

CHAPTER 3

LITHIUM-ION BATTERIES

Yuliya Preger, Loraine Torres-Castro, Sandia National Laboratories, Jim McDowall, Saft America Inc.

Abstract

Lithium-ion batteries are the dominant electrochemical grid energy storage technology because of their extensive development history in consumer products and electric vehicles. Characteristics such as high energy density, high power, high efficiency, and low self-discharge have made them attractive for many grid applications. The ability to significantly modify materials properties of the electrodes and electrolytes has made it possible to tailor Li-ion batteries for many different operating conditions and applications. Current research is aimed at increasing their energy density, lifetime, and safety profile.

Key Terms

battery, cell design, energy density, energy storage, grid applications, lithium-ion (li-ion), supply chain, thermal runaway

1. Introduction

This chapter is intended to provide an overview of the design and operating principles of Li-ion batteries. A more detailed evaluation of their performance in specific applications and in relation to other energy storage technologies is given in Chapter 23: Applications and Grid Services. A detailed assessment of their failure modes and failure prevention strategies is given in Chapter 17: Safety of Electrochemical Energy Storage Devices.

Lithium-ion (Li-ion) batteries represent the leading electrochemical energy storage technology. At the end of 2018, the United States had 862 MW/1236 MWh of grid-scale battery storage, with Li-ion batteries representing over 90% of operating capacity [1]. Li-ion batteries currently dominate the grid-scale battery market due to their extensive history in consumer products and growing production volumes for electric vehicles. Characteristics such as high energy density, high power, high efficiency, and low self-discharge have made them attractive for many grid applications. Figure 1 shows the global dominance of Li-ion technology in the electrochemical grid energy storage market.

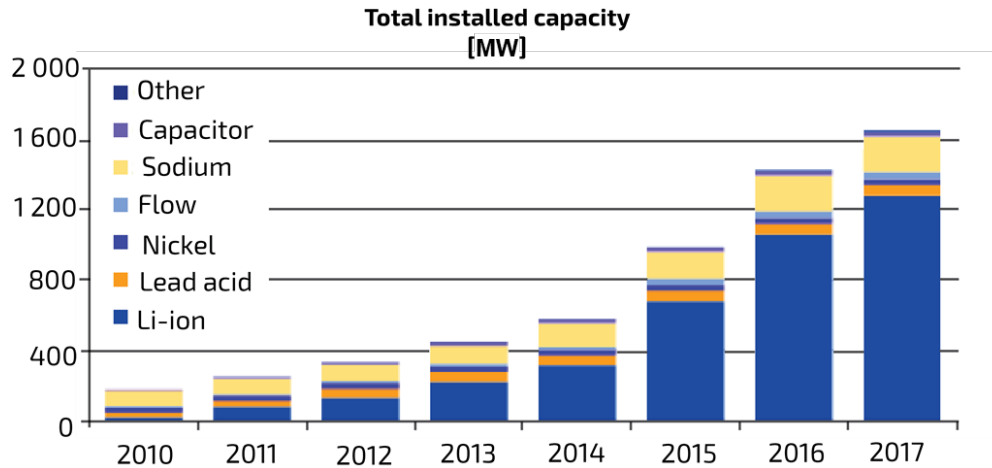


Figure 1. Global cumulative installed capacity of electrochemical grid energy storage [2]

The first rechargeable lithium battery, consisting of a positive electrode of layered TiS_2 and a negative electrode of metallic Li, was reported in 1976 [3]. This battery was not commercialized due to safety concerns linked to the high reactivity of lithium metal. In 1981, layered LiCoO_2 (LCO) was first proposed as a high energy density positive electrode material [4]. Motivated by this discovery, a prototype cell was made using a carbon-based negative electrode and LCO as the positive electrode. The stability of the positive and negative electrodes provided a promising future for manufacturing. In 1991, Li-ion batteries were finally commercialized by Sony Corporation. The commercialized cells could deliver an energy density of $120\text{--}150 \text{ Wh kg}^{-1}$ with a high potential of 3.6 V [5]. In the three decades since then, the structure and operation of Li-ion batteries have remained largely the same, although researchers have discovered many new configurations of negative electrode-electrolyte-positive electrode that provide enhanced performance in terms of energy output, safety, and cost. Figure 2 summarizes the numerous positive and negative electrodes under consideration for future generations of Li-ion batteries.

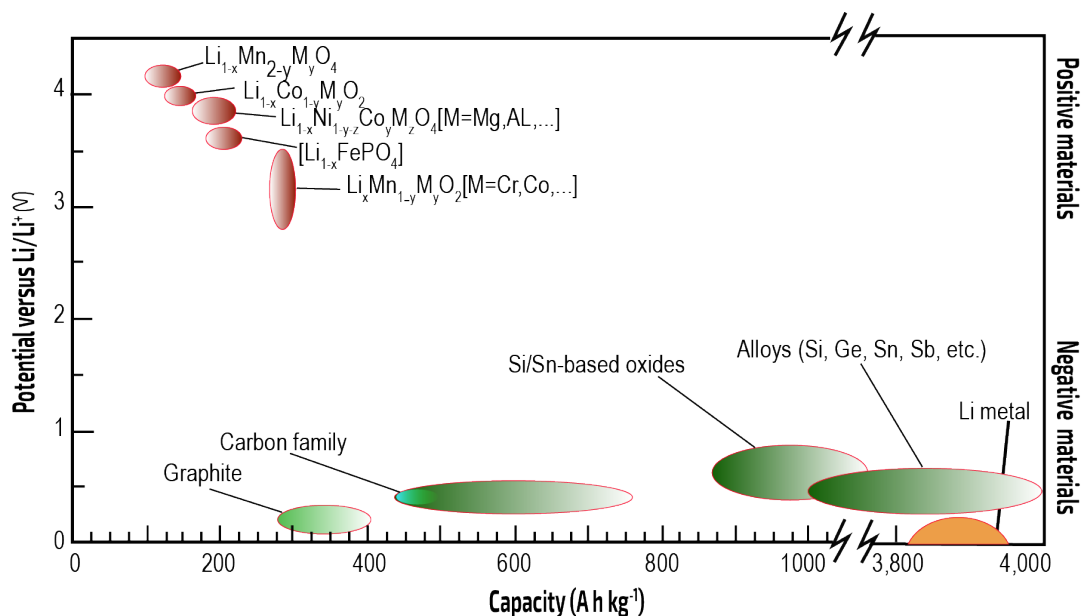


Figure 2. Comparison of positive and negative electrode materials under consideration for the next generation of rechargeable lithium-based batteries [6]

1.1. Nomenclature

Colloquially, the positive electrode in Li-ion batteries is routinely referred to as the “cathode” and the negative electrode as the “anode.” This can lead to confusion because which electrode is undergoing oxidation (anode) and which electrode is undergoing reduction (cathode) changes depending on whether a Li-ion battery is charging or discharging. To avoid this confusion, this chapter refers to positive and negative electrodes, rather than cathodes and anodes, respectively.

2. State of Current Technology

2.1. Current Implementation of Li-ion Batteries

2.1.1. Battery Structure

2.1.1.1. Cell Reaction

A Li-ion battery is composed of the active materials (negative electrode/positive electrode), the electrolyte, and the separator, which acts as a barrier between the negative electrode and positive electrode to avoid short circuits. The active materials in Li-ion cells are the components that participate in the oxidation and reduction reactions. These components operate by incorporating lithium ions in an intercalation process in which lithium ions are removed or inserted into a host without significant structural changes [7]. Typically, the positive electrode is a lithium metal oxide, and the negative electrode is graphite. The electrolyte is composed of a lithium salt (e.g. LiPF_6) in a mixture of organic solvents (e.g. ethylene carbonate [EC] and dimethyl carbonate [DMC]). The commonly used current collectors for the positive electrode and negative electrode are aluminum and copper, respectively.

During the discharging process, the positive electrode is reduced and the negative electrode is oxidized. In this process, lithium ions are de-intercalated from the negative electrode and intercalated into the positive electrode. During charge, lithium ions are de-intercalated from the positive electrode and intercalated into the negative electrode. The movement of Li is driven by the potential difference between the electrodes upon charge and discharge. The electrons flow through an external circuit generating the current. Parasitic reactions with the electrolyte during the first few cycles create a passivation layer on the surface of the negative electrode, the solid-electrolyte interphase (SEI). This leads to irreversible loss of Li inventory, which may result in capacity loss in some technologies. However, the rated capacity of a Li-ion cell is always net of the lithium ions consumed during this initial SEI formation. Furthermore, the passivation layer acts as a barrier and reduces further decomposition of the electrolyte during the cycle life of the cell. The graphical representations of these processes in a Li-ion battery are illustrated in Figure 3.

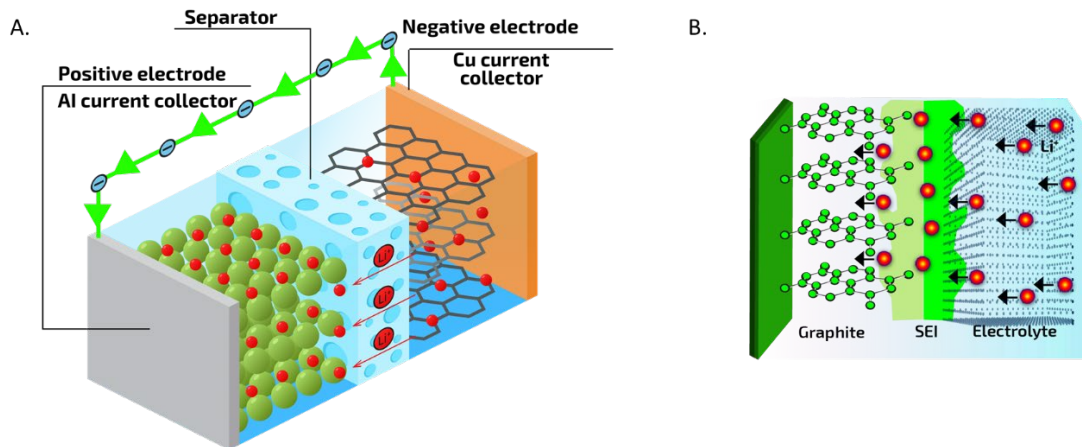


Figure 3. A) Lithium-ion battery during discharge. B) Formation of passivation layer (solid-electrolyte interphase, or SEI) on the negative electrode.

2.1.1.2. Key Cell Components

Li-ion cells contain five key components—the separator, electrolyte, current collectors, negative electrode, and positive electrode—all of which can be substantially modified depending on the application.

Separator

The separator is a membrane located between the electrodes to prevent physical contact without compromising the flow of lithium ions. Chemical and electrochemical stability against the electrolyte and electrodes are one of the key requirements of separators, as well as small pore size (<1 μm). The pore size involves trade-offs between larger holes to optimize ion transport and smaller holes to avoid short circuiting the cell. Commercial Li-ion batteries with liquid electrolytes most often use microporous polymer membranes. In general, the microporous polymer membranes are made of polyethylene (PE), polypropylene (PP), or combinations of both (PP/PE/PP). The combination PP/PE/PP is a multilayer separator known as the “shutdown separator.” The layers have different phase transition temperatures. If the cell temperature increases beyond the allowed limit, the PE layer melts and fills out the pores of the outer PP layers, blocking ion transport and current flow in the cell to prevent battery failure.

Electrolyte

The role of the electrolyte is to act as a medium for ionic conduction and a barrier for electronic conduction to avoid self-discharge of the cell [8]. The electrolyte must be stable against oxidation and reduction reactions and withstand the potential window of the electrochemical reaction without substantial degradation. Other essential requirements are (1) good Li^+ conductivity over a wide temperature range, (2) adequate diffusion of Li-ions at operating temperatures and charge/discharge rates, (3) does not dissolve the SEI, (4) thermal stability, (5) low toxicity, and (6) low cost [9]. Li-ion batteries generally use a liquid electrolyte, made with a lithium salt, typically LiPF_6 , dissolved in carbonates such as EC, DMC, and diethyl carbonate (DEC) [10]. Various additives may be incorporated to increase lifetime [11].

Current collectors

A current collector facilitates electron flow from large area electrodes to the cell terminals. The positive electrode uses aluminum foil as a current collector while the negative electrode uses copper foil. While copper is denser and more expensive than aluminum, aluminum is electrochemically unstable at the potential of the graphite electrode. The exception is the lithium titanate (LTO) negative electrode, where the higher operating potential allows the use of aluminum. The copper collector of graphitic negative electrodes can dissolve during overdischarge and form microshorts on recharge. Preventing this is one of the functions of the battery management system (see 2.1.3). The electrode foils represent inert materials that reduce the energy density of the cell. Thus, they are made as thin as possible.

Negative electrode

Graphite is the preferred material for the negative electrode due to its stability over many cycles of expansion during charge, contraction during discharge, abundance, and low cost. It also has a reasonably low potential. The difference in potential between the negative and positive electrodes is the cell voltage, a major factor in energy density. Thus, lower potential materials are preferred for the negative electrode. Graphite also has a relatively low capacity of $\sim 370 \text{ mAh g}^{-1}$, leading to extensive research into alternative carbonaceous materials with more active sites for lithium intercalation to increase capacity.

Demand for negative electrodes capable of charging and discharging quickly (for high power applications) has led to the development of LTO. The most common LTO negative electrode is $\text{Li}_4\text{Ti}_5\text{O}_{12}$, with a theoretical capacity of 175 mAh g^{-1} . Its capacity is lower than that of graphite, but the material is more stable during lithiation/delithiation and can sustain tens of thousands of cycles.

Positive electrode

The following section provides an overview of the basic material properties of the most popular classes of Li-ion battery positive electrodes and links these properties to their preferred uses and applications. The classification of positive electrode materials for Li-ion batteries is generally based on the crystal structure of the compound: olivine, spinel, and layered [12]. The olivine positive electrodes are materials with more open structures such as LiFePO_4 (LFP), which delivers an experimental capacity of 160 mAh g^{-1} at an average potential of 3.5 V. For compounds with a spinel structure, like LiMn_2O_4 (LMO), the experimental capacity is lower (120 mAh g^{-1}); however, the average potential is significantly higher (4.1 V). Olivine and spinel structures lead to flat discharge voltage profiles, which are suitable for constant-power discharges but bad for cell balancing during prolonged operation at partial state of charge. The positive electrodes with a layered structure provide capacities ranging from 150 mAh g^{-1} to 200 mAh g^{-1} with an average potential above 4.0 V. The layered structures produce cells with sloping voltage profiles, where cell balancing is straightforward at any state of charge. The positive electrodes that are most common in Li-ion batteries for grid energy storage are the olivine LFP and the layered oxide, $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC). Their different structures and properties make them suitable for different applications [13].

- ***Olivine structure/LiFePO₄***

LFP has a lower average potential (vs. Li/Li^+) than all other popular commercial positive electrodes, and a correspondingly lower energy density. This initially limited its use in electric vehicle applications, where energy density is at a premium. However, low cost and thermal stability have fueled its broad adoption in grid energy storage applications. The

low-cost stems from the absence of metals like Co. LFP is more thermally stable because unlike the metal-oxide bond in most other positive electrodes, the phosphorus-oxygen bond is strong, and oxygen does not evolve during degradation (See *Chapter 17: Safety of Electrochemical Energy Storage Devices*). The use of carbon additives to enhance electronic conductivity and improve capacity at high discharge rates was critical to the broad adoption of this electrode.

- ***Spinel structure/LMO***

The potential use of LMO as a positive electrode for Li-ion batteries was reported in 1983 [14]. The benefits associated with the spinel structure, specifically the high average potential and specific energy, attracted major attention. The use of Mn instead of Co or Ni also provided a wide range of benefits due to the low cost. However, LMO suffers from several drawbacks including low theoretical capacity and dissolution of Mn in the electrolyte at elevated temperatures. Positive electrodes that use LMO alone are uncommon in grid energy storage systems, but it is often used in a blended positive electrode with the layered NMC.

- ***Layered structure***

Positive electrodes with a layered structure have been the most popular material for Li-ion batteries since the commercialization of LCO. This structure facilitates intercalation; however, complete charge or discharge of the electrode leads to the collapse of the structure. Practical capacity is thus lower than theoretical capacity.

LCO dominated the Li-ion battery industry for over two decades due to its easy synthesis and long cycle life. However, it has a low maximum delivered capacity (140 mAh g⁻¹) and a high cost. Therefore, the replacement of Co with more abundant transition metals is ongoing and LCO positive electrodes are not employed in grid energy storage applications.

LiNiO₂ (LNO) is a layered positive electrode material with a structure similar to LCO. The material has been extensively studied because it has a higher practical capacity of 200 mAh g⁻¹. Additionally, it has the capability to be discharged below 2 V. Safety concerns around the lower thermal stability of LNO have halted its commercialization as a positive electrode material and there are no commercial positive electrodes that use pure LNO.

Efforts to incorporate other transition metals into the layered structures of pure LCO and LNO ultimately led to the development of NMC and LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ (NCA) positive electrodes. The first commercialized NMC positive electrode was LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC 111). This was followed by LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ (NMC 532), which offers higher energy density, lower cost, and longer cycle life. Researchers are currently optimizing positive electrodes with even higher nickel content such as LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC 622) and LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC 811) to increase energy density and lower production cost by reducing the utilization of cobalt. In NCA, the partial replacement of nickel with cobalt and aluminum made it possible to stabilize the structure, aiding its commercialization as a high nickel positive electrode material. However, thermal stability and long-term cycling are still a concern for both NMC 811 and NCA, particularly due to the energetic thermal runaway of these cells when exposed to abnormal conditions.

- ***Practical Comparisons***

Figure 4 shows application-oriented comparisons of the positive electrodes most relevant for grid energy storage. Each has advantages and disadvantages. Thus, the use of blended positive electrodes, such as NMC-LMO, to fine-tune the characteristics of a cell for a

particular application is increasingly common. Additionally, metrics may vary depending on electrolyte additives and the formulation of the cathode (for example, the energy density of NMC increases and the safety decreases with increasing Ni content). Thus, Figure 4 is just intended to provide rough comparisons. A breakdown of common compositions for different applications is provided in Chapter 23: Applications and Grid Services.

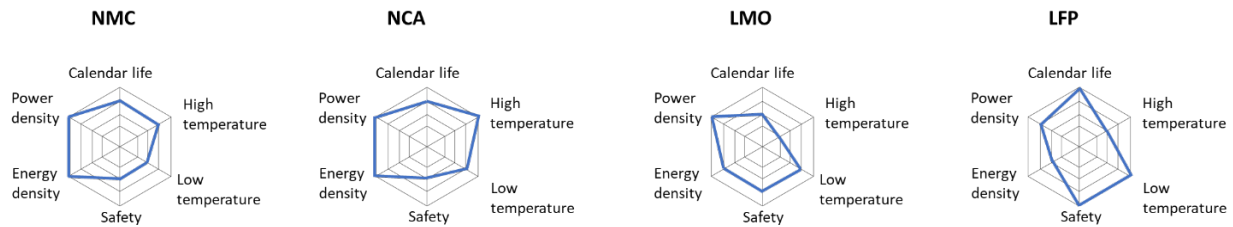


Figure 4 Comparison of common positive electrodes across several metrics. Metrics may vary depending on electrolyte additives

2.1.2. Cell Design

2.1.2.1. Form Factor

The cylindrical form factor has been the preferred design of Li-ion batteries for consumer electronics over the last three decades due to ease of manufacturing. The most significant benefit is the ability of the cylinder to resist high internal pressure and support the expansion and contraction of the electrodes during intercalation. Moreover, cylindrical pack configurations minimize heat transfer from cell to cell and reduce the risk of failure propagation. However, the geometric inefficiency of cylindrical cells limits the volumetric energy density, as significant space is lost in the pack design.

The increasing demand for high energy density Li-ion batteries has diverted the focus to prismatic cell formats, as shown in Figure 5B. Prismatic cells are generally constructed with electrode strips and separators folded into a stack and enclosed in a hard casing. Pouch cells are another type of prismatic cell that are enclosed in a small amount of polymer wrapping (mylar foil). Prismatic cells, either hard casing or pouch, provide space maximization and higher energy density; however, the manufacturing cost is higher compared to cylindrical cells.

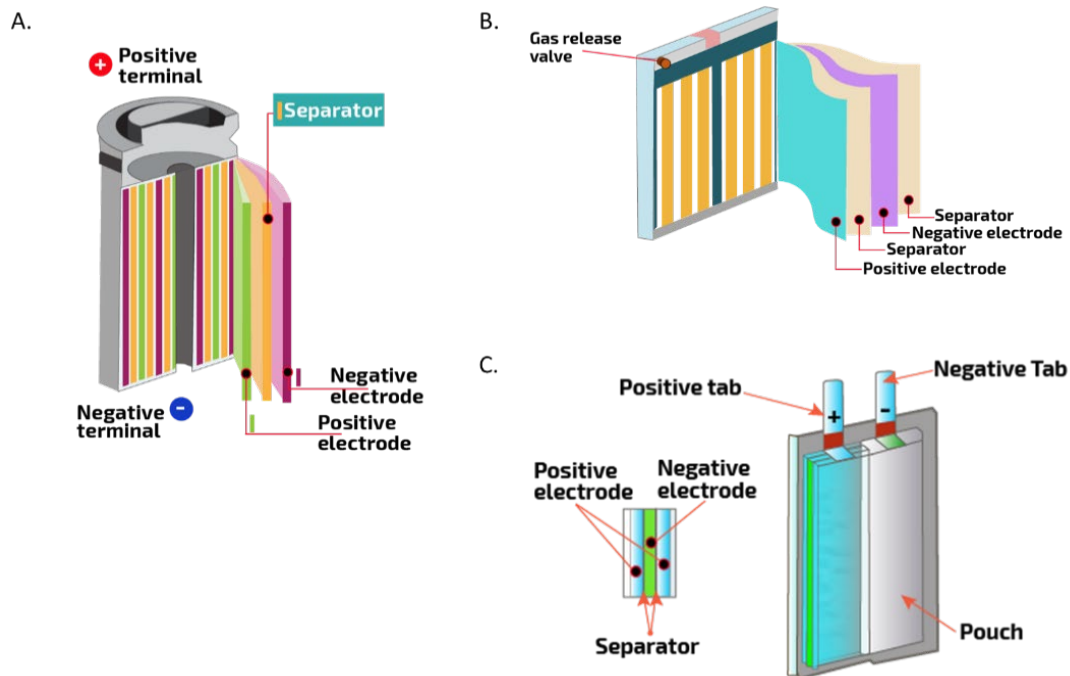


Figure 5. Schematics of various form factors for Li-ion cells, including: A) cylindrical, B) prismatic, and C) pouch

2.1.2.2. Power vs. Energy

Over the last three decades, there have been extensive iterations on cell design and chemistry to achieve application-specific requirements. Improved positive and negative electrodes, along with thoughtful cell engineering, have led to cells with high volumetric energy densities. However, the requirements to obtain a high energy density cell are inversely proportional to the requirements for a high-power cell. A breakdown of power- and energy-oriented applications in grid energy storage is provided in Chapter 23: Applications and Grid Services.

One of the methods for controlling power versus energy is the electrode coating process. The precision-coating process uses active material slurries that are deposited onto current collectors. Low coating thickness increases the power capability while at the same time reducing the available energy. Power cells can be designed to fully discharge in minutes, which is required for some applications. When the application requires discharge over several hours, a high energy density cell is needed. High energy density is achieved by coating thicker layers of active material onto the current collectors. However, there are some limitations to how thick the electrode can be without affecting the overall performance of the cell. For example, thicker electrodes can limit the speed of lithium ion diffusion through the SEI and the battery constituents, as well as cause local non-uniformity in currents, temperatures, and aging rates. Therefore, thoughtful consideration is required while designing a cell to identify if power or energy is the priority.

2.1.3. Modular Design

Individual Li-ion cells (or groups of cells in parallel) are combined in series to form modules, the core building blocks of large-scale energy storage systems. The number of cells in parallel and series used to create modules depends on a specific manufacturer's design. Design factors include the desired voltage range for the power electronics (See Chapter 13: Power Conversion Systems)

and the desired relationship between power and energy. The cells in a module are arranged to maximize heat dissipation and reduce the potential of thermal runaway propagation from one cell to another. Modules include a solid frame to protect against external shock, heat, and vibration. They are connected in series to form strings of the desired voltage, then strings are connected in parallel for the desired energy and power ratings.

The above paralleling aids in cell balancing by a BMS. Each module, or string of modules, can have its own BMS with circuits to measure the voltage of each cell (or group of parallel cells). Their voltage is adjusted either “passively” or “actively” to match other cells in the module. In passive balancing, the most common approach, switchable shunt resistors bleed off excess charge from higher voltage cells. In active balancing, capacitors are used to shuttle charges between cells, or a small power supply connects successively to chosen cells. There are also typically several temperature sensors throughout a module, but rarely at the cell level. The string-level BMS is also responsible for monitoring operation within a safe envelope, managing the string contactor(s), and communicating operating parameters, alarms, and warnings up to the next level. Contactors are electromechanical switches that connect and disconnect the battery from the load device. They ensure that the battery connects to the load only when required and disconnects in the event of a critical fault.

2.1.4. System Design

For safety purposes, grid-scale batteries include numerous components beyond the modules and string-level BMS [15]. For multi-string systems connected to a common DC-bus, there is normally a single point of connection to the host system to communicate aggregate battery data. This primary unit may be a separate piece of hardware, or it may take the form of a dynamic primary-secondary setup between the string-level BMSs. Additionally, isolation, or ground fault detection, ensures that users are not exposed to hazardous voltages. Various new sensors are being explored to detect battery failures such as cell venting and internal short circuits. Systems may also incorporate fire suppression technologies, such as sprinklers, inert gases, or aerosols.

All of these components should be contained in an enclosure that is suitable for the operating environment. For grid-scale batteries, two common units are a shipping container and cabinet-based systems. In the former, racks of batteries are arranged along the walls of the container. Appropriate spacing between racks and the modules within them is critical to preventing the spread of fire if a few cells go into thermal runaway. Cabinet-based systems can be shipped fully assembled and units are duplicated as many times as needed to build a utility-scale site.

System level thermal management is another critical consideration. Temperature and temperature uniformity both significantly affect the lifespan, performance, and safety of Li-ion batteries. Without proper thermal management, overheating cells will degrade, malfunction, or even go into thermal runaway. Minimizing the temperature spread between cells will also minimize variation in the cells’ performance and degradation. The primary source of heat in a grid-scale system is the batteries themselves (from resistive heating), however, other heat sources include the DC bus and the external environment.

3. Challenges and Opportunities

3.1. Cost and Manufacturing

Li-ion batteries currently dominate the grid-scale battery market due to their extensive history in consumer products and the supply chain for electric vehicles. EV battery pack prices have fallen from \$1100/kWh in 2010 to \$156/kWh in 2019 due to expanding order size and production capacity [16]. They are expected to reach \$100/kWh by 2023. Module-level costs for grid-energy storage systems are following a comparable trajectory. However, there is concern that increasing demand and political instability in the regions of extraction could lead to a shortage of raw materials, notably the cobalt used in NCA and NMC positive electrodes. This caused the price of cobalt spike to three times its normal level in 2017 and 2018. In recent years, attention has turned to reduce materials costs by exploring new electrode formulations. For example, there has been much research into low- and no-Co positive electrodes. The proportion of metals in NMC positive electrodes has undergone an evolution from the original “111” mix (with an equal amount of nickel, manganese, and cobalt) to 532, 622, and 811 alloys.

The United States is unlikely to have the Li-ion battery supply chain to support growing energy storage demand. According to an analysis by BloombergNEF, in early 2019 there were 316 GWh of global lithium cell manufacturing capacity. China was home to 73% of this capacity, followed by the United States at 12% [17]. The US fraction of manufacturing capacity is expected to drop in the next few years as China makes substantial investments in infrastructure. Furthermore, within the last year, the European Union (EU) has decided to spend billions of dollars expanding their own Li-ion battery manufacturing capacity [18]. The US government and various industry groups have recognized the declining leadership of the United States in Li-ion battery manufacturing. To support domestic development, the Department of Energy recently launched the Energy Storage Grand Challenge, a “comprehensive program to accelerate the development, commercialization, and utilization of next-generation energy storage technologies and sustain American global leadership in energy storage [19].”

3.2. Recycling and Related Issues

In addition to challenges in manufacturing Li-ion batteries, it is also important to consider challenges in decommissioning and disassembling energy storage systems. The current recycling rate for Li-ion batteries in the US and EU is around 5%, whereas 95% of lead acid batteries are recycled [20]. The low recycling rate is due to a combination of technical constraints, economic barriers, logistic issues, and regulatory gaps (particularly for small batteries in consumer devices). Current Li-ion batteries come in a variety of shapes and sizes that are not designed to be disassembled. As the first generation of EV and grid-scale batteries approaches end-of-life, it is important to consider how to handle them. Two pathways are currently being explored: 1) extraction of individual metals via smelting and/or acid leaching, and 2) extraction of intact alloy positive electrodes [21]. Initially, only positive electrode components and the copper foil from the negative electrode were considered worth recycling. However, companies have recently established processes for lithium recycling as well.

Another avenue under consideration for electric vehicle batteries is repurposing them for grid energy storage use, or second life. Once a battery pack has reached the end of its first life in an EV, possibly due to power loss and the resulting reduction in acceleration, it still has a high residual capacity and can continue to be used in a less demanding grid application. There have been

numerous demonstrations of this concept [22], but it may be more difficult to implement than recycling due to liability concerns. For example: How can used cells be certified as “safe”? How long can they be insured? Who is accountable if there is a violent failure? For more information on this subject, refer to Underwriters Labs recently published UL 1974, Standard for Evaluation for Repurposing Batteries, which lists extensive characterization protocols for second life batteries.

There is a growing movement toward battery “ID tags” that would help identify individual batteries and keep track of their usage histories. This would facilitate the transfer from first life to second life. It is also important to consider while second life battery cells will be less expensive than fresh cells, there are additional costs associated with physical repackaging and development of new BMS protocols for aged cells with different electrochemical profiles. The rapid pace of development in battery technology may also eventually make “second life” a less attractive prospect. In 5 to 8 years, the EV batteries sold today will likely be competing with new batteries that are safer, longer lasting, and more energy dense.

3.3. Increasing Lifetime

Li-ion batteries are known for their long service life; however, their operational lifetime can vary widely with the environmental conditions and use cases. Aging is caused largely by parasitic reactions at the electrodes that occur even when a battery is not being cycled (calendar aging) and stress that occurs during charge and discharge (cycle aging). Calendar and cycle aging are largely independent of each other and are additive. For most cycling conditions, aging is linear down to 80% capacity and for some, it is linear down to 60% capacity.

The influence of various operating conditions on calendar and cycle aging is covered in greater depth in Chapter 17: Safety of Electrochemical Energy Storage Devices. Briefly, cycle aging is affected by depth of discharge, charge/discharge rate, and temperature. Each chemistry responds slightly differently to each variable and there is no precise set of ideal operating conditions. For depth of discharge, a narrower window reduces the mechanical stress of volume change on the electrodes. Higher discharge rates put more mechanical stress on the electrodes and increase resistive heating, but they have a far less significant influence than charge rates. There is a limit to how quickly Li can pass through the SEI and diffuse into the graphite during charging. When this limit is exceeded, the Li plates on the SEI, where it reacts with electrolyte to form more SEI. In addition to increasing the cell resistance, this process reduces the capacity of the cell and can pose a safety risk in the form of potential dendrite formation. Temperature-dependent degradation is a continuum between Li plating at lower temperatures and SEI formation at higher temperatures [23]. Calendar aging is largely influenced by the state-of-charge (SOC) and temperature. The impact of temperature on calendar aging follows an Arrhenius relationship, with aging rates increasing with temperature [24, 25].

Various battery modifications are currently being considered to increase lifetime, with new electrolyte formulations representing the most active area of research [11]. Choosing the appropriate electrolyte additive blend for each application is important because different formulations are optimized for different conditions (e.g., temperature, charging rate, etc.). Different degradation modes may become possible for a particular formulation, even for seemingly harmless changes to cycling conditions, such as moving from 40°C to 20°C.

Given the influence of operational variables on Li-ion battery degradation, it is also critical to have a BMS that tightly controls the battery operational window. For example, the BMS can minimize

exposure to deep discharge. Each battery chemistry has slightly different operational preferences and it is important to factor those in when programming the BMS rather than using a one size fits all approach. One other action currently being considered is restricting how batteries might respond to grid demand. This involves factoring in the cost of battery degradation into operational cost optimization algorithms.

When trying to create an environment that minimizes battery degradation, it is also important to consider the impact on degradation of other components in the full system. For example, increased lifetime of the electrochemistry can be achieved through lower temperatures, but in humid locations lower temperatures increase the risk of condensation and corrosion of the electrical connections when containers are opened for servicing.

3.4 Increasing Energy Density

The energy density requirement for Li-ion batteries in grid energy storage applications is lower than that for EV applications. This has boosted the use of LFP cells, which are considered safer than metal oxide positive electrodes but are generally avoided in automotive applications due to their lower energy density. However, there has been a recent trend to increase energy density to drive down costs.

Higher energy densities can be achieved both by cell-level materials and module to system-level balance-of-plant modifications. New materials are being explored for both the positive and negative electrodes. Recently, positive electrodes with higher nickel content have attracted attention due to the correlation between large Ni content and greater intercalation of lithium ions. The first commercialized NMC was $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, more commonly known as “NMC 111.” Currently, researchers are optimizing materials with even higher Ni content such as NMC 622 and NMC 811. Additionally, there are significant efforts to develop higher energy density variants of LFP such as LMFP (lithium manganese iron phosphate). This new composition preserves the thermal stability of an LFP positive electrode, but the addition of Mn allows operation at higher voltages, increasing energy density up to 25%.

One of the most promising negative electrode materials for Li-ion batteries is silicon due to its high theoretical capacity of 4200 mAh g^{-1} . The main problem with silicon is a 400% volumetric change during lithium intercalation/de-intercalation. This volume change causes other structural issues such as self-pulverization and fracture that ultimately lead to loss of electrochemical contact. Several approaches to solve these issues include new electrolytes, merging graphite with silicon, and designing different silicon structures. Nonetheless, there are already commercial cells with graphite electrodes containing up to 10% silicon and many start-up companies with backing from major automotive manufacturers pursuing predominantly silicon electrodes.

In the longer-term, higher energy densities may be achieved with solid state batteries. The replacement of the organic liquid electrolyte with a solid-state electrolyte enables the use of Li metal negative electrodes in place of graphite. Solid state batteries are currently being developed for automotive applications.

Beyond new materials, higher energy densities have been achieved using non-cylindrical cells, making individual modules larger, and minimizing the space between larger units (either by eliminating the servicing aisle in intermodal containers or minimizing the distance between cabinet-based systems). This increased energy density has significant implications for safety and

fire suppression, potentially making it difficult to avoid cell-to-cell propagation within cell modules. The challenge would then be to prevent module-to-module propagation.

3.5 Increasing Safety

Although Li-ion batteries are widely used, there are increasing challenges from the safety perspective as applications have transitioned from Wh consumer devices to MWh systems. High energy density becomes a disadvantage when a cell is operated outside of recommended conditions and failure liberates large quantities of chemical and electrical energy. This release of energy has the potential to generate heat faster than it can be dissipated and can cause a thermal runaway of the cell, creating fire, smoke, and particulate ejecta.

Li-ion batteries using metal oxide positive electrode materials possess all the components required for combustion or even explosion once thermal runaway occurs—fuel, oxygen, and an ignition source. Organic electrolyte is the fuel as it is unstable at elevated temperatures and easily ignited once it is exposed to air. Once the positive electrode is exposed to elevated temperatures during thermal runaway, it releases oxygen. A more extensive discussion of thermal runaway is provided in Chapter 17: Safety of Electrochemical Energy Storage Devices. The sections below briefly summarize some recent directions for enhancing the safety of Li-ion batteries.

3.5.1 New Materials

The majority of short-term research on improving the safety of Li-ion batteries is focused on the electrolyte. The organic liquid electrolyte contributes significantly to the energetics of thermal runaway. Several approaches currently being pursued include replacing LiPF_6 with more stable salts, incorporating fire retardants, and incorporating additives to prevent electrolyte degradation during overcharge.

Since 2000, companies have also tried to commercialize solid-state electrolytes because they can address leakage and short circuit problems. However, solid-state electrolytes present a significant challenge because improved safety is accompanied by a decline in battery performance due to lower ionic conductivity. There is currently no single most promising candidate for solid-state electrolytes, but the general classes of material being pursued include polymers (solid, gel, polymerized ionic liquids) and inorganics (oxides and sulfides) [26].

Beyond electrolytes, there have been efforts to enhance the safety profile of the separator. Conventional separators made of polyolefins short-circuit the cell when they melt at 130-170 °C. Applying a ceramic coating on polyolefin separators can raise the melting point. Another strategy is switching from polyolefins to high-melting temperature polymers that do not shrink upon heating, including polyimide and various polyesters [27]. Additionally, there have been efforts to develop separators that break in a pre-defined geometry when the battery is physically damaged. This effectively isolates the damaged portion of the separator and minimizes the short circuit.

3.5.2 New Designs

Li-ion battery safety has generally involved a reactive approach to failure although that is changing with increasing codes and standards. A predictive approach involving early detection of internal faults in batteries is critical to mitigate the consequences of failure. A predictive approach requires techniques that can detect and decipher pre-failure signatures, including physical and chemical changes. These techniques are currently being developed and commercially available equipment

is limited. One approach involves tracking cell impedance to identify subtle changes in electrochemical performance and stability.

More reactive approaches involve identifying single cell failure early enough to prevent propagation in large systems. Thermal runaway detection methods can be broken down into the following categories: terminal voltage detection by the BMS, battery mechanical deformation detection by creep distance sensors, temperature monitoring by thermocouples or fiber optic sensors, and gas sensors [28].

After failure has propagated, system-level responses include the activation of fire suppression systems. The most common medium of fire suppression is a gaseous clean agent such as Novec. These clean agents typically operate via a cooling effect. Oxygen-depleting suppressants like CO₂ are only effective as cooling agents against metal oxide positive electrodes, which release their own oxygen during thermal runaway. However, increasing system energy densities have made it difficult for such clean agents to fully stop propagation. Water-based fire suppression systems have also been implemented. One of the issues with active fire suppression systems is that they can lead to the build-up of combustible gases (which are no longer being consumed by an active fire). Thus, companies are beginning to include sensors for gases like CO in their systems. The introduction of deflagration, or vent, panels is intended to channel explosive blasts upwards, away from people and other battery units.

3.5.3. New Standards

The present standards for Li-ion battery safety at the cell and system level are covered in greater depth in Chapter 17: Safety of Electrochemical Energy Storage Devices. Currently, most standards focus on factory testing, commissioning, and emergency response. Accidents are still occurring and there is an increasing recognition that more guidance is needed on maintenance after an energy storage system is installed.

4. Concluding Remarks/Summary

Li-ion batteries will likely dominate the electrochemical energy storage market for the next decade, despite safety concerns from recent fires. These safety concerns are encouraging more stringent codes and standards, leading to evolving system designs. However, cells are likely to retain the same fundamental intercalation structure with materials modifications in the negative electrode, positive electrode, and electrolyte to achieve higher lifetime, energy density, and safety. As economies of scale continue to drive down prices, Li-based batteries will become an increasingly attractive candidate for more energy storage applications. A detailed evaluation of their present performance in specific applications and in relation to other energy storage technologies is discussed in Chapter 23: Applications and Grid Services.



Dr. Loraine Torres-Castro is a Senior Member of Technical Staff in the Power Sources Research and Development Group at Sandia National Laboratories. She joined Sandia in 2016, where her work has focused on the safety and reliability of batteries, particularly under abusive conditions. Her work in the Battery Abuse Testing Laboratory (BATLab) is focused on understanding the mechanisms that lead to energy storage system safety incidents which guide her in developing strategies to mitigate energy storage cell and system failures. Loraine earned her B.S. in Physics in 2010 and Ph.D. in Chemical Physics in 2016, both at the

University of Puerto Rico-Rio Piedras. Her dissertation work focused on the development of positive electrode materials for high energy Li-ion batteries.



Dr. Yuliya Preger is a Senior Member of Technical Staff in the Energy Storage Technology and Systems Group at Sandia National Laboratories. Her current work is centered on the safety and reliability of lithium ion batteries for grid-level energy storage applications. This work ranges from high precision analysis of cell level cycling and thermal characterization of cell components to development of new module arrangements in conjunction with new power electronics architectures. She earned her PhD in Chemical Engineering at the University of Wisconsin-Madison and her BS in

Chemical Engineering from MIT.



Jim McDowall has worked in the battery industry since 1977 and is currently in the position of Senior Technical Advisor with Saft, primarily associated with grid systems. Involved in the energy storage market since 1998, Jim was a Director of the Energy Storage Association for 14 years and is a past Chair of the organization. Jim is an IEEE Fellow and is Standards Coordinator and Past Chair of the IEEE Energy Storage and Stationary Battery Committee, and Chair of three of its working groups. Jim is a frequent speaker at energy storage conferences and related events.

References

- [1] <https://www.eia.gov/todayinenergy/detail.php?id=41813>
- [2] I. Tsiropoulos, D. Tarvydas, N. Lebedeva, "Li-ion batteries for mobility and stationary storage applications – Scenarios for costs and market growth" EUR 29440 EN, Publications Office of the European Union, Luxembourg, ISBN 978-92-79-97254-6, doi:10.2760/87175, JRC113360, 2018
- [3] M. S. Whittingham, "Electrical energy storage and intercalation chemistry," *Science*, vol. 192, p. 1126, 1976.
- [4] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, " Li_xCoO_2 ($0 < x \leq 1$): A new cathode material for batteries of high energy density," *Solid State Ionics*, Vols. 3-4, p. 171, 1981.
- [5] A. Yoshino, K. Sanechika and T. Nakajima, "Secondary battery," USA Patent 4,668,595., 1987.
- [6] J. M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature*, vol. 414, p. 359, 2001.
- [7] D. Linden and T. B. Reddy, *Handbook of Batteries*, New York: McGraw-Hill Companies, 2001.
- [8] M. Yoshio, R. J. Brodd and A. Kozawa, *Lithium-Ion Batteries: Science and Technologies*, New York: Springer, 2009.
- [9] C. Daniel and J. O. Besenhard, *Handbook of Battery Materials*, Wiley, 2011.
- [10] K. Xu, "Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries," *Chem. Rev.*, vol. 104, p. 4303, 2004.
- [11] E. R. Logan, K. L. Gerin, X. Ma, J. R. Dahn, "Electrolyte Development for High-Performance Li-Ion Cells: Additives, Solvents, and Agreement with a Generalized Molecular Model" *Electrochem. Soc. Interface*, 2019, 28, 49.
- [12] A. Manthiram, A reflection on lithium-ion battery cathode chemistry. *Nat Commun* 11, 1550 (2020). <https://doi.org/10.1038/s41467-020-15355-0>
- [13] N. Mohamed and N. K. Allam, "Recent advances in the design of cathode materials for Li-ion batteries," *RSC Adv.*, vol. 10, p. 21662, 2020.
- [14] M. M. Thackeray, W. David, P. G. Bruce and J. B. Goodenough, "Lithium insertion into manganese spinels," *Materials Research Bulletin*, vol. 18, p. 461, 1983.
- [15] P. Weicker, *A Systems Approach to Lithium-Ion Battery Management*, Boston: Artech House, 2014.
- [16] <https://insideevs.com/news/386024/bloombergnef-battery-prices-156-kwh-2019/>
- [17] <https://www.forbes.com/sites/rrapier/2019/08/04/why-china-is-dominating-lithium-ion-battery-production/#3f42d9fd3786>
- [18] <https://www.bloomberg.com/news/articles/2019-07-03/europe-thinks-like-china-in-building-its-own-battery-industry>

- [19] DOE Energy Storage Grand Challenge <https://www.energy.gov/energy-storage-grand-challenge/energy-storage-grand-challenge> (2020).
- [20] <https://cen.acs.org/materials/energy-storage/time-serious-recycling-lithium/97/i28>
- [21] G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, P. Anderson, “Recycling lithium-ion batteries from electric vehicles” *Nature*, 2019, 575, 75.
- [22] E. Martinez-Laserna, I. Gandiaga, E. Sarasketa-Zabala, J. Badedo, D.-I. Stroe, M. Swierczynski, A. Goikoetxea, “Battery second life: Hype, hope or reality? A critical review of the state of the art” *Renew. Sust. Energ. Rev.* 2018, 93, 701.
- [23] T. Waldmann, M. Wilka, M. Kasper, M. Fleischhammer, M. Wohlfahrt-Mehrens, “Temperature dependent ageing mechanisms of Lithium-ion batteries – A Post-Mortem study” *J. Power Sources*, 2014, 262, 129.
- [24] P. Keil, S.F. Schuster, J. Wilhelm, J. Travi, A. Hauser, R.C. Karl, A. Jossen, “Calendar Aging of Lithium-Ion Batteries I. Impact of the Graphite Anode on Capacity Fade” *J. Electrochem. Soc.*, 2016, 163, A1872.
- [25] M. Naumann, M. Schimpe, P. Keil, H.C. Hesse, A. Jossen, “Analysis and modeling of calendar aging of a commercial LiFePO₄|graphite cell” *J. Energy Storage*, 2018, 17, 153.
- [26] J.C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S.F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, “Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction” *Chem. Rev.* 2016, 116, 140.
- [27] K. Liu, Y. Liu, D. Lin, A. Pei, Y. Cui, “Materials for lithium-ion battery safety” *Sci. Adv.*, 2018, 4.
- [28] Z. Liao, S. Zhang, K. Li, G. Zhang, T. G. Habetler, “A survey of methods for monitoring and detecting thermal runaway of lithium-ion batteries” *J. Power Sources*, 2019, 436, 226879.