIBs. These chemical processes generate heat in an auto-acceleratory process leading to cell failure and the generation of combustible volatiles that burn or explode in closed compartments such as aircraft cargo holds. Our approach is to use electrical resistance (Joule) heating to drive an 18650 cell into thermal runaway inside the closed pressure vessel of a bomb calorimeter filled with an inert gas and measure the total energy at failure as a function of the stored electrical energy, thereby obtaining the total chemical energy of the failure reactions by difference. In this way, the cell contents are confined to the pressure vessel (bomb) and the chemical processes that release heat and volatiles at failure occur in an inert environment that precludes burning or oxidation of combustibles.

2. Thermodynamics of battery failure in a bomb calorimeter

Rechargeable lithium ion cells perform electrical work by exchange of lithium ions through electrolytes between positive and negative electrodes separated by ion-permeable polymer membranes. The electrolytes are typically lithium salts dissolved in high purity linear and cyclic organic carbonates that are combustible [1–7]. During normal use electrons flow through the terminals and lithium ions flow through the electrolyte from the anode to the cathode in a quasi-reversible process with negligible change in the chemical structures of the cell components. When a lithium ion cell fails due to an internal short circuit, the resistance of the cell approaches zero and the current flows irreversibly between the electrodes, generating internal power of magnitude ε^2/Ω , where ε and Ω are the cell potential (V) and internal resistance (Ohms) of the cell, respectively. The power generated by an internal short circuit quickly exceeds the external heat losses, so the cell temperature increases until the polymer separator melts and the electrodes and electrolytes mix, react and thermally decompose.

When this process of cell failure happens in an *adiabatic* bomb calorimeter at constant volume [15,16], the temperature of the calorimeter increases from T_1 to T_2 , but no work is done and no heat is transferred to the environment. Applying the first law of thermodynamics to the calorimeter system, the change in internal energy is zero for failure of the lithium ion cell, i.e., $U_2 - U_1 = 0$. However, if the masses and heat capacities of the reactants (virgin cell) and products (failed cell) are not significantly different, the internal energy change of the cell at failure in the pressure vessel ΔU can be obtained from a fictive process in which the heat required to raise the calorimeter temperature from T_1 to T_2 is estimated from the heat capacity C of the system (cell + calorimeter) [15],

$$\Delta U = -C(T_2 - T_1) = \Delta U_{ext} + \Delta U_{elec} + \Delta U_{rxn} \quad (1)$$

In this paper we assume that the internal energy change measured in the bomb calorimeter test is the result of three processes represented by the right hand side of Eq. (1). These are the external electrical resistance (Joule) heating of the cell to failure (ΔU_{ext}), the discharge of stored electrical energy via an internal short circuit

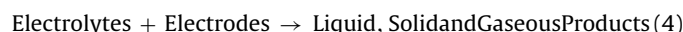
when the separator melts (ΔU_{elec}), and the exothermic, auto-acceleratory chemical and physical changes of the cell contents during the ensuing temperature rise (ΔU_{rxn}). The Joule heat used to force the lithium ion cells into thermal runaway in the bomb calorimeter is,

$$\Delta U_{ext} = U_{ext} = -\int_0^{\tau} VI dt = -V I \tau \quad (2)$$

In Eq. (2), V and I are the measured voltage and current in a resistance heating wire connected to an external power source at time t , and τ is the duration of Joule heating. The stored electrical energy released by an internal short circuit when the separator fails is,

$$\Delta U_{elec} = -\int_0^{\infty} \frac{\varepsilon^2}{\Omega} dt = -\int_0^{\infty} \varepsilon i dt \approx -\varepsilon \int_0^{t_c} I dt = -\varepsilon Q = -E \quad (3)$$

In Eq. (3), i is the internal current associated with a short circuit and Q is the charge on the cell in Coulombs (A-s) after being connected to an external current source (charging device) for duration t_c . The release of electrical energy E when the polymer separator melts results in a rapid increase in the cell temperature, causing the cell components to mix, chemically react, and thermally decompose to liquid, solid and gaseous products in an irreversible process, i.e.,



The internal energy change for the mixing, chemical reactions and thermal decomposition of the cell components is ΔU_{rxn} in Eq. (1). From Eqs. (1)–(4), the internal energy change of an adiabatic calorimeter system associated with lithium ion cell failure is,

$$\Delta U = -C\Delta T = -E + \Delta U_{rxn} - V I \tau \quad (5)$$

The internal energy change of the lithium ion cell at failure is therefore,

$$\Delta U_f = -E + \Delta U_{rxn} = -C\Delta T + V I \tau \quad (6)$$

The energy released when a lithium ion cell fails at constant (atmospheric) pressure P is the enthalpy, which is related to the quantities measured in the bomb calorimeter at constant volume,

$$\Delta H_f = \Delta U_f + \frac{m_g R T_1}{M_g} \quad (7)$$

Ideal gas behavior is assumed for Eq. (7), with m_g and M_g the mass and average molecular weight of the volatiles produced at failure, respectively, and R is the gas constant. Empirically it is found that ΔU_f and ΔH_f are negative with respect to the system because these are the change in these state functions at cell failure is accompanied by an increase in the temperature of the system (calorimeter) so that heat seeks to flow to the surroundings. From our perspective in the surroundings, these quantities have positive values and this convention will be used throughout the paper for convenience, after properly accounting for the signs in Eq. (7).

3. Materials

The batteries used in this study consist of lithium transition metal oxide cathodes (LiCoO₂, LiNiCoO₂, LiNiCoAlO₂, LiMn₂O₄, etc.) in contact with an aluminum terminal, and a graphitic carbon anode attached to a copper terminal and are shown in Fig. 1. A liquid electrolyte is contained between the electrodes comprised of a lithium salt and organic solvents [1–7]. In the rechargeable LIBs of this study, the cell is made in sheet form and rolled to fit inside a cylindrical steel jacket measuring 18 mm in diameter and 65 mm in length, hence the designation 18650. These cells were purchased from commercial sources. Assemblies of these lithium

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