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Lithium battery thermal models

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Abstract

Thermal characteristics and thermal behavior of lithium batteries are important both for the batteries meeting operating life requirements and for safety considerations. Sandia National Laboratories has a broad-based program that includes analysis, engineering and model development. We have determined thermal properties of lithium batteries using a variety of calorimetric methods for many years. We developed the capability to model temperature gradients and cooling rates of high-temperature primary lithium thermal batteries several years ago. Work is now under way to characterize the response of ambient-temperature rechargeable lithium-ion batteries to thermal abuse. Once the self-heating rates of lithium cells have been established over a range of temperatures, the thermal response can be estimated under a variety of conditions. We have extended this process to isolate the behavior of individual battery components and have begun to understand the chemical nature of the species responsible for heat evolution within the cells. This enhanced level of understanding will enable more accurate modeling of cell thermal behavior and will allow model-based design of safer, more abuse-tolerant lithium batteries for electric vehicles (EVs) and hybrid electric vehicles (HEVs) in the future. Progress toward this goal and key information still needed to reach it are discussed.

Keywords: Thermal battery; Lithium-ion cell; Calorimeter; Thermal model; Electrochemical model; Abuse tolerance; Safety

1. Introduction and motivation

Interest in lithium battery thermal modeling is divided into two general areas. High-temperature thermal batteries are designed as primary (non-rechargeable) power sources that only remain active as long as the molten salt electrolyte does not freeze. The operating life of the battery is therefore, usually dependent on the design parameters and can range from minutes to a few hours. Modeling of the temperature profile of a battery, both spatially and over time, is an important tool to improve designs and select materials for enhanced battery performance. The model also serves as a repository for past design experience and knowledge for use by new staff. Existence of a model also enables testing protocols to be much more efficient, since it can be used to evaluate preliminary designs and reduce the number of tests that need to be run. Final validation tests can focus on critical areas highlighted by the model, thereby expediting the overall design process.

Modeling the thermal performance of the second general technology area of rechargeable ambient-temperature lithium-ion batteries also falls into two categories: (1) ensuring proper thermal management under normal operating conditions and (2) predicting and mitigating thermal abuse response. These modeling tools also improve the efficiency of the design process, thus reducing product development time and should lead to better battery designs. If the fundamental properties of the battery components and materials can be included in the model and the primary chemical interactions responsible for heat generation are identified, then the model can also be a valuable tool for development of improved battery materials.

2. Thermal battery thermal modeling

High-temperature lithium thermal batteries are primarily used in defense applications and therefore, high reliability is required. The standard chemistry is Li (alloy)/FeS_2 with a lithium halide molten salt electrolyte (Fig. 1). This reserve battery is inactive until time of use when the Fe–$KClO_4$ heat powder mixture is ignited to bring the battery up to operating temperature. Operating time is limited by the temperature profile and can generally continue as long as the electrolyte remains liquid (above ~350 °C). Reduced cycle time and cost for battery selection and development for specific applications are needed for this battery. This will require better tools for battery design and performance evaluation.

A thermal model has been completed that can simulate thermal performance and establish baseline characteristics for thermal batteries [1]. This reduces the number of tests

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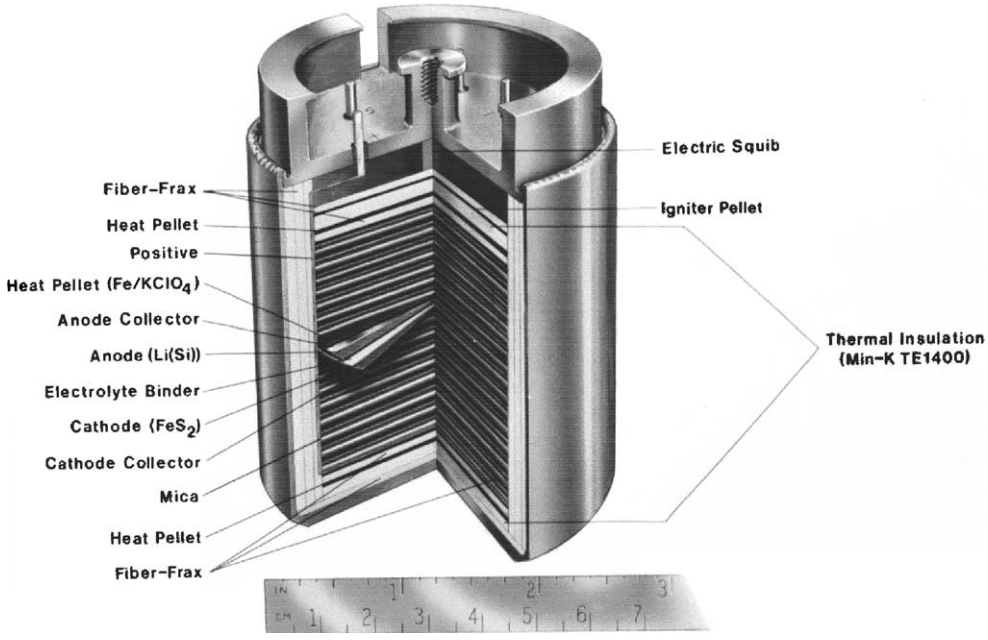

Fig. 1. Typical Li (alloy)/FeS_2 thermal battery configuration.

required to establish a design. Both internal and external battery temperatures can be predicted. As shown in Fig. 2, internal temperature rises nearly instantaneously to a little over 500 °C and then begins a slow decline over about an hour in this instance. The outer case, in contrast, does not reach its maximum temperature of about 100 °C until after about 15 min. Also shown in the graphs are the effects of improved insulation (aerogel sleeve) and the addition of a 5 W heater, which reduce the rate of decline of the internal battery temperature, thereby extending operating life. Fig. 3 shows the internal temperature gradients calculated for a different thermal battery using the thermal model.

An electrochemical model is also under development for thermal batteries that will enable the electrical performance and chemical reaction/transport to be simulated along with battery temperature [2]. This enhanced model will perform a

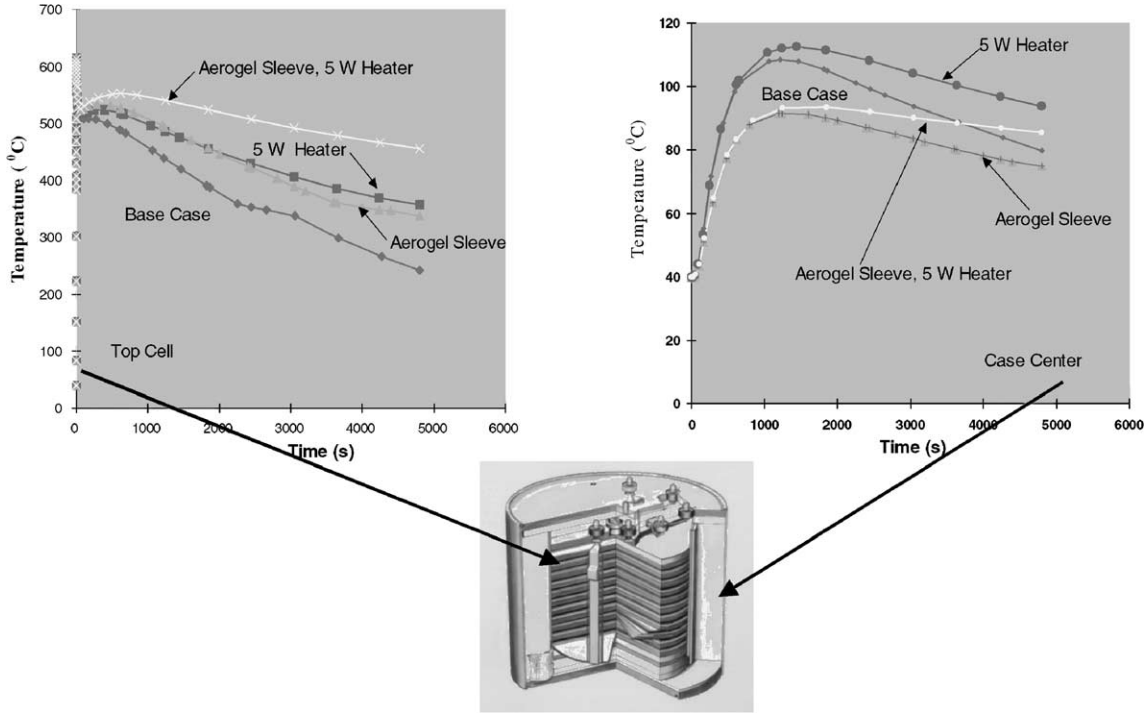

Fig. 2. Thermal battery internal and external temperatures.

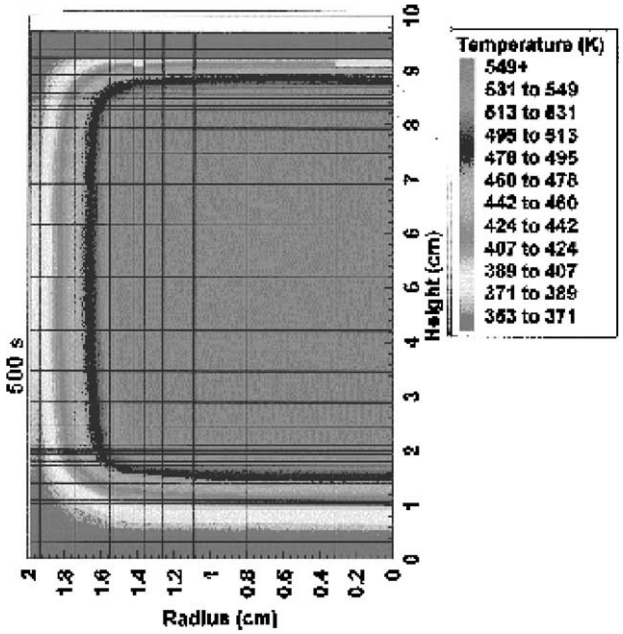

Fig. 3. Calculated thermal battery temperature profiles from the thermal model.

detailed parametric simulation of all cell processes and will enable a link between cell chemistry and performance to be established. Other goals for the complete thermal battery model are prediction of voltage versus time within 10% of actual, capability to model all thermal battery chemistries (flooded and unflooded anodes; standard, low melting, and all-lithium electrolytes, and FeS_2, CoS_2, and other cathodes). In addition, the model must be useable on a desktop PC by battery design staff. Current activities in the thermal and electrochemical model development include migrating the existing codes from a workstation platform to a web-based network. Also, both models are being upgraded in that process. Ultimately, the two models will be combined into a single design and prediction tool.

3. Lithium-ion cell thermal modeling

Lithium-ion cells typically consist of carbon anodes containing a binder and conductivity-enhancement additive, an organic solvent electrolyte with a salt such as $LiPF_6$, and metal oxide cathodes, which also contain binder and conductive graphite/carbon. Lithium cobalt (or nickel, or a mixed metal oxide) is typically used in the cathode, although there are other possible variations. Thermal runaway and gas generation result in cell venting and vigorous exotherms. Thermal abuse conditions are simulated when cells are subjected to a thermal ramp, as shown in Fig. 4. If these reactions can be understood and controlled, then abuse tolerance can be improved.

There are two general approaches that can be used to build thermal abuse models of lithium-ion cells. These are the calorimetry-based approach developed by Dahn and coworkers [3–5] and the chemical reaction approach. The calorimetry approach is based on a simplified model of cell construction comprised of concentric cylinders. It uses measured thermal properties of cell components, which are characterized by reaction rate equations using Arrhenius thermal activation energy terms. These properties are determined as a function of state-of-charge (SOC) and can include anode/electrolyte, cathode/electrolyte, and electrolyte decomposition reactions. Cycle/ageing history can be accounted for from measurements on aged cells. Other data required are accurate determination of cell component heat capacities and thermal conductivities along the cell dimensions. These could be calculated from bulk material proper-

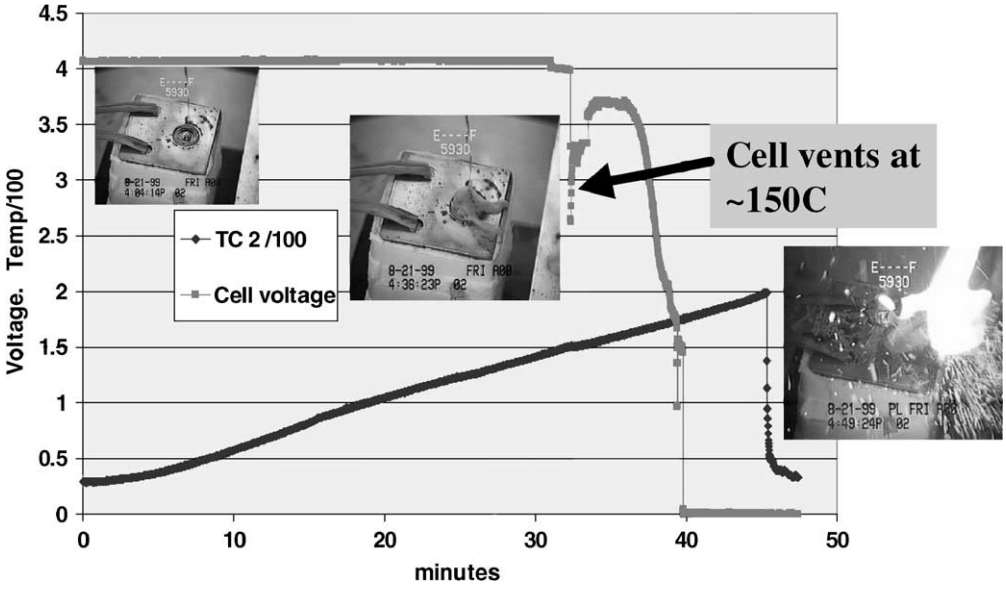

Fig. 4. Thermal ramp test on a lithium-ion cell at 80% state-of-charge.

ties, if known. A complete model of cell thermal response under operating conditions also requires calculation of total internal cell heat generation rates as a function of state of charge, charge/discharge rate, and temperature as well as the individual cell component reactions. Heat generation at different charge/discharge rates requires determination of the thermoneutral potential for each cell chemistry variation. The thermoneutral potential is the entropy-corrected open circuit potential. From this parameter, calculation of the total heat generation in the cell is possible for any load profile. This value is rate independent but is a function of electrode chemistry and crystallographic structure.

The chemical reaction approach requires the identification of the chemical reactions responsible for each of the dominant thermal events. Reaction rates and activation energies must be determined for each of these reactions. A model is also needed for predicting the reaction product species on the electrodes, which will serve as source terms contributing to the heat producing reactions. Finally, the chemical terms must be combined with details of the cell construction in order to simulate thermal behavior for the overall cell. This requires knowledge of bulk thermal properties of the cell materials [6,7].

As in most cases, there are trade-offs involved in choosing between these two thermal modeling approaches. The calorimetry-based phenomenological approach has the advantage that the model input data are easier to acquire, but the understanding obtained is less detailed and the range of prediction capability is narrower. The chemical reaction model requires the complete set of reaction parameters, which may be difficult to obtain especially if effects such as particle size change the kinetics of the reactions. Changes in the dominant reaction also may occur as temperature increases, further increasing the model complexity. However, the benefit is better mechanistic understanding of the thermal events, which will enable poor thermal abuse tolerance to be improved using better materials and designs. A mechanistic model should also have the best chance of extrapolating correctly to other conditions.

Modeling based on the calorimetric phenomenological approach requires the measurement of full cells and cell materials in thermal abuse type environments [8–10]. Full cells are placed in various states of charge and monitored for heat and gas generation during a thermal runaway reaction. Anode and cathode materials are prepared in representative states of charge and measured in the presence of electrolyte in sealed capsules under conditions simulating thermal runaway. A key piece of instrumentation for characterizing the thermal response properties of lithium-ion cells and cell components is the accelerating rate calorimeter (ARC). The ARC measures cell or cell material thermal response to increasing temperature in an adiabatic environment. Discrete thermal reactions may be observed in different temperature regimes and the thermal runaway point for the cell can be determined in order to predict its response to extreme operating conditions. Other conditions such as SOC and prior ageing or thermal abuse can also significantly affect the ARC test results. Gas evolution from cell component materials and vented cell gases can also be measured during these thermal runaway regimes. A gas sampling system is available to capture evolved gas for analysis. Fig. 5 shows the cell holder, heating unit, blast shield and a portion of the gas collection system for the ARC system used at Sandia.

Fig. 6 shows ARC data for three different types of lithium-ion cells. All of these samples are spiral wound, 18650-size cells at 100% SOC. The Sony cells were an earlier generation of a commercial product, while Gen 1 and 2 are cells built specially for the Advanced Technology Development (ATD) Program [11]. ATD is sponsored by the US Department of Energy and the Partnership for a New Generation of Vehicles (PNGV) to characterize and improve battery life and abuse tolerance in hybrid electric vehicles. Development of low cost battery materials, designs and fabrication processes is another ATD objective. The Gen 1 cells contain an anode with ‘‘MCMB’’ carbon that consists of synthetic spherical carbon particles, a mixed Ni/Co oxide cathode, and an ethylene carbonate/diethyl carbonate (EC/DEC/$LiPF_6$) electrolyte. The Gen 2 chemistry is similar with a ‘‘MAG10’’ graphite anode consisting of smaller, flaky carbon particles, an aluminum-doped Ni/Co oxide cathode, and an ethylene carbonate/ethylmethylcarbonate (EC/EMC/$LiPF_6$) electrolyte.

As shown in Fig. 6, Sony and Gen 2 cells show similar ultimate heating rates, although the heating rate for the Sony

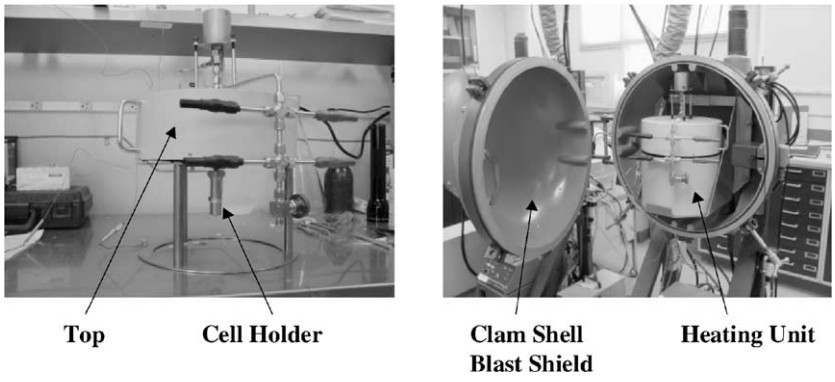

Fig. 5. Accelerating rate calorimeter and cell holder.

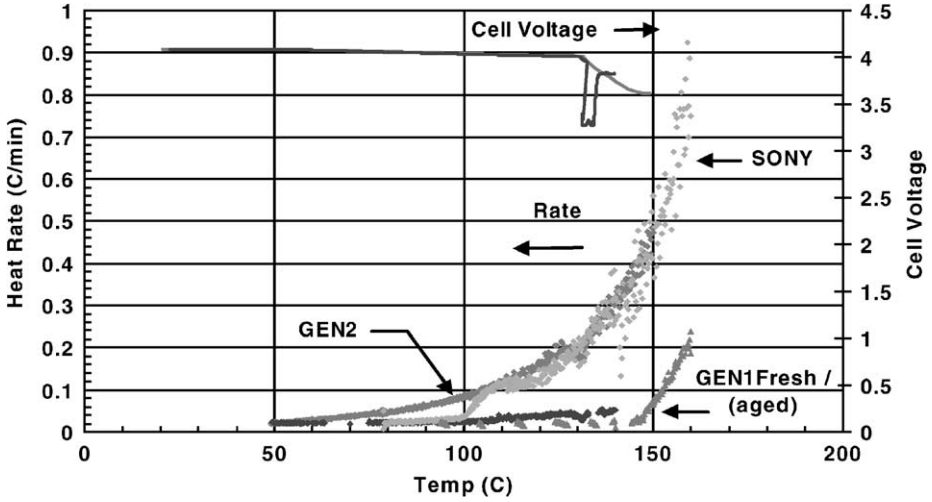

Fig. 6. Accelerating rate calorimeter data showing onset of thermal runaway for Sony, Gen 1 and 2 cells at 100% state-of-charge.

cell does undergo a step upward just above 100 °C probably due to a sudden breakdown in the protective solid–electrolyte interphase (SEI) layer [5]. In contrast, the Gen 1 cells (either fresh or aged) demonstrate a much lower heating rate that does not begin to accelerate until about 140 °C. This behavior is interpreted as indicating that the anode SEI layers are more robust in the Gen 1 cell design.

Figs. 7 and 8 compare the effect of cell SOC and elevated temperature ageing on the Gen 2 cell-heating rate. Lower heating rates are observed at lower SOC and after elevated temperature ageing. These data also show a feature at about 130 °C that is due to the melting of the separator.

ARC tests can also be used to study cell components or materials that are contained in a small spherical bomb sample holder. Fig. 9 shows both heating rate and pressure traces for Gen 2 electrolyte and solvents alone. Thermal activity and gas pressure are higher for the electrolyte, which is attributed to the reactivity of the $LiPF_6$ salt.

Similar types of thermal data are being measured on other sizes of lithium-ion cells for development of thermal models. In one example, the properties of 190 Ah cells are being determined for NASA. The application is a proposed use on the NASA space shuttle for the electric auxiliary power unit program. Tested parameters include heat capacity, thermal conductivity, thermoneutral potential, and thermal abuse tolerance in the ARC. The thermal runaway and heat capacity of these large cells were tested using a special ARC from Thermal Hazards Technology Co. (UK), which provides a 15 in. high, 9 in. i.d. test chamber that allows destructive testing of large cells at up to 400 °C under adiabatic conditions.

Another useful technique for obtaining thermal data on cell components and materials is differential scanning calorimetry (DSC). Small samples (typically a few milligrams) are placed in sealed pans that allow sensitive measurement of thermal reactions. As opposed to the multi-hour measurements in the ARC bombs, higher heating rates (typically 10 °C/min) are employed in these measurements that enable more rapid screening of multiple samples in various combinations and states. Cell component interactions can be studied to determine thermal stability and understand safety and lifetime variables. Electrode materials are placed in a particular electrochemical SOC in a laboratory cell prior to the DSC test. Fig. 10 compares the DSC

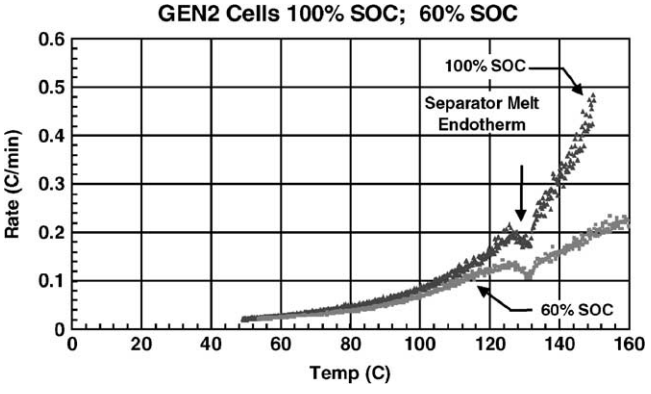

Fig. 7. State-of-charge effect on thermal runaway.

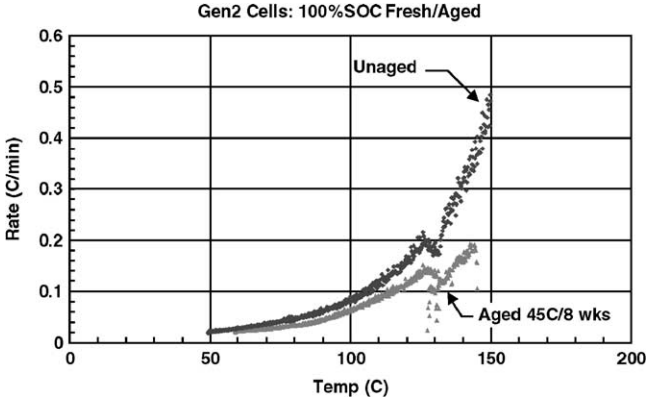

Fig. 8. Cycle/ageing effect on thermal runaway.

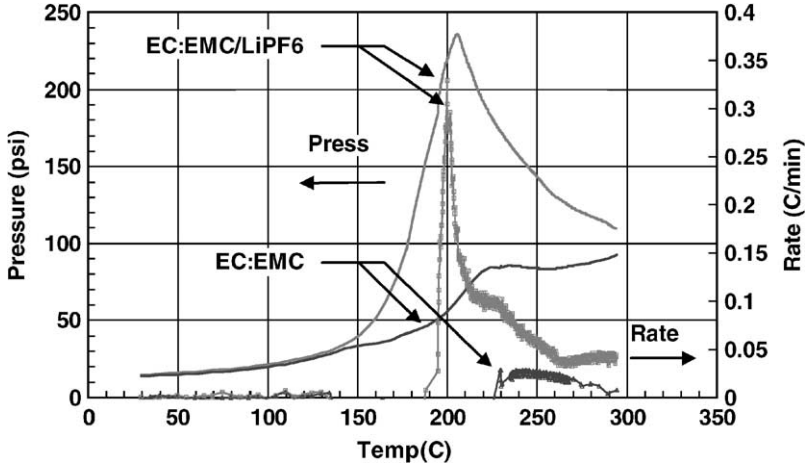

Fig. 9. Accelerating rate calorimeter data on cell materials showing greater heat and pressure from electrolyte compared to solvents alone.

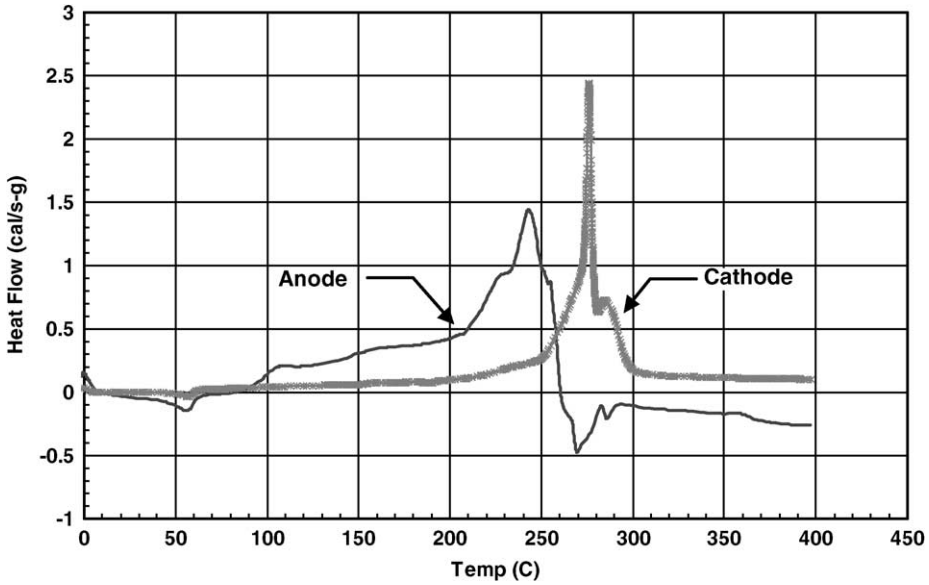

Fig. 10. Differential scanning calorimetry data for charged Gen 2 anode/cathode in Gen 2 electrolyte.

results for Gen 2 anode and cathode materials in Gen 2 electrolyte. The data show thermal reactions beginning below 100 °C for the anode, followed by higher temperature reactions in the cathode.

Applications of this type of thermal data and models to batteries for hybrid electric vehicles provides better definition of heat sources, which is necessary for development of effective thermal management systems for both normal operating conditions and abusive environments. This information also can be used to determine safe operating limits and the possible consequences of off-normal events.

4. Summary and data needs

Thermal models have been developed to describe temperature profiles and time evolution of temperature in lithium thermal batteries. This information is valuable for predicting the performance envelope of the battery and reduces the cycle time and cost for designing and developing a thermal battery for a specific application. The model is being enhanced by coupling with an electrochemical model of the cell so that electrical performance can also be simulated.

Rechargeable lithium-ion cells appropriate for hybrid electric vehicles and other applications are being characterized by various calorimetric methods in order to provide data for thermal models that will also reduce the time for battery development. These tools will enable thermal abuse tolerance and cell safety to be improved, as well as defining thermal management requirements and safe operating limits for use of the battery in HEVs. Both calorimetric and chemical reaction approaches are being used. The calorimetric approach requires a complete description of the cell design (dimensions and materials), measurement of either materials or whole cell thermal properties (e.g. heat

capacity, thermal conductivity), calculated or measured thermal response properties for cell materials/cells, and information on the effect of ageing on the thermal response properties. A chemical reaction approach relies on determination of a different set of parameters, which include identification of the dominant chemical reactions for the system and the evolved chemical species. Reaction rates and activation energies must be measured for all of the relevant chemical reactions.

A detailed understanding of the chemical nature of thermal abuse tolerance will enable materials and cell designs to be selected for optimum safety as well as improved electrical performance. This will lead to enhanced battery safety in HEVs and in other applications as well.

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