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Thermal runaway of lithium-ion batteries and hazards of abnormal thermal environments

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Batteries are chemical energy storage devices subject to thermal runaway (ignition) under abnormal thermal environments. We discuss the processes that can lead to thermal runaway in the context of lithium-ion batteries, a particularly common battery with a relatively high energy density. These processes share much in common with traditional combustion and fire safety. Relevant processes include multiphase reactions including hydrocarbon spray flames and metal oxidation. Multi-physics modeling techniques must include couplings between turbulent fluid mechanics, gas and solid phase combustion, participating media radiation (PMR) and object heat-up through conjugate heat transfer (CHT). The critical question to address in identifying thermal runaway is the balance between heat dissipation and the release of chemical energy in common with the classical thermal ignition theories, but there are multiple stages of chemical heat release that can complicate the problem.

An important concern for battery safety is the propagation of thermal runaway from an initial heat source to multiple battery cells. Application-scale computational fluid dynamics (CFD) can predict many of the relevant processes associated with this propagation, and we address the potential for predicting this spread of thermal runaway through demonstration calculations.

1 Introduction

Battery use in transportation and grid-scale energy storage is increasing, but recent high-profile incidents point to challenges in determining adequate levels of safety and reliability testing to ensure the safety of these systems. Under a variety of accident scenarios, batteries can undergo thermal-runaway where the stored chemical energy is converted to thermal energy. In some cases, the initial discharge and heat release is primarily electrical as occurs with an inadvertent short circuit. However, in other cases material reactivity, often enhanced under external heating, leads to a chemical process with similarities to more traditional fires, though significant differences remain. Some of these processes have been reviewed in Refs.

Lithium-ion batteries are particularly desirable for energy storage applications requiring high energy and power density [1]. However, with energy densities approaching petroleum, inadvertent energy release is a significant safety concern. A century of experience with petroleum-based systems led to high safety standards, but there is a gap in our understanding of lithium-ion and related battery systems exhibited in recent high-profile fire incidents (Singapore Airlines, Boeing 787, Chevy Volt, Tesla). While individual battery cells are highly reliable and safety mechanisms are often built into batteries [2], failure probabilities increase in large-scale systems where thousands of cells may be linked. Further, heat dissipation is more difficult at larger scales, increasing the probability of thermal runaway.

The current industry and regulatory agency approach to studying battery failures at the system level relies on testing. There are no system-level simulation tools that adequately predict material degradation and heat release during abnormal environments to make decisions regarding the balance between heat dissipation and thermal runaway. Further, there are no predictive simulation capabilities of most chemical and transport processes relevant to thermal runaway at the individual cell level. Since there is a significant cost barrier to full-scale, system-level testing for large-scale energy storage applications, the development of predictive capabilities offers potentially significant financial benefits. In this paper we describe some aspects associated with the physics and chemistry of thermal runaway in lithium-ion batteries relevant to predicting system level failure that would allow exploration of the safety parameter space. Other reviews of the relevant physics and chemistry [2, 3] provide additional details.

2 Problem description

Batteries are composed of an anode and a cathode separated by an electrolyte through which ions flow but not electrons, the electrons being required to perform work by flowing through whatever circuit the battery is attached to. The energy stored in batteries comes from the difference in the Gibbs free energy between the charged state and the discharged state of the anode and cathode. For lithium-ion batteries discussed here, the most typical anodic material is graphite, which is intercalated with lithium in the charged state, represented as $\mathrm{C_6Li}_x$ here. The cathode is one of several metal oxides, of which $\mathrm{CoO_2}$ is typical in current batteries. The Gibbs free energy of reaction for this process is

$$\mathrm{C_6Li} + \mathrm{CoO2} \rightarrow \mathrm{C_6} + \mathrm{LiCoO_2} \qquad \Delta G \approx 400\,\mathrm{kJ\,mol^{-1}\,Li}. \tag{1}$$

Considering the mass of just the active materials, this leads to a theoretical energy density of approximately 1.5 MJ kg^{-1}, but a practical battery including packaging would have an energy density closer to 0.5 MJ kg^{-1} [4]. While this energy density appears low in relation to many fuels, the battery also contains a flammable electrolyte and polymers with additional energy content.

In the quest for high-energy density batteries, lithium has emerged as the front runner in part due to its high reactivity, having a strong reducing potential. This leads to high reactivities with water as is typical of alkali metals so the electrolytes in batteries are typically alkyl carbonates including ethylene carbonate (EC) [5, 6], propylene carbonate (PC), dimethyl carbonate (DMC) [7, 8] and diethyl carbonate (DEC) [9]. In order to carry the charge, a salt is added to the electrolyte with $\mathrm{LiPF_6}$ being the most common. While less reactive than aqueous solutions, the alkyl carbonates do react with materials in the cell, especially at temperatures above ambient. The relevant chemistry is introduced in the Chemistry of thermal runaway section.

For the present we recognize the fact that alkyl carbonates react with lithium in the anode (forming a passivation layer) and at higher temperatures will react with the salt and with the oxygen from the metal oxide cathode materials. Each of these processes can be exothermic and occur at sufficiently fast rates at temperatures below our expectations for hydrocarbon fire ignition. As detailed below, exothermic processes begin as low as 160 C (see Chemistry of thermal runaway section).

3 Potential battery in fire scenario

A wide range of scenarios can be imagined for potential interactions between a fire and battery. In many incidents, internal failure of one or a small number of cells leads to an internal short circuit that generates enough heat to initiate thermal runaway. In these cases, it is important to prevent a cascading failure that progresses from the thermal runaway of a single cell to the runaway of a large pack of cells, where an electric vehicle might hold one thousand cells in a pack. Similarly, a fire external to a pack of batteries might lead to thermal runaway of those batteries. As will be discussed in the Thermo-fluids aspects of thermal runaway section, these problems bear some resemblance to the classic Frank-Kamenetskii ignition problem. Recently, Ditch et al. reported on a study of battery involvement in a warehouse storage fire [10]. Calorimetry of batteries in fires have also been reported by Ribiere et al. [11] and by Huang et al. [12].

In a move toward predicting the interaction of a fire and batteries, we have begun simulations of fire environments with conjugate heat transfer linking the fire to the battery pack using the Sierra low Mach reacting flow code module, which is part of the Sierra multi physics codes suite at Sandia National Laboratories. At this stage there is no exothermic evolution of the battery, but the simulations predict the heat transfer through combined conduction, advection and radiative heat flux from a fire to an object in the fire to examine the battery heating relative to heat dissipation under a range of environments like degrees of ventilation.

This usage of a simulation tool for high consequence predictions has been deployed to support Science-based Stockipe Stewardship within Engineering Sciences ([13]). Recently, both scalability and stability properties of the underlying numerical method have been studied. For example, in a recent Sandia study ([14]), near-optimal weak scaling in linear solve time and assemble have been demostrated up to 525k core on approximately nine billion element unstructred hex elements. As the computational domain size increases, a scalable tool will prove essential to properly predicting the fire enviornment. Moreover, verification and validation of the implemented model suite will also be required in a manner consistent with high consequence studies ([15]).

As already noted, fire environment coupling to an object that is thermally heated is complex in that it requires multiple physical couplings. A brief overview of the coupling is now presented. Coupling between the gas phase reacting flow and participating media radiation (PMR, or also known as thermal radiation) occurs through the divergence of radiative flux. The divergence of the radiative flux is furnished by the PMR solve and requires the gas phase temperature and absorption field. The PMR solve also provides the irradiation onto an object which is required for the object/PMR boundary condition. The thermal solve requires the convective loading (through the gas phase coupling) and, along with the irradiation, computes the surface temperature which forms the boundary condition for both the intensity and gas phase static enthalpy equation set. The addition of a spray, which may be due to a fire suppression strategy or electrolytic de-pressurizing jet, adds additional coupling terms to both the fluids, PMR and object equation set. Verification strategies for a subset of this application space is given by [15].

4 Chemistry of thermal runaway

Before discussing thermal runaway, it is necessary to describe the state of the battery. Batteries are constructed with the lithium in the metal oxide cathode, $LiCoO_2$ here, and upon charging the lithium ion is transported into the anode to form the C_6Li. In this form, the lithiated graphite is reactive with the alkyl carbonate electrolytes, and these react to form a passivation layer on the surface of the anode. In the literature this passivation layer is referred to as the solid electrolyte interface or SEI layer. A prototypical global reaction describing this process would be [16]

$$2\mathrm{Li} + \mathrm{C_3H_4O_3(EC)} \rightarrow \mathrm{Li_2CO_3} + \mathrm{C_2H_4}. \tag{2}$$

Here Li_2CO_3 is a salt that forms the passivation layer, and we also observe gas generation in the form of ethene. Other possible processes will form organic salts that are subject to thermal decomposition to similar products

$$2\mathrm{Li} + 2\mathrm{C_3H_4O_3(EC)} \rightarrow \mathrm{(CH_2CH_2OCO_2Li)_2} \rightarrow \mathrm{Li_2CO_3} + \mathrm{C_2H_4} + \mathrm{CO_2} + \frac{1}{2}\mathrm{O_2}. \tag{3}$$

The products of the above reactions, Li_2CO_3 and $(CH_2CH_2OCO_2Li)_2$ can be assumed to exist as a passivation layer under all conditions (being generated during manufacture) while the second reaction in Eq. 3 occurs under heating to temperatures around 90-120 C [16]. The process in reaction Eq. 2 and the first reaction of 3 occur slowly under operation in a process thought to be transport limited (largely by electron transport through the salt layer). This transport process was measured to have an activation energy of 36 to 38 kJ mol^{-1} in one study [17] and 48 to 55 kJ mol^{-1} in another [18]. As discussed below, this transport process is likely to also be limiting under some thermal runaway conditions. The thermal decomposition of this passivation layer occurs around temperatures of 200 C and has recently been measured with activation energies for this process ranging between 50 and 100 kJ/mol [19]; this would correspond to both the second process in Eq. 3 as well as the continued global passivation process described by both Eqs. 2 and 3. We note that the variability of specific materials leads to substantial variation in the chemistry in the same way that a variety of fuels exist for fires; this makes analysis a challenging problem requiring material-specific measurements.

Thermal runaway is generally a sequence of processes involving exothermic reactions and gas generation, which build up pressure in the cell. At temperatures in the vicinity of 160 C to 200 C reaction of the alkyl carbonate electrolyte with a typical electrolyte salt, $LiPF_6$, begin and this occurs in parallel with the above anode passivation layer decomposition reactions (above). $LiPF_6$ decomposes as $LiPF_6 \rightarrow LiF(s) + PF_5(g)$ and PF_5 is a strong Lewis acid that can react with many alkyl carbonates along with trace water forming reactive HF [**?**].

These lowest temperature reactions are only mildly exothermic, but they do result in significant gas generation. Measurements suggest slightly more than 1 L/Ahr of gas vapor at STP is released during this gas-generation process [20]. In a sealed cell, this will lead to pressurization and venting is likely to occur. Venting will involve a jet of gaseous products including some alkyl carbonate vapors as well as gases like CO_2 ($\approx 60\%$), CO, C_2H_4, CH_4 (together $\approx 20\%$), H_2 ($\approx 10\%$) among others [21]. Liquid alkyl carbonates will also be emitted in a spray that often results in a dramatic burst of flame (see below).

Prior to addressing the oxidation of the electrolyte and vapors in air we address reactions between the cathode and the electrolyte. As temperatures rise, the metal oxide can undergo phase transformations that release oxygen,

$$\begin{aligned} \mathrm{Li_xCoO_2} &\rightarrow \mathrm{xLiCoO_2} + \frac{1-\mathrm{x}}{3}\mathrm{Co_3O_4} + \frac{1-\mathrm{x}}{3}\mathrm{O_2} \\ \mathrm{Co_3O_4} &\rightarrow \mathrm{CoO} + \frac{1}{2}\mathrm{O_2} \end{aligned} \tag{4}$$

and this oxygen can react with the electrolyte at the particle surface.

$$\mathrm{C_3H_4O_3(EC)} + \frac{5}{2}\mathrm{O_2} \rightarrow \mathrm{3CO_2} + \mathrm{2H_2O}. \tag{5}$$

These reactions are strongly exothermic, being typical combustion oxidation. However, the amount of oxygen released by the cathode is only sufficient to oxidize a small fraction of the electrolyte, so that the direct electrolyte flammability is a significant issue.

The gas generation and exothermic processes described above will often (when the thermal energy is not rapidly dissipated) lead to pressurized venting of gases and liquid electrolyte from the cell in a relatively sudden spray process. The potential for ignition of this spray and the resultant heat generation are of significant concern since the heat generation from the alkyl carbonate electrolyte oxidation can represent several times the energy content of the battery itself. For example a kilogram of batteries might contain 0.5 MJ of stored electrical energy along with 0.1 kg of electrolyte having an enthalpy of combustion in the vicinity of 15 MJ $\mathrm{kg^{-1}}$ of electrolyte and 1.5 MJ $\mathrm{kg^{-1}}$ of battery ($\Delta H_{comb} = 13.3$ MJ $\mathrm{kg^{-1}}$ for $\mathrm{C_3H_4O_3}$ (EC) and 17.5 MJ $\mathrm{kg^{-1}}$ for $\mathrm{C_6H_6O_3}$ (PC)). Ribiere et al. suggested the enthalpy of electrolyte combustion was as high as 1.92 MJ $\mathrm{kg^{-1}}$ of battery in their calorimetry experiments [11]. Fortunately, these alkyl carbonates have generated some interest as biofuel components and ignition and combustion chemistry models are available for a couple (DEC and DMC) [7–9]. Thermodynamic properties for other alkyl carbonates are also available in the literature, for example [5, 6]. The chemical heat release from these electrolytes is less than typical alkanes but flaming is regularly observed if ignited in the form of a pressurized spray.

While we do not address the involvement of plastics used in the battery, the contribution of plastic oxidation in fire calorimetry tests has been estimated to be as great as the contribution of the electrolyte in terms of heat release (2.5 MJ for plastics versus 1.92 MJ for electrolyte per kilogram of batteries) [11].

In the description of the above processes, it should be noted that the anode chemistry was listed with the lithium present in Eq. 2 and 3 and the cathode material was listed with the lithium deficient in Eq. 4. This is the charged state for the battery, the state for which the energy is highest and the active materials are most unstable. The involvement of the active battery materials in the thermal runaway process through the above reactions is dependent on the battery being in the charged state. For this reason, regulations typically require batteries be transported, etc., in the discharged state, at least below some critical state of charge. While the battery calorimetry literature has carried out analyses of exothermicity over a range of states of charge [19, 21–24] this dependence on the state of charge is perhaps most dramatic in recent fire calorimetry studies [11, 12]. In those studies the heat release rates for charged cells were much higher than discharged cells with mass loss occurring perhaps an order of magnitude faster in fully charged batteries relative to fully discharged batteries. This is despite the fact that the majority of the energy release is not associated with the stored electrical energy; the increased reactivity provides for the rapid ignition of the flammable components.

To address the hazards of electrolyte flammability, research is ongoing to develop flame retardant additives, although the results are mixed because the additives frequently have an adverse effect on cell performance. Many additives include phosphorous-containing or halogen-containing compounds the introduce radical termination into the gas-phase chemistry with some success [3, 20]. One challenge to note is that the flammability environment created by high temperature and pressure sprays is more volatile than the typical cup-burner test. Reduced gas generation and exothermicity within the cell, prior to venting and flaming combustion, is thus desirable and has been attained in some cases [20].

The processes described above have been studied using differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC) both with full cells and with cell components [19, 21–24]. This is the primary data that provides the separation of the runaway process into the sequential stages of electrolyte breakdown, SEI (passivation layer) decomposition, cathode oxygen release and electrolyte oxidation and oxidation of the electrolyte in surrounding air. Further, this data provides guidance for predicting heat release rates as a function of temperature. Such estimates are required to determine the required heat dissipation to prevent runaway.

5 Thermo-fluid aspects of thermal runaway

A battery in an environment where a thermal insult is applied to that battery is in danger of transitioning to thermal runaway if the above described chemical processes are initiated. It is critical to determine the transition criteria and relate these to mitigation strategies. The problem exists at three levels of complexity: (1) reaction between individual anode or cathode particles and electrolytes (2) thermal runaway of a single, for example, cylindrical cell including venting and spray flames and (3) thermal runaway of an array of cells in a battery pack. The consequences for the latter process are of course much more dangerous, but the initiation comes down to the former processes with the particle-electrolyte reactions providing the basis for the single cell runaway and this providing thermal conditions for cascading failure at the pack scale.

At a various levels the ignition can be thought of as a balance between the exothermic processes as a function of temperature and the rate of dissipation as per the classical theories of Semenov and Frank-Kamenetskii. For example, theoretical ignition criteria are available for cylinders and slabs that might represent individual cells [25]. However, several complications arise. First, reactant depletion needs to be considered for the early processes that are only mildly exothermic as does transport-limited reaction processes discussed below. Second, advanced batteries have improved (i.e. reduced) heat release characteristics so that multiple processes need to be chained together to reach thermal runaway and the details of the heat release (reactant depletion and transport limitations) need to be taken into account so that simple Arhennius expressions are inadequate. Third, battery packaging leads to asymmetries in the heat transfer that can be important in limit processes like ignition.

To address the third item above, three-dimensional computational simulations are suitable to address the complexities of geometry. They can take into account the thermal insulation capabilities of battery packaging that is specifically designed to inhibit cell-to-cell propagation and at the same predict the heat transfer along conduction paths, there being a close alignment between electrical and heat conduction properties. Predictions of fluid mechanics behavior like gas flow or sprays, while more complicated than heat conduction, is accessible for advanced simulation codes [13, 15].

To begin to address the challenges of chemical source terms, Dahn and coworkers developed global expressions for heat release associated with thermal runaway to match their calorimetry measurements [22, 26]. These expressions are highly simplified, ignore transport limitations, and have not necessarily fit more recent measurements well although they have been implemented into multidimensional simulation codes [27, 28]. At the single particle level passivation or less reactive layers will exist and grow as the reaction progresses. On the anode this layer is the SEI layer described above that limits breakdown of the electrolyte while on the cathode there will be oxygen depleted layers that limit rates of oxygen transport to the electrolyte.

Here we formulate a particle reaction model with a surface reaction and a passivation or reactant depleted layer. We assume a spherical particle of radius, r_p, with a passivation layer of thickness, δ. Transport of the limiting reactant through the passivation layer occurs based on activity gradients with a diffusion coefficient having Arhennius temperature dependence, $D = D_0 \exp(-E_D/RT)$. Without loss of generality we assume that the reactant R is limiting and that the flux is adequately described by a difference in activities across the layer δ. A reaction, R $\rightarrow$ P, occurs at the outer surface $r_p + \delta$ with an Arhennius rate constant $k = A_0 \exp(-E_r/RT)$ and a reversible rate given by $\omega = k a_R - k a_P / K_{eq}$ where K_{eq} is the reaction equilibrium constant and a_R and a_P are the chemical activities of the complete set of reactants and products. For an ideal gas the activities are the product of the concentrations, for example, but with solids and liquids activity coefficients can alter these significantly. Either the reaction rate or the diffusion rate may be limiting. Equating the diffusive and reactive fluxes at the interface and setting these equal to the growth rate of the product layer yields

$$\frac{\partial \delta}{\partial t} = D \left(\frac{r_p}{r_p + \delta} \right) \left(\frac{a_{R,in} - a_{R,out}}{\delta} \right) = k \left(a_{R,out} - \frac{a_{P,out}}{K_{eq}} \right) \tag{6}$$

We assume here that the activities have been made dimensionless and k has dimensions of growth rate (velocity) so that this expression nominally provides a growth velocity for the product layer. A Damköhler number is formed $Da = k_0 r_p^2 / D_0$ along with a dimensionless layer thickness $\tilde{\delta} = \delta / r_p$. Eliminating the intermediate activity $a_{R,out}$ yields an expression for the layer growth rate

$$\frac{\partial \tilde{\delta}}{\partial t} = \frac{k_0 \exp(-E_r/RT)}{r_p \left[1 + Da(1+\tilde{\delta})\tilde{\delta} \exp\left(\frac{E_D - E_r}{RT} \right) \right]} \left(a_{R,in} - \frac{a_{P,out}}{K_{eq}} \right). \tag{7}$$

In thermal runaway, the Damköhler number, Da, can be large. As the layer grows so that $Da\tilde{\delta} > 1$ the reaction rate is reduced due to diffusion limitations and the activation energy changes. Typically $E_r > E_D$ and the above expression helps to fit more recent calorimetry results where heat release occurs in relatively small bursts followed by further induction [21, 24]. In addition to this expression for the layer growth, the energy and reactant conservation equations must be solved.

6 Outlook

An important challenge with lithium-ion batteries is the relatively low temperatures at which reactions start, listed above as 160 C, which is somewhat below flash point temperatures for typical fuels (> 200 C). Another challenge is the potentially long induction time with the lower temperature processes occurring at slow rates followed by sudden thermal runaway. Experience in dealing with these systems will grow with time, but improved safety can be engineered into these systems.

While the hazards associated with lithium-ion cells might appear severe, it is important to note that the technology is evolving. While the system described here is in common use today, new materials are reported monthly in the research literature with improved safety properties. As an example, we address the cathode material. Many other cathode materials are under consideration as alternatives to $LiCoO_2$ including $LiMn_22O_4$ and $LiFePO_4$, both of which are significantly less reactive than $LiCoO_2$. Similarly, batteries contain a range of safety mechanisms including self sealing separators and positive temperature coefficient resistors, both of which inhibit sudden discharge and the associated energy release. Lithium-ion battery safety mechanisms have been reviewed by Balakrishnan et al. [2].

7 Summary

Lithium-ion batteries are increasingly common for energy storage. With energy storage comes the potential for inadvertent energy release under abnormal conditions. We discussed the chemistry and physical processes unique to lithium-ion batteries that can lead to thermal runaway. The chemistry is associated with the high reactivity of battery materials, which is related to high energy storage density, and these materials are key to the early stages of thermal runaway. Later in the thermal runaway process, flammable electrolytes and other packaging can contribute much greater enthalpy to what at that point would be a fire scenario. We suggest that modeling of the coupled physical and chemical processes associated with the thermo-fluid system evolution can provide insight to mitigation approaches.

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