Simulation of Abuse Behavior of Lithium-Ion Batteries

by Robert Spotnitz and Richard Muller

The last decade has seen tremendous progress in the capability to simulate and so improve the abuse tolerance of lithium-ion batteries. This progress has been driven by both the need to improve the safety of small cells used in consumer electronics and the need to design large packs used in automotive applications.

The energy density of small lithium-ion cells, for example 18650 (18 mm dia., 65 mm tall), used in consumer electronics has increased steadily since their commercial introduction by Sony in 1991. By 2000, these higher energy cells faced challenges in passing the abuse tests. Modeling and simulation provided validation of experimental results and useful insights to improve design.

Of particular concern for consumer cells is the ability to pass an oven exposure test. The cell should not burn or rapidly disassemble when exposed to elevated temperatures for a reasonable period of time. Hatchard *et al.*[1] found that the ability of a cell to pass an oven exposure test depended on the label. Cells with low values of emissivity failed a 140°C oven exposure test, while cells with high values of emissivity passed. This finding was explained by considering radiative heat transfer where calculations revealed that during the oven exposure test the heat transfer coefficient contained a substantial contribution from radiative heat transfer.

Hatchard *et al.*[2] also developed a model for simulation of the oven exposure test. The model used a simple 1-dimensional energy balance that included the heat generation due to thermal decomposition of the individual active materials. The heat generation rates of the individual active materials (positive and negative) were modeled by kinetic equations that were validated by ARC and DSC studies. The model provided very good quantitative agreement with experimental results (see Fig. 1).

Spotnitz and Franklin[3] generalized the approach of Hatchard *et al.* to consider a wide variety of possible reactions in the battery such as reaction of the binder with the negative active material. Further, an extensive review of available thermal data was compiled and used to prioritize the most important reactions. This work confirmed the view that reactions of the negative gave rise to an increase in temperature, but thermal runaway occurred when the reaction between the positive active material and solvent was activated. Kim *et al.*[4] extended this work to consider 3-dimensional cells and so more precisely identify where thermal runaway initiated (see Fig. 2).

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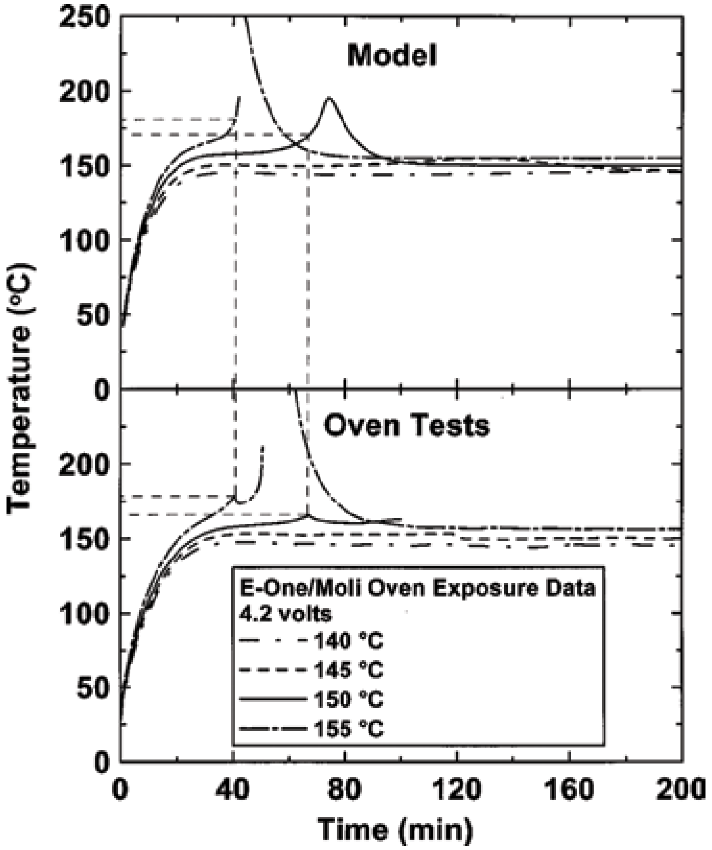

Fig. 1. *Comparison of simulation (top) and experimental (bottom) results for oven exposure tests at various temperatures.*[2]

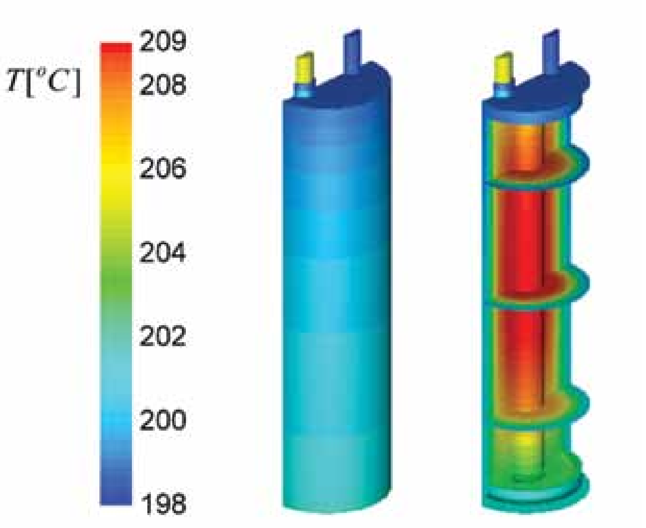

Fig. 2. *Three-dimensional simulation of 155°C oven test for an 18650-size cell.*[4]

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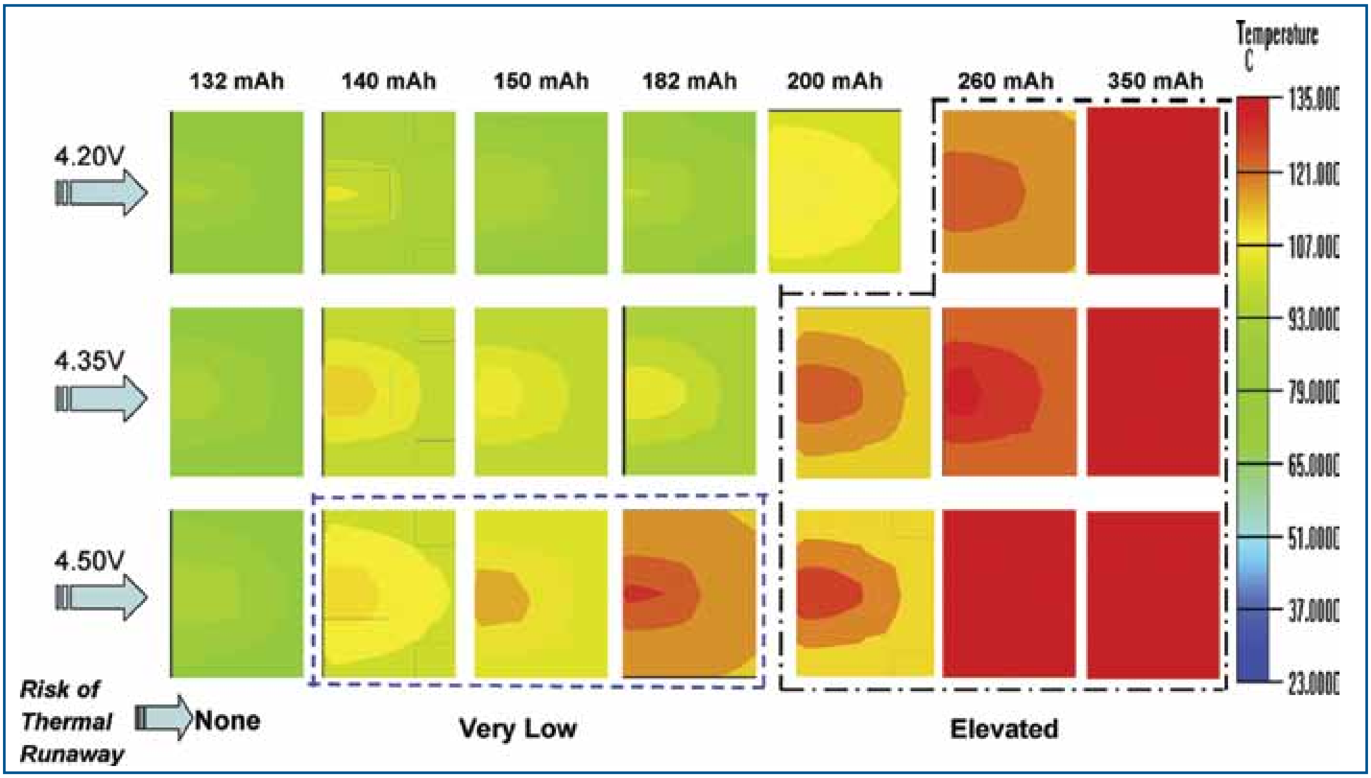

Fig. 3. *Thermal modeling profiles of a 4mm x 4 mm separator surrounding an internal short circuit location. Maximum temperature is set at melting point of polyethylene separator (135°C).*[5]

Around 2005, a large number of safety incidents dealing with thermal runaway of lithium-ion batteries used in laptop computers were reported that resulted in recalls of hundreds of thousands of batteries. The root cause of these safety incidents was traced to the occurrence of internal short circuits. This problem created an urgency to develop methods for identifying the vulnerability of cells to internal short circuits and for preventing internal short circuits. To prevent internal short circuits, Matsushita (Panasonic) introduced "heat-resistant layer" technology. The heat-resistant layer consisted of a porous ceramic coating that served as a thermally stable separator between the electrodes so that at high temperatures (>160°C) where conventional separators lost physical integrity, the heat resistant layer maintained integrity and prevented direct contact between the electrodes. Validating that heat resistant layer actually works has proved challenging. Maleki and Howard[5] have evaluated various experimental techniques for creating internal short circuits and used simulation to help validate their results (see Fig. 3). Their simulation results and experimental data indicate that pouch cells with capacity greater than 250 mAh at ^{3}4.2 Volts are susceptible to thermal runaway by an internal short circuit as temperatures can be reached that exceed the melting point of the separator.

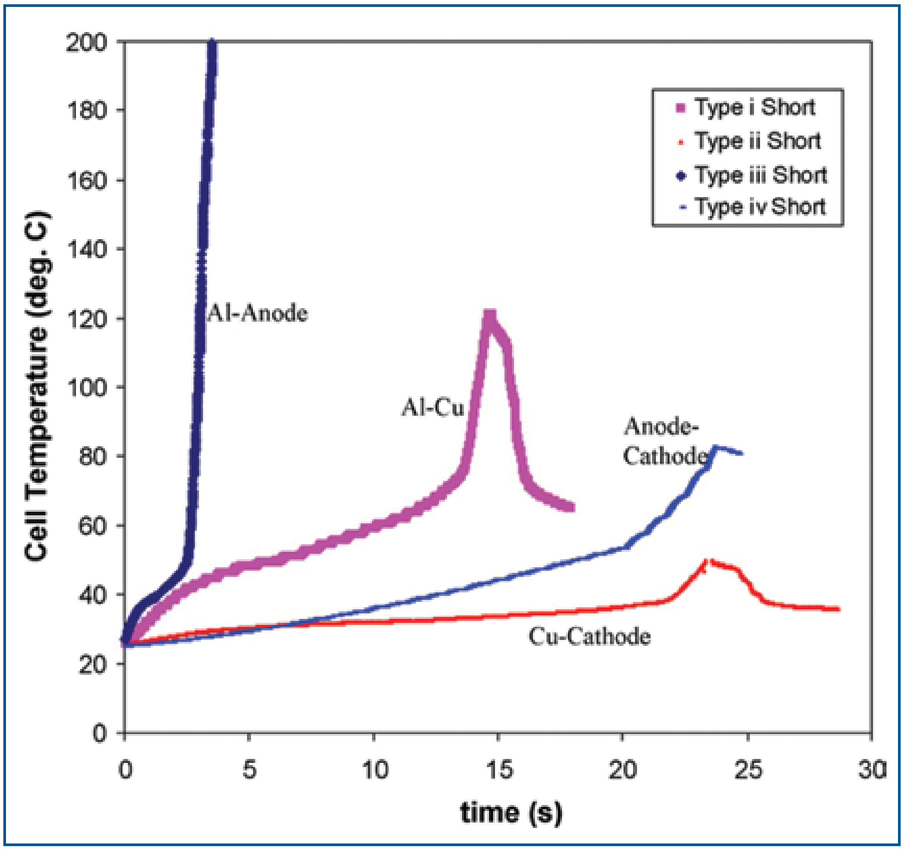

Fig. 4. *Simulation of various types of internal short-circuits in a lithium-ion cell. A short circuit between the positive collector (aluminum foil) and the negative electrode (carbon anode) is most likely to result in thermal runaway.*[6]

Santhanagopalan *et al.*[6] considered the effect of the location of the internal short circuit in spirally-wound cells. They enumerated the various types of internal short circuits that could occur between different components in the battery, that is (1) the aluminum current collector of the positive and the negative active material, (2) the aluminum current collector of the positive and the copper current collector of the negative, (3) the positive and negative active materials, and (4) the positive active material and the copper current collector of the negative. The model indicated that the most dangerous short was when the negative active material contacted the aluminum current collector (see Fig. 4). To prevent this type of internal short circuit, the aluminum current collector can be insulated with tape and this practice is now universally used.

As mentioned above, another major driver for simulation of abuse is the need to design large packs used in automotive applications. The approach used to simulate abuse of small cells[4] can be directly applied to large cells. However when modules or packs are considered, the problem of propagation of runaway emerges. If one cell in a pack goes into thermal runaway, there is a possibility that the heat released can drive neighboring cells into thermal runaway. Since there is some finite probability that one cell could go into thermal runaway, all efforts should be made to design the pack to tolerate thermal runaway of a single cell.

Spotnitz *et al.*[7] suggested an approximate but simple approach to simulate propagation of thermal runaway. The exotherm corresponding to thermal runaway of an individual cell is approximated by a Gaussian curve and one cell in the pack is brought to a temperature to initiate thermal runaway. This approach revealed that propagation could occur depending on the ability of the neighboring cells to dissipate heat. This approach was used by Kizilel *et al.*[8] to demonstrate the safety advantage of using phase change materials in packs. Kim *et al.*[9] showed that the cell interconnects affected the propagation of thermal runaway in modules. The importance of the automotive market has attracted the interest of large providers of Computer Aided Engineering (CAE) software like CD-adapco whose software can account for not only detailed geometry but also convective cooling (see Fig. 5).

At present, efforts are underway to simulate the effect of mechanical impact on batteries[10] (for example see Fig. 6) with the ultimate aim of predicting crash performance of batteries.

In conclusion, simulation has played an important role in both understanding and improving the abuse tolerance of lithium-ion batteries. That major CAE software providers now offer battery simulation software indicates that simulation is becoming a routine part of the battery design process, and that the capabilities will increase over time. ■

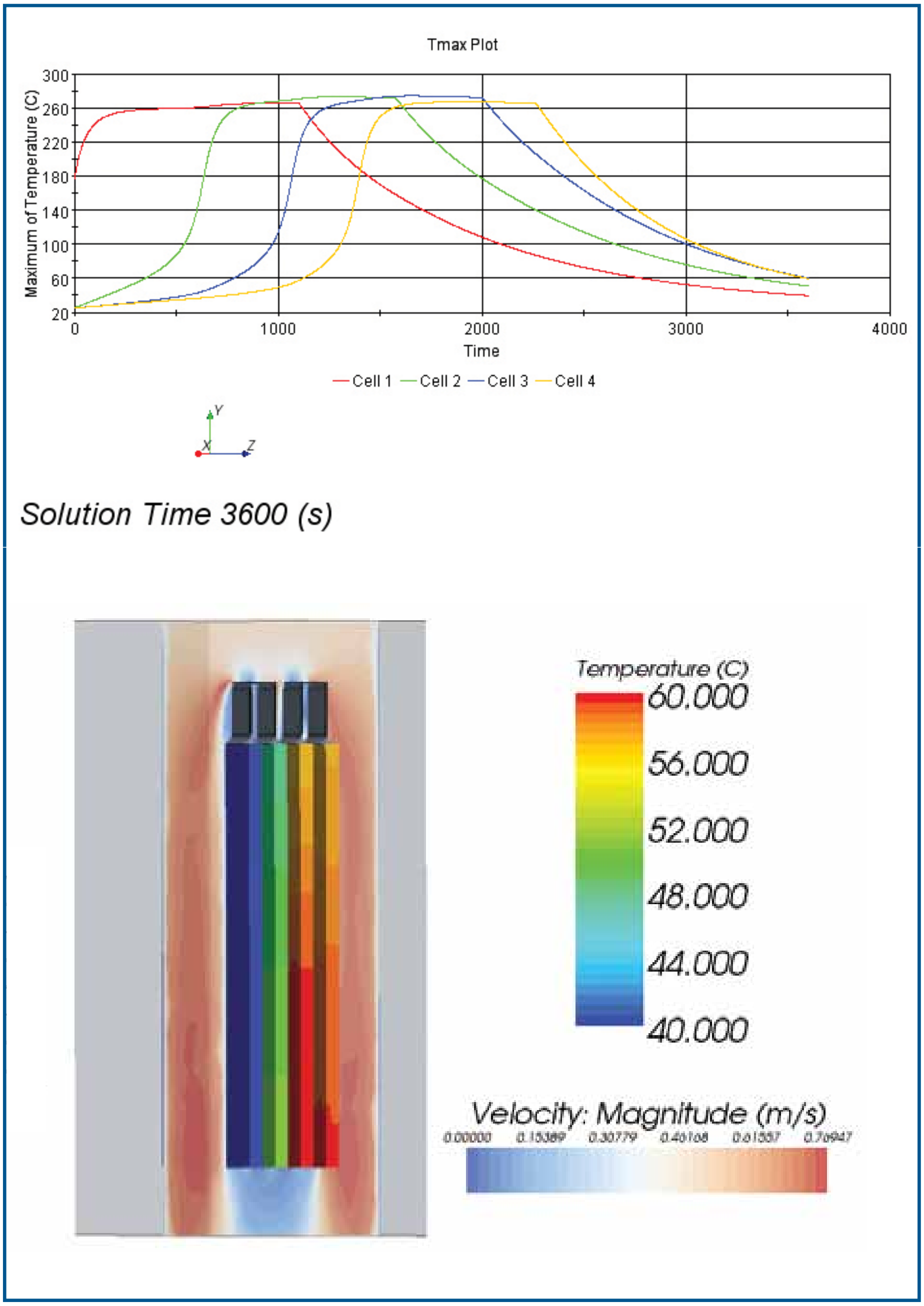

Fig. 5. *Simulation of propagation of thermal runaway. The image shows four cells cooled by forced air. Cell 1 is forced into thermal runaway and the other cells follow. Courtesy of N. Halliday (CD-adapco).*

Acknowledgment

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

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Robert Spotnitz leads Battery Design LLC, a company that provides consulting and software for battery developers and users. He is a well-known speaker on various aspects of battery engineering. After starting Battery Design LLC in 1999, he developed Battery Design Studio®, a virtual environment for battery design and simulation (see www.

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batdesign.com). He has also participated in the start-up of two battery developers: American Lithium Energy Corporation and Enovix Corporation. Before Battery Design LLC, he was a Director at PolyStor where he led efforts to develop lithium-ion batteries for hybrid electric vehicles. Earlier he worked for Hoechst, where he started a battery applications laboratory, and W. R. Grace & Co., where he made several inventions, including the multi-layer battery separator that is widely used today. He received a PhD in chemical engineering from the University of Wisconsin-Madison. He may be reached at rspotnitz@batdesign.com.

Fig. 6. *Simulation of drop test of a Li-ion battery pack. Courtesy of T. Wierzbicki (MIT).*

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