Consumer Product Safety Commission (CPSC) Staff's Statement on Naval Surface Warfare Center, Carderock Division's (NSWCCD) Report on "Emerging Energy Storage Technologies"
October 2020

The "Report on Emerging Energy Storage Technologies," presents the results of research conducted by NSWCCD for CPSC, under CPSC Contract No. CPSC-I-17-0002. CPSC funded this research to learn about emerging high-energy-density battery technologies and to identify strategies to mitigate the fire hazards related to battery failures. The research focused on technologies with viability for consumer applications.

CPSC staff is using the results to guide future efforts to promote development of safer high-energy-density batteries for consumer applications and possibly to develop recommendations for improvements to standards for batteries and battery-powered products.

Naval Surface Warfare Center
Carderock Division
West Bethesda, MD 20817-5700

Emerging Energy Storage Technologies

by

Gordon H. Waller, Jonathan K. Ko, Thomas H. Hays, and Daphne A. Fuentevilla

NSWCCD-63-TR–2020/39   Emerging Energy Storage Technologies

Emerging Energy Storage Technologies
by

Gordon H. Waller, Jonathan K. Ko, Thomas H. Hays, and Daphne A. Fuentevilla

REPORT DOCUMENTATION PAGE		*Form Approved* *OMB No. 0704-0188*
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Richmond Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**		

1. REPORT DATE *(01-29-2019)* 10-09-2020	2. REPORT TYPE Technical Report	3. DATES COVERED *(From - To)* 10/01/18 – 9/30/19
4. TITLE AND SUBTITLE Emerging Energy Storage Technologies		**5a. CONTRACT NUMBER** CPSC-I-17-0002
		5b. GRANT NUMBER N/A
		5c. PROGRAM ELEMENT NUMBER N/A
6. AUTHOR(S) Gordon Waller, Jonathan Ko, Thomas Hays, and Daphne Fuentevilla		**5d. PROJECT NUMBER** N/A
		5e. TASK NUMBER N/A
		5f. WORK UNIT NUMBER N/A
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) AND ADDRESS(ES) Expeditionary Power and Energy Branch, Naval Surface Warfare Center Carderock Division 9500 MacArthur Blvd, Bldg. 11 West Bethesda, MD 20817		**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S Consumer Product Safety Commission 4330 East West Hwy, Bethesda, MD 20814		**10. SPONSOR/MONITOR'S ACRONYM(S)** CPSC
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) N/A

12. DISTRIBUTION / AVAILABILITY STATEMENT
DISTRIBUTION A. Distribution unlimited.

13. SUPPLEMENTARY NOTES
N/A

14. ABSTRACT:

This report summarizes various rechargeable battery technologies with a particular emphasis on lithium-ion batteries (LIB), which are commonly used in consumer electronics applications of all sizes. A main limitation of lithium-ion batteries is their relatively poor safety compared to other technologies. Methods to mitigate safety issues are described. Technologies covered in this report include lithium-ion alternatives, modifications to lithium-ion active and passive components, packaging materials, which can prevent cell-to-cell propagation and "early failure detection" technologies, which monitor the state of health of LIB and prevent unsafe scenarios.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF: UNCLASSIFIED			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. RESPONSIBLE PERSON Gordon Waller
a. REPORT UNCLASSIFIED	b. ABSTRACT UNCLASSIFIE	c. THIS PAGE UNCLASSIFIE	N/A	61	19b. TELEPHONE NUMBER 301-227-1649

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

CONTENTS

FIGURES

TABLES

ADMINISTRATIVE INFORMATION

EXECUTIVE SUMMARY

This report summarizes academic and industrial trends in the field of energy storage which have particular relevance to the Consumer Product Safety Commission (CPSC), namely in their application to consumer electronics. Lithium-ion batteries (LIB) have grown to dominate the consumer electronics field due to their high energy density, good cycle life, and falling prices. However, the high energy density that makes LIB desirable also introduces safety concerns, especially for devices that are designed with minimal or no protective packaging or circuitry. The contents of this report are divided into two categories. First, a survey of energy storage technologies including state-of-the-art lithium ion batteries as well as an introduction to emerging technology areas which may one day compete with or replace LIB in consumer electronics. In particular, technologies that may influence the safety of energy storage of consumer electronics devices, such as the use of lithium metal or solid-state electrolytes, are discussed in more detail. In the second part of the report, "early failure detection" technologies are discussed. In this section, technologies that can help mitigate the safety drawbacks of LIB are described and their relative technical maturity is discussed. Several technologies are discussed in both categories of the report, however the overall conclusion from the authors of this report is that LIB are likely to maintain if not increase application in consumer electronics. For this reason, the safety of these devices may have to be engineered through secondary technologies which may or may not be suitable for small, low cost applications.

ACRONYMS

A	Amperes (electrical current)
Ah	Capacity, in Ampere-hours
ARPA-e	Advanced Research Project Agency - Energy
BITS	Battery Internal Temperature Sensor
BMS	Battery Management System
COTS	Commercial Off-The-Shelf
DAQ	Data Acquisition System
EIS	Electrochemical Impedance Spectroscopy
INL	Idaho National Lab
JHUAPL	Johns Hopkins University Applied Physics Lab
kWh	Electrical energy, in kilo-Watt hours
LIB	Lithium Ion Battery(ies)
LCO	Lithium Cobalt Oxide
LFP	Lithium Iron Phosphate
LTO	Lithium Titanium Oxide
NASA	National Aeronautics and Space Administration
NCA	Nickel Cobalt Aluminum cathode material
NREL	National Renewable Energy Laboratory
NRL	Naval Research Laboratory
NSWC	Naval Surface Warfare Center
NSWCCD	Naval Surface Warfare Center, Carderock Division
OCV	Open Circuit Voltage
RIB	Rapid Impedance Box
RRTO	Rapid Reaction Technology Office
RTSD	Real Time Short Detector
SBIR	Small Business Innovative Research
SEI	Solid Electrolyte Interphase
SSB	Solid State Batteries
SOC	State Of Charge
SOH	State Of Health
SOS	Sum-Of-Sines
V	Electrical Voltage, in Volts
W	Electrical power, in Watts
Wh	Electrical energy, in Watt-hours

This page intentionally left blank.

1. Introduction

Energy storage technologies for portable electronics and consumer devices are in most instances electrochemical cells, or as commonly referred to, batteries. Battery technologies for civilian and consumer applications include many cell sizes and configurations but generally utilize an alkaline chemistry (i.e. Zn anode, MnO_2 cathode, and KOH electrolyte) for primary (non-rechargeable) applications. Secondary (rechargeable) variants including lead-acid (Pb anode, PbO_2 cathode, and H_2SO_4 electrolyte), nickel-metal hydride (Metal hydride anode, $Ni(OH)_2$ cathode, and KOH electrolyte), and lithium-ion (graphite anode, lithium transition metal oxide cathode, and organic solvent electrolyte with lithium salt). In this report, we describe the commercial state of the art and current research trends in the area of secondary electrochemical cells which are common in consumer devices ranging in size from a ~1 Wh found in a wearable "smart watch" to hundreds of kWh in an electric vehicle. For these applications, lithium-ion batteries are the clear leader due to superior energy density and cycle life compared to common alternatives. Some of these properties are summarized in Table 1 (1). Note that the properties highlighted in Table 1 are typically not maximized simultaneously for a single cell design, and cycle life assumes a 100% depth of discharge. Furthermore, the relative cost for each battery technology reported in Table 1 are in reference to the frequently emphasized "$/Wh" figure or simply the cost of the device divided by the nameplate energy content, whereas cost values which include the number of useful cycles for a given application can result in lithium-ion batteries becoming cost-competitive with other technologies. While lithium-ion batteries have clear advantages for energy intensive applications, these are the only rechargeable batteries in Table 1 utilizing a non-aqueous electrolyte. Because of the inherent safety risks of the organic solvent electrolyte used in lithium-ion batteries there has been increasing concern over the potential for catastrophic battery failures. Exploring methods to improve the safety of high energy rechargeable batteries is a focal point of this report. The information in this report was obtained through a combination of literature review, hands-on evaluation of batteries and associated technologies, and subject matter expertise of the authors. Wherever appropriate, references are cited, however, the citations provided are by no means an exhaustive survey of all available literature.

Table 1 Selected Properties of Commercially Available Rechargeable Batteries

Property	Lead-acid	Nickel-metal hydride	Lithium-ion
Specific Energy (Wh/kg)	10-40	47-110	100-270
Energy Density (Wh/L)	50-90	177-430	570-700
Nominal cell voltage (V)	2.0	1.2	3.6-3.8
Cycle life	200-700	500-1000	1000-3000
Relative cost ($/Wh)	Low	Medium	High

2. Energy Storage Technologies

2.1 Lithium-ion batteries

2.1.1 Key features

Lithium-ion batteries (LIB) have the greatest specific energy (Wh/kg) and energy density (Wh/L) of any rechargeable energy storage technology available today, and for this reason have experienced a rapid growth in many application spaces since they were first introduced in the early 1990s. All commercial LIB utilize intercalation or insertion type electrodes in which lithium-ions are inserted and removed from atomic scale "gallery space" present in the host material (2). This arrangement is very effective for achieving a high coulombic efficiency, which is simply the ratio of charge released during discharge through a load to charge stored in a cell during charge. LIB can demonstrate coulombic efficiencies exceeding 99.5%, whereas battery chemistries which utilize formation reactions (i.e. the precipitation of a new phase during cycling, which includes both Ni-metal hydride and lead-acid) tend to be less efficient. The first LIB utilized a graphite anode and a $LiCoO_2$ (LCO) cathode. As shown in Figure 1, both graphite and several lithium transition metal oxides with the formula $LiMO_2$ (where M is the transition metal cation) have a layered gallery space allowing for lithium-ion intercalation (3). While simplistic, Figure 1 is a fairly accurate depiction of the crystal structure for many electrodes used in modern LIB.
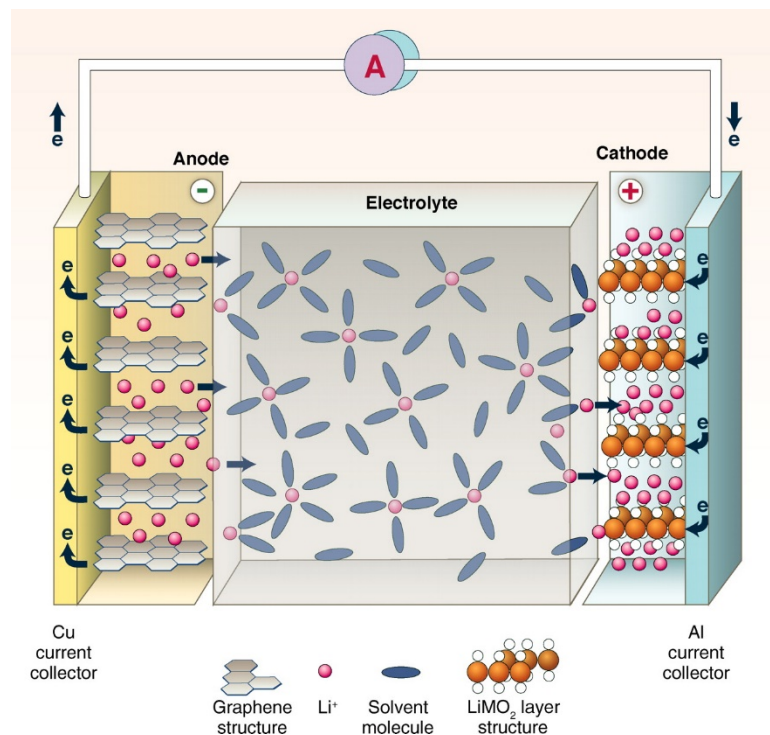
Figure 1 Schematic depicting a lithium-ion battery during discharge

The organic electrolyte in a LIB allows for the use of electrode active materials with electrochemical potentials outside of the limits of water based electrolytes which restricts cell voltages to ~2V and below. Conversely, LIB have a nominal voltage between 3V and 4V, with

some newer variants approaching 5V when fully charged. LIB electrolytes typically consist of a mixture of carbonate ester solvents (e.g. ethylene carbonate, dimethyl carbonate, diethyl carbonate, propylene carbonate and many derivatives), a lithium salt (e.g. lithium hexafluorophosphate, lithium perchlorate, lithium bis(trifluoromethanesulfonyl)imide), and various additives. Unlike water-based electrolytes, the solvents used for LIB electrolytes are flammable and as a result can greatly contribute to the energy released during cell failure. Furthermore, the high operating potential of LIB can lead to decomposition of the electrolyte through oxidation at the positive electrode and reduction at the negative electrode. This decomposition can in fact be beneficial for the lithium-ion battery, as encouraging the formation of the solid electrolyte interphase (SEI) layer at the anode through electrolyte selection was a critical step in the development of LIB. The first commercialized LIB utilized a graphite anode, which as shown in Figure 2 lies nearly 1 V outside of the lower potential limit of a typical LIB electrolyte (2).
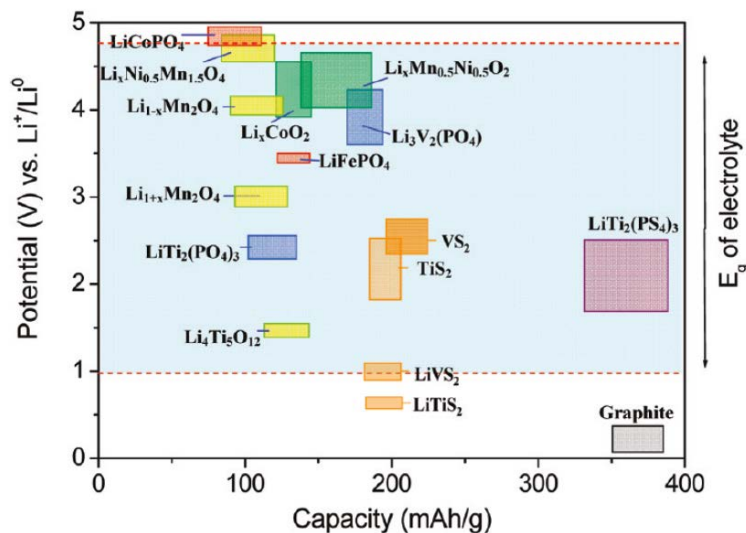
Figure 2 Voltage and capacity of several LIB electrode materials relative to the voltage stability window of 1M $LiPF_6$ salt in EC/DEC (1:1) solvent

Several decades of study of the SEI, initiated in large part by Peled et al., has revealed that on anodes operating below the reduction potential of a LIB electrolyte the SEI is a composite film containing organic and inorganic products of electrolyte reduction (4). Stability of the SEI is a hallmark of modern LIB and is an absolute requirement for any new anode materials, most notably non-intercalation based materials.
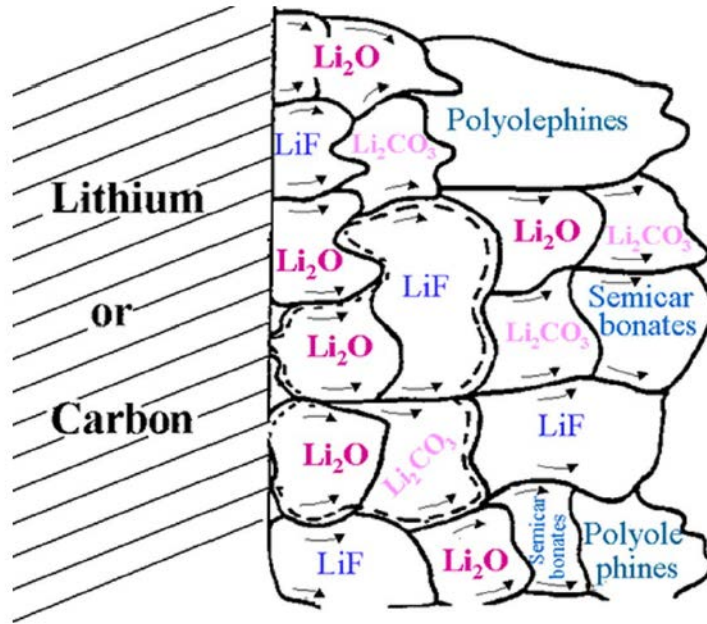
Figure 3 The Peled model of the solid electrolyte interphase

2.1.2 Commercial state-of-the-art

As described in the previous section, all commercial LIB utilize an organic solvent and intercalation based anode (graphite) and cathode (lithium transition metal oxide). Furthermore, all commercial LIB contain electrolyte additives, which improve the properties of the SEI, without which the 1000+ cycles referenced in Table 1 would be impossible. While LCO cathodes and graphite anodes are still commonly used for many applications, a few other cathode and anode options are used commercially as summarized in Table 2 (5). The selection of a cathode or anode material is largely driven by whether the envisioned application requires a maximized energy density or power density. In most cases, cells designed for applications requiring high power have lower energy density by a factor of 2-3 compared to cells designed for high energy. This is particularly evident in cells utilizing either LFP cathodes or LTO anodes which have lower and higher nominal voltages than alternative cathode and anode materials, respectively. Both LFP and LTO based cells are capable of extremely high-power operations with sustained current densities in excess of a 10C rate (6 minutes for complete discharge), but usually have a lower specific energy of around 100 Wh/kg. LTO also has a key advantage over graphitic anodes in that it's higher operating voltage, while lowering energy density, allows for high power charging (i.e. "fast charging") without concern for lithium plating on the anode surface. Other factors, such as the raw materials cost and global availability are more heavily considered for large format applications like electric vehicles. In particular, the availability and cost of cobalt is one reason electric vehicles have shifted away from LCO cathodes, however due to the large production volumes some references suggest LIB utilizing LCO cathode are in fact the cheapest available in terms of $/kWh (6).

Table 2 Capacities, voltages, and application of commercialized LIB electrode materials

Material	Typical Capacity (mAh/g)	Nominal Voltage (V vs. Li)	Applications
$LiCoO_2$ (LCO, cathode)	145	3.8	Moderate energy / moderate power
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA, cathode)	200	3.7	High energy / moderate power
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM333, cathode)	170	3.7	High energy / moderate power
$LiMn_2O_4$ (LMO, cathode)	120	4.1	High power
$LiFePO_4$ (LFP, cathode)	165	3.4	High power
$Li_4Ti_5O_{12}$ (LTO, anode)	150	1.55	High power – high power charge possible
LiC_6 (graphite/carbon, anode)	350	0.1	All applications – high power discharge only

LIB are available in many capacities and geometric configurations. The internal components of all cell types are virtually identical, consisting of foil current collectors (aluminum for the

cathode and copper for the anode, except in the case of LTO which can also use an aluminum current collector due to its high operating potential) coated with a composite film of active material, polymeric binder, and conductive additive (usually carbon black), and a polymeric separator (1). Flat cells, either packaged in flexible polymer pouches (pouch cells) or in rigid metal cans (prismatic cells) are produced with a wide range of dimensions, and are often designed specifically for a certain product in order to maximize the packing density of cells into the available space. As shown in Figure 4, electrode sheets in flat cells can be wound, however stacked or folded configurations, which allow the distance from the active film to the cell terminals to be minimized are also utilized (7). The electrode winding includes at least one positive and one negative current collector, but may include multiple current collecting tabs welded onto the current collecting foil to improve current distribution during high-rate operation. Improvement in pouch cell designs has enabled the development of very thin portable electronics, namely smart phones and tablet computers. Through these improvements, pouch cells for smartphones have energy densities as high as 750 Wh/L.
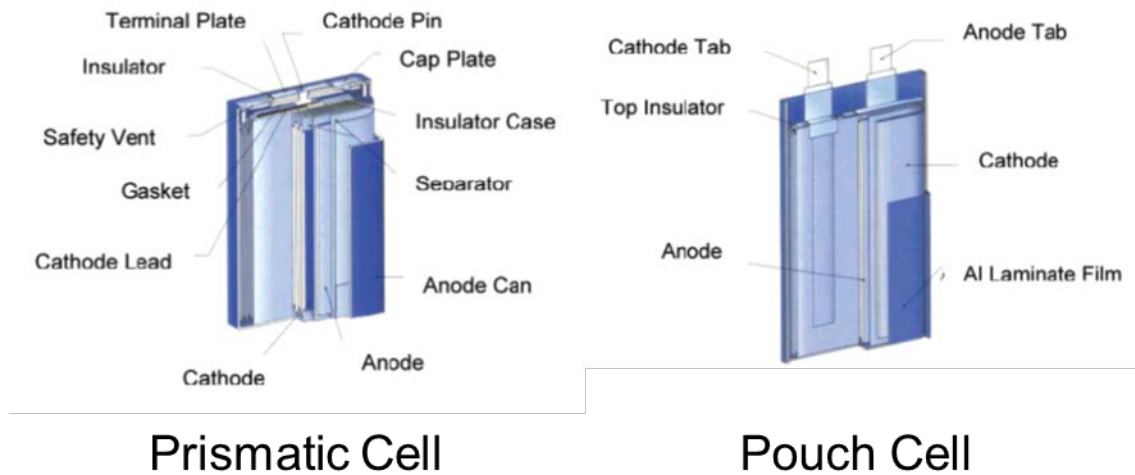
Figure 4 Prismatic and pouch cell construction used for LIB

Cylindrical cells, specifically those with the "18650" standard size (18 mm diameter and 65 mm length) are common in many applications and have become one of the most widely produced cell types used in battery packs for many applications. As shown in Figure 5 cylindrical LIB cells have a wound "jelly roll" electrode structure (7). Like with prismatic and pouch cells, cylindrical cells can have multiple current collecting tabs, which is common for high power cells, while low-rate cells designed for high energy may only have one positive and one negative tab on opposing ends of the jellyroll winding.
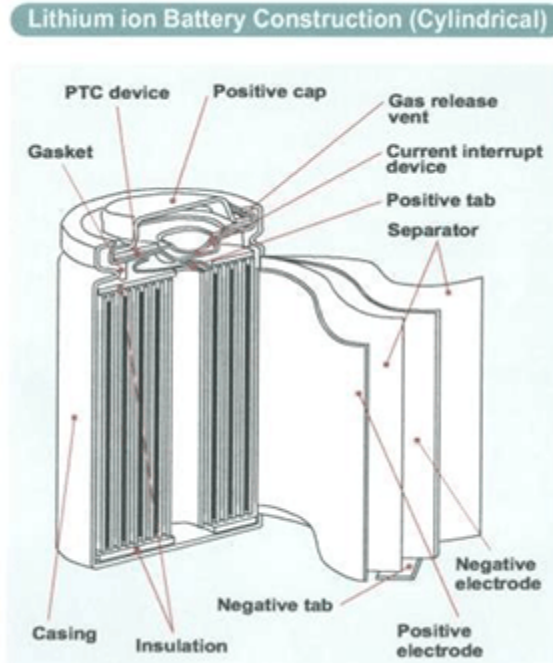
Figure 5 Cylindrical cell construction used for LIB

Cylindrical cells often include many passive safety features usually located in the top cap of the cell. Two common examples are the positive temperature coefficient or "PTC" device and the current interrupt device or "CID", as shown in Figure 5. The PTC is activated by an over-current event, usually caused by an external short circuit through a low resistance pathway, which rapidly heats the PTC (8). Above a critical temperature, the electrical resistivity of the PTC greatly increases thereby preventing a rapid temperature rise in the rest of the cell. When cooled, the PTC can revert to the lower resistivity state and allow the cell to continue to pass current. Conversely, the CID is an irreversible mechanism in which an open-circuit is formed within the cell in response to increased cell pressure. A schematic depiction of a pressure activated CID is shown in Figure 6, in which the aluminum burst disc is forced upward by increasing pressure inside the cell can (7). As a result, the electrical contact between the cathode lead and the top of the can (the positive terminal) is lost.

(a) Prior to operation   (b) After operation
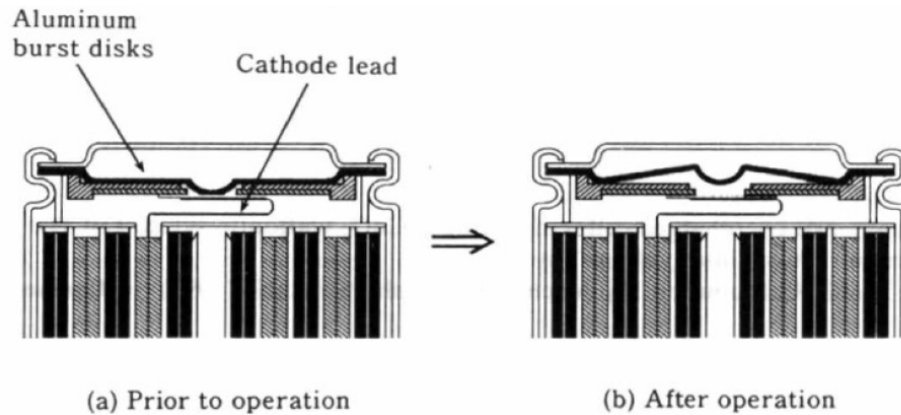
Figure 6 Schematic depiction of CID activation

Pressure rise inside the cell can be due to temperatures exceeding the specifications for use causing an increase in the electrolyte vapor pressure, or from the generation of gas due to electrochemical abuse such as an overcharge, which causes the electrode potentials to exceed the electrolyte stability window as discussed in section 2.1.1. Several designs of CID are used, however all result in a loss of cell functionality and the inability to read voltage or pass current through the cell. Safety vents are also typically included in the top cap, or in some newer cell constructions both on the top and bottom ends of an 18650 sized cell (9). Like the CID, opening of safety vents are pressure related, irreversible, and render the cell unusable.

The energy content of an 18650 cell is one method used to benchmark the increasing energy density of the LIB chemistry. As shown in Figure 7 specific energy has more than tripled since the commercialization of the 18650 sized cell (7). For the first two decades of 18650 LIB, the originally introduced LCO cathode // graphite anode chemistry was relatively unchanged. Consequently, improvements in 18650 energy content were the result of steady optimizations of the internal cell components, specifically reduced thicknesses of the separator, current collector foils, and cell can as well as improved electrode coatings and electrolyte stability which resulted in a roughly linear increase in energy density over time. More recently, improvements to the electrode materials, specifically the incorporation of small amounts of Si in the anode, have allowed for a continued increase in energy density.
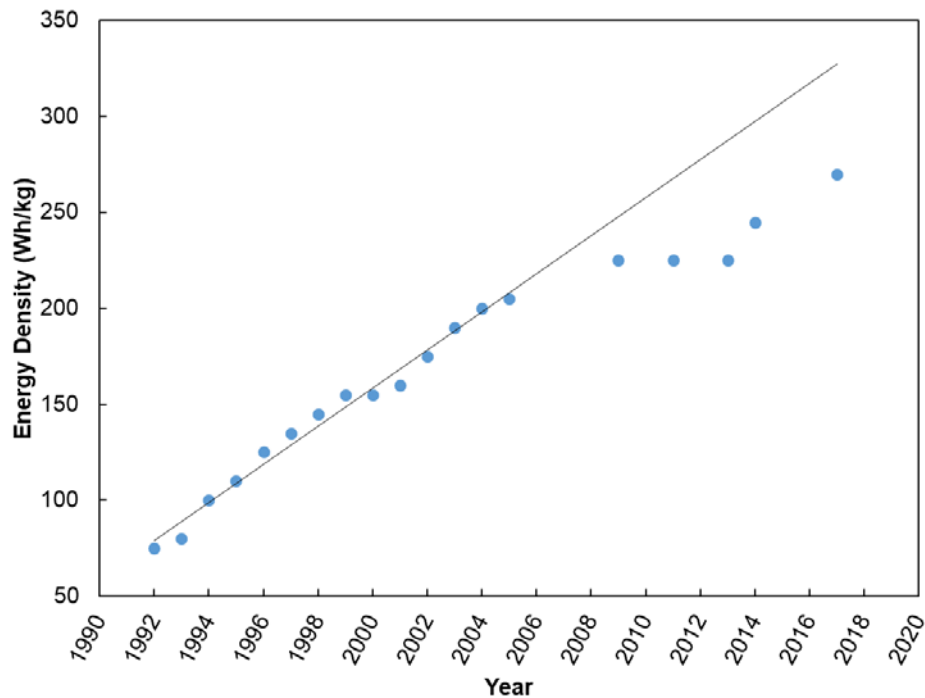
Figure 7 Energy Density of LIB in 18650 Sized Cylindrical Cell

2.1.3 Literature trends

Recent research into improving the performance of lithium-ion batteries has focused primarily on developing new or modified anode, cathode, and electrolyte materials. Research into advanced cathode materials has emphasized "high voltage" compounds which have nominal voltages vs. Li approaching or exceeding 5 V, in contrast to those around 4 V and below shown in Table 2 (10). Because the anode potential is already near 0 V vs. Li/Li+, increasing the cathode potential is the only option to increase the operating potential of the cell and thereby improve the overall cell energy density. While several factors including crystal structure and processing route can contribute to the observed operating potential of an electrode material, for lithium transition metal oxides like those listed in Table 2 the species and oxidation state of the transition metal cation is often the key determinant as shown in Figure 8 (11). An important consequence of increasing the operating potential of the cathode is that this can lead to decomposition of the electrolyte at the cathode surface, which does not necessarily form a protective SEI analogous to that formed on the anode (12). In fact, the electrolyte decomposition products formed at the cathode can migrate through the electrolyte to chemically degrade the anode SEI and generate excessive gas buildup when fully charged. For this reason, incorporating a high-voltage cathode material into an existing LIB design also requires modifying the electrolyte. In COTS cells, the electrolyte solution has been optimized for graphitic anodes, which limits the applicability of high voltage cathode materials as a "drop in" replacement for existing cathode materials.
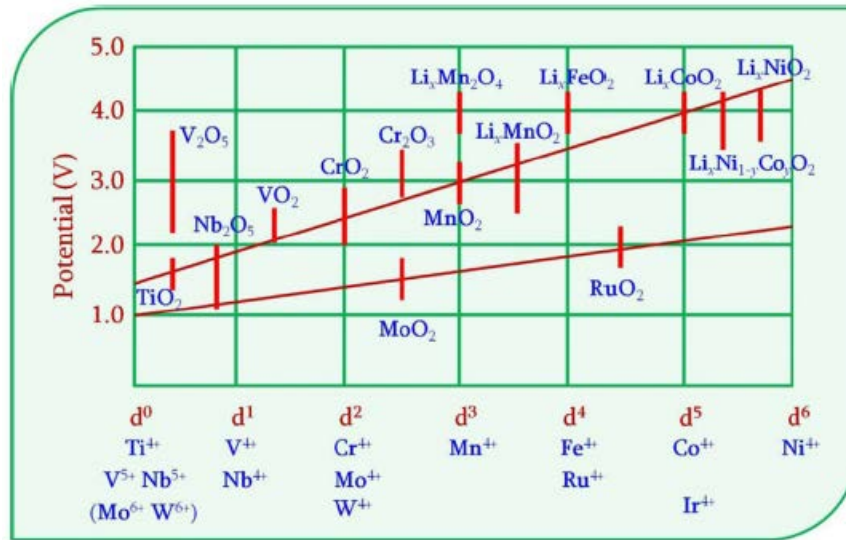
Figure 8 Relationship between operating potential and transition metal species for lithium-ion battery electrodes

Cation mixing or doping in layered type lithium transition metal oxides, of which $LiCoO_2$ is the prototypical example, has been another effective way to improve cell energy density by increasing the available charge storage capacity of the cathode. Based on the molecular mass of $LiCoO_2$ and the charge associated with 1 mole of Li^+ ions, the theoretical capacity of $LiCoO_2$ is 275 mAh/g, however, in practice only about half of this capacity can be reversibly cycled resulting in an effective capacity of 145 mAh/g (Table 2). Extracting more than half of the Li^+ cations leads to instability in the remaining CoO_2 structure and a resulting rapid capacity fade. Decades of investigations have found that solid solutions between $LiNiO_2$, $LiMnO_2$, and $LiCoO_2$, as well as the insertion of non-transition metal cations such as aluminum, can improve the specific capacity of the layered type lithium transition metal oxide to above 200 mAh/g. As shown in Figure 9, layered compounds in which Ni constitutes the majority of the transition metal content (referred to as "nickel rich") offer more capacity than LCO, however, these compounds have correspondingly lower thermal stability and worse capacity retention in comparison to compounds with more manganese and cobalt (5) (13). Several academic works have demonstrated that cathode materials with composition variation at the micron to nanometer scale, such as core-shell or continuous gradient particles, can combine the desirable properties of a Ni rich core while maintaining the stability of Mn and Co rich outer layer.
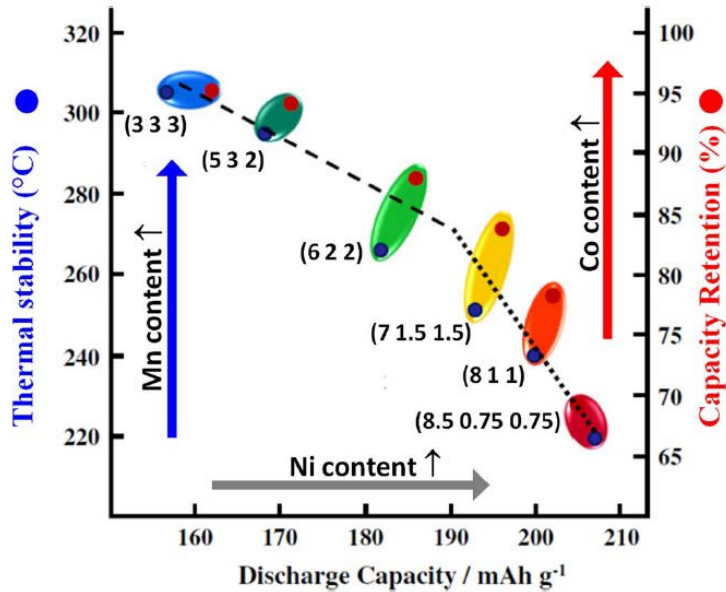
Figure 9 Comparison of thermal stability, discharge capacity, and capacity retention of Li(Ni$_x$Mn$_y$Co$_z$)O$_2$ compounds with varying composition

Conversion based electrode materials, which were briefly mentioned in section 2.1.1 in reference to the formation reactions occurring in Ni-metal hydride and lead-acid batteries, are another area of heavy research activity. In contrast to intercalation materials, which includes all of the transition metal oxide compounds discussed to this point as well as graphite, conversion materials involve the formation and dissolution of a structurally and or physically distinct phase during the charge and discharge process. This can be achieved through alloying with a starting compound or by precipitation of a completely new phase from components in the electrolyte. As shown in Figure 10 the conversion reaction mechanism allows for a much larger charge storage capacity compared to those compounds limited to intercalation, but tend to have less desirable operating voltages (i.e. lower voltages for cathodes and higher voltages for anodes) (5).
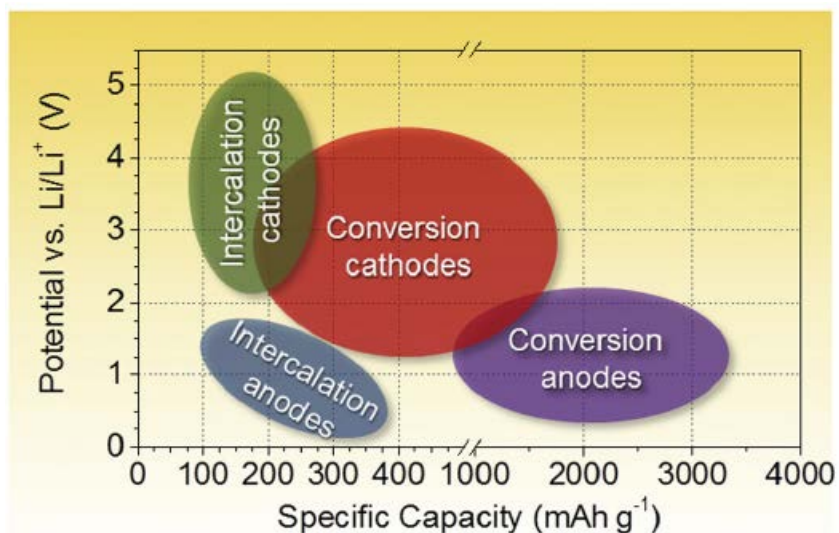
Figure 10 Comparison of typical discharge potentials and specific capacities for intercalation and conversion-based anode and cathode materials in lithium batteries

While several compounds are capable of undergoing formation reactions with lithium, two have been highlighted as the most promising: silicon-based anodes and sulfur-based cathodes. Silicon and sulfur both have the advantage of a very high theoretical capacity when completely reacted with Li – 1675 mAh/g for sulfur and 3579 mAh/g for silicon, and are considered as potentially inexpensive alternatives to current electrode materials (5). However, both materials have significant challenges that have yet to be addressed, namely, very poor cycling efficiency and a high rate of capacity loss. In silicon based anodes, a large volume expansion accompanies the lithiation and delithiation of the anode, which can lead to cracking or pulverization of anode particulates, delamination of electrode films, and continuous growth of the SEI, all of which conspire to reduce the available capacity of the cell (Figure 11) (14). For sulfur-based cathodes, volume expansion is also a significant issue, and in addition, some of the discharge products (polysulfides) are soluble in conventional LIB electrolytes. Another limitation of sulfur and some other conversion-based cathodes (e.g. transition metal fluorides) is that they are lithium free, which necessitates that lithium is available at the anode when the cell is assembled. In a laboratory setting, this is easily achieved by using a lithium metal anode with excess capacity, however, in a practical device lithium metal is extremely difficult to implement. Commercial cells are typically assembled in the discharged state with lithium being present only on the cathode side instead of the anode side. Several methods of anode "pre-lithiation" which would allow for high capacity lithium-free cathode materials have been explored, however, none of these techniques have been commercialized. While plausibly a pre-lithiation step would not influence the final function or capabilities of a LIB, this process is a significant deviation from the high-throughput manufacturing processes used for today's LIB, and, therefore, would be expected to be a major impediment to commercialization of these materials.
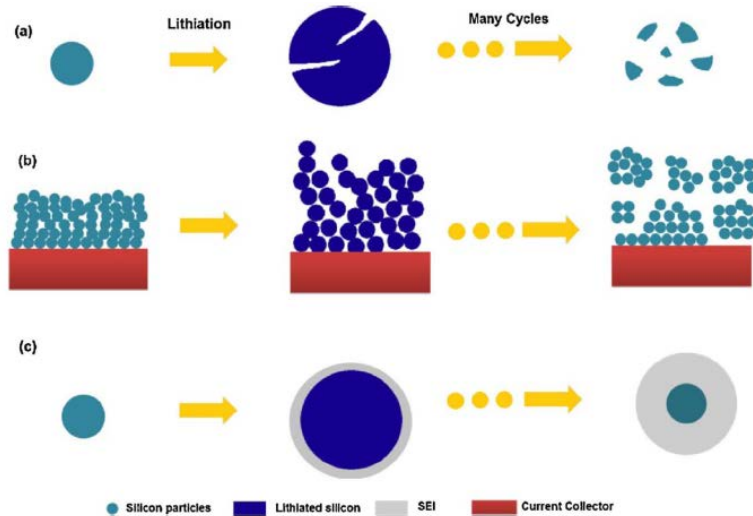
Figure 11 Schematic depiction of capacity loss mechanisms in silicon anodes due to active particle pulverization (a), delamination of the electrode film (b), and continuous growth of the SEI (c)

While the mechanisms for this poor performance are different for the anode and the cathode, a commonly pursued mitigation strategy is through reducing the utilization of the active material by careful cell balancing (i.e. adjusting the capacity ratio of the anode and cathode such that one electrode is limited). Other strategies are based on the incorporation of inactive materials into the electrode composite intended to compensate for the large volume expansion of the active materials (often referred to as encapsulation), and the nanoscale geometry control of active materials to avoid particle fracture. These approaches have been particularly effective at improving Si based anodes, and as a result, several companies have attracted millions of dollars in public and private funding with reported successful tests of improved energy density cells containing some fraction of Si in the anode. Recent reports from the Department of Energy highlight the expected future role of conversion based materials in driving down battery costs in electric vehicles (Figure 12), however, the practical limitations of conversion based electrode materials will likely yield only modest improvements in the foreseeable future (15) (16). While commercialization of cells with anodes containing a small fraction of Si has already begun (Figure 7), a silicon dominant anode, which demonstrates superior energy density to conventional graphite anodes while maintaining good cycle life and reasonable cost requires further development.
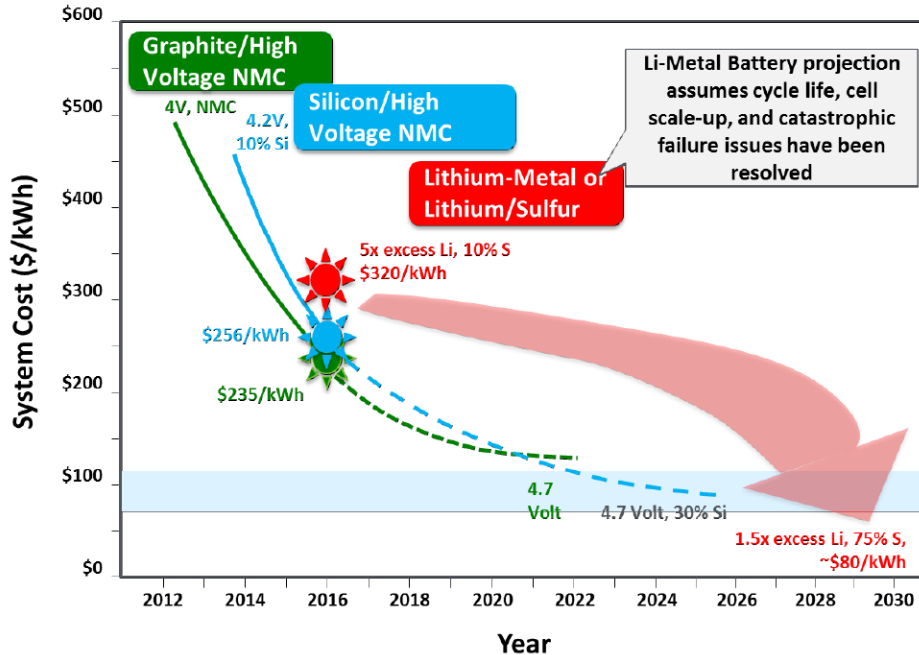
Figure 12 DOE Projections for cost reduction of LIB by introducing new electrode materials

2.2 Emerging secondary battery technologies

The market share of LIB is expected to grow relatively uncontested for the foreseeable future, however, some intrinsic limitations of LIB are frequently highlighted in the literature as a motivation for the development of new rechargeable battery chemistries. As already introduced in this report, the use of organic solvent-based electrolytes in LIB is a significant safety concern, so several approaches including water based (aqueous) electrolytes have been explored. Also pointed out is the relative lack of abundance of lithium relative to other potential cations, most notably sodium that is significantly more plentiful and at lower cost.

2.2.1 Na+ Ion

Sodium-ion batteries operate with an identical mechanism to LIB, in that intercalation-based anode and cathode materials "host" Na+ ions during charge and discharge. As stated in the introduction to this section, Na is significantly more plentiful than Li, which is typically cited as the key to a lower cost battery (Na salts have reportedly 5% of the cost-per-ton of Li salts). Furthermore, concerns about global suppliers of Li and other key components of LIB (e.g. graphite and cobalt are produced almost exclusively in People's Republic of China and the Democratic Republic of the Congo, respectively) introduce a political motivation to find alternative technologies. Early work into sodium-ion batteries focused on materials analogous to those used in LIB such as carbon-based anodes and layered transition metal oxide cathodes (17). As shown in Figure 13, a large number of cathode and anode materials have been envisioned for sodium ion batteries, however very few full cells (i.e. cells not containing sodium metal) have been demonstrated with attractive results.
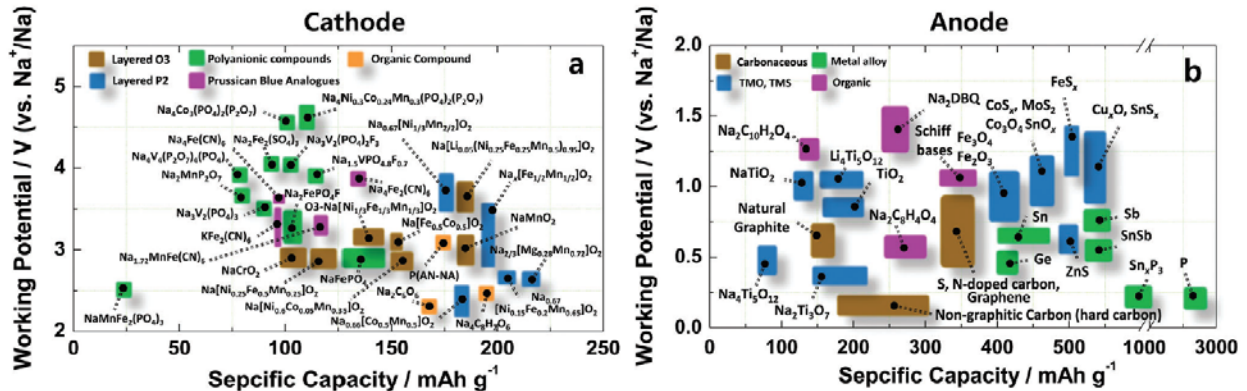
Figure 13 Theoretical capacities and voltages of potential sodium-ion anode and cathode materials

Some fundamental limitations also impede the development of sodium-ion batteries. The larger size of crystalline gallery spaces of sodiated intercalation materials also makes them particularly susceptible to water absorption, which requires dry room processing (also a requirement of LIB), and in some cases reduces the rate capability of active materials relative to lithium analogues. Furthermore, the operating potential of sodium ion cells tends to be slightly lower than that of LIB, which contributed to a lower energy density (18). A careful consideration of the implied "cost saving" of replacing lithium with sodium is also warranted. Detailed reports on the cost breakdown of lithium-ion batteries are produced by the Department of Energy, which report that at the cell level, lithium containing components (positive active material and electrolyte) contribute only 20% of the total production cost for a 52 kWh electric vehicle battery (Figure 14) (19).
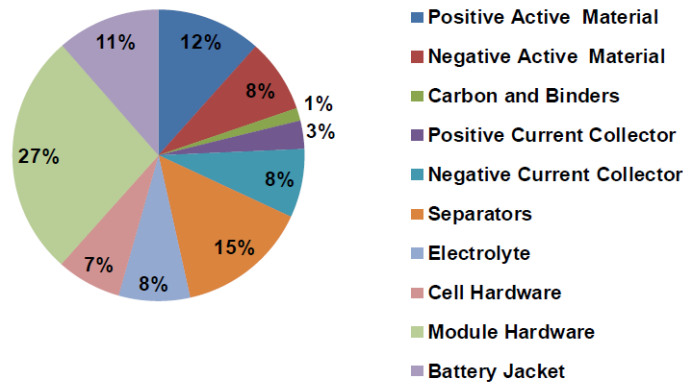
Figure 14 Materials contribution to production cost of LIB

Sodium-ion batteries still utilize organic solvent-based electrolytes (with some exceptions discussed in Section 2.2.3), and the majority of the positive active material would still be transition metal oxides, therefore the cost reduction for these components would likely not be dramatic. This, combined with a lower reported energy density for sodium-ion batteries, draws into question the argument that sodium-ion batteries would be significantly less expensive to produce (in terms of $/kWh) than lithium-ion batteries. In fact, despite boasting lower electrode and electrolyte costs, $/Wh estimates provided by Choi and Aurbach for a hypothetical Na-ion

cell utilizing a layered transition metal oxide cathode and hard carbon anode were higher than that of an equivalent LIB due to the lower energy content of the sodium ion cell (20). Future demand for lithium around the world, which is expected to increase, may change this however. Provided a sodium-ion battery was brought to market, its success in consumer products, as well as its potential safety issues, would largely be dependent on the energy content of the cells. As mentioned above, most demonstrations of sodium-ion batteries utilize an organic solvent-based electrolyte analogous to that used in lithium-ion batteries, which comes with the same potential issues for exothermic electrolyte-electrode reactions, sensitivity to overcharge, and flammability.

2.2.2   Metal air batteries

Rechargeable lithium-metal anodes are seen as the ultimate goal for LIB development (Figure 12), however pairing a reactive metal with an "oxygen breathing" cathode represents an opportunity for an order of magnitude increase in battery energy content. Two anodes of interest are lithium and zinc, which will be focused on in this report, though, others including aluminum and magnesium have also been proposed. A comparison of "practical" energy contents of $Li-O_2$, along with commercially available rechargeable batteries, and other developmental battery chemistries are shown in Figure 15 (21). A noticeable feature of Figure 15 is the large range in practical energy contents for the chemistries under development (metal air, Li-S, and advanced Li-ion), which is due to their relative technical immaturity. Some reports even estimate a fully developed $Li-O_2$ battery could have an energy density comparable to that of gasoline use in internal combustion engines, which are limited by the Carnot efficiency (22). "Practical" internal combustion engines that do not feature multiple thermodynamic cycles in series are limited to about 30-40% efficiency, while electrochemical devices can have 100% theoretical efficiency.
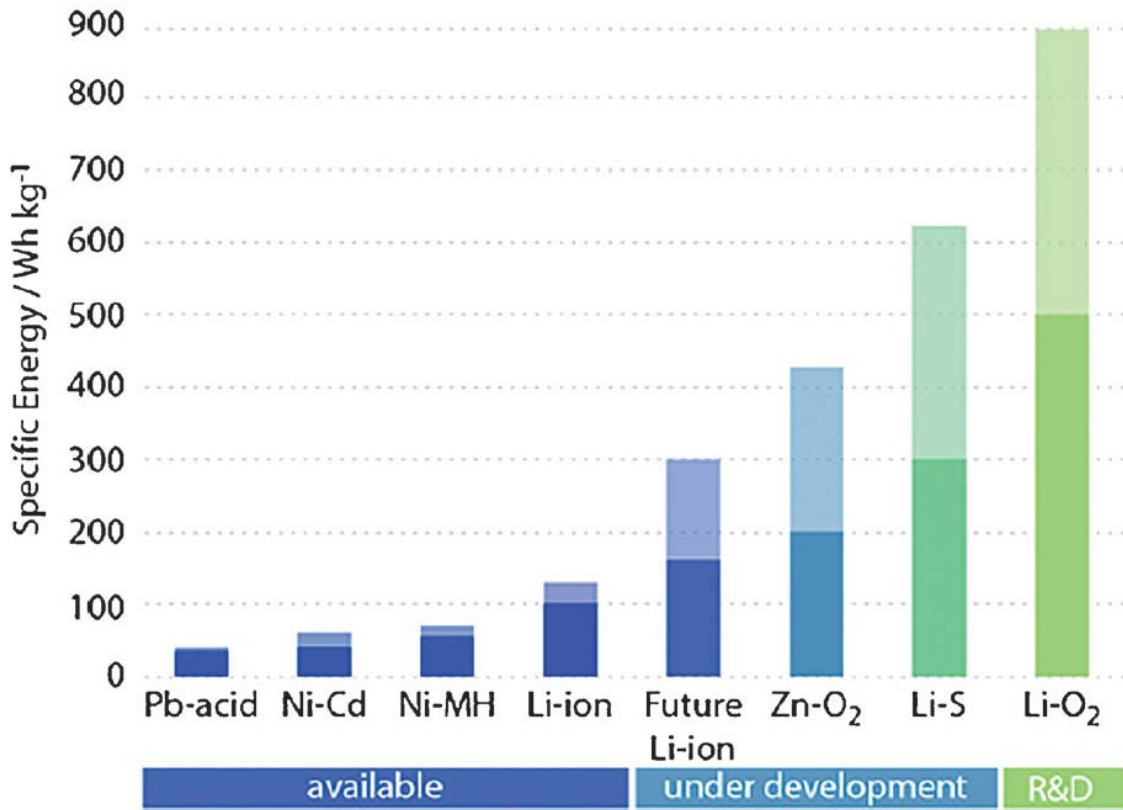
Figure 15 Comparison of energy density of metal-air couples vs. commercial batteries

Limitations of metal-air batteries are due to the discharge products, typically metal oxides (though reactions with water, carbon dioxide and other atmospheric gases are also possible), which are precipitated onto the air breathing current collector. These oxides are typically electronically insulating and form near the air-electrolyte interface, effectively blocking further discharge from occurring. A comparison of energy density for a Li-O_2 battery utilizing a cathode made entirely of carbon nanofibers to a typical $LiCoO_2$ LIB cathode is shown in Figure 16 (23).
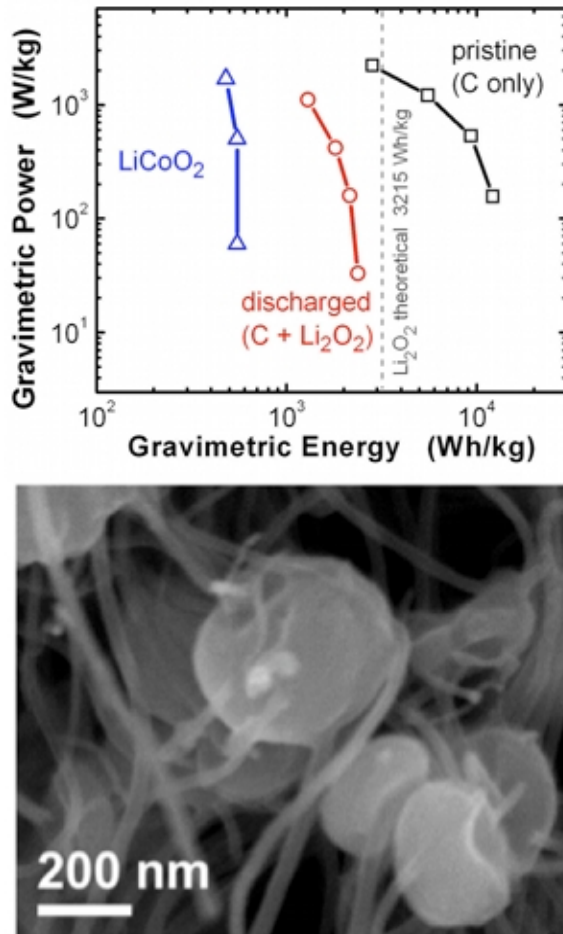
Figure 16 Ragone plot (top) and SEM image (bottom) for Li-O₂ battery showing formation of Li₂O₂ discharge product

Lithium-oxygen compounds are notoriously difficult to decompose in an electrochemical cell. While the nominal recharging mechanism for a metal air battery involves the formation of a binary compound (e.g. Li_2O_2) during discharge and the release of pure O_2 during charge, the reality is less straightforward. Demonstration systems are often restricted to dry O_2 rather than "air", which enables the formation of alternative discharge products with ambient water vapor and CO_2, as well as direct chemical reactions between the metal anode and O_2, which must have some degree of solubility in the electrolyte, and are therefore difficult to avoid. Schemes involving specialty coatings of the cathode to control exactly where the air-electrolyte interface occurs, dual-layer electrolytes, which separate the anolyte from the catholyte, and various electrolyte solutions have been investigated. Catalysts intended to enable the decomposition of metal oxides have also been reported, however, in practice confirming that the discharge product is in fact exclusively O_2 gas (rather than gas due to electrolyte decomposition) has been difficult and is rarely done in academic works. For these reasons, much of the recent fervor for rechargeable lithium-air systems has dissipated (24). Still, primary Li-air batteries (which were first demonstrated in the lab in 1996 (25)), may still have some potential application in consumer electronics. While very few commercial demonstrations of Li-air have been made, one example is from the company PolyPlus, which developed a lithium conducting glass ceramic suitable for use with aqueous electrolytes. PolyPlus demonstrated a relatively high energy density lithium air

battery at 800 Wh/kg, however, this was limited to extremely low power densities and was not rechargeable (26).

Zinc-air batteries have a generic construction analogous to Lithium-air batteries, namely a metallic anode and a porous "air-breathing" cathode. While lithium-air batteries have certainly received the most attention in academic research, primary zinc-air batteries have been commercialized for several decades for small, low-drain applications like hearing aids. Commercialized zinc-air batteries share much of their electrochemistry with common alkaline cells (e.g. Zn anode vs. MnO_2 cathode in KOH electrolyte), where MnO_2 cathode is replaced with an air-breathing variant. Many research works have focused on simply improving the electrochemical reversibility of the reaction used in the primary Zn-air cells. Several issues with this approach have been highlighted. The first issue is electrolyte dry out due to the air-exposed cathode can limit the shelf life of a metal-air battery. For this reason, primary Zn-air cells are stored in a sealed configuration and must be opened prior to use. Packaging solutions such as special air permeable but hydrophobic membranes can be used on the cathode side to mitigate this issue but are not foolproof. A second issue is the inhomogeneous deposition of Zn metal during recharge, typically described as dendrites. This issue also occurs when using a lithium metal anode (either lithium ion or lithium air) but can be controlled by charging at low rates. Prevention of zinc dendrites has been demonstrated by using porous or "three dimensional" zinc anode structures, which reduce the current density of the electroplating process during recharge below the threshold for forming dendrites. Researchers at the Naval Research Laboratory (NRL) have demonstrated this approach to produce anodes for Zn-air and Ni-Zn batteries (27) (28). A third issue affecting zinc-air cells is that Zn metal is highly reactive with the aqueous electrolyte and the anode forms a passivating layer of ZnO. The NRL approach deliberately introduces a continuous ZnO layer to prevent isolation of Zn particles, however, an alternate approach involves the use of non-aqueous electrolyte. While almost no technical data is available, the company NantEnergy (formerly known as Fluidic Energy) has reportedly commercialized a rechargeable Zn-air battery utilizing an ionic liquid electrolyte, which greatly improves the cycleability of the Zn anode. Ionic liquids are salts with melting temperatures below room temperature, such that they form a solvent free electrolyte with very high stability (29) (30). NantEnergy has received over $200M in funding through both public grant (ARPA-e) and private funding. The limited information available on the NantEnergy technology indicates that the batteries operate at a very low rate, which is suitable for certain grid storage applications, but not currently seen as a head-to-head competitor with higher power lithium-ion batteries for portable electronic devices.

The safety of metal-air batteries would largely depend on the specific construction. Li-air has been demonstrated in laboratory cells using organic solvent-based electrolytes similar to those used in lithium-ion batteries, but also using a water-based electrolyte with an encapsulated Li anode. Furthermore, the use of lithium metal has many potential issues, especially in a rechargeable system where re-deposition of lithium during charging can cause dendrites to form. Today, lithium metal is only used in non-rechargeable batteries and requires more stringent regulations during shipping and handling. Zn-air batteries, or other metal-air batteries using a less reactive anode, which in theory could be quite safe from a thermal runaway/flammability perspective, however, the caustic KOH electrolyte used for most zinc-based batteries is a potential concern. The "open" nature of metal-air batteries may also introduce certain design issues that are not present in hermetically sealed cells.

2.2.3 Aqueous systems

Rechargeable batteries with aqueous electrolytes have been commercialized for over 150 years (the lead acid battery) but, as indicated in Table 1, typically have much lower energy densities than lithium-ion batteries using organic electrolytes. While lithium-ion batteries are starting to replace all but the most demanding applications of aqueous rechargeable cells (e.g. lead acid is still used in extremely high current applications like automotive starter batteries and uninterruptable power supplies), some opportunities for new aqueous chemistries have also been investigated. As indicated in section 2.2.2, zinc anodes in KOH electrolytes are used for some rechargeable systems. Ni-Zn batteries were first commercialized 100 years ago but never gained significant market share. At least two companies are pursuing commercial opportunities for Ni-Zn batteries. First, ZincFive is pursuing the commercialization of Ni-Zn batteries using a traditional electrode structure for application in uninterruptible power supplies (UPS) (31). Another company, EnZinc, has also advanced Ni-Zn technology using a porous anode structure developed by NRL. However, as shown in Figure 17, even a 100% utilization of the zinc anode (which is prohibited by the aforementioned passivation reactions) is only competitive with lower energy lithium-ion batteries and comparable to the already commercialized nickel-metal hydride (28). For this reason, the "selling point" of Ni-Zn has been the improved safety of the aqueous electrolyte.
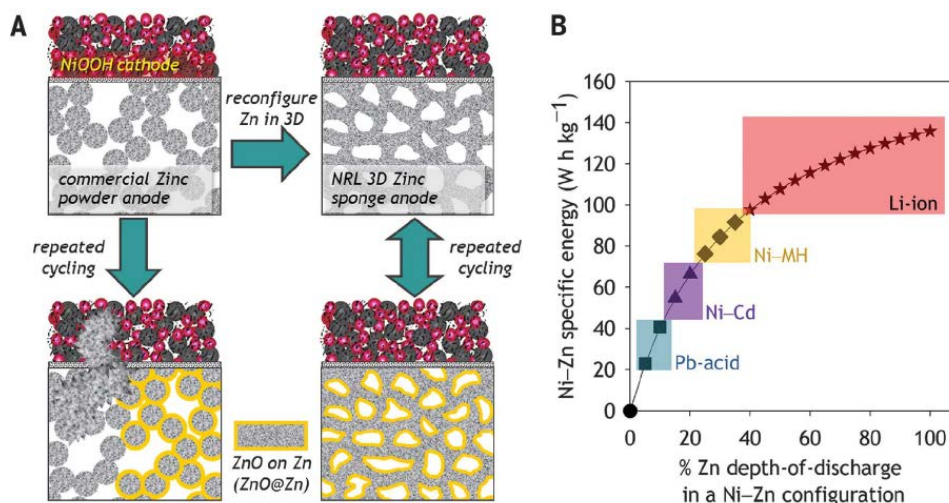
Figure 17 Schematic depiction of porous Zn anode developed by NRL relative to conventional powder bed anode in a Ni-Zn battery (A) and projected energy density of Ni-Zn based on utilization of Zinc anode (B)

Most aqueous electrolytes are limited to an operating voltage of about 2V or below, which is directly related to the electrochemical stability window of the solvent (water). As shown in Figure 2, lithium-ion batteries operate outside of the electrochemical stability window of the organic salt by forming an SEI, which prevents further reaction between the anode and electrolyte. No SEI is formed in conventional aqueous electrolytes, and deviations outside of the electrolyte stability window, for instance due to overcharging or decreases in electrolyte conductivity due to low temperature, will cause electrolysis to occur. The nominal products of water electrolysis are hydrogen and oxygen gas, however, depending on the pH of the electrolyte water soluble ions can also be formed. In some aqueous rechargeable batteries, notably lead-acid and some more recent nickel-metal hydrides cells, a recombination reaction can occur within the

cell to prevent excessive gas buildup and restore water to the electrolyte. Still, many compounds can operate within the electrochemical stability window of water with good electrochemical reversibility. A popular approach involves intercalation compounds analogous to those used in LIB. Provided both electrodes operate well within the electrolyte stability window, extremely long cycle lives can be demonstrated. MnO_2 and related compounds have been demonstrated to reversibly intercalate both Na+ and Li+ ions in aqueous solutions with good results (Figure 18) (32), but with lower capacity and voltage than conventional LIB materials (Table 2).
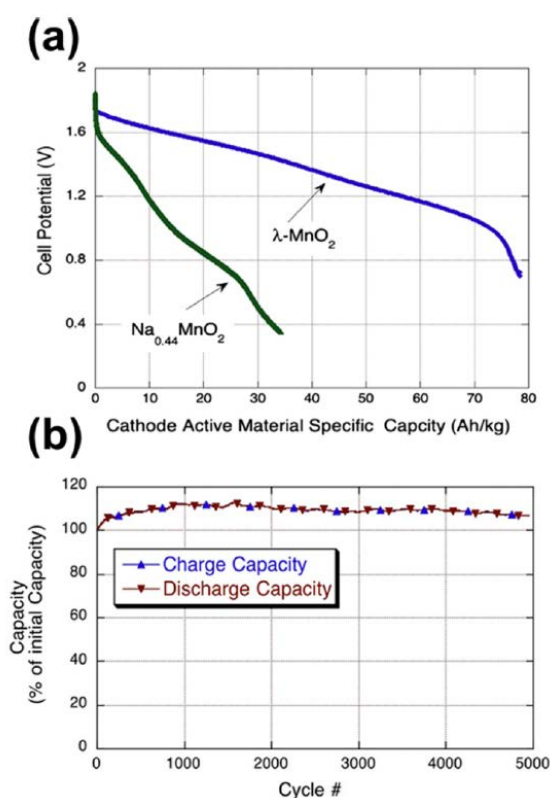
Figure 18 Voltage profile (A) and cycle life (B) of MnO₂ compounds in a 1M Na₂SO₄ aqueous electrolyte

Some commercial ventures utilizing intercalation compounds in aqueous electrolytes have also been pursued. Aquion Energy raised $180M in public and private capital and began selling batteries based on an aqueous sodium-ion intercalation chemistry in 2014. In 2017 Aquion Energy filed for bankruptcy and was restructured, and as of 2018 has not yet resumed production of batteries (33). In 2015, researchers at the University of Maryland and Army Research Lab introduced an intriguing new concept – the formation of an SEI from an aqueous electrolyte, which was accomplished by using an extremely high concentration of lithium salt (i.e. 21 molar Lithium bis(trifluoromethanesulfonyl)imide or LiTFSI) in water (34). The resulting electrolyte was more salt than solvent by mass, which prevented electrolysis from occurring. The resulting electrolyte had a stability window of approximately 3V, which was paired with more attractive intercalation materials than those used in conventional aqueous electrolytes, including some standard LIB electrode materials (Figure 19). Subsequent work has demonstrated that lower concentration aqueous solvents can also show improved electrochemical stability, however, all are significantly more concentrated than the typical 1-2 molar

concentration used in all other commercial batteries. As highlighted in Figure 14, the electrolyte solution is already a significant contributor to the cost of lithium-ion batteries, with most of this cost associated with the lithium salt. Several follow-on studies have taken the water-in-salt electrolyte concept further, showing that improved safety is in fact achieved over lithium-ion batteries. A press release from Johns Hopkins University Applied Physics Lab (JHUAPL) demonstrated a water-in-salt prototype cell, which continued to function with no harmful effects after mechanical abuse (35).
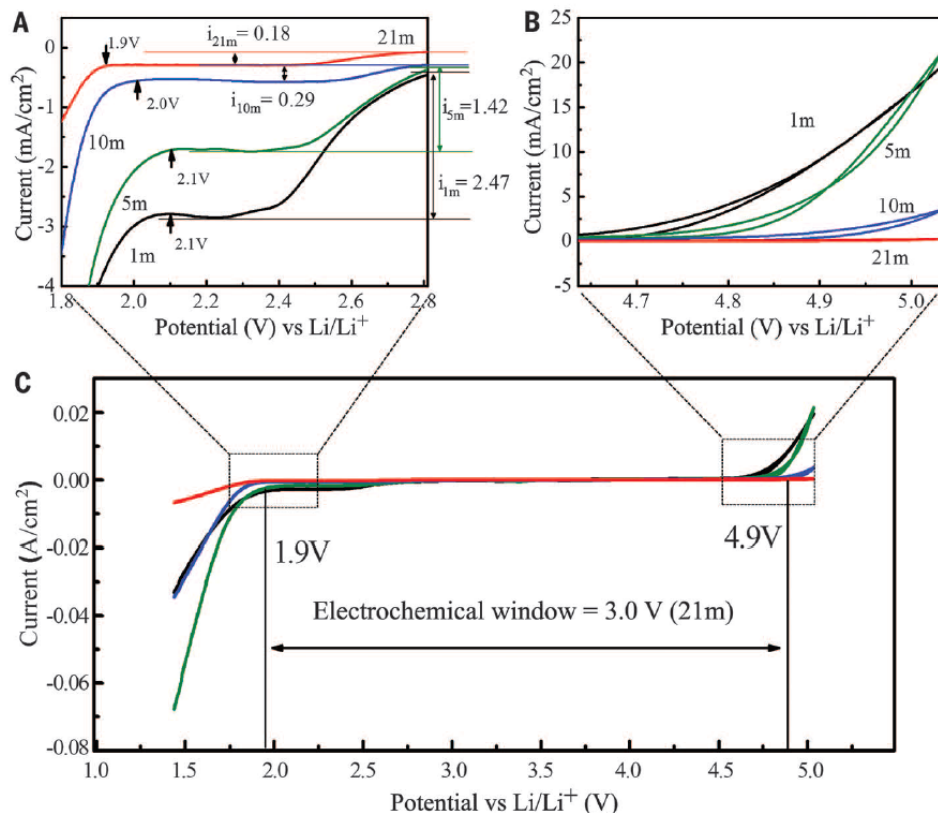
Figure 19 Electrochemical stability of "water in salt" electrolyte showing anodic stability (a), cathodic stability (b), and overall stability window as a function of LiTFSI concentration in water

Relative to lithium-ion batteries, all versions of aqueous rechargeable batteries are expected to be fairly safe, however, the potential for energetic failures is always present in high-energy batteries. One safety concern, which is more common in aqueous rechargeable batteries than in lithium-ion is the possibility of electrolyte electrolysis and associated hydrogen generation during charge. This can be suppressed to some extent by electrolyte and electrode design, or as in the case of some lead-acid batteries allowed to occur but moderated by a catalytic reformation of the electrolysis products.

2.2.4 Solid-state

Solid-state batteries (SSB) are an emerging energy storage technology with many desirable qualities, and are the focus of significant research and development activities in many academic institutions and commercial enterprises. While lithium ion batteries have rapidly become the benchmark of energy storage methods, there are inherent drawbacks and challenges

posed by their usage. Of primary concern are the potentials for the release of hazardous and flammable gas, fires, and spontaneous disassembly of lithium ion cells when subjected to electrical, thermal, or mechanical abuse (36). One of the root causes of this behavior is the use of organic liquid electrolytes in lithium ion cells (37). SSB solve this by using solid and non-flammable electrolyte materials, which are much less sensitive to temperature changes. These materials are also generally stable in contact with pure lithium metal unlike organic liquid electrolytes. This allows SSB to use lithium metal anodes, theoretically increasing energy density of SSB above state of the art lithium ion cells (38) (39) (40). This superior stability also allows for the use of higher-voltage cathode materials, such as $LiNi_{0.5}Mn_{1.5}O_4$, which are incompatible with conventional lithium ion electrolytes (41). The potential for a safer, higher voltage and more energy dense batteries are driving interest in SSB.
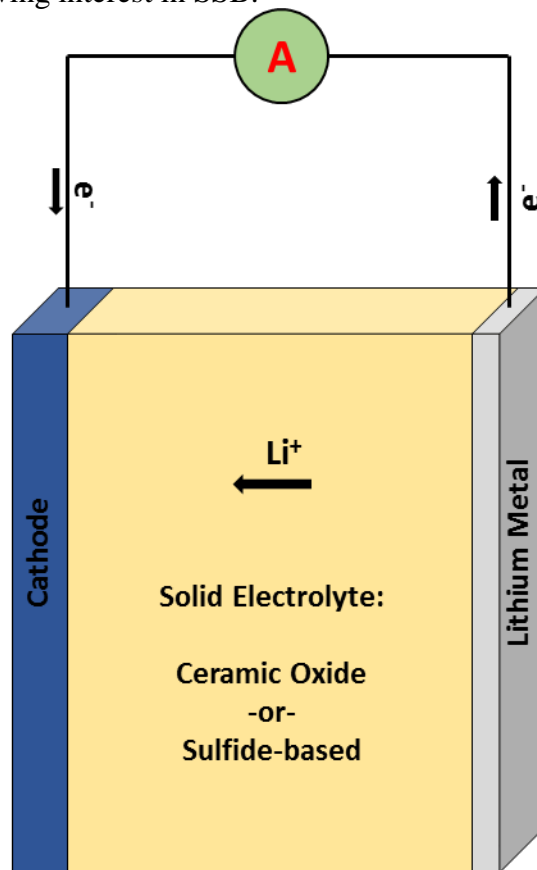
Figure 20 Concept Schematic of solid-state lithium battery with lithium metal anode

The structure of a SSB is usually composed of three layers: a metallic anode, an ion-conducting glass or ceramic electrolyte, and a cathode (Figure 20). During discharge, lithium ions from the anode pass through the electrolyte and enter the cathode layer. For each lithium ion that moves across the cell, an electron must travel in the same direction through an external circuit to balance the overall charge. The reverse action occurs when the cell is charged, plating lithium metal on to the anode-side of the solid electrolyte. The main focus of research and development efforts in the field of SSB is on the electrolyte layer, due to currently lackluster ionic conductivity in these materials. The two primary classes of electrolyte materials are ceramic oxides and sulfide-based lithium conductors. Sulfide electrolytes currently have superior ionic conductivities, in the range of $10^{-5} – 10^{-2}$ S cm^{-1}, compared to ceramic oxide electrolytes

which are generally an order of magnitude less conductive (38) (39). Oxide electrolytes exhibit significantly improved conductivities at elevated temperatures, and are more chemically stable, which simplifies processing. Sulfide electrolytes require very careful control of processing environments due to their poor chemical stability (38).

Despite the large amount of interest in SSB, there has only been limited commercialization of the technology. This is due to a combination of factors, most notably interfacial challenges and large-scale manufacturing difficulties, with high cost being the chief concern (40) (42). In comparison to lithium ion batteries, where the electrolyte-electrode interface is a liquid-solid interface, layer interfaces in SSB are between two solid materials. Therefore, any deviation from perfectly planar faces results in "dead" areas where there is no contact and an effective reduction in battery area. This is being addressed with the use of surface coatings to promote good contact. The production of most solid lithium conducting materials must be done in a controlled atmosphere. Lithium conducting sulfide materials are extremely moisture sensitive and oxide electrolyte materials are affected by the formation of insulating carbonate species on surfaces (39).

Automotive companies have been some of the largest investors in commercial solid-state lithium battery development. This usually takes the form of funding grants to small start-up companies with promising technology, or partnerships with those companies. Due to the high level of secrecy surrounding their development efforts, it is very difficult to get firm details. Some of the leading companies in this space are listed below, with some of the available detail.

PolyPlus
- Glass film electrolyte, roll to roll processing with lithium metal anode
- Leader in developing very clean lithium metal surface, which is key for success

Ionic Materials
- Solid polymer electrolyte with good performance at room temperature
- Has received funding from ARPA-E, Renault, Nissan, Mitsubishi

QuantumScape
- Very secretive about technology specifics, has done some work with oxide electrolytes
- Large investment by Volkswagen

Solid Power
- Secretive about electrolyte composition, but likely oxide or sulfide based
- Partnership with BMW

Bathium
- Using variation of academically well-established polymer electrolyte
- Partner with Bluecar, an electric vehicle company

Research efforts toward development of an all-solid-state lithium battery have been ongoing since the 1970s, and is accelerating with the proliferation of portable electronics and growing electric vehicle market (39) (40). The reported conductivity of solid electrolyte materials suitable for use in lithium SSB has improved by several orders of magnitude in the past three decades and is approaching that of commercial liquid electrolytes (39). Even if

performance parity with conventional lithium-ion is achieved in the near future, likely there will still exist significant hurdles to manufacturing at commercial scale. While manufacturing of these devices is complicated by requirements for controlled atmosphere and extremely dry conditions, similar challenges have been surmounted in other industries such as semiconductor processing (40). Additionally, proposed manufacturing process chains for SSB are similar to those for lithium-ion devices and there is potential for gradual integration of SSB processes into existing production lines (40) (43). If fully developed, SSB may find an immediate market niche in consumer electronic devices, as in theory these batteries could have greatly improved volumetric energy densities and cycle life. Furthermore, the cost of early versions of these devices may be prohibitive for large format applications like electric vehicles, which makes smaller format applications more attractive.

2.3 Battery safety

Lithium-ion batteries are notable in their safety limitations due to their ability to undergo "thermal runaway", which can result in fires and explosions of cells with sufficient energy to propagate to an entire battery pack. Thermal runaway initiates when sufficient heat is generated internal to a cell, such as due to a short circuit, external or internal to the cell (typically caused by mechanical damage to the cell or a manufacturing defect), high-rate operation, improper charging protocols, or by an external heat source. Exothermic reactions begin with the decomposition of the solid electrolyte interface (SEI) at the anode-electrolyte interface. While the SEI is a critical component in the stability of LIB anodes and allows for thousands of high-efficiency charge and discharge cycles, SEI decomposition can begin below 100 °C (44) (45), and for some anode and electrolyte combinations exothermic reactions are detected as low as 50 °C (46). Melting of typical separator materials such as polyethylene and polypropylene, which is endothermic, occurs between 120-140°C. Separator melting allows for local short circuits to form and further heat small areas internal to the cell. Boiling points for many LIB electrolyte solvents are also comparable to that of melting separator (dimethyl carbonate Tb=91 °C, diethyl carbonate Tb=126 °C, ethyl methyl carbonate Tb=107 °C) and can lead to swelling of pouch cells and distortion of electrode layers, which can strain the melting separator to form short circuit pathways or cause venting introducing flammable vapors into the local environment. As cell temperatures approach 150 °C and above, decomposition of electrode and electrolyte materials rapidly increases the self-heating rate of the cell to a point that cannot be arrested by external cooling. This process can take seconds or hours to develop, and is not always apparent from external pack monitoring, especially when cells are not individually instrumented. Processes leading to a cascading thermal runaway are shown schematically in Figure 21 (47).
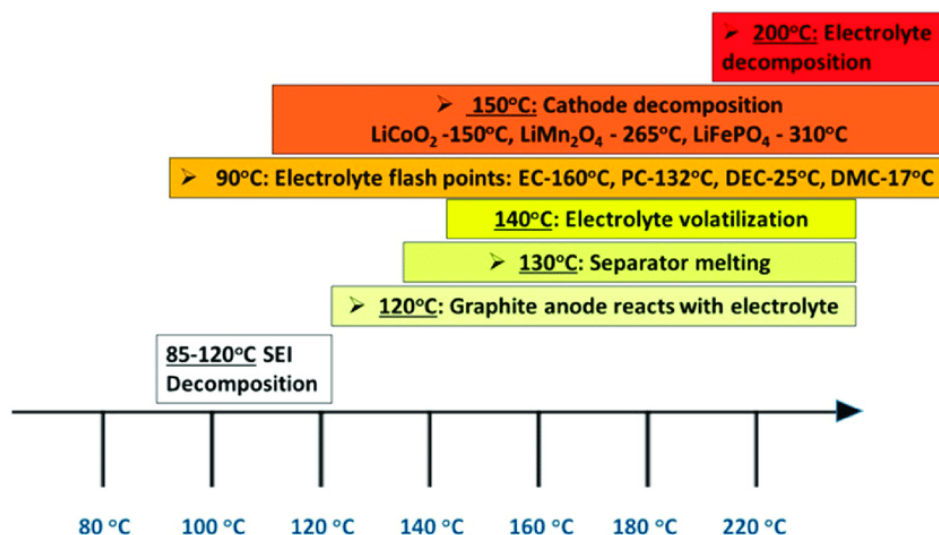
Figure 21 Summary of reactions contributing to thermal runaway in LIB

Alternatives to LIB with plausibly improved safety have been highlighted in section 2.2, however, methods to improve the intrinsic safety of LIB, or the safety of packs containing LIB, have also been reported and will be covered in this section. It is important to emphasize that while the discrete processes of thermal runaway in LIB has been extensively studied in that context, they are by no means limited to LIB. Any electrochemical system in which the electrode working potentials extend beyond the stability window of the electrolyte will lead to the oxidation or reduction of the electrolyte. This could lead to the beneficial formation of an SEI, which could in turn be thermally unstable, or simply lead to gas generation, which even for non-flammable aqueous electrolytes produces flammable hydrogen. Abusive conditions such as overcharge, external short, mechanical damage, or external heating can all generate extreme energetic failures even for an otherwise "safe" cell. Component testing is certainly one aspect of a safe rechargeable battery, however, testing of a complete cell in a relevant environment is always recommended.

2.3.1   Safety at the cell level

Protecting against internal short circuits

Thermal runaway can be initiated by internal short circuits between the anode and cathode. These short circuits cause localized heating which in turn initiates the reactions depicted in Figure 21. Internal short circuits are considered particularly problematic for LIB because they can be introduced by manufacturing defects and are difficult to detect without extensive monitoring. Reports from NASA on lot acceptance testing for a batch of >4000 LIB from a top-tier manufacturer found that 4.9% of these cells had signs of high-resistance internal short circuits (i.e. "soft shorts") which led to OCV anomalies (48). Depending on the exact electrical pathway and cycling history of a cell, soft shorts can transition into lower resistance short circuits and begin to generate heat. Alternatively, short circuits can develop due to certain cycling conditions (e.g. the formation of dendrites during high rate and/or low temperature charging) or mechanical damage to the cell. Several companies have introduced product lines intended to mitigate heat generation due to internal shorts by modifying the inactive components

used in LIB, specifically the separator and current collectors, which can strongly influence battery safety (49).

Battery separators are required in LIB to provide an ionic pathway between the anode and cathode while keeping them electrically isolated, but also represent a common point of failure (50). Whether pierced by a manufacturing defect such as a foreign metallic particle or due to mechanical forces on the cell casing, a hole or thinning of the separator can lead to a localized short circuit and rapid heating of the electrode stack. At relatively low temperatures (<150 °C), polymeric separators can melt allowing for broad internal shorting across the cell which rapidly generates enough heat to initiate a thermal runaway. Ceramic coated or fully ceramic separators have been recently commercialized which improve the melting temperature to above 200 °C, and as a result can delay the onset of thermal runaway and significantly reduce the severity of cell failure (51). A ceramic-coated separator can delay the onset of thermal runaway in response to an overcharge by approximately 60 ℃ and withstands nearly double the overcharge percentage (with 100% corresponding to a cell charged to the nominal capacity) relatively to a standard polymeric separator Figure 22 (7).
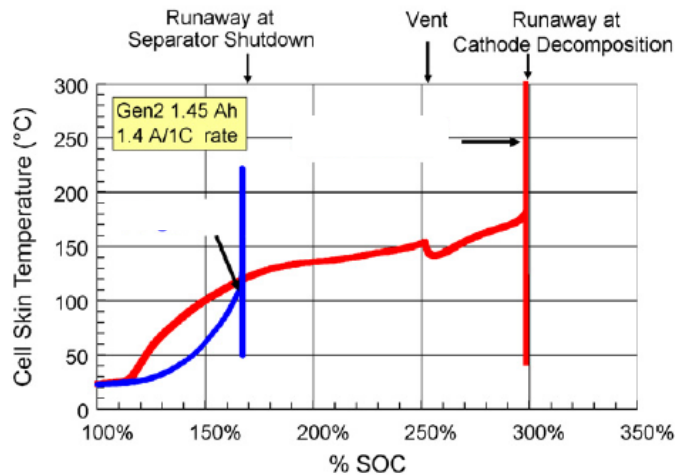
Figure 22 Comparison of overcharge response using standard polymeric separator (blue) and ceramic coated separator (red)

While ceramic-coated separators can delay the onset of thermal runaway, other technologies seek to interrupt current flow in response to an internal short circuit, preventing heat generation altogether. Two similar approaches are presented by the Amionx (SafeCore PTC coating) and Soteria (metallized polymer current collector) (52) (53). Both companies utilize a similar concept, namely, a response to localized heating produced by an internal short circuit which prevents further current flow and arrests thermal runaway. The Amionx approach involves a thin coating on the current collector, which swells in response to heating (analogous to the positive thermal coefficient device shown in Figure 5). The swelling effect separates the current collector from the active material, thereby preventing subsequent current flow in the affected region (Figure 23) (52).
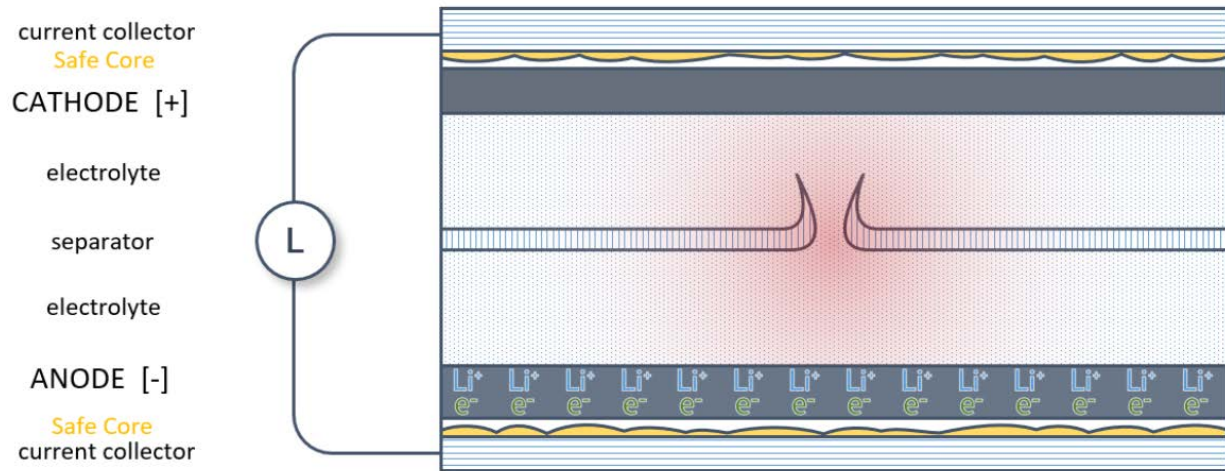
Figure 23 Schematic of an LIB with an activated SafeCore layer

According to the manufacturer's testing of LIB containing the SafeCore coating (Figure 24) resulted in improved safety response when subjected to overcharge and nail penetration (simulated internal short).
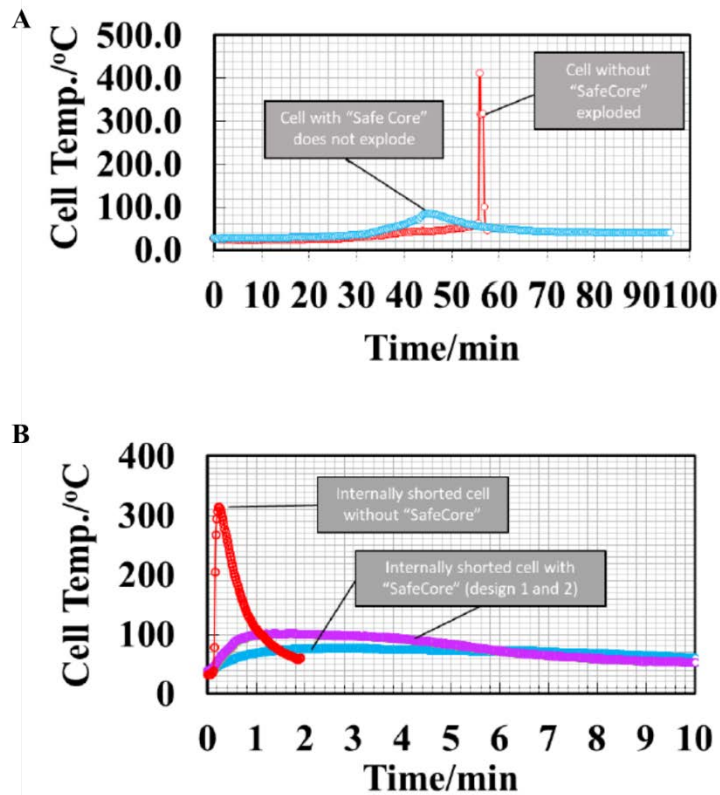
Figure 24 Temperature response of LIB containing SafeCore technology in response to overcharge (A) and nail penetration (B)

In the approach presented by Soteria, rather than a thermally responsive coating on the current collector, the current collector itself is thermally responsive. This is achieved by using a metalized polymer which is melted and shrinks in response to localized heating (Figure 25). The Soteria architecture also involves a thermally stable "non-woven" separator to further prevent the expansion of internal short circuit due to localized heating. An additional benefit to the Soteria approach is that the metallized polymer current collector can save mass by an estimated 10-20% over conventional metal foil current collectors.

LEGACY ARCHITECTURE   SOTERIA ARCHITECTURE
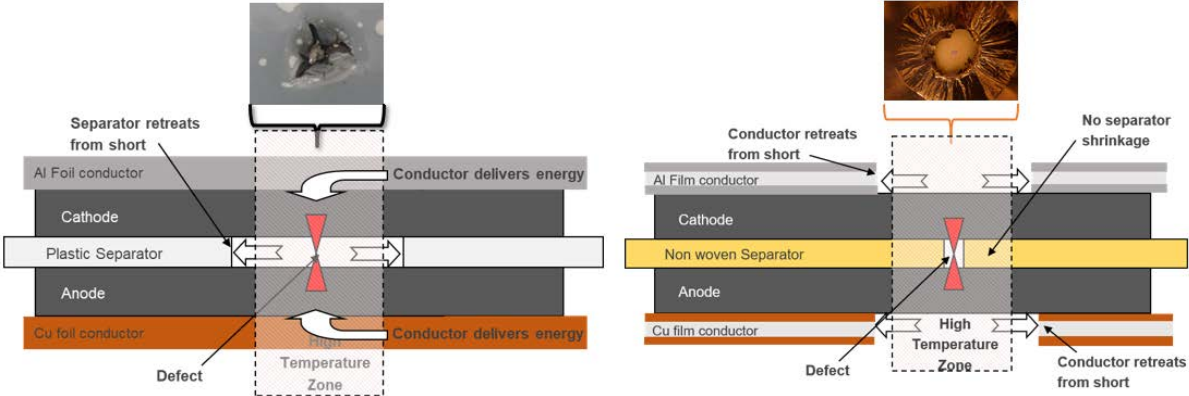
Figure 25 Schematic depiction of LIB utilizing a metalized film current collector from Soteria

Nail penetration testing for LIB containing the Soteria current collector/separator architecture is shown in Figure 26. Because the Soteria current collector shrinks away from the site of the nail penetration, the OCV of the cell is maintained and no cell heating is observed (54).
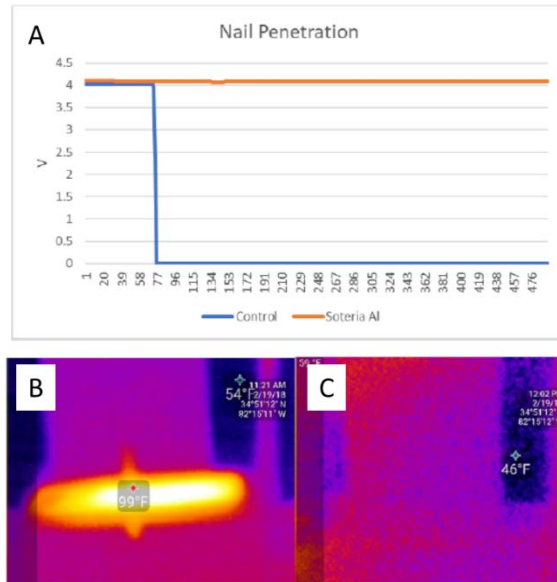
Figure 26 Voltage response (A) and thermal imaging (B,C) of LIB without (B) and with (C) Soteria metalized polymer current collector and thermally stable separator

While some prototype cells have been demonstrated for both Amionx and Soteria, both companies state that their intended "go to market strategy" will be to license their technology rather than develop and sell it to battery manufacturers.

High stability electrode materials

As can be reasonably surmised from the description of thermal runaway provided in the section 2.3 introduction, the severity of a battery failure event is determined by the quantity and species of reactants involved. Practically speaking, this means there is a direct relationship

between the energy density and physical size of the electrochemical cell and the observed response to abusive testing (55). Unfortunately, limiting the density or amount of stored energy is rarely a useful suggestion when this impacts mission capabilities. Still, there are opportunities for improving the failure response of LIB while maintaining good performance. The most commonly employed approach is through replacing the cathode active material. As shown in Figure 27, the cathode can strongly influence the heat release rate of LIB with identical anodes and electrolytes. While this can reduce the total heat release observed during thermal runaway when it occurs, it does not preclude the low-onset temperature processes, which can lead to a cascading exothermic reaction, and cannot prevent the process of thermal runway in all scenarios.
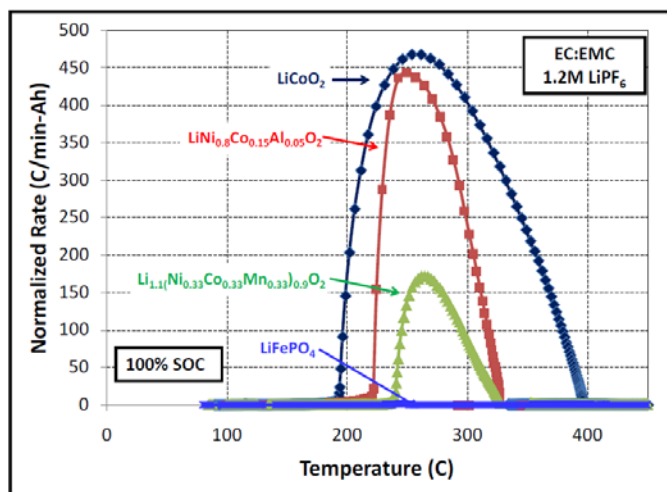
Figure 27 Capacity Normalized Self-heating Rates of LIB with Various Cathode Materials

Layered transition metal oxide cathode compounds, which include everything in Figure 27 except for $LiFePO_4$ (LFP), have been utilized in industry since the earliest commercialized LIB but have the unfortunate drawback of being highly thermally unstable. Furthermore, in response to certain abusive conditions, such as an overcharge, these compounds can release oxygen from the cathode lattice and react with the electrolyte, exacerbating the cell failure. Doped compounds like $Li_{1.1}(Ni_{0.33}Co_{0.33}Mn_{0.33})_{0.9}O_2$ or "NCM" are markedly more stable than the prototypical layered compound $LiCoO_2$, however, LFP is still preferred when safety is critical (13). Unfortunately, cells containing LFP provide much less energy compared to those utilizing layered compounds, making the utilization of the less safe alternatives mandatory when high energy content is mission essential.

An alternative approach to utilizing lower-energy cathode materials is to coat electrode materials such that reactions between the electrode and electrolyte can be shifted to higher onset temperatures or greatly reduced in intensity. Recent research has demonstrated that thin (a few nm) surface coatings of inert materials, typically oxides, halides or phosphates, deposited by atomic layer deposition (ALD) can have a dramatic and positive impact on the safety of layered compounds (Figure 28) (45). Coatings on anode materials (e.g. graphite) have also been shown to improve thermal stability (56). Other benefits, such as reduced capacity loss, both under normal operating conditions and when using elevated temperatures or increased upper voltage cutoffs, and improved rate capability have also been reported (57) (58) (59) (60).
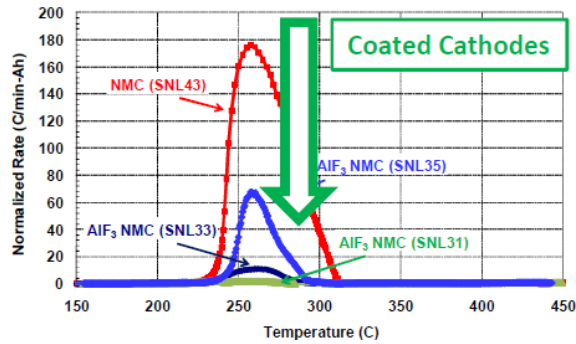
Figure 28 AlF₃ Coated NCM Coated Showing Reduced Heating Rate in the Presence of LIB Electrolyte

Many academic works have demonstrated that ALD coatings are an effective way to improve the thermal stability of LIB electrodes, however, only one company, ForgeNano, has commercialized a high-throughput ALD coating process. Their "PicoShield" line of cathode and anode materials feature state of the art LIB compounds which have been modified in bulk (up to several metric tons per year) to realize the advantages described above (61).

Reduced flammability electrolytes

Reducing the flammability of the electrolyte is a key aspect required to improve the safety of LIB. Careful selection of the individual electrolyte components, as well as certain flame-retardant additives, can be leveraged to improve the safety of lithium ion batteries (49). Example electrolyte alternatives include electrolyte solvents based on ionic liquids (IL). Compared to organic solvents used for Li-ion electrolytes, some of the ionic liquids have much greater thermal stability (>250°C), wider electrochemical stability and reasonable Li-ion conductivity. Several companies are pursuing LIB electrolytes based on ionic liquids, with one noteworthy example being Physical Sciences Inc. Recent test data showed reasonable rate capability in a LIB compared to conventional organic solvent based electrolytes, while the IL based alternative was non-flammable even when aerosolized in the presence of an open flame (Figure 29) (62). LIB containing the IL electrolyte were also subjected to puncture testing and showed no energetic failures.

Figure 29 Aerosolized electrolytes subjected to open flame testing comparing conventional LIB electrolyte and solvent (DMC) with an ionic liquid (IL) based electrolyte developed by Physical Sciences Inc.

In another approach, replacing the typically used electrolyte salt $LiPF_6$ with LiF and an "anion bonding agent" (ABA) required to dissolve LiF, has also been shown to improve the thermal response of LIB (63). Heating rates for full-cells containing a standard electrolyte (1.2 M $LiPF_6$ in EC:EMC) compared to several alternatives, including alternative salts (LiF-ABA in black and LiTFSi in light blue), and inclusion of proprietary additives (flame retarded FM2 in green and "organosilicon" materials from Silatronix OS#1 and OS#2 in dark blue and orange) are shown in Figure 30. In this example, the LiF-ABA based electrolyte shows virtually no self-heating due to electrode-electrolyte interactions.
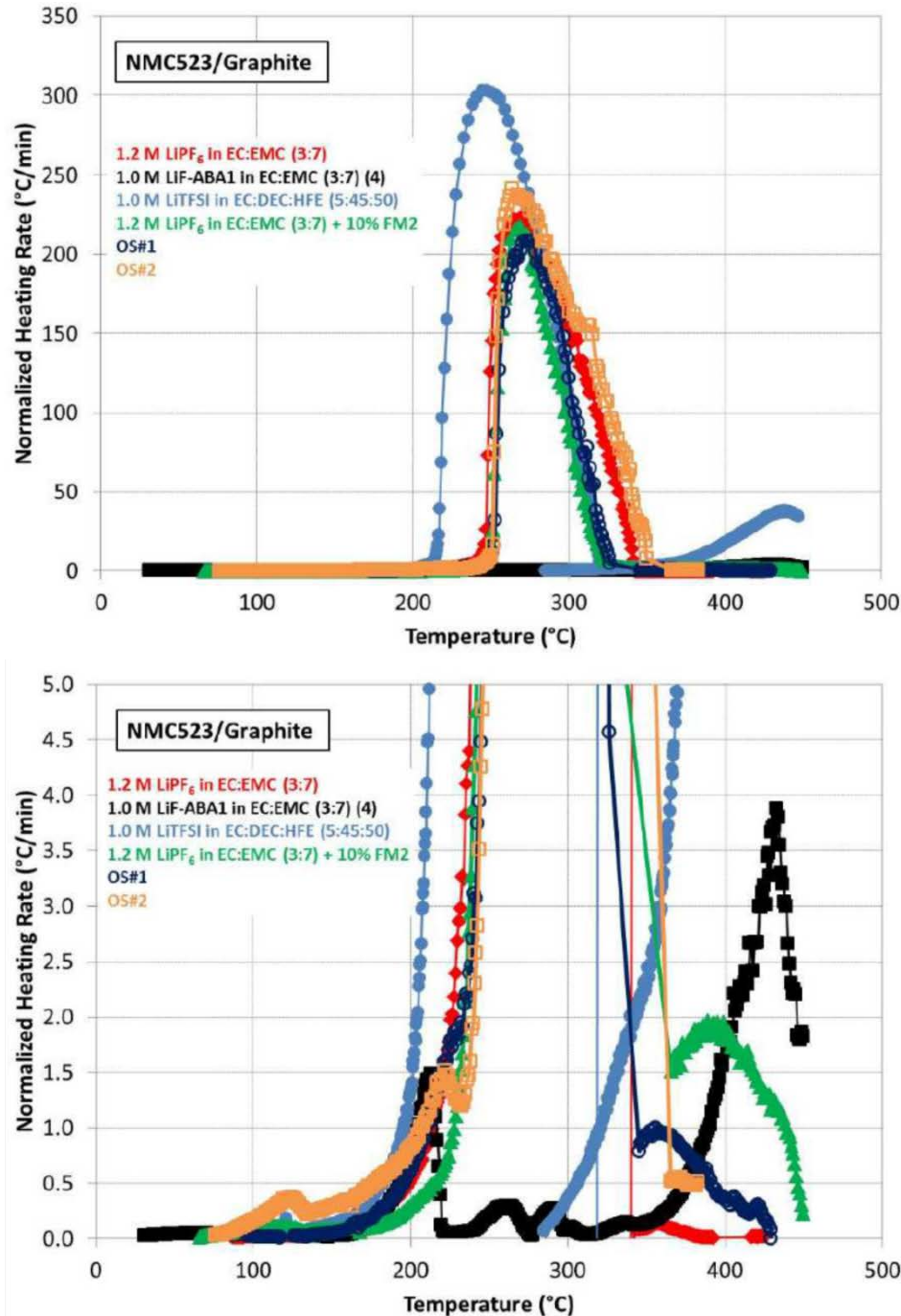
Figure 30 Normalized Heating Rate for LIB Containing Various Electrolytes

One common limitation of alternative electrolyte materials is a reduced ionic conductivity relative to the optimized baseline electrolyte blends. While lower conductivities were observed for the alternative electrolyte blends evaluated in Figure 30, this was not found to be predictive of relative rate capability. As depicted in Figure 31, several electrolyte blends with lower conductivity than the standard electrolyte were observed to have improved rate capabilities when evaluated in full-cells, which was attributed to an improved electrode-electrolyte interface resistance. Some of the limitations of non-standard electrolytes, such as an increased viscosity or

reduced conductivity, may also be partially mitigated by the use of modified separator and electrode components.
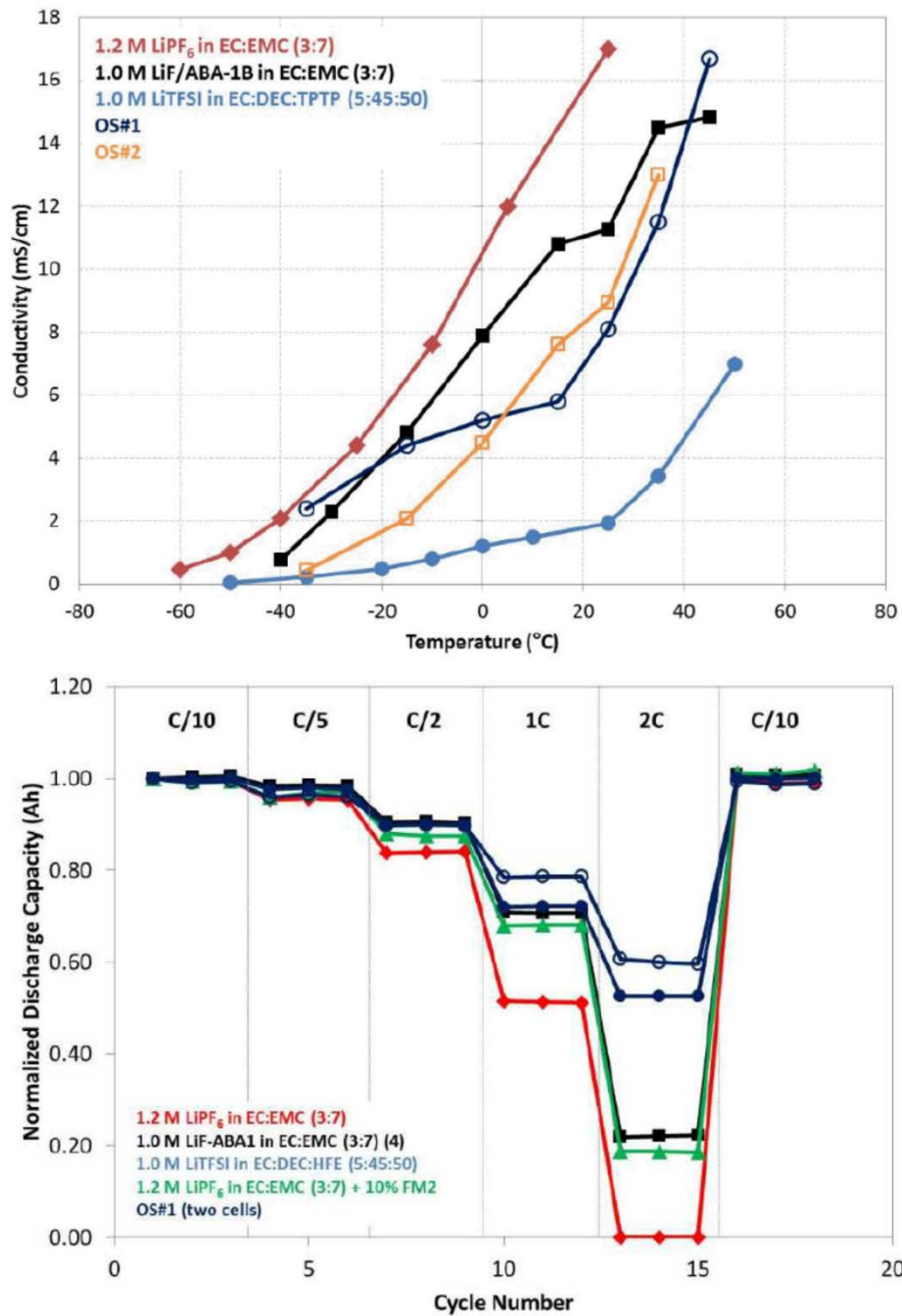
Figure 31 Comparison of ionic conductivity of various LIB electrolytes (left) to observed rate capability (right)

2.3.2   *Non-propagating battery design*

A major limitation to the approaches identified in section 2.3.1 is that they are often difficult to scale into large-scale production. As a result, these technologies, while promising, rarely make it into COTS cells. An alternative approach to improving the safety of LIB is to

contain battery failures when they occur, and prevent a cascade of failures, which can be much more hazardous. "Non-propagating" batteries seek to isolate or redirect the energy of a single cell failure, and ideally maintain some functionality of the device.

Typically, cells are assembled into modules by spot-welding the positive and negative tabs on each cell into the desired series or parallel arrangements. In more complex modules passive safety mechanisms (e.g. fuses, channels for vent gases, intumescent materials) and/or active mechanisms (e.g. forced air or circulated liquid cooling) may be included but in many instances, cells are simply restrained with epoxy and sealed into a suitable enclosure. Alternative module assemblies deliberately designed for improved safety have also been demonstrated, but are not widely adopted by industry. While intrinsic safety at the cell level, either by modifying the LIB chemistry or adopting a safer alternative, non-propagating battery designs are a valuable second layer of protection for cells and can contain thermal runaway should it occur.

Two examples of this approach stand out as particularly mature and effective, and both have been evaluated by NSWCCD with good results. First, the "super cell" design from Cadenza Innovation features multiple electrode windings (jelly rolls) within a single hermetically sealed case. Each winding is then surrounded by a ceramic housing which absorbs heat during thermal runaway, preventing cell-to-cell propagation, and releases non-flammable gases to enable a quick and safe vent opening which also activates cell level fuses (Figure 32) (64).
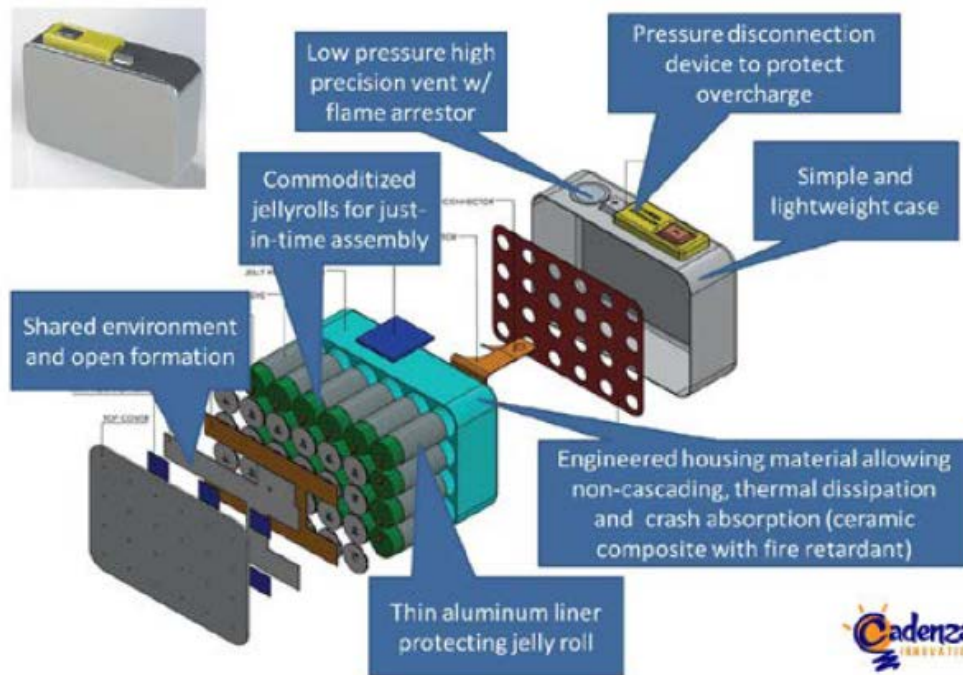
Figure 32 Schematic of the Cadenza Super Cell Design

The Cadenza Innovation design is independent of subcomponent choice, meaning it could be completely compatible with any desired anode, cathode, electrolyte, or separator material. Even when subjected to an internal short circuit (produced using the NASA and NREL developed internal short circuit device) supercells produced using the Cadenza architecture and a standard LIB chemistry did not undergo propagating thermal runaway (Figure 33) (64). Testing of modules containing six supercells in series conducted at NSWCCD showed that overcharge,

nail penetration, external short circuit, crush and over temperature testing all showed either no thermal runaway, or thermal runaway occurred only under extreme test conditions (crush above 100 kN load and over temperature > 200ºC). Development of the Cadenza super cell and evaluation by NSWCCD was sponsored by the Advanced Research Project Agency – Energy (ARPA-e).
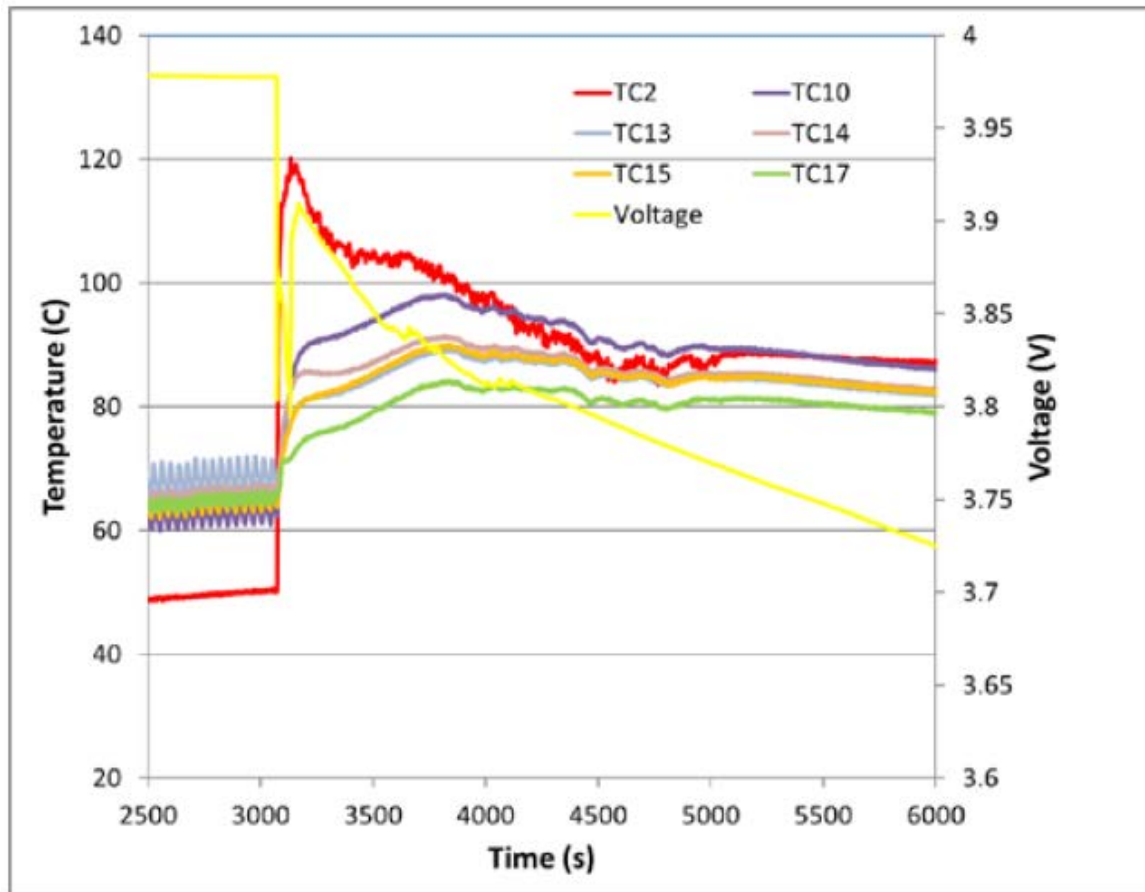
Figure 33 Temperature and voltage response of Cadenza supercell after activation of internal short circuit device

Another alternative module assembly has been demonstrated by NASA through the development of a propagation resistant space-suit battery. The NASA design is similar to the one developed by Cadenza in which cells are surrounded by a special housing intended to protect adjacent cells in the event of a single cell experiencing thermal runaway. The NASA approach relies on five design features to minimize the possibility of cell-to-cell propagation. These are:

1) Minimize sidewall ruptures, which can occur when high-energy cells with thin can walls (cylindrical cells) are used. However, this prevents proper design of vent openings and makes it difficult to predict and redirect the heat released from a failed cell.
2) Provide adequate cell spacing to minimize cell-to-cell heat transfer.
3) Individually fuse parallel cells to prevent external short circuit pathways between parallel cells and a failed cell.
4) Protect adjacent cells from hot thermal runaway ejecta (solids, liquids, and gases) achieved with pathways for vent ejecta and assumed no sidewall ruptures occur.

5) Prevent flames and sparks from exiting the battery enclosure which can ignite flammable vapors.

Battery packs designed following the five guidelines above start with cell selection – lower energy content cells are less likely to exhibit sidewall ruptures (for 18650 sized cells). Design guidelines #2 and #4 were accomplished by introducing solid heat sinks between cells. While early version of the NASA design utilized an aluminum heat sink, subsequent versions showed that incorporating a vaporizing heat sink from KULR could lead to significant mass savings and enabled the demonstration of a 227 Wh/kg battery pack (all parasitic masses included) that was capable of preventing cell-to-cell propagations (Figure 34) (65).
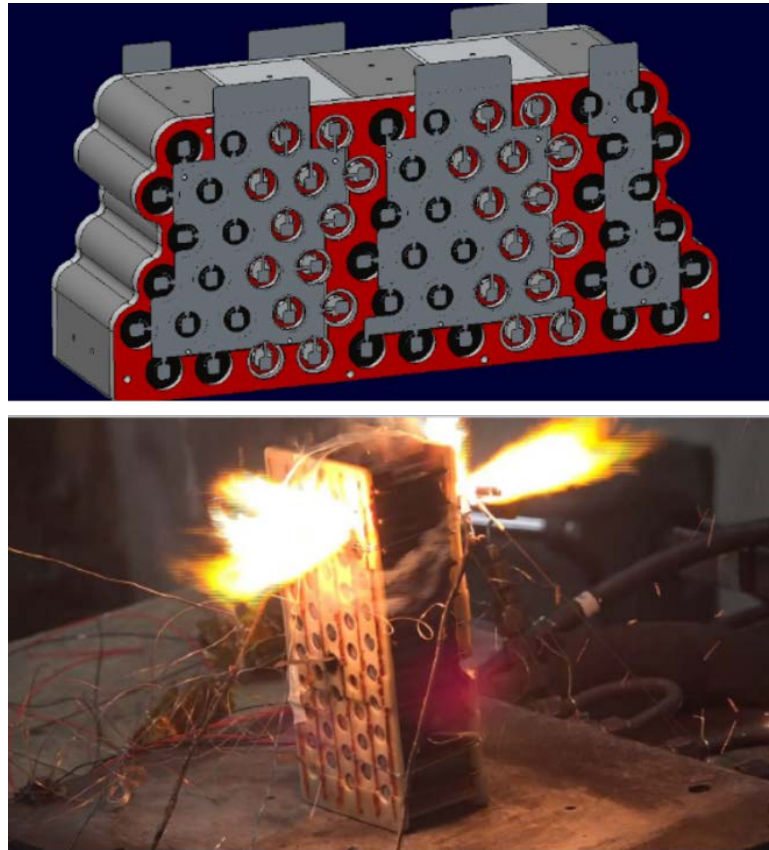
Figure 34 NASA Battery Pack Design (top) and Testing of Pack with KULR Vaporizing Heat Sink (bottom)

Packs assembled and tested at NSWCCD with the KULR material (the Thermal Runaway Shield or "TRS") were found to be highly effective at resisting cell-to-cell propagation when a trigger cell was externally heated to failure. Meanwhile, identical cells with identical configuration but no TRS underwent a complete cell-to-cell propagation under the same test conditions. Unlike the Cadenza technology, which is produced as a complete battery module, the KULR material must be integrated by a separate battery manufacturer.

3. Early Failure Detection Technologies

3.1 Overview

There are multiple ways in which a lithium-ion battery can fail, which include overcharge, thermal abuse, and short circuit. These failures can occur as a result of either personnel or system error. To prevent these kinds of failure, many applications require a Battery Management System (BMS) to monitor, protect and if possible evaluate the health of the battery. Existing state of the art BMS systems perform these functions by measuring the voltage, current, and external temperature of the individual electrochemical cells, which make up the battery. However, not all failures can be prevented with current existing BMS. Some failures occur due to manufacturing defects, damage to the integrity of the cell, or development of an internal short circuit due to lithium plating. The Expeditionary & Developmental Power and Energy Branch, Code 635 of NSWCCD evaluated a number of different prototype technologies that provide more sophisticated techniques for monitoring lithium-ion batteries and identifying faults more rapidly than existing established techniques. The evaluation will provide a starting point for future applications of early failure detection techniques into new battery technologies.

Testing at Code 635 was performed on two rechargeable 18650 lithium-ion cells from LG Chem with different capacities: 2.2 Ah and 2.6 Ah. Both cells have the same dimensions, 18 mm diameter by 65 mm length, with the same nominal voltage, 3.7 V, weigh about 44 g and contain a PTC to protect the cell from excessive charge and discharge currents.

Figure 35 View of the pink 2.2 Ah (left) and gray 2.6 Ah (right) 18650 cells.

3.2 CAMX Power LLC "Blue Demo Box" Description

CAMX Power LLC has developed a device that is capable of detecting internal shorts. The CAMX Short Detection device (Figure 36), also called the blue demo box, is a 127 mm x 102 mm x 50.8 mm blue box with a standard USB 2.0 type B connection on one side and a rectangular power connection on the other side. The rectangular power connection contains 13 wires with ring type connections at the ends for scanning up to 12 channels sequentially. Each channel is associated with a pair of wire leads to connect either a single cell or several in series or parallel. On the opposite side, the USB connection connects to a computer. As well as running the software interface, the computer provides power and communication to the blue demo box. Although the USB port of the laptop is limited to 5V and 500 mA of power, CAMX has indicated that the device can test battery systems up to the full voltage of twelve series units of lithium-ion cells or cell blocks. This enables the device to test battery systems with multiple cells in series or parallel.

The blue demo box is a proprietary system designed to detect small changes in cell behavior that are indicative of future safety hazards. Although the exact design of the system

remains the intellectual property of CAMX, it is possible to assess the likely hazards of working with the system. The blue demo box utilizes a nondestructive method for determining internal shorts. This method implements a specific proprietary electrical interrogation protocol used to detect and grade the severity of an internal short in a cell. Each scan will take from as little as 15 seconds to 2 minutes depending on the set scan time. There is no upper limit on scan time, and longer scan times can be employed to achieve greater sensitivity. An example of a scan is shown in Figure 37. Different resistors are used to simulate internal shorts and the blue demo box was used to scan cells immediately after applying the short. The blue demo box determines the health of the cell by applying certain analyses to the response obtained when the technology's electrical interrogation protocol is applied. A figure of merit is determined from the detection data taken during a scan of a cell or group of cells. This is reflected in a score number provided after the completion of each scan, with an increasingly positive score indicating an increasingly significant internal short. It will be up to the operator to determine at what score number i.e. short level is considered bad and will be hazardous to the cell.

Before the blue demo box is used for detection, it needs to be calibrated to the cell. This calibration includes determining certain settings for the control algorithm, and determining resistances of connection lines between the blue demo box and the cells of the battery under test.
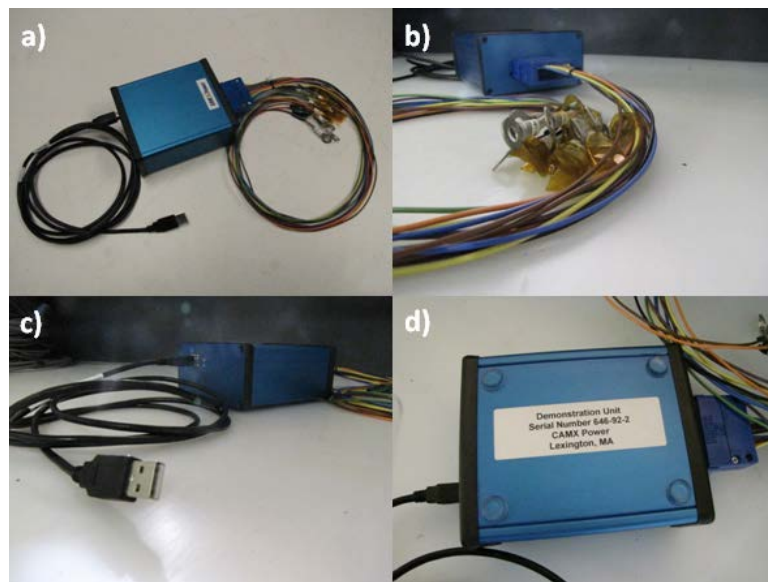
Figure 36 Display of the blue demo box: a) is the overall view, b) and c) are side views of the device, and d) is the bottom side.
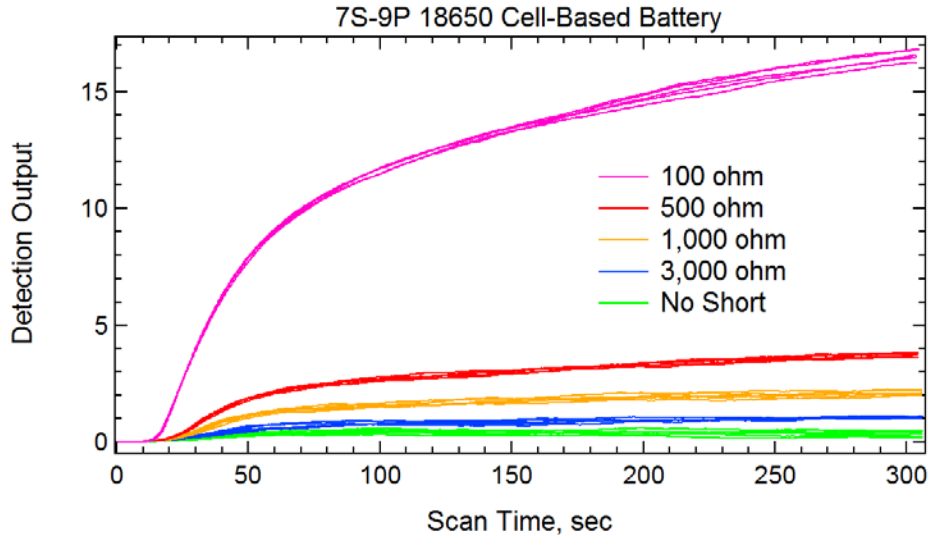
Figure 37 Example scan of simulated internal shorts generated by CAMX.

3.2.1 Discussion

The blue demo box from CAMX seems promising, as it is capable of detecting the simulated shorts. The leads of the wire will have to be connected to each of the cell terminals. However, testing shows that before the technology could be implemented in applications, it will need to be calibrated for each distinct cell and temperature. As shown previously, different cell type and different temperatures can affect the score output. In addition, the box cannot be used while the cell is cycling as charge and discharge can affect the response of the box. The box relies on the cell to be at rest where the OCV is stable. If the cell voltage fluctuates, for example due to temperature changes, the score number will change and give a false positive reading. The time length for a cell's voltage to stabilize depends on several factors, which include cell type, capacity, and temperature. To some extent, temperature fluctuation issues can be minimized by carrying out the tests with the cell in a temperature-controlled environment. Future testing would require some method for the box to adapt to this relaxation voltage.

Because the blue demo box has two wire leads per channels, it required the user to input the internal resistance of the wire. This resistance can change with temperature and contact resistance between the box, wires, and cell. CAMX has addressed this problem with their next generation "red demo box." This reduces the need for user input. NSWCCD has not performed any testing with this device yet.

For future applications, the blue demo box can potentially be used with applications such as emergency backup battery supplies. These batteries are not constantly cycled, but are left on a trickle charger so that it can be fully utilized when needed. However, trickle charging batteries may develop soft internal short and may not be easily detectable with current BMS. The blue demo box could periodically check the health of the cell to identify and determine when these shorts pose a risk to the warfighter or ship integrity. From a consumer product standpoint, this could be implemented in certain devices that are not constantly being used (in contrast to a typical personal electronic device like a smartphone, which is typically on even when not in use) such as an e-mobility device or electric vehicle. The device can check the battery pack during standby periods to determine if a soft short is developing. In both cases, the device does not have to be integrated with the product but could be part of the device battery pack's charger.

In a recent discussion, CAMX conveyed that significant progress has been made with this technology, however, these claims have not been verified independently by NSWCCD. CAMX has reduced the size of the circuit board incorporating the detection engine to a package that measures less than 2" x 2". They are in the process of adapting this circuit board technology for use in battery packs including unmanned underwater vehicles. They are calling this technology Universal Detection Technology or UDT.

3.3   Johns Hopkins University Applied Physics Lab BITS Prototype Description

Johns Hopkins University Applied Physics Laboratory (JHUAPL) has developed a prototype device called the Battery Internal Temperature Sensor (BITS), which is claimed to be capable of detecting changes in internal cell temperature using external electrical connections (66). The design of the prototype enables a cell temperature to be measured every ~40 milliseconds and can operate while the cell is cycling.

Although the exact design of the system remains the intellectual property of JHUAPL, it is possible to describe the basic design and operation of the BITS from a high level. The BITS is a two-part device, capable of monitoring a battery with tens of cells. The first part senses cells' internal temperature, internal impedance at multiple frequencies, and cell voltage. A current version of the 76 mm x 76 mm x 7 mm prototype board is shown in Figure 38. The second part has multiplexers, at the rate of two multiplexers per cell in the battery. For example, an 8-cell battery would require 16 multiplexers, and a PC board carrying the 16 multiplexers would have a footprint of 76 mm x 76 mm x 7 mm. A previous version of BITS that was tested at NSWCCD had a wiring harness that connected up to 10 cells in series or parallel. One pair of sensing leads for each cell in the battery system and a pair of leads to provide the excitation signal for a total of 22 wires for a 10 cell battery.
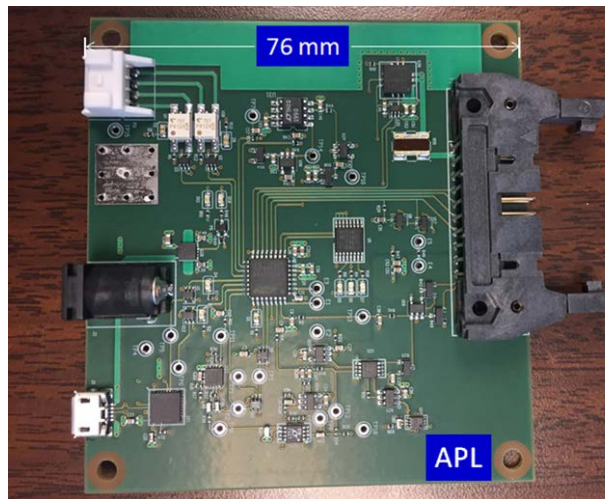
Figure 38 BITS prototype hardware.

The BITS device utilizes a nondestructive method known as electrochemical impedance spectroscopy (EIS). EIS uses a small sinusoidal input signal to measure the impedance of a cell

or battery as a function of frequency. The excitation and response currents are typically small, below 100 milliamps (mA) even for large-format (55-Ah) cells. For 18650 cells (1.5 Ah to 3.5 Ah), the excitation and response currents are below 25 mA. The cell's impedance (measured at multiple frequencies) can provide valuable information about the internal temperature and electrolyte resistance of the cell. Although the total impedance can change with State of Charge (SOC), specifically when measuring in the low frequency range (<1 Hz), the portion that the BITS device is monitoring is virtually invariant with State of Charge, but highly sensitive to the cell's internal temperature. Frequencies used in measuring internal temperatures of cells with ≤5-Ah capacity are 10 Hz and 70 Hz; for cells with higher Ah-capacity, lower frequencies may have to be used. For all cells, aging of the cell has very little influence on the measured impedance. Impedance at high-frequency (>400 Hz) is not influenced by temperature, but only by aging of the cell. JHUAPL claims that changes in the impedance at 70 Hz and 10 Hz are associated only with changes in temperature of the negative electrode and the positive, respectively, and independent of SOC, therefore provides a method for determining the cell's internal temperature during charging and discharging (67).

The BITS hardware itself directly measures the cell voltage, and the phase and magnitude of the impedance at the frequency of interest, allowing it to act as a battery management system (BMS). A Matlab script, written into the BITS' microcontroller, converts these measurements to indicate the anode temperature and cathode temperature, using an empirical equation developed by APL. The system has been previously tested by JHUAPL on three different Li-ion cell models of different cell chemistries (LCO, NMC and LFP), and capacities ranging from 2.3 Ah to 53 Ah (68).

3.3.1 Discussion

From the limited testing conducted to date it is difficult to provide a comprehensive assessment of the BITS technology. For batteries containing pre-selected "matched" cells (similar impedance values for nominally identical cells), the internal temperature values appear to be accurate, however, this is from a single test using the same exact cells which were originally used in the calibration. For the poorly matched cells (randomly selected but otherwise identical cells), it is unclear whether the variations were due to the battery assembly process or due to normal variations in the cell manufacture. Ideally, additional cells should be tested both before and after assembling into a battery pack. However, it was observed that the general shape of the temperature profiles is consistent even for the poorly matched cells, therefore, the BITS does appear to accurately indicate the changes in temperature. According to the development team at JHUAPL, these changes in temperature gradient align with phase transitions in the lithiated graphitic carbon anode, although this has not been validated at NSWCCD and would be difficult to confirm experimentally.

As mentioned previously, it was noted, the BITS operates without noise problems when a battery is under discharge and during the constant-current mode of charging. BITS will not operate during constant-voltage charging mode, because when operating in constant voltage mode, the impedance of the charger is low, comparable or even smaller than the impedance of the battery pack. When the BITS system applies the excitation signal, at least a part of the current will flow into the charger instead of the battery pack. This limitation cannot be overcome in impedance technique, and should be understood when considering compatibility issues with any potential applications and how the system's charger will operate for that application.

BITS, in its current format, works in conjunction with controls systems, to function as a battery management system. JHUAPL calls it as BITS-BMS (Figure 39).

Overall, initial testing of the technology has shown the potential to quickly detect unexpected changes in internal temperature and may be able to provide this information before it would otherwise be detected in the cell voltage or surface temperature. It is also possible to use the tool to quickly scan batches of cells to ensure that only well-matched cells are used in pack assembly. In order to validate the veracity of BITS-BMS under rigorous operating conditions of a battery, further testing under different conditions and cycling rates is required.
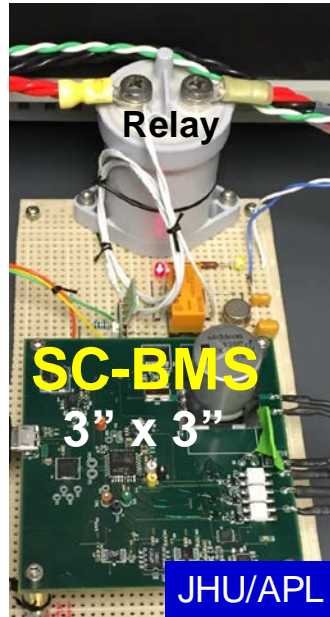
Figure 39 BITS-BMS prototype hardware.

The BITS could be implemented as part of a charger to monitor the internal temperature of cells as they are being charged. Because BITS-BMS combines internal temperature with electrolyte resistance and cell voltage, it can be used to manage charging and discharging. Additional work may help reduce its size in an integrated-circuit format. JHUAPL has licensed out this technology for commercialization.

3.4   Other Prototypes

There are a number of other early detection devices that still require evaluation. Some uses similar techniques in determining internal shorts.

3.4.1   *CAMX Real-time Detection Technology (RDT)*

Along with the universal detector (blue and red demo box), CAMX has been developing another early failure detection device that capture real-time data as the battery is under use. The box is intended for use with batteries containing multiple modules or cells in parallel and will not work with cells connected only in series. Discussions with the company indicated that this device

is larger than the blue demo box. This technology is more applicable to battery packs where multiple cells/modules are connected in parallel, such as in grid energy storage. This device could determine the problematic battery, which could be switched out without dramatically affecting the entire system. CAMX is calling this the Real-time Detection Technology or RDT.

CAMX Power reports that this technology is also being adapted for use in battery packs. They have developed prototypes for battery packs used in miner's cap lamp as well as for unmanned underwater vehicles.

3.4.2 INL/Dynexus Prototype (iRIS)

Idaho National Lab (INL), in collaboration with Montana Tech of the University of Montana, has developed a prototype sensor to improve the overall accuracy and reliability of SOH assessment techniques for electrochemical energy storage devices. The principle of operation for this inline Rapid Impedance Spectroscopy (iRIS) system is to capture impedance spectra rapidly over a broad frequency range using simple hardware and control software that processes unique algorithms to determine the spectra based on a sum-of-sines (SOS) excitation signal that yields data comparable to standard commercial off-the-shelf (COTS) equipment measurements at a number of individual frequencies. The technology was exclusively licensed for commercialization by Dynexus Technology.

The iRIS system represents a piece of engineering equipment as opposed to a commercial tool and has not yet, been miniaturized for individual system integration (Figure 40). The analysis methodology is relatively computationally simple, which uses synchronous detection without the need to compensate for crosstalk error, and could be implemented as an embedded software analysis tool. Dynexus plans on eventually miniaturizing the device down to a chip to be able to integrate it with a BMS. NSWCCD has to acquire this device for in-house testing.

Figure 40 Photograph of Dynexus Technology inline Rapid Impedance Spectroscopy prototype.

3.4.3 NRL Diagnostic Prototype- Bat$_{MD}$

The Naval Research Laboratory (NRL) with support from the Rapid Reaction Technology Office (RRTO) has developed a prototype diagnostic device to improve the safety of lithium-ion batteries and prevent catastrophic failures. This technology is similar to the BITS in that it measures the impedance of a lithium-ion battery at a single frequency invariant to the state

of charge and unique to the cell chemistry to provide critical state-of-health (SOH) information and detect internal damage prior to catastrophic failure occurring. The SOH information provided by this new technology is inaccessible to existing monitoring methods. The difference between the JHUAPL developed BITS device and NRL prototype is that the NRL prototype does relies on empirical evaluation of the imaginary component of the complex impedance and does not claim that the device measures the internal temperature of the cell. NRL has finished making a prototype device to send to NSWCCD for future testing.

3.4.4 Nexceris Li-ion Tamer

Nexceris, LLC. has been developing a device through the Navy's Small Business Innovative Research (SBIR) program capable of detecting a cell failure by detecting battery electrolyte vapor in the environment (Figure 41). The size of the device is 28.6 mm in diameter by 25.4 mm with three wires: one for power and two for signal. The device constantly monitors the environment for a change in the composition of the gas that it senses. This is beneficial for detecting cells that have been punctured or not sealed properly. In addition, it is capable of detecting cell venting during failure. Nexceris has provided data that shows that the device, Li-ion Tamer AWARE, can detect cell-venting minutes before thermal runaway can occur. NSWCCD has previously done some limited testing with the device while the device was in Phase I. NSWCCD has reached out to Nexceris for follow on testing and has received 5 prototype devices.

Figure 41 Photograph of Nexceris Lion Tamer AWARE prototype.

3.4.5 Feasible ResoStat

Feasible has been developing a device, ResoStat, for detecting changes in the battery cell through the use of sound waves. Although it was originally developed for quality control purposes, the device could be further developed as an early failure detection tool. Two devices (emitter and receiver) are placed on opposite sides of a cell or electronic device (Figure 42). The emitter will cycle a range of frequencies through the sample and with the receiver, a resonance profile can be generated that is unique to the cell. Feasible has used this device and were able to generate unique resonance profiles of different smartphones. Through conversations, the company has noted that the resolution of the device decreases as the distance between the emitter and receiver increases. Due to the size of the device, it is not ready to be implemented in any commercial BMS.
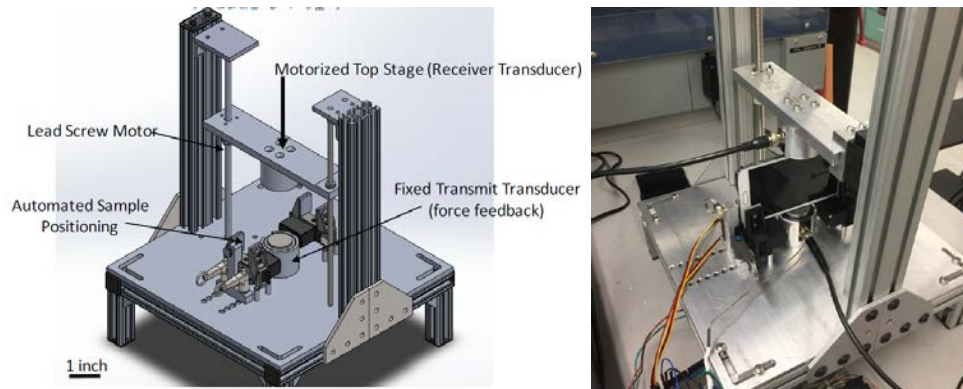
Figure 42 Schematic (left) and photograph (right) of Feasible ResoStat prototype.

3.4.6   *NSWCCD in-house strain gauge sensor*

NSWCCD has a project on studying the effects of stress on a cell with the buildup of internal pressure. Testing was performed on large-format Li-ion cells. A puncture fitting and a pressure transducer was used to monitor the pressure while a strain gauge mounted on the side of the cell was used to monitor the stress and strain on the cell casing. Cells were subjected to normal cycling, overcharge, and thermal abuse. Pressure, temperature, voltage, and strain were monitored. Testing shows good correlation between strain and pressure measurements up until 120°C. This is due to a combination of low temperature epoxy and solder that was used on the strain gauge. The benefit of using strain measurements is to be able to monitor the internal pressure of the cell without the need to puncture the cell. This is much easier to implement in battery packs without damaging the integrity of the cells.

4. Conclusions and Findings

This document provides a summary of rechargeable batteries used for consumer electronic devices, specifically LIBs, and survey several alternative technologies. In the opinion of the authors, no technologies are likely to replace LIB in the near future (next 5-10 years), while modifications of LIB active materials and electrolyte are seen every year resulting in incremental improvements to battery capabilities. Battery safety remains a pressing issue for LIB, and despite their ubiquity in many markets, the trends for future LIB are to become more energy dense and cheaper, but not necessarily safer. Certain modifications to the active cell components (electrodes and electrolyte) and passive cell components (separator, current collector, and cell packaging) have been presented in academic and industrial literature, however, most of these efforts are not supported by the large multinational LIB producers which dominate the industry. For this reason, integrating COTS LIB into packaging, which improves safety, or using "early failure detection" technologies, which can protect against some of the failure mechanisms associated with LIB may be a more workable alternative. For consumers of products containing LIB, the most effective strategy in improving safety may be careful adherence to manufacturer specifications regarding storage conditions such as temperature, handling, and charging.

5. References

1. **Linden, D and Reddy, TB.** *Handbook of Batteries.* 4th. s.l. : McGraw-Hill, 2011.

2. *Challenges for Rechargeable Li Batteries.* **Goodenough, JB and Kim, Youngsik.** 2010, Chemistry of Materials, Vol. 22, pp. 587-603.

3. *Electrical Energy Storage for the Grid: A Battery of Choices.* **Dunn, B, Kamath, H and Tarascon, JM.** 6058, 2011, Science, Vol. 334, pp. 928-935.

4. *Review-SEI:Past, Present, and Future.* **Peled, E and Menkin, S.** 7, 2017, Journal of the Electrochemical Society, Vol. 164, pp. A1703-A1719.

5. *Li-ion battery materials: present and future.* **Nitta, N, et al.** 5, 2015, Materials Today, Vol. 18.

6. *The lithium ion battery market: supply and demand.* **Navigant Research.** 2014. ARPA-e RANGE Conference.

7. *Lithium Ion Cell and Battery Safety.* **Doughty, DH.** s.l. : Battery Safety Consulting Inc, 2018. Presentation to NAVSEA.

8. *Designing Safe Lithium-Ion Battery Packs Using Thermal Abuse Models.* **Pesaran, AA., et al.** 2008. Lithium Mobile Power .

9. *18650 Cell Bottom Vent: Preliminary Evaluation into its Merits for Preventing Side Wall Rupture.* **Anderson, N, Tran, M and Darcy, E.** 2016. S&T Meeting.

10. *Higher, Stronger, Better … A Review of 5 Volt Cathode Materials for Advanced Lithium-ion Batteries.* **Kraytsberg, A and Ein-Eli, Y.** 2012, Advanced Energy Materials, Vol. 2, pp. 922-939.

11. *Understanding Electrochemical Potentials of Cathode Materials in Rechargable Batteries.* **Liu, C, Neale, Z.G. and Cao, G.** 2, 2016, Materials Today, Vol. 19, pp. 109-123.

12. *The Cathode-electrolyte interface in the Li-ion battery.* **Edstrom, K, Gustaffson, T and Thomas, JO.** 2004, Electrochmica Acta, Vol. 50, pp. 397-403.

13. *Review-Li-Rich Layered Oxide Cathodes for Next-Generation Li-Ion Batteries: Chances and Challenges.* **Rozier, P and Tarascon, JM.** 14, 2015, Journal of the Electrochemical Society, Vol. 162, pp. A2490-A2499.

14. *Silicon based lithium-ion battery anodes: a chronicle perspective review.* **Zuo, X, et al.** 2017, Nano Energy, Vol. 31, pp. 113-143.

15. *Batteries and Electrification R&D Overview.* **Boyd, Steven.** s.l. : US Department of Energy, 2018. DOE Annual Merit Review.

16. *Theoretical Limits of Energy Density in Silicon-Carbon Composite Anode Based Lithium Ion Batteries.* **Dash, R and Pannala, S.** 27449, 2016, Scientific Reports, Vol. 6.

17. *Sodium-ion Batteries: Present and Future.* **Hwang, JY, Myung, ST and Sun, YK.** 2017, Chemical Society Reviews, Vol. 46, p. 3529.

18. *Recent developments in electrode materials for sodium-ion batteries.* **Wang, LP, et al.** 2015, Journal of Materials Chemistry A, Vol. 3, p. 9353.

19. **Argonne National Laboratory.** *Modeling the Performance and Cost of Lithium-ion Batteries for Electric-Drive Vehicles.* s.l. : Department of Energy, 2012. ANL-12/55.

20. *Promise and reality of post-lithium-ion batteries with high energy densities.* **Choi, JW and Aurbach, D.** 16013, 2016, Nature Reviews Materials, Vol. 1.

21. *Challenges Facing Lithium Batteries and Electrical Double-Layer Capacitors.* **Choi, Nam-Soon, et al.** 2012, Angewandte Chemie International Edition, Vol. 51, pp. 9994 – 10024.

22. *Metal-air batteries: from oxygen reduction electrochemistry to cathode catalysts.* **Cheng, F and Chen, J.** 2012, Chemical Society Reviews, Vol. 41, pp. 2171-2192.

23. *All-carbon-nanofiber electrodes for high-energy rechargable Li-O2 batteries.* **Mitchell, RR, et al.** 8, 2011, Energy and Environmetnal Science, pp. 2952-2958.

24. *Lithium ion, lithium metal, and alternative rechargable battery technologies: the odyssey for high energy density.* **Placke, T, et al.** 2017, Journal of Solid State Electrochemistry, Vol. 21, pp. 1939-1964.

25. *A polymer electrolyte-based rechargable lithium-oxygen battery.* **Abraham, KM and Jiang, Z.** 1, 1996, Journal of the Electrochemical Society, Vol. 143.

26. **PolyPlus Battery Company.** *Manufacturing of Protected Lithium Electrodes for Advanced Lithium-air, Lithium-water, and Lithium-sulufur batteries: Final Technical Report.* Deparment of Energy. 2015. DE-EE0005757.

27. *Retaining the 3D Framework of Zin Sponge Anodes upon Deep Discharge in Zn-Air Cells.* **Parker, JF, et al.** 2014, ACS Applied Materials and Interfaces, Vol. 6, pp. 19471-19476.

28. *Rechargable nickel-3D zinc batteries: An energy-dense, safer alternative to lithium-ion.* **Parker, JF, et al.** 2017, Science, Vol. 356, pp. 415-418.

29. **Penn, Ivan.** Cheaper Battery Is Unveiled as a Step to a Carbon-Free Grid. *The New York Times.* 2018.

30. **ARPA-e.** Zinc-Air Grid Energy Storage. [Online] 2016. https://arpa-e.energy.gov/?q=impact-sheet/fluidic-grids.

31. **Whitlock, R.** The world's first nickel zinc smart battery: An interview with Tim Hysell and Todd Higinbotham of ZincFive Inc. *Renewable Energy Magazine.* [Online] 2016. https://www.renewableenergymagazine.com/interviews/the-worlda-s-first-nickel-zinc-smart-20161213.

32. *Aqueous Recharagble Li and Na Ion Batteries.* **Kim, H, et al.** 2014, Chemical Reviews, Vol. 114, p. 11788–11827.

33. **Spector, Julian.** Saltwater's Second Wave: Aquion Has Emerged From Bankruptcy Under a New Owner. *GreenTech Media.* [Online] July 24, 2017. https://www.greentechmedia.com/articles/read/saltwater-aquion-emerged-from-bankruptcy-new-owner#gs.RNaG0b28.

34. *"Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries.* **Suo, L, et al.** 6263, s.l. : Science, 2015, Vol. 350.

35. **Johns Hopkins Applied Physics Laboratory.** Breakthrough Cuttable, Flexible, Submersible and Ballistic-Tested Lithium-Ion Battery Offers New Paradigm of Safety and Performance. *Johns Hopkins APL Press Release.* [Online] 2017. https://www.jhuapl.edu/PressRelease/171016.

36. **Hendricks, Christopher and Fuentevilla, Daphne.** 12B - Procedures for Incident Investigations. *Electrochemical Power Sources : Fundamentals, Systems and Applications - Li-Battery Safety.* Cambridge : (Jürgen Garche and Klaus Brandt). Elsevier., 2019, pp. 524-537.

37. *Characteristics of lithium-ion batteries during fire tests.* **Larsson, Fredrik, et al.** 2014, Journal of Power Sources, Vol. 271, pp. 414-420.

38. *Review on solid electrolytes for all-solid-state lithium-ion batteries.* **Zheng, Feng, et al.** 2018, Journal of Power Sources, Vol. 389, pp. 198-213.

39. *Progress in solid electrolytes toward realizing solid-state lithium batteries.* **Takada, Kazunori.** 2018, Journal of Power Sources, Vol. 394, pp. 74-85.

40. *All-solid-state lithium-ion and lithium metal batteries - paving the way to large scale production.* **Schnell, Joscha, et al.** 2018, Journal of Power Sources, Vol. 382, pp. 160-175.

41. *Reasearch Progress in Improving the Cycling Stability of High-Voltage LiNi0.5Mn1.5O4 Cathode in Lithium-Ion Battery.* **Xu, Xiao Long, et al.** 22, 2017, Nano-Micro Letters, Vol. 9, pp. 1-19.

42. *A review of lithium and non-lithium based solid state batteries.* **Kim, Joo Gon, et al.** 2015, Journal of Power Sources, Vol. 282, pp. 299-322.

43. *The Manufacturing of Electrodes: Key Process for the Future Success of Lithium-Ion Batteries.* **Günther, Till, et al.** 2016, Advanced Materials Research, Vol. 1140, pp. 304-311.

44. **Exponent Failure Analysis Associates, Inc.** *Lithium-Ion Batteries Hazard and Use Assessment.* s.l. : The Fire Protection Research Foundation, 2011. 1100034.000 A0F0 0711 CM01.

45. *A General Discussion of Li Ion Battery Safety.* **Doughty, D and Roth, EP.** 2, 2012, The Electrochemical Society Interface, Vol. 21, pp. 37-44.

46. *Accelerating Rate Calorimetry Study on the Thermal Stability of Lithium Intercalated Graphite in Electrolyte.* **Richard, MN and Dahn, JR.** 6, 1999, Journal of the Electrochemical Society, Vol. 146, pp. 2068-2077.

47. *Looking Deeper into the Galaxy Note 7.* **Loveridge, MJ and al., et.** 3, 2018, Batteries, Vol. 4.

48. *Battery Technology and Safety for Manned Space Applications.* **Darcy, Eric.** 2018. Presented to NAVSEA at Washington Navy Yard.

49. **Orendorff, CJ, et al.** *Advanced Inactive Materials for Improved Lithium-Ion Battery Safety.* s.l. : Sandia National Laboratory, 2012. SAND2012-9186.

50. *Battery Separators.* **Arora, P and Zhang, Z.** 2004, Chemical Reviews, Vol. 104, pp. 4419-4462.

51. *The Role of Separators in Lithium-ion Cell Safety.* **Orendorff, Christopher J.** s.l. : The Electrochemical Society Interface, 2012, Vol. Summer.

52. **Amionx.** Amionx SafeCore - Battery safety from the inside-out. [Online] 2018. http://www.amionxsafecore.com/technology.html .

53. **Morin, Brian.** How I Stumbled into Something BIG: The Founding of the Soteria Battery Innovation Group. *Battery Power.* [Online] August 13, 2018. https://www.batterypoweronline.com/news/how-i-stumbled-into-something-big-the-founding-of-the-soteria-battery-innovation-group/.

54. *Soteria Architecture Cell Materials.* **Hu, Carl.** 2018. Proceedings of the 48th Power Sources Conference. 6-4.

55. *Quantifying Thermal Runaway and Improvements Through Materials Development.* **Orendorff, CJ, et al.** 2015. Next Generation Batteries 2015. SAND2015-2970C.

56. **Orendorff, CJ.** *Abuse Tolerance Improvements.* s.l. : Sandia National Laboratories, 2012. Energy Storage Annual Merit Review Presentation. ES036.

57. *Enhancing the High-Voltage Cycling Performance of LiNi0.5Mn0.3CoO.2O2 by Retarding Its Interfacial Reaction with an Electrolyte by Atomic-Layer-Deposited Al2O3.* **Su, Yantao, et al.** 2015, Applied Materials and Interfaces, Vol. 7, pp. 25105-25112.

58. *Modification of Ni-Rich FCG NMC and NCA Cathodes by Atomic Layer Deposition: Preventing Surface Phase Transitions for High-Voltage Lithium-Ion Batteries.* **Mohanty, Debasish, et al.** 2016, Scientific Reports, Vol. 6, p. 26532.

59. *Unexpected high power performance of atomic layer deposition coated Li[Ni1/3Mn1/3Co1/3]O2 cathodes.* **Kim, Ji Woo, et al.** 2014, Journal of Power Sources, Vol. 254, pp. 190-197.

60. *Ultrathin Direct Atomic Layer Deposition on Composite Electrodes for Highly Durable and Safe Li-Ion Batteries.* **Jung, Yoon Seok, et al.** 2010, Advanced Materials, Vol. 22, pp. 2171-2176.

61. **Forge Nano.** An Introduction to Particle ALD. [Online] July 11, 2017. http://www.forgenano.com/uncategorized/introduction-particle-ald/.

62. *Development of a Nonflammable Electrolyte for Li-ion Batteries.* **Lang, Christopher, Moran, P and Herb, J.** 2018. 48th Power Sources Conference. VG-2018-47.

63. **Orendorrf, CJ, et al.** *Abuse Tolerance Improvements (SNL).* s.l. : Sandia National Laboratories, 2015. SAND2015-9391R.

64. **Cadenza Innovation, Inc.** *High Capacity and Low Cost Lithium-ion Cell for Peak Energy Demand (Advanced Clean Power Program).* 2017. NYSERDA Report 70422.

65. *Update on Cell Thermal Runaway Calorimeter.* **Darcy, E, et al.** 2017. 6th IAPG Li Battery Safety Meeting.

66. *Monitoring dynamic thermal behavior of the carbon anode in a lithium-ion cell using a four-probe technique.* **Srinivasan, R.** 2012, J. Power Sources, Vol. 198, pp. 351-358.

67. *The five modes of heat generation in a Li-ion cell under discharge.* **Srinivasan, R., et al.** 2014, J. Power Sources, Vol. 262, pp. 93-103.

68. *Instantaneous measurement of the internal temperature in lithium-ion rechargeable cells.* **Srinivasan, R., et al.** 2011, Electrochim. Acta, Vol. 56, pp. 6198-6204.

69. *What are batteries, fuel cells, and supercapacitors?* **Winter, Martin and Brodd, Ralph J.** 10, 2004, Chemical Reviews, Vol. 104, pp. 4245–4270.