WHITE PAPER

Lithium Battery

Overcoming Lithium-Ion Battery Obstacles for the Alternative Energy Revolution

Global climate initiatives, in conjunction with an increase demand for battery reliant technological innovations, are driving the alternative energy revolution. Rapidly emerging as a cornerstone technology in this revolution are lithium-ion batteries (LIBs). Libs are providing key energy advantages to enable innovations in the energy, automotive and tech sectors.

LIBs made their debut in consumer electronics in 1991, with a bulky design and limited energy capacity. Since then, LIBs have evolved a more compact design and greater energy storage. Energy storage is described as energy density, the total energy divided by the batteries' weight or volume. By increasing energy density, LIB manufacturers could produce smaller batteries with greater energy capacities. Energy density is one reason lithium is so attractive, the third element of the periodic table is super lightweight, delivering a lot of energy in a small package. In addition to their high energy densities, LIBs have long lifetimes and low toxicity, positioning themselves as one of the dominant battery technologies.

However, there are two major obstacles that the LIB industry is facing that need to be overcome to stay dominant: raw material acquisition and battery failure prevention. As the LIB industry increases with growing demand, added pressures will be placed on procurement of key raw materials. Specifically, the demand for lithium, cobalt, and graphite is projected to increase significantly in the coming decades. Procurement of raw materials for LIBs have a variety of environmental and social considerations that need to be addressed to ensure ethical development practices.

The LIB industry must also tackle the issues that drive LIB failure and thermal runaway. While most lithium battery failures are small, isolated incidents, there have also been large scale accidents. Such battery failures have led to explosions and fires, resulting in significant damage and deaths. Fortunately, there are now resources and advances designed to prevent battery failure and thermal runaway. In this white paper, we shall investigate the issues surrounding raw material procurement and battery failure, with an emphasis on the newest innovations and technologies to solve them.

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LIB Raw Materials

LIBs normally consist of a separator, electrolyte, negative electrode (commonly graphite), and positive electrode (typically layered lithium transition metal oxides i.e. cobalt, nickel, and manganese), see Figure 1. The separator, acting as electronic insulation, is saturated with an electrolyte (i.e. lithium hexafluorophosphate), which is dissolved in organic carbonate solvents.

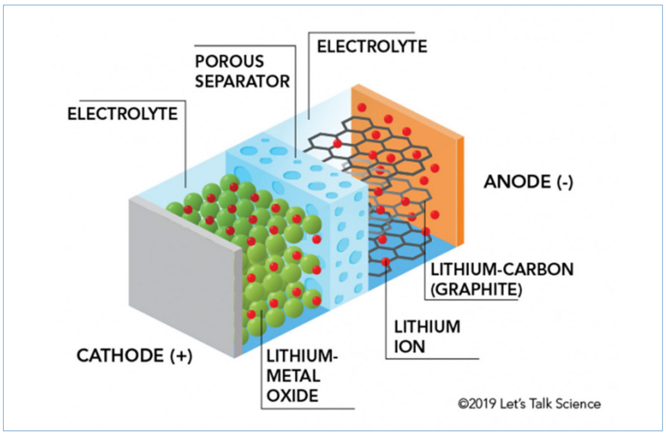

Figure 1: General Anatomy of a Lithium-Ion Battery.

The raw material extraction of these metals relies on an expanding mining industry and high purity metal processing that will continue to increase complexity of processing techniques for the future. The primary mechanisms that are driving the evolution of mining's technological innovations are safety considerations and operational benefits.

Safety

Exposure to high levels of metal particulates found in dust during extraction and other high-risk operational tasks has pushed the mining industry to replace laborers with remote-controlled and autonomous robotic equipment. Remote-controlled and autonomous robotic equipment has led to enhanced exploration of flooded mines and deep-sea deposits. Additionally, the COVID-19 pandemic has revealed that remote-controlled and autonomous robotic equipment can help manage COVID-19 risk, and risk of future pandemics, by mitigating close contact situations during operation.

Technological innovations including remote operations, robotics and automation are transforming mineral extraction industry into what is being referred to as Industry 4.0, see Figure 2. The increase in digitally connected and integrated systems has enabled a variety of new technology developments such as the internet of things and advanced analytics. These technological innovations are primed to optimize the industry by providing operators better analytical tools to make better decisions and improve production efficiency.[1]

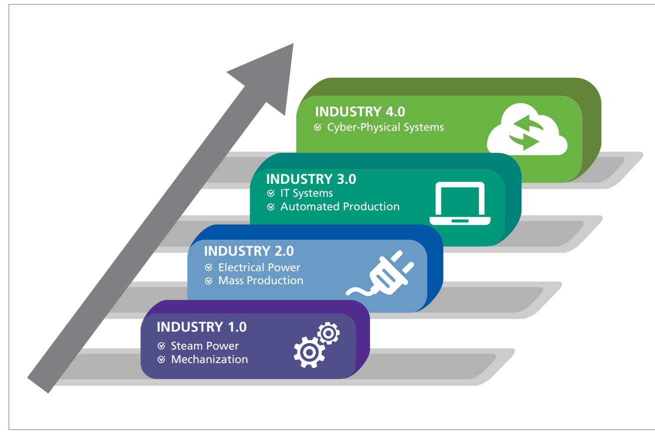

Figure 2: Industrial Revolutions.

Environmental Impact of LIBs

Lithium battery innovations continue to set a gold standard for, and reinforce the promise of, more efficient battery systems. However, even though LIBs may hold the potential to push green energy solutions into ubiquity, paradoxically, one of the biggest hinderances to LIB's expanded development is the cost raw materials acquisition places on the environment.

LIB cells are primarily responsible for the energy and carbon footprint in the production of lithium batteries. 40% of the total climate impact of LIBs is due to the mining, conversion and refining of the active materials of the cell.[2] The cell production is the second most energy consuming process with 20% total CO2/kWh.[2] In order to mitigate the environmental impact of LIBs several innovative processes are being developed.

Environmental Solutions for LIB Development

Geothermal Powered Lithium Extraction

Vulcan Energy has developed their Zero Carbon Lithium™ extraction technique utilizing geothermal power. As part of the EU's climate agenda, Vulcan aims to produce lithium for 1 million batteries per year. Their production is set for the beginning of 2024 and will significantly develop the EU's ability to produce its own domestic car batteries.

Subsurface Brine Extraction for High Purity Lithium

Lithium salts, lithium carbonate or lithium hydroxide monohydrate, have the current standard of 99.5% pure. However, there is an increased market for high purity lithium that delivers a 99.99% pure product. Higher purity lithium salts ensure battery performance and remove the risk of impurities, such as sodium, that can lead to battery failure and overheating.

Prairie Lithium has developed an unconventional Li approach using Li enriched brine reserves in western Canada. Their method utilizes subsurface brines that contain 15-300 ppm

Lithium, which is significantly more enriched than conventional seawater at 0.2 ppm Li.[3] The Li brines are analyzed using atomic absorption (AA), an effective test to find higher metal impurities, and inductively coupled plasma (ICP) testing, used to evaluate range and concentration of metal impurities. Once the brine location is established, it is surfaced for the DLE process where Li is removed from the brine. Finally, the lithium concentrate is converted to battery grade LiX.[3]

A cornerstone technology for the determination of impurities in high-purity metal raw materials is ICP-OES. PerkinElmer Avio 550 ICP-OES possesses the required sensitivity to perform high purity analyses, making it an excellent option for high-purity lithium extraction. Additionally, its sample introduction systems are resistant to high salt matrices and highly corrosive samples. Table 1 shows various analytes identified in high-purity lithium carbonate raw materials used in LIB production.

Table 1: Analytes in High-Purity Raw Materials Used in Li-Battery Production-Lithium Carbonate.

Analyte	Lithium Carbonate (mg/kg)
Al	0.76
Ca	79.5
Cr	0.082
Cu	0.295
Fe	3.86
K	228
Mg	35.5
Mn	0.36
Na	480
Pb	2.75
Zn	2.70

Recycling LIBs

It is estimated that nearly 11 million tons of previously used LIBs will exist by 2030.[4] Currently, there is not an adequate framework to handle this excess waste. Recycling LIBs is going to be instrumental in ensuring an adequate supply of raw materials while mitigating damage to the environment.

The process of recycling LIBs starts with deactivating and shredding of the old battery module, which is discharged and dismantled. The dismantling of the module happens under inert atmospheric conditions to avoid thermal runaway. Volatile electrolyte residues are removed, and hydrometallurgical procedures are carried out using pH dependent precipitation of salts to recover materials like lithium and cobalt. Characterization of LIB materials using elemental analysis and cell chemistry are paramount in order ensure effective recycling efficiencies.[5]

Repurposing LIBs

Repurposing of these spent batteries is another strategy to reduce the toxic waste and pollution burden associated with this projected LIB expansion. After an electric vehicle battery drops below 70-80%, they lose the ability to power the car.[6] However, they retain enough capacity for other functions requiring stationary storage such as household and industrial power applications. Currently, the primary limitations of repurposing LIBs are the lack of data-sharing to support the residual value of battery capacity, battery standards, and limited clarity regarding liability.[6]

Battery Failure

There are several abuse factors that can lead to battery failure, but the most common to consider are overcharging, battery misuse, overheating, manufacturing defects and short circuits caused by dendrites. Any of these abuse factors can lead to thermal runaway, as it is created in a battery when the rate of internal heat generation exceeds the rate of heat that can be expelled.[7]

Overcharging can create a chemical reaction between the electrode and electrolyte, initiating the transition of the liquid electrolyte into a gas. Overheating also causes this liquid electrolyte to transition to a gaseous state. As the gas builds, pressure increases beyond what is able to vent. Once the separator is compromised by this pressure, chemical interactions between the cathode and anode lead to a short circuit and thermal runaway.

Thermal Runaway

Thermal runaway begins after the cell has been compromised and starts a chain reaction that produces significant amounts of trapped thermal energy. During the process of thermal runaway, the battery can heat up from room temperature to nearly 700°C in a matter of seconds. The heat degrades the electrolyte into flammable and toxic gases, while the cathode begins to decompose releasing oxygen, accelerating the thermal runaway chain reaction. Once the flammable gases react with oxygen and heat, a combustion reaction is created. The risk of explosion during thermal runaway increases as the pressure continues to build in the battery cell. Thermal runaway is an exothermic reaction and once it starts it will generate its own oxygen, making it very difficult to extinguish.[8]

There have been numerous incidents of thermal runaway in LIBs that have led to the destruction of electric vehicles, cell phones, laptops, and even whole industrial energy facilities. The reason why every smart phone doesn't turn into a fire hazard while charging overnight is due to the battery management system (BMS). LIBs utilize the BMS to manage charge and discharge controlling, faulty diagnosis, parameter detection (total voltage, numeric temperature, total current), balance control, and thermal management.[9]

Even though the BMS is designed to mitigate thermal runaway risk, it occasionally fails at managing one of these parameters due to manufacturing defects in the BMS (also the battery) or an abuse factor. It is vital that the proper quality and development strategies are applied to LIBs, and their associated components, along with the utilization of off-gassing technologies to provide robust thermal runaway prevention.

Preventing Thermal Runaway

With the initiation of an abuse factor, thermal runaway can lead to destroyed equipment and dangerous meltdowns. Prevention of thermal runaway can be conducted at several points during development of the LIB and throughout the lifetime of the LIB in the field. During development careful analytical analysis of the separator, electrolyte and binder can prevent the formation of impurities and provide vital information on material compositions to support thermal runaway prevention. Post-production, detection of off-gassing compounds in the battery using TG-IR-GCMS and thermal runaway sensors, provides LIB operators fail safes to prevent thermal runaway before it starts.

Separator Analysis

Lithium battery failure is often caused by degradation of the battery separator. The synthetic polymers used in separators in the LIB industry provide both thermal and physical properties that can ensure battery integrity and prevent battery failure. Poor quality polymers, or polymer blends, utilized during manufacturing can lead to LIB failure, thus, verification and quality testing of those materials during every stage of manufacturing is necessary. Infrared (IR) spectroscopy is ideal for qualitative analysis of polymer starting materials and finished products as well as quantification of components in polymer mixtures.

Fourier transform infrared (FT-IR) spectroscopy is a rapid and non-destructive analytical technique which delivers a sort of compositional "snapshot", as the measured data is specific to covalent bonds present in the tested material. This information helps LIB manufacturers to verify they have received the correct raw materials and can also be used in a "forensic" approach, through analysis of failed components to help identify the root cause.

Degradation can occur during charging and discharging, and results in changed chemical bonds and structure, which provides insights when inspecting binder or separator materials. These analyses can be conducted in bulk, using an instrument such as the Spectrum 3 FTIR, or in microscale, using the Spotlight 200i or 400 infrared microscopes. Figure 3 shows microspectroscopic measurements of a degraded separator, acquired with a Spotlight 400 microscope equipped with an ATR imaging accessory[10].

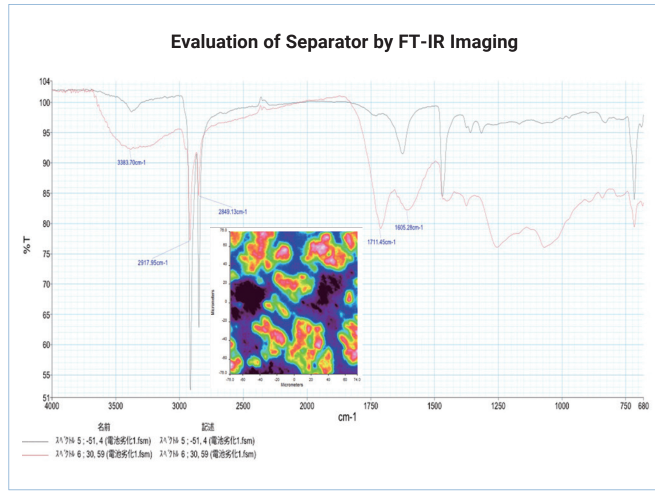

Figure 3: IEvaluation of oxidative degradation is shown here through ATR imaging of the separator.

Evaluation of separator materials can also be conducted by differential scanning calorimetry (DSC), which is used to study the melting profile, electrolyte decomposition, the enthalpy of phase transitions, thermal stabilities, and other thermal properties.[10]

Binder Analysis

Lithium battery binders are responsible for holding coating particles together and reinforcing the coating to the metal or separator membrane. Additionally, binders can aid in film formation, encourage optimal particle dispersion in the solvent and help the coating disperse to deliver a uniform slurry and discrete particles to the anode and cathode. A binder's functionality, helping to maintain LIB capacity, is dependent on their stability and it is imperative that the binder resists degradation.[11]

Thermogravimetric analysis (TGA) is an indispensable tool in determining thermal stability and the decomposition profile of materials used in lithium batteries under controlled heating conditions. In Figure 4, operators were able to generate thermogravimetric data from a sample of ethylene vinyl acetate binder on the electrodes of a LIB Using a PerkinElmer TGA 8000™ thermogravimetric analyzer.[10]

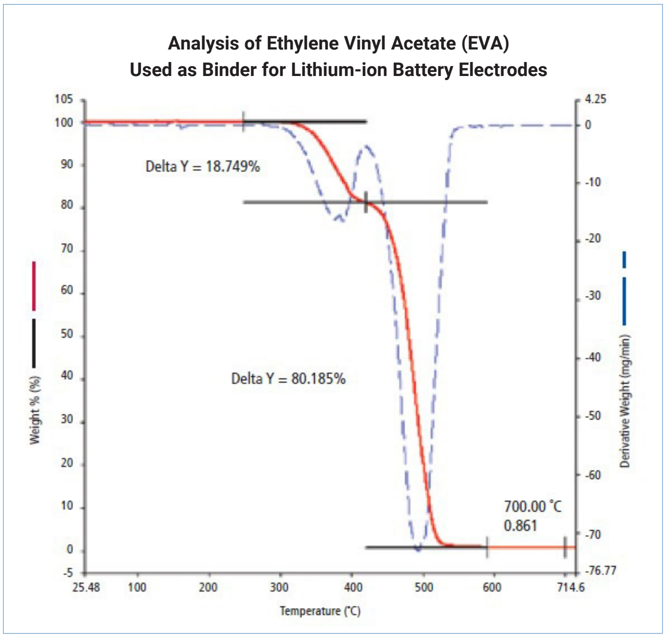

Figure 4: Thermogravimetric data generated from the analysis of EVA sample.

Electrolyte Analysis

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is used for a variety of analyses in the Li battery industry and can be very useful in the analysis of impurities in LIB electrolytes. The presence of electrolyte impurities increases the risk of battery inefficiency and failure. In Table 2, the following electrolyte impurity analysis was carried out utilizing PerkinElmer's Avio® 550 ICP-OES, offering excellent insights on electrolyte composition.[10]

Table 2: Impurities in DMC Electrolyte.

Analyte	DMC Electrolyte (µg/L)
Al	2480
Ca	96.4
Cd	43.6
Fe	158
K	136
Mg	2.20
Na	3172
Pb	192

Compositional testing, such as determining the composition and ratio of cyclic carbonates, offers valuable insights into the degradation of components resulting from repeated charging and discharging in LIBs. In Table 3, users calculated method detection limits and method quantitation limits of a variety of cyclic carbonates with PerkinElmer's Clarus® SQ 8 GC/MS.[10]

Table 2: Calculated Method Detection Limits (MDL) and Method Quantitation Limits (MQL).

Analyte	MDL (µg/mL)	MQL (µg/mL)
Dimethyl Carbonate	0.111	0.444
Ethyl Methyl Carbonate	0.176	0.705
n-Propyl Propionate	0.171	0.684
Diethyl Carbonate	0.172	0.690
Vinylene Carbonate	0.166	0.664
Fluoroethylene Carbonate	0.104	0.415
Ethylene Carbonate	0.146	0.584
Propylene Carbonate	0.086	0.343
1,3-Propanesultone	0.080	0.320

Off-Gassing Monitoring and Sensors

After an abuse factor initiates off-gas generation, there is a window of time where the gas production can be detected, and strategies can be set in place to remove the abuse factor or shut the battery down entirely. It is within this window that off-gas monitoring and sensors can be instrumental to thermal runaway prevention.

Once off-gasses are detected, manual or automated processes can be implemented to shut down the battery pack and continue to monitor for smoke as a preventative action. The key question becomes which gases are important to monitor? Given that the components of LIB are constantly changing, due to the dynamic nature of material optimization, it is important to get your batteries unique off-gas signature.[12] Once established, you can determine key gasses to monitor along with their concentrations over time. Getting this off-gassing signature can help LIB manufacturers find the correct sensor or provide the necessary data to detect and design their own sensor, unique to their battery system. To detect off-gases, it is important that sensors or monitors be capable of detecting a cocktail of off-gases that are uniquely dependent on the LIB used.

Off-Gas Monitoring Technologies

Due to the wide variety of lithium salts used in the cathode of LIBs, such as lithium cobalt oxide, lithium manganese oxide, lithium nickel cobalt aluminum oxide, and lithium iron phosphate, off-gassing profiles will differ depending on the internal elements of the LIB. Volatile organic compounds are common denominators in most LIBs. Once an abuse factor initiates the battery failure process, VOCs will be released along with carbon monoxide, methane, ethane, ethylene, hydrogen chloride, hydrogen fluoride, and hydrogen.[12]

Analytical testing methods using TG-IR-GCMS are ideal technologies for a comprehensive analytical testing option of off-gas signatures. Individual gas compounds may not provide enough of a signal prior to thermal runaway to give proper notice, so a TG-IR-GCMS method that calculates off-gas signatures together will provide robust post-monitoring sensor capabilities.

TGA analysis enables quantification of the weight loss of a material at specific temperatures. Mass spectrometry (MS) enhances the technique by providing the ability to identify the species that evolved during thermal analysis. If complex gases, such as the cocktail of off-gasses and VOCs, evolve during an event, the MS data is difficult to interpret. The use of TG-GC/MS adds chromatographic separation of co-evolved gases, enabling identification of individual components, making data interpretation easier than TG-MS.

Overcoming Obstacles

Investment in reliable equipment offers a significant ROI for those involved in LIB development. Analytical solutions that assess separators, binder, electrolytes, and other LIB components will ensure battery integrity and reduce the risk of battery failure. Safeguards in off-gassing monitoring provide additional security against thermal runaway, preventing injury, death and significant costs.

Utilizing the proper analytical instrumentation can help provide high-purity lithium and other metals for LIB development and manufacturing. These high-purity applications will yield better end products with greater battery functionality and lower failure rates.

There is no doubt that lithium battery innovations will continue to play an important role in energy, automotive and tech sectors. Overcoming the obstacles of raw material procurement and reducing battery failure are imperative for LIB manufacturers to achieve a dominant position in the alternative energy revolution.

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