From material properties to multiscale modeling to improve lithium-ion energy storage safety

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Energy storage using lithium-ion cells dominates consumer electronics and is rapidly becoming predominant in electric vehicles and grid-scale energy storage, but the high energy densities attained lead to the potential for release of this stored chemical energy. This article introduces some of the paths by which this energy might be unintentionally released, relating cell material properties to the physical processes associated with this potential release. The selected paths focus on the anode–electrolyte and cathode–electrolyte interactions that are of typical concern for current and near-future systems. Relevant material processes include bulk phase transformations, bulk diffusion, surface reactions, transport limitations across insulating passivation layers, and the potential for more complex material structures to enhance safety. We also discuss the development, parameterization, and application of predictive models for this energy release and give examples of the application of these models to gain further insight into the development of safer energy storage systems.

Introduction

Lithium-ion batteries have reached relatively high energy densities by electrochemical standards, allowing compact transport of energy that fuels our portable electronic lifestyles.^{1,2} However, the high energy density coupled with the compact nature of its storage requires relatively unstable materials by electrochemical standards. Energy storage is unstable by nature. Inadvertent release of the stored energy can be hazardous, as when a short circuit occurs. These concerns are amplified as lithium-ion becomes predominant for vehicle and grid-scale electrochemical storage solution. What is it that prevents the inadvertent release of this stored energy? At the cell level, preventing the flow of electrons through a circuit will stop the electrochemical discharge, but there is still the potential for chemical energy release (thermal runaway) without electrochemical reactions occurring. Preventing this are various energy barriers associated with kinetic or transport processes that hinder the stored chemical energy from exothermically progressing toward its more stable states.

When material-scale activation barriers inhibit kinetic or transport processes, rates generally have Arrhenius or similar temperature dependencies, with rates that increase rapidly as temperatures rise. Because the inadvertent release of stored energy tends to generate further heating, the process can self-accelerate into what is referred to as thermal runaway, with rapid release of stored chemical energy. Thermal runaway can occur at the cell level under various abuse conditions, but dangers increase for larger energy storage systems comprised of many cells as in electric vehicles and grid-scale storage. Failure at one cell/location can propagate to other points in a cascading manner. Materials science comes into play in the full range of behaviors from atomistic understandings of energy content and activation barriers through grain and particle-scale transport processes up through full electrochemical cells and arrays of cells in understanding cascading failure.

This article provides a series of vignettes as to how materials science acts across the range of relevant scales. The literature contains a number of more comprehensive reviews.^{3–5} While much is understood, we point out opportunities and

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needs for refined knowledge. The ability to predict phenomena like thermal runaway is rooted in determining the balance between the driving force for the release of stored energy and the kinetic or transport barriers that prevent its release. The next paragraph provides some macroscopic thermal runaway context, identifying some of the important parameters that need to be understood.

Thermal runaway can be prevented if any heat produced can be dissipated fast enough to prevent continued temperature rise. Heat-production rates are given generically by a term such as $\Delta H_{rxn}\phi(C)A\exp(-E_a/RT)$ where ΔH_{rxn} is the heat of the reaction, $\phi(C)$ is a generic composition-dependent indication of reactivity and $A\exp(-E_a/RT)$ is an Arrhenius reaction rate expression with an activation energy barrier, E_a . Material properties determine ΔH_{rxn} , $\phi(C)$ and $A\exp(-E_a/RT)$ appearing even in this simple expression. Materials science also comes into other processes leading toward the initial breakdown of kinetic and transport barriers. For example, desirable fast charging can lead to lithium dendrite growth that can penetrate separators and induce energy release via a short circuit;^{4,6–9} separator failure/melting can have a similar effect^{6,7,10}. Mechanical strain might be associated with changes in transport properties including particle cracking or strain induced defects; these topics arise in anode passivation and are significant in some cathode failure modes.

In cell thermal runaway, three main reactions are typically of concern. The first is the discharge reaction, where lithium from the anode can react with the oxidizing cathode electrochemically or through some direct chemical reaction. Separators are intended to prevent this, though thermal runaway eventually reaches temperatures that make most separators ineffective. The other two reactions involve the anode reacting with the electrolyte and the cathode reacting with the electrolyte. As anode–electrolyte reactions often begin at slightly lower temperatures, these are discussed in the next section, followed by cathode–electrolyte reactions, including discussions of the tradeoff between safety and energy density in some of the newer cathode materials. A particular need is for predictive models that can translate from material-scale measurements or predictions up to an ability to design cell-level systems and beyond. To develop predictive models, model parameters must be identified from a combination of first principles and fundamental measurements as discussed in Material screening for safer batteries.¹¹ This understanding is brought together in Predicting multiscale behavior and in the final Summary section.

Anode–electrolyte interactions

While many batteries operate with aqueous electrolytes, it has been difficult to make lithium behave itself in the presence of water with lithium's strong preference to oxidize, and water's willingness to oblige. To address this, commercial lithium-ion batteries generally employ electrolytes with alkyl carbonate solvents together with lithium salts (LiPF₆ being

the most typical).² While less reactive than water, they are not completely inert.

For the anode, where lithium is stored in its unstable charged state, these electrolytes are reactive, and the formation of a high-quality passivation layer is essential to safety and long-life battery operation. This passivation layer, referred to as the solid-electrolyte interphase (SEI), results from lithium oxidation by the electrolyte.¹² Depending on the extent of the reaction fairly stable oxidized forms of lithium can result, and the release of potential energy by this reaction alone can be very significant. Typically referenced products of this reaction involve lithium carbonate, Li₂CO₃, which is a passivation layer component, along with ethene, C₂H₄, or similar gases. The heat of reaction for Li₂CO₃ and C₂H₄ formation from lithium and ethylene carbonate is 281.4 kJ/mol Li.¹³ This is sufficient to heat typical cells by several hundred degrees if much of the cell's lithium content is oxidized in this way, with greater temperature rise for higher energy density cells.

The anode contributions to thermal runaway mainly involve this same exothermic reaction that forms the SEI passivation layer. When the thermal evolution of the anode–electrolyte interface is measured using differential scanning calorimetry (DSC), the heat release exhibits several features, as shown in **Figure 1a**. At temperatures around 100°C, significant heat release begins but with a limited magnitude. This SEI reaction is limited by electron transport through the SEI that may involve an electron tunneling process, creating a plateau in the heat release observable in DSC measurements like **Figure 1a**.^{14,15} However, the SEI thickness exceeds typical tunneling dimensions, suggesting the importance of lattice defects in facilitating transport.¹⁶ Recent density-functional theory calculations have suggested that strain associated with delithiation affects the defect density.¹⁷ This has been used to extend early anode–electrolyte models to account for the later accelerated heat release observed above 200°C (**Figure 1a**), allowing more comprehensive predictions of heat production over a wide range of conditions.^{13,14} There are other possible explanations for the changing heat release rates including mechanical strain leading to exfoliation of the passivation layer.¹⁸ Some anode–electrolyte DSC measurements include endothermic pulses in the heating rate that might be evidence of the energy absorbed by this exfoliation, as in **Figure 1a**. Because the anode–electrolyte heat release is such a strong contributor to potential heat release, there remain opportunities to improve upon the protection afforded by the SEI passivation layer.^{19,20}

Cathode–electrolyte interactions

As if the challenges associated with the reactivity of the lithium with electrolyte were not sufficient, the cathode can also transform exothermically and release oxygen that can react with the electrolyte.^{21–24} The majority of cathodes are composed of layered transition-metal oxides of a form Li_{1–x}MO₂ where M is a transition metal; Ni, Co, Mn, and combinations

Figure 1. Thermodynamics and kinetics of anode and cathode heat release. (a) Differential scanning calorimetry (DSC) measurement¹⁸ and models of lithiated graphite with electrolyte.^{13,14,15} Adapted with permission from Reference 13. © 2018 IOP Science. (b) Global and stepwise thermodynamic heat release from typical $\text{Li}_{0.5}\text{MO}_2$ cathodes decomposing with electrolyte; open/solid bars show reaction enthalpy without/with solvent oxidation. Adapted with permission from Reference 21. © 2020 IOP Science. (c) Heat release from NMC decomposition with electrolyte. Lines are thermodynamic calculations, symbols are calorimetry measurements. Adapted with permission from Reference 37. © 2020 IOP Science. (d) Correlation of thermal stability and capacity retention with discharge capacity for a range of NMC cathode compositions. Reprinted with permission from Reference 42. © 2013 Elsevier. SEI, solid electrolyte interface.

of these are typical examples. When built in the discharged state, $x=0$, but charging moves some Li to the anode, $x>0$, giving the cathode a stronger oxidation potential. The partially delithiated $\text{Li}_{1-x}\text{MO}_2$ might be thought of as a solution of the stable LiMO_2 and the less stable MO_2 , with the latter having the potential to release O atoms.²¹

Before proceeding further, we note another important class of cathode materials, olivines, with the general form Li_xMPO_4 of which lithium iron phosphate (LFP) is the commercialized example.^{23,24} Phosphate cathodes have oxygen bonded covalently in phosphate groups, and reaction with typical electrolytes is rare for LFP.^{25–27} From a safety perspective, LFP is quite desirable,^{6,26–29} but it has a lower energy density and a number of other challenges.^{23,24} LFP cells are not immune to thermal runaway because anode thermal decomposition can still occur,^{28,29} but the sudden onset of cathode heat release is rarely observed, making them significantly safer. LFP cells are used in many safety-conscious applications.^{6,23,24}

In layered metal oxides (LiMO_2), lithium and transition metals occupy octahedral sites in alternate layers between oxygen layers arranged in a cubic close packed array.^{23,24,30} When cells are charged (cathodes delithiated) the partially emptied lithium layer becomes less stable due to the oxygen-layer repulsion, and there is a tendency for the transition

metal to migrate toward the lithium layer resulting in a spinel such as LiM_2O_4 . Thermodynamically, this is shown to almost always be favorable and exothermic,^{31,32} but the kinetic barriers vary with the transition metal and with the degree of delithiation.³³ Moderately large energy barriers are predicted for Co cations that are known to provide good structural stability;³⁴ comparable, though slightly lower, barriers are measured using calorimetry.³⁵ It is likely that the first exothermic cathode transformation observed is related to this formation of a lithium-containing spinel.^{21,36,37}

Subsequent heat release can occur with reactions between the electrolyte and oxygen atoms released from the cathode. This involves the conversion from MO_2 or LiM_2O_4 to a spinel M_2O_4 and/or a rock salt MO .^{21,36–39} The oxygen release must occur at the surface and excess metal cations will need to move further into the bulk.³⁰ The exact limiting physics associated with this oxygen atom loss to react with the electrolyte is not well described at this point. Thermody-

namics indicates that the oxygen release itself is endothermic, but can be driven forward by the heat release and entropic gain associated with gas-phase products.^{21,40} Figure 1b shows the global heat release (R1) as well as the heat release associated with the first spinel formation step (R4) and this second step (R6) where oxygen release combines with electrolyte oxidation for two typical cathode materials. Figure 1b values correspond to 50% delithiation ($\text{Li}_{0.5}\text{MO}_2$), but greater heat release can occur at higher degrees of delithiation, as shown by the calorimetry measurements plotted on the left half of Figure 1c. Furthermore, excess delithiated MO_2 at higher degrees of delithiation allows cathode decomposition to proceed via multiple oxygen-producing reactions after the initial formation of LiM_2O_4 . This accounts for the observation of multiple exotherms in calorimetry of highly charged cathodes shown in Figure 1c.^{21,37}

Early commercialized cathodes were largely based on cobalt, LiCoO_2 , and have been reasonably well characterized.^{35,38,39,41} Using nickel as the transition metal gives a higher energy density, but yields a less thermally stable cathode material than needed (with similarly reduced cycle life). To optimize cathode properties, modern cathodes have trended toward combinations of nickel, manganese and cobalt in the

LiMO₂ layered structure.^{42–44} For example, equal quantities of each transition metal would be LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ commonly denoted as NMC-111. The nickel as Ni²⁺ is electrically active (able to shift to Ni⁴⁺ with delithiation) and provides high energy density. Cobalt provides good structural stability, inhibiting the Li–Ni cation mixing. Manganese has strong oxygen bonding and provides improved thermal stability.^{34,44} With this combination of materials as NMC-111, the thermal stability and hence the safety is generally improved over LiCoO₂ cathodes while modestly improving energy density.⁴⁵

It is desirable to increase the energy density by increasing the nickel content of the NMC mixture (increasing the number of two electron conversions between Ni²⁺ and Ni⁴⁺), and this has led to a range of compositions considered. Studies of NMC thermal stability in electrolytes were conducted using accelerating rate calorimetry⁴⁶ (ARC) and DSC.⁴² In general, the increase in nickel fraction leads to an increase in the discharge capacity but also a simultaneous reduction in the thermal stability as shown in Figure 1d,⁴² where capacity retention

declines in much the same way as the thermal stability. This is useful to note since similar kinetic and transport barriers are associated with both thermal stability and capacity retention, and literature on capacity retention can provide useful insights into many aspects of safety and thermal stability. While the trends are clear, the thermal stability trends all go against the desired increased cell capacity and voltage that increase the cell energy density. To alleviate this issue, core–and–shell and composition-gradient approaches have been evaluated. These apply more thermally stable surface coatings to high-nickel cathode particle cores, and results show improved thermal stability characteristics as well as reduced capacity loss.^{44,47–51} There remain opportunities to find the optimal combination of capacity and thermal stability, and this is an ongoing effort within the electrochemistry community with real needs in materials characterization and understanding.

Solid-state electrolytes

In the previous two sections, the reactions of the electro-

lyte with either the anode or cathode were presented. A less reactive electrolyte system (solid-state electrolyte) can better prevent anode–cathode interaction. Here, we contrast the thermal decomposition of microcells with traditional and solid-state electrolytes. **Figure 2a** compares the DSC profiles of Li-ion microcells with conventional liquid electrolyte, but with different cathode materials.⁵² Several major exotherms can be observed in samples with NCA (LiNi_{0.80}Co_{0.15}Al_{0.05}O₂) and NMC cathodes that appear broadly consistent with the processes described in the preceding sections. The results indicate that this NMC has somewhat reduced/delayed heat production relative to this NCA. However, the exothermicity of either cathode with conventional electrolytes is significantly larger than the solid electrolytes presented next.

A less reactive solid-state electrolyte potentially offers a solution for battery safety issues; additionally, it also significantly inhibits lithium dendrite growth to mitigate short circuits. Figure 2b describes the DSC profile of Li-ion micro-cells using lithium lanthanum zirconium niobium oxides (LLZNO) solid electrolyte but with different assemblies of anode and cathode

Figure 2. Thermal signature of lithium-ion battery electrolyte. (a) Liquid electrolyte with different cathode materials. (b) Solid electrolyte with different anode materials. Reprinted with permission from Reference 52. © 2017 American Chemical Society.

materials.⁵² Thermal signatures of samples with lithium titanate (LTO) and artificial graphite (AG) exhibit only one broad reaction peak that marks interaction between oxygen liberation and intercalated lithium, indicating a simpler thermal runaway mechanism. A reduced specific heat flow suggests enhanced thermal stability compared with liquid-electrolyte samples. Moreover, solid-electrolyte microcells with Li metal anode exhibit one endothermic peak followed by two exothermic peaks, which correspond to the melting of lithium metal and subsequent interaction with oxygen released from the decomposition of cathode crystal structure and solid-electrolyte skeleton.⁵²

Materials screening for safer batteries

To go from material-level properties to system-scale performance and safety predictions require knowledge of reaction kinetic parameters ΔH , A , E_a and $\phi(C)$. DSC shown in **Figure 3a**⁵³ and ARC in **Figure 3b**⁵⁴ are two standard techniques that facilitate predictions of thermal abuse severity. Mathematical modeling of heat release and heat transfer provides insight into the limits of thermal runaway, but relies on the extraction of suitable kinetic parameters from the calorimetric measurements. Common strategies for estimating kinetic parameters include a model-free approach using Kissinger's method and a model-based approach using nonlinear optimization algorithms. **Figure 3c** exemplifies Kissinger's method⁵³ where the shifting of reaction peaks with increased DSC scanning rates can be correlated using linear regression analysis. The activation energy and frequency factor, E_a and A , can be derived

from the slope and intercept of linear regression. **Figure 3d** illustrates an example of carrying out nonlinear optimization algorithms, allowing more complex reaction models to be parameterized.⁵⁵

These material screening methods can be applied to assess the significance of changes in materials and also changes in geometry over the range of scales. **Figure 3e** shows the DSC response of the anode–electrolyte reaction as a function of various types of carbon particles with spiky, graphite and spherical morphologies.⁵⁶ Parameters are extracted from these measurements to develop macroscale models that predict in advance the behavior under safety tests,⁵⁶ as shown in **Figure 3f**. **Figure 3g** demonstrates applying these same techniques of extracting parameters from DSC to a range of materials followed by parameter sweeps that map out the space of safe cell capacity/operational space; here, that parameter space is described in terms of predicted response in oven tests as a function of cell capacity.^{10,55}

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Predicting multiscale thermal behavior

Up to this point, discussion has focused on properties at the atomic to micron-scale particle level, but applications exist at the macroscale where interactions between physical phenomena can be complex. Next, we discuss the interactions between phenomena at different length scales and highlight the safety-related efficacy of electrode engineering at the particle surface scale (less than 1 μm), particle-scale (10–20 μm), microstructure scale (10 to 100 μm), and full cell scale (10–20 cm).

Beyond basic Arrhenius forms, particle geometry and surface characteristics affect the thermal runaway kinetics of cell components. Recent model development predicting anode–electrolyte reactions during thermal runaway highlights the differences of the graphitic edges or prismatic surfaces relative to basal-plane surfaces toward lithium-electrolyte reactions.^{13,14} There is also evidence from nickel-rich NMC that surface layers play a key role in thermal safety. Core-and-shell designs where more thermally stable coatings are applied to high-nickel cathodes were discussed above as improving thermal stability characteristics.^{44,47–51}

Electrode microstructure-informed physics models extended to macroscale problems have helped understanding thermal and lithium-plating concerns. For example, altering carbon particle morphology (commercial graphite, spherical

carbon, and spiky carbon) at the particle surface scale (Figure 4a) is shown to influence intercalation dynamics, electrochemical performances, and thermal runaway propensity.⁵⁶ The potential evolution of spiky carbon is closer to theoretical open-circuit voltage (OCV) than spherical carbon, indicating more lithium storage, the deferred onset of adverse lithium plating, and a lower side reaction rate.

At the electrode scale in Figure 4b, the differences in anode and cathode response sensitivity to changes in design parameters (porosity, wt%, binder fraction) are reflected by showing differences in thermal, electrochemical, and plating signatures at the cell level.⁵⁷ The variations in electrode design parameters influence the kinetic and transport limitations within the anode and cathode distinctly. As a result, Figure 4c compares how the morphologies of particles dictate the potential profile and side reaction versus extent of lithiation.⁵⁶ Figure 4d shows that coupled microstructure-resolved crosstalk between anode and cathode leads to inhomogeneous intercalation, plating, and heat generation signatures at the cell level.⁵⁷ Here, the cell performance is closely related to the anode structure, while temperature rise and hence safety is more linked to the cathode specification. In contrast, plating shows a co-dependence on both electrodes.

At the cell scale in Figure 4e, inhomogeneity in thermal and plating signatures arise near tabs reflecting their sensitivity to cell-level design.^{58,59} The regions near the positive tab experience a higher temperature due to high current density and Ohmic heating after charging (4C). The improved kinetics in warmer regions facilitate electrochemical reactions through lower overpotentials. Such a scenario leads to inhomogeneous

intercalation within the cross-section of the electrode. Furthermore, the constant high current density at the hotter locations triggers the local anode potential to fall below 0.0 V and stimulates localized lithium plating.

Moving from the development and onset of thermal runaway to the potential for large-scale cascading failure where thermal runaway propagates from cell to cell, modeling provides insight into the physical processes that mitigate propagation.^{60,61} The cited studies show mitigation is a balance between microscale transformations and macroscale thermal properties of the system. In at least one case, results suggest the kinetics relevant in lower temperature screening tests are not the same kinetics that limit large-scale propagation. It is instead suggested that the limiting process shifts at high temperatures

from a kinetic barrier to a diffusion process with lower activation barriers.⁶¹

Summary

The high energy densities attained by lithium-ion cells bring with it the potential to inadvertently release stored energy as heat in a thermal runaway event. In addition to a potential reaction between the anode and cathode materials that hold the stored chemical energy, reactions are also possible between typical electrolytes and both the anode and cathode. This article introduces these potential transformations focusing on some of the material barriers that prevent the inadvertent energy release under most conditions. For both the anode and cathode, the driving thermodynamics processes have been identified along with an understanding of the important limiting kinetic or transport processes for battery materials commonly in use. However, significant uncertainties remain for newer materials. These can be addressed through fundamental characterization studies at a range of scales.

As energy densities increase to meet demands, potential risks of thermal runaway also increase, and we discuss the simultaneous research efforts to enhance safety jointly with energy densities. Much of this research parallels research on cell lifetimes or cycling stability where barriers to decomposition or decay are similar as those that inhibit thermal runaway. Still needed are improved understanding of the limiting processes associated with thermal decomposition in nickel-rich cathode materials and the potential decomposition of the various solid-electrolyte materials under consideration.

A continued challenge is identifying the interaction of phenomena from atomic to device scales. To extend the materials-level understanding to more macroscopic systems, we describe the development of models from fundamental measurements and provide several examples of the applications of these models. Models allow exploration of parameter space, and as physical understanding improves and model fidelity increases, there are opportunities to explore more complex phenomena. Of particular interest are the interactions of inhomogeneities in state and properties with nonlinear physical processes (i.e., Arrhenius rates); for these challenging problems, models provide a window into the complex system response. The application of these techniques to, for example, cathode composition gradients and particle morphology is just beginning.

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Conflict of interest

The authors declare no conflicts of interest beyond the above Acknowledgments.

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