

ENERGETICS OF LITHIUM ION BATTERY FAILURE

Richard E. Lyon, Richard N. Walters, Sean Crowley and
James G. Quintiere*

Federal Aviation Administration
William J. Hughes Technical Center
Fire Safety Branch ANG-E21
Atlantic City International Airport, NJ 08405

*Department of Fire Protection Engineering, University of Maryland, College Park

The high energy density of lithium ion cells/batteries (LIB) makes safe shipment of this commodity as bulk cargo on commercial aircraft a concern due to its potential to initiate a fire by overheating and contribute to a fire by burning of the organic electrolytes ejected during thermal runaway. Full-scale tests in aircraft have shown that fires involving large quantities of lithium ion cells/batteries when shipped as cargo can be catastrophic. To quantify the thermal hazard of LIBs, cells having different cathode chemistry were heated to failure in a bomb calorimeter under inert conditions at various states of charge. Cell failure involves rapid heating of the cell initiated by an internal short circuit (thermal runaway), thermal decomposition and reaction of the electrolytes and electrodes, rupture of the cell, and ejection of the contents into the sealed calorimeter bomb or fire calorimeter. For a cell potential ε (V) and charge Q (A-s), the total thermal energy release at cell failure due to electrochemical processes ΔH_{ec} as measured in the bomb calorimeter is the sum of the stored electrical (free) energy, εQ and the chemical energy of thermal decomposition and reaction of the electrolytes and electrodes, ΔH_{rxn} ,

$$\Delta H_{ec} = \varepsilon Q + \Delta H_{rxn}$$

Figure 1 shows the total electrochemical energy ΔH_{ec} measured in a bomb calorimeter at cell failure versus the stored electrical energy, εQ and reaction energy, ΔH_{rxn} (obtained by difference) for 18 mm x 650 mm cylindrical (18650) lithium ion cells having the indicated cathode chemistries, with similar cell potentials (3.7V) and weight (44 grams). It is seen that the energy released by the chemical reactions of the cell contents ΔH_{rxn} is a significant fraction of the total electrochemical energy release ΔH_{ec} and increases with εQ to a plateau value beginning at about 50% of the maximum εQ . Subsequent combustion of the volatile cell contents ejected at failure in a fire calorimeter (or conflagration) contributes an additional heat of combustion ΔH_{comb} to the thermal energy ΔH_{ec} plotted in Figure 1. Figure 2 is a plot of the heat of combustion ΔH_{comb} of the LiCoO₂ 18650 LIB versus stored electrical energy εQ measured in a cone calorimeter at 500W external heating power. It is seen that ΔH_{comb} in Figure 2 decreases with εQ by approximately the same amount that ΔH_{rxn} increases in Figure 1, indicating that the cell contents are partially combusted/oxidized during the thermal runaway reactions- which occur at temperatures proportional to ΔH_{ec} .

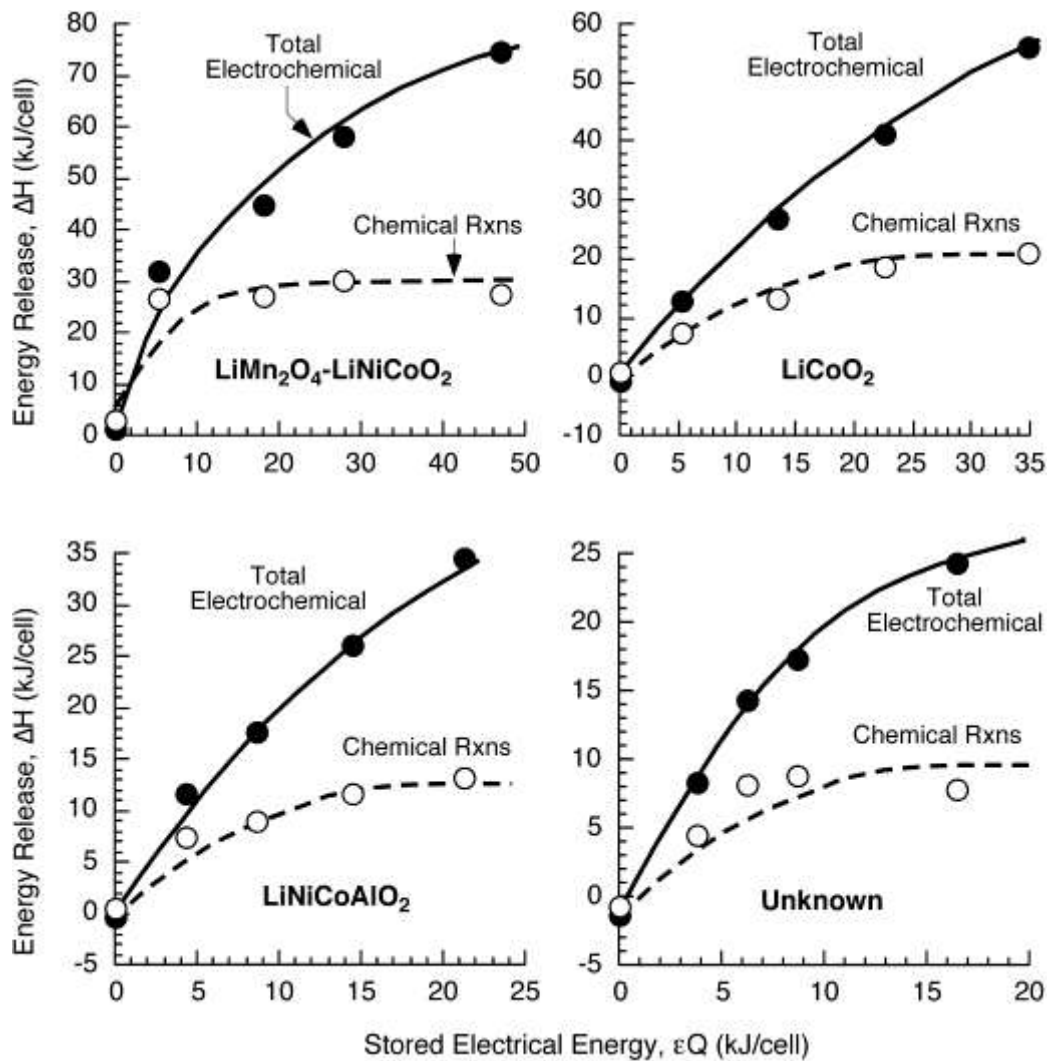


Figure 1. Energy Release of LIBs Versus Stored Electrical Energy

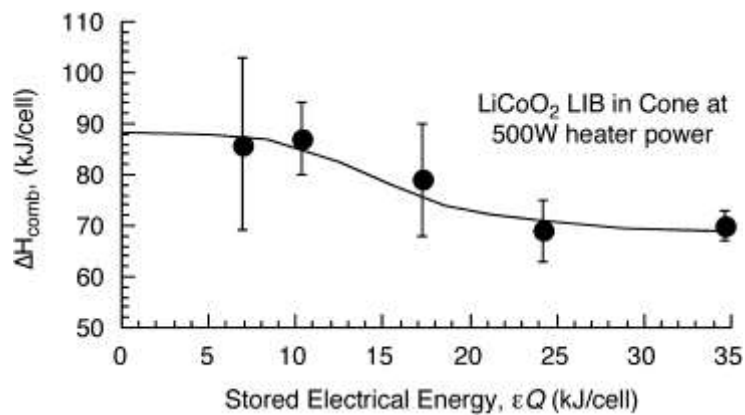


Figure 2. Heat of Combustion of LiCoO_2 LIB Cell Contents at Failure in Cone Calorimeter at 50 kW/m^2 External Heat Flux.