

Improved Safety Lithium-ion Chemistry Development

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R&D

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Abstract

Safer Lithium-ion (Li-ion) chemistries and batteries are needed to support various new high-energy and power applications. Li-ion batteries under abuse conditions can undergo thermal runaway, leading to a battery fire. EaglePicher Technologies has developed a reduced flammability (RF) electrolyte that increases cell safety while maintaining cell performance, including high rate and cold temperature discharge conditions. Cell safety and performance were demonstrated for the RF electrolyte using 26650 cells with a lithium iron phosphate (LFP) cathode and 18650 cells with lithium nickel manganese cobalt oxide (NMC111). Both the LFP 26650 and NMC111 18650 demonstrated improved safety with the RF electrolyte compared to the control cells that use a standard Li-ion carbonate-based electrolyte for the overcharge, overheating and external short tests. 7P2S representative aircraft battery modules subjected to overheating and external short tests did not catch fire when using LFP 26650s with the RF electrolyte. Preliminary results of the RF electrolyte with high Ni (Ni>80%) cathodes will also be presented be highlighted.

Keywords

lithium ion; safety; reduced flammability electrolyte; post suppressant materials

Introduction

Lithium-ion batteries (LIBs) are the most common energy source in many everyday applications such as portable electronics, zero-emission vehicles and renewable energy storage. The global production of LIBs increased one order of magnitude during the 2010s and is expected to do so again in the 2020s. Performance, cost, supply chain stability and safety are current challenges that battery manufacturers are seeking to improve through R&D efforts. Mission-critical defense applications in extreme and harsh environments further require even safer LIBs. This paper focuses on methods to improve the safety of LIBs.

The energy density of mass-produced commercial off the shelf (COTS) Lithium-ion cells has increased threefold from 264 Wh L⁻¹ of the 18650s introduced by Sony in 1991 to 760 Wh L⁻¹ of the 21700s used today in the Tesla Model 3. This substantial increase of energy in the same volume can lead to dramatic safety events when its release

is not controlled. Battery fires have been widely reported by the media and are generally caused by manufacturing defects or misuse. Battery fires are caused by thermal runaway. Thermal runaway occurs when the temperature inside a cell reaches the point that causes an unwanted chemical reaction that produces heat, which propagates further chemical reactions that create more heat eventually causing the cell to deform, vent and in the worst cases fire.

Li-ion batteries are especially prone to thermal runaway events due to their flammable electrolyte. The need for many safety measures could be eliminated by moving to a fully nonflammable electrolyte. However, a nonflammable electrolyte has yet to be commercialized due to difficulties in manufacturing or poor electrochemical performance. For example, attempts to build completely solid cells based on ceramic conducting materials have failed due to the low conductivity of the electrolyte and high interfacial resistance between the electrolyte and electrodes.

This paper will discuss the challenges in incorporating a reduced flammability electrolyte into a Li-ion cell. Cell and module-level electrochemical and safety performance of various Li-ion chemistries using a RF electrolyte will be compared to that of cells with a conventional electrolyte. Finally, additional methods to improve battery safety at the module and pack level will be highlighted.

Reduced Flammability Electrolyte

This paper focused on the inclusion of a RF additive that worked by scavenging free radicals that lead to continuous combustion. Generally, RF additives improve cell safety at the cost of high-rate and cold-temperature performance. The RF additive demonstrated in this work does not suffer from these issues. Additionally, the additive may have improved safety and cycling performance by affecting the solid electrolyte interphase (SEI) composition and uniformity. Finally, the RF electrolyte exhibits a decreased vapor pressure compared to common Li-ion electrolytes.

Figure 1 compares the heat generation using differential scanning calorimetry (DSC) of a RF and a conventional electrolyte used as a baseline (BL). The onset of heat generation is delayed by the RF electrolyte. The total magnitude of heat generated is also decreased by the RF electrolyte.

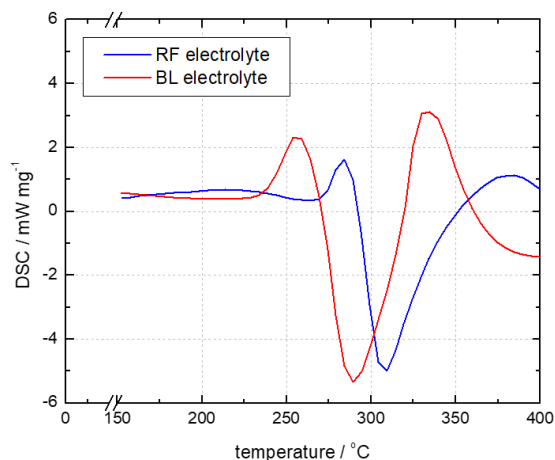


Figure 1. Effect of RF additive on heat generation for electrolytes.

Figure 2 shows the RF electrolyte has no effect on the discharge energy of this same chemistry over the wide temperature range of -20 to 50 °C. The discharge energy is actually improved by 25% at -30 °C most likely due to a thinner, more conductive SEI. Figure 3 shows that the RF electrolyte has no effect on the discharge capacity of 26650 cylindrical cells with a graphite anode and LFP cathode to an 8C rate.

The cells with RF electrolyte all passed the overcharge, overheating and external short circuit tests. Cells without the RF electrolyte often caught fire. 18650s with graphite and NCM111 also demonstrated these same results. The summary of these test are not shown due to space constraints.

Module Level Safety Improvement

The LFP 26650s were then incorporated into a 7P2S module as shown at the top of figure 4. This module is representative of an aircraft battery. The modules, with and without the RF electrolyte, were then subjected to the High-Temperature Test per the S9310-AQ-SAF-01 standard.

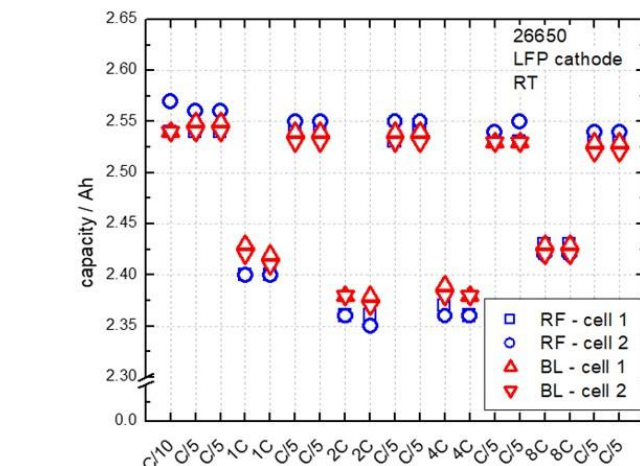
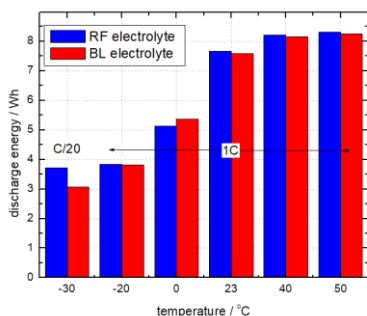


Figure 3. Effect of RF electrolyte on discharge capacity of LFP 26650s at various rates.

The module was heated at a rate of 10 to 20 °C per minute in the presence of a spark emitter. The voltage and temperature profiles of the modules during this test are shown in figure 5. The module with the RF electrolyte-containing cells demonstrated a lower maximum of 200 °C compared to over 300 °C for the BL module. The RF electrolyte also delayed the onset of the module voltage decrease by 20 minutes. The bottom left picture in figure 4 shows the BL module. There is evidence of fire and 13 out of 14 cells vented. The bottom right picture of figure 4 shows the RF module where there is no evidence of fire and only 7 out of 14 cells vented. This demonstrates that safer cells will lead to slower propagation of events between cells and pack thermal runaway.

RF electrolyte with high Ni cathodes

Many new applications require higher energies that cannot be delivered with LFP or NCM111. NMC with Ni content over 70 percent can deliver >25% more energy on an active material basis. However, it is generally considered less safe due to the higher capacity and voltage, as well as the chemical structure.

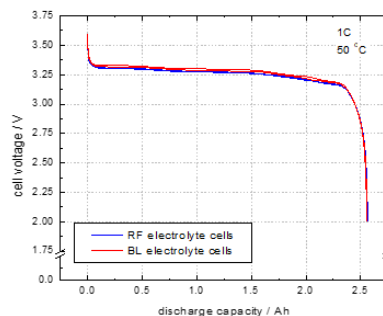


Figure 2. Effect of RF electrolyte on discharge energy of LFP 26650s at various temperatures (left). Discharge curve comparison of LFP 26650s using RF or BL electrolyte.

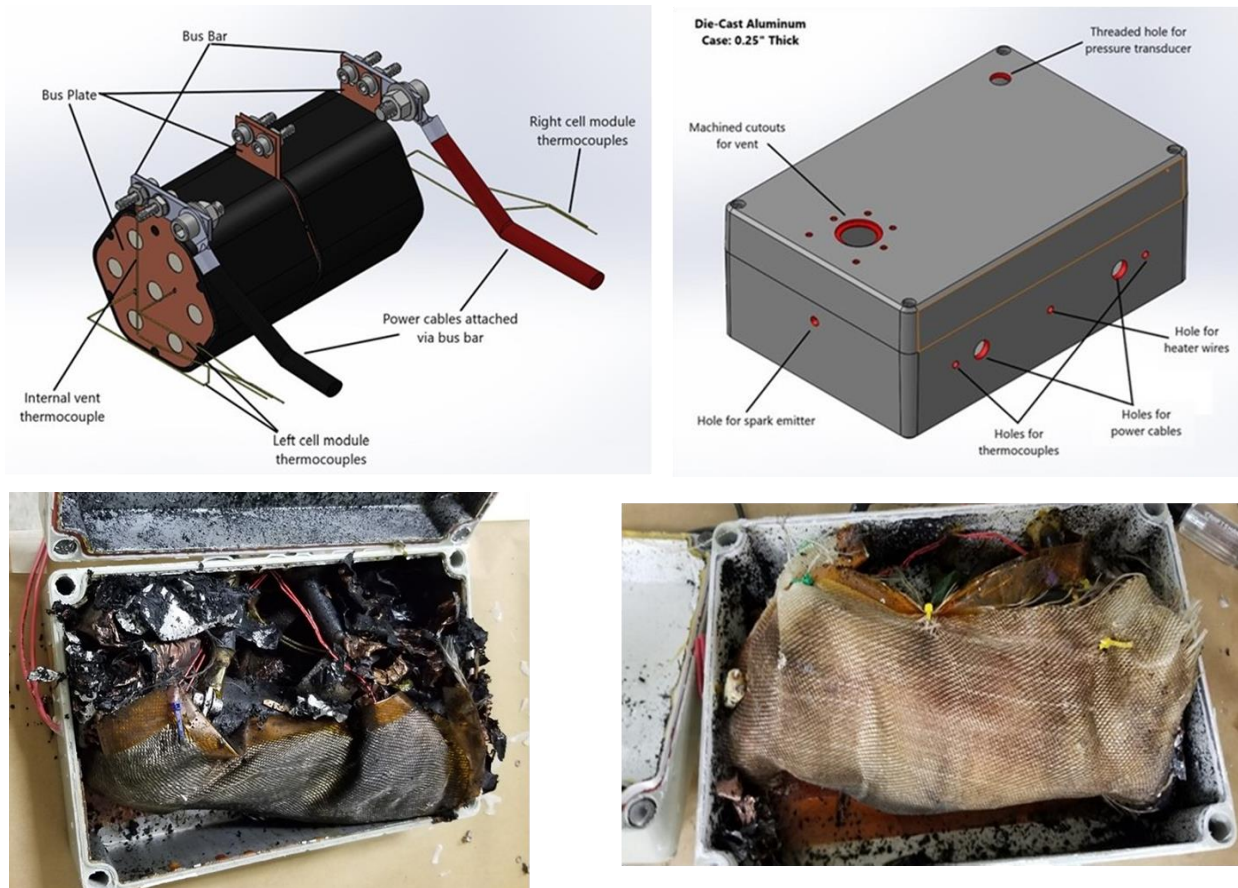


Figure 4. Design drawing of the High-Temperature Test fixture of 7P2S module (top). Picture of the module after the test (bottom)

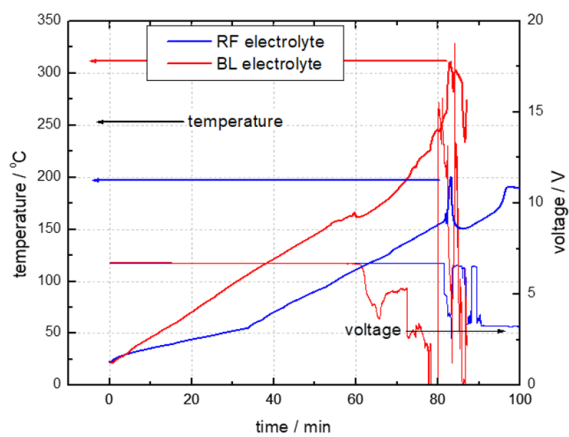


Figure 5. Effect of RF electrolyte on temperature and voltage response of a 7P2S LFP 26650 module during the High-Temperature Test

Initial compatibility of the RF electrolyte with this high Ni cathode is demonstrated by the capacity retention during cycling of 10 Ah pouch cell data in figure 6. The cells with the RF electrolyte demonstrate similar performance to at

least 500 cycles. The safety performance of this chemistry will be presented at the conference.

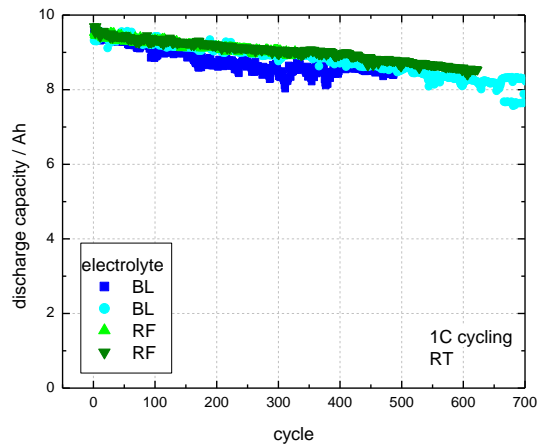


Figure 6. Cycling behavior of RF electrolyte with high Ni cathode.

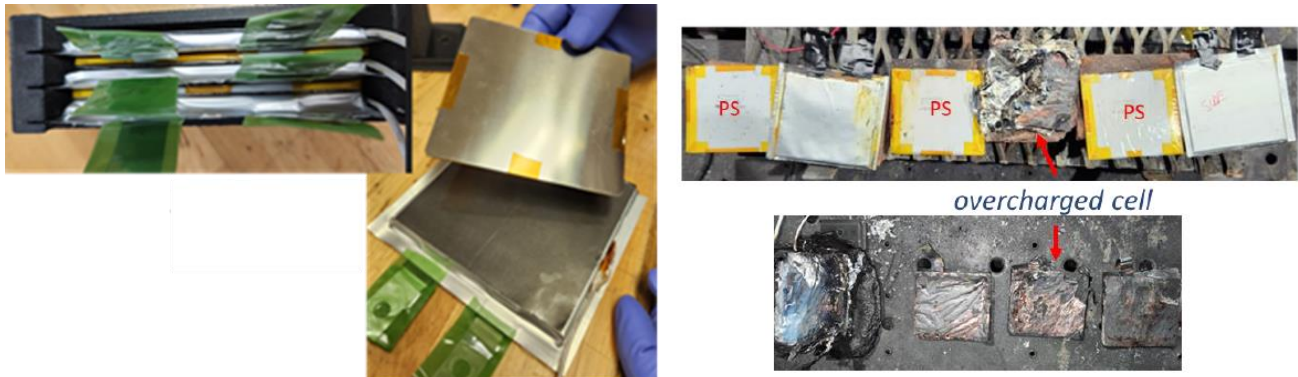


Figure 7. Schematic of 3 cell packs used to demonstrate the PS materials (left). Cells remaining intact after the center cell was forced into thermal runaway in the pack with PS materials (right top). Adjacent cells were completely destroyed in three cell pack without PS materials (right bottom).

Post Suppressant Materials

The RF electrolyte demonstrates improved cell and module safety as part of cell chemistry. Post Suppressant (PS) materials improve pack safety by mitigating propagation between cells after a thermal event has started. Figure 7 shows two different three 10 Ah pouch cell modules. One pack just contained the cells and the other pack had PS materials separating the cells. In each pack, the middle cell was forced into thermal runaway via overcharge. The adjacent cells were destroyed in the pack with no PS materials. The adjacent cells from the pack with the PS materials were able to discharge after the thermal runaway

event. This test shows the merits of PS materials and this will be discussed in more detail at the conference.

Conclusions

The RF electrolyte demonstrates improved cell and module safety as part of cell chemistry in LFP as well as NMC cells. Post Suppressant (PS) materials mitigate propagation in a thermal event. Greater details on both topics will be presented at the conference.

Acknowledgments

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