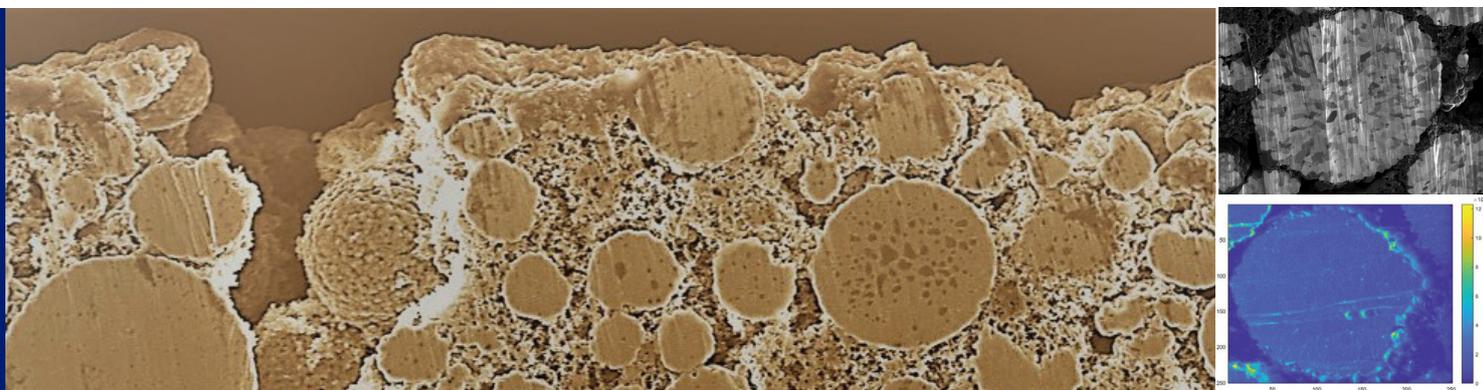


Why Batteries Fail and How to Improve Them: Understanding Degradation to Advance Lithium-Ion Battery Performance



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Fundamental research on lithium-ion batteries (LIBs) dates to the 1970s, with their successful commercialisation delivered by Sony in 1991. Since then, LIBs have revolutionised the world of portable electronics, owing to their high energy density and long lifespan. Whilst LIB uptake initially powered small devices, they are now enabling global growth in electric vehicles (EVs), as well as having an increasing presence in new areas such as grid storage. Whilst LIBs will continue to lead electrification in multiple sectors, there are still requirements for improvements in lifetime, performance and safety. To achieve these researchers need to better understand – and find ways to mitigate – the many causes of battery degradation.

Introduction

In 2021, the battery industry will mark the 30th anniversary of a remarkable scientific invention that led to great commercial success, and the awarding of the 2019 Nobel Prize in Chemistry: the rechargeable lithium-ion battery. Three decades of performance improvements have occurred because of innovative research, with enhanced manufacturing efficiency bringing about mass-market penetration. This has made LIBs ubiquitous, although cost and performance obstacles still need to be overcome to ensure sustainable business cases for volume automotive and to enable new sectors, such as aerospace. Critical to clearing these hurdles and unlocking the massive market potential for LIBs is a deeper scientific understanding of why batteries ultimately fail. This Insight provides clarity into the current state of knowledge on LIB **degradation**¹ and identifies where further research might have the most significant impact.

Battery degradation is a collection of events that leads to loss of performance over time, impairing the ability of the battery to store charge and deliver power. It is a successive and complex set of dynamic chemical and physical processes, slowly reducing the amount of mobile lithium ions or charge carriers. To visualise battery degradation, it is useful to first consider what cells² are composed of. Figure 1 represents a simplified view of a typical battery cell, i.e., two opposing electrodes impregnated by an **electrolyte** solvent and electrically isolated by a porous **separator** (to prevent a short circuit). The electrodes (both positive and negative) are fabricated from coatings that contain active and inactive particles; a magnified view of the morphology of the negative electrode is represented in Figure 1.

For maximised cell performance, an optimised coating structure or architecture is required. This is directly dependent on a uniform distribution of sub-components with

Scanning electron microscopy images. Left: cross sections of a nickel manganese oxide cathode showing macro-scale cracking. Top right: a focused ion beam section of an NMC cathode particle with smaller secondary structures of "crystallite grains" clearly visible. Bottom right: secondary ion mass spectrometry oxygen map of an NMC particle.

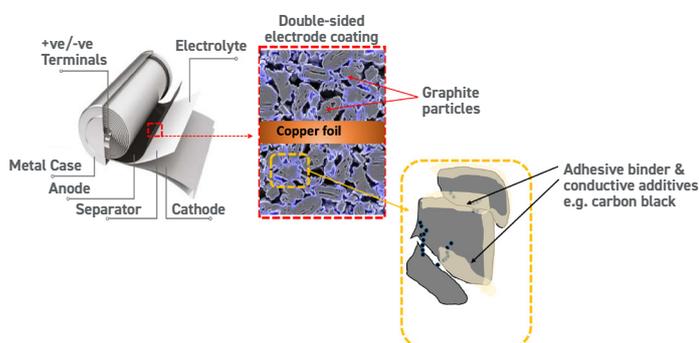
¹ Technical terms and acronyms used in this Insight in bold text are clarified in a glossary in the appendix.

² Batteries are collectives of individual cells.

desired properties, and is critical to ensuring complete mass and charge transport during operation. However, there are numerous chemical, electrochemical and physical processes that occur during operation of the battery that can lead to incomplete charge/mass transfer. This invariably results in degradation and eventual failure – a process that happens more rapidly if the battery is subjected to repeated fast charging.

Over the past decade, the battery research agenda has been predominantly led by the needs of the automotive industry. The main focus has centred on improving energy density³ to provide a driving range that is competitive with vehicles powered by internal combustion engines. With the sale of new petrol and diesel vehicles in the UK ending by 2030, there is a need to further reduce costs and improve performance to convince consumers that electrification can meet their usage requirements. Improvements are needed in the EV range, to increase the speed with which batteries can be charged and deliver power (which is enabled by power density levels) and, of course, to safety during both operation and storage. Suppressing and ultimately circumventing the degradation of LIB technology is critical for achieving the performance and safety demands required over the next decade.

Figure 1: Illustration of a cylindrical cell and a magnified view of the morphology of a typical negative electrode (anode)



Not all LIB usage cases have the same energy and power requirements – LIBs can be optimised to suit different applications, each of which will degrade in subtly different ways. The need for basic and applied research to continue advancing understanding is critical, as there are still considerable fundamental scientific challenges to overcome with Li-ion energy storage. This is expanded upon comprehensively in a recent article in Nature Communications.⁴

Why Batteries Degrade

Understanding how LIBs operate on an atomistic level provides a true sense of the degradation challenge. Lithium ions must be able to move freely and reversibly between and within the battery's electrodes. Several factors can impede this free movement and can cause a battery to prematurely age and degrade its **state-of-health (SoH)**. Over time, successive charging and discharging causes damage to the battery's materials. The usage conditions when recharging the battery – for example, frequent rapid charging – can accelerate the damage. The environment within which the battery operates (factors such as temperature, duty cycle and pack construction) will also have a profound effect on how quickly the battery ages.

Degradation Modes and Capacity Fade

One of the major issues that has hindered step-change advances in LIB performance is the decline over time in the charge that a battery can deliver (defined as '**capacity fade**'), and its impact on performance. A key location for electrochemical **degradation** processes is the interface between the electrolyte and the electrode active particles. This is the location where lithium ions and electrons unite before becoming stored via several mechanisms. These are based on either **intercalation** (insertion between layers),⁵ **alloying** (the combination of two or more metals), **conversion chemistry** (chemical reactions)⁶ or by the direct plating as Li metal.⁷ There is an incomplete understanding of what happens at the electrode-electrolyte interfaces and a lack of knowledge about how to control and stabilise the associated reactions.

When a LIB is charging or when it is powering a device, lithium ions move reversibly between electrodes, through an insulating porous film (the separator) and an organic solvent (the electrolyte), to convey charge between the **anode** and **cathode**. For the reactive lithium ions, these journeys are treacherous, with multiple physical and chemical fates that await them. Over time, the resulting loss of active lithium available for charge-carrying is the reason battery performance deteriorates. This is commonly referred to as 'battery ageing'. Consumers notice this when, after a few years of use, a device like a mobile phone needs to be charged more frequently than it had previously. Figure 2 outlines the range of causes of degradation in a LIB, which include physical, chemical, mechanical and electrochemical failure modes. The common unifier is the continual loss of lithium (the charge currency of a LIB).

³ The amount of energy stored by the battery in a given weight or volume.

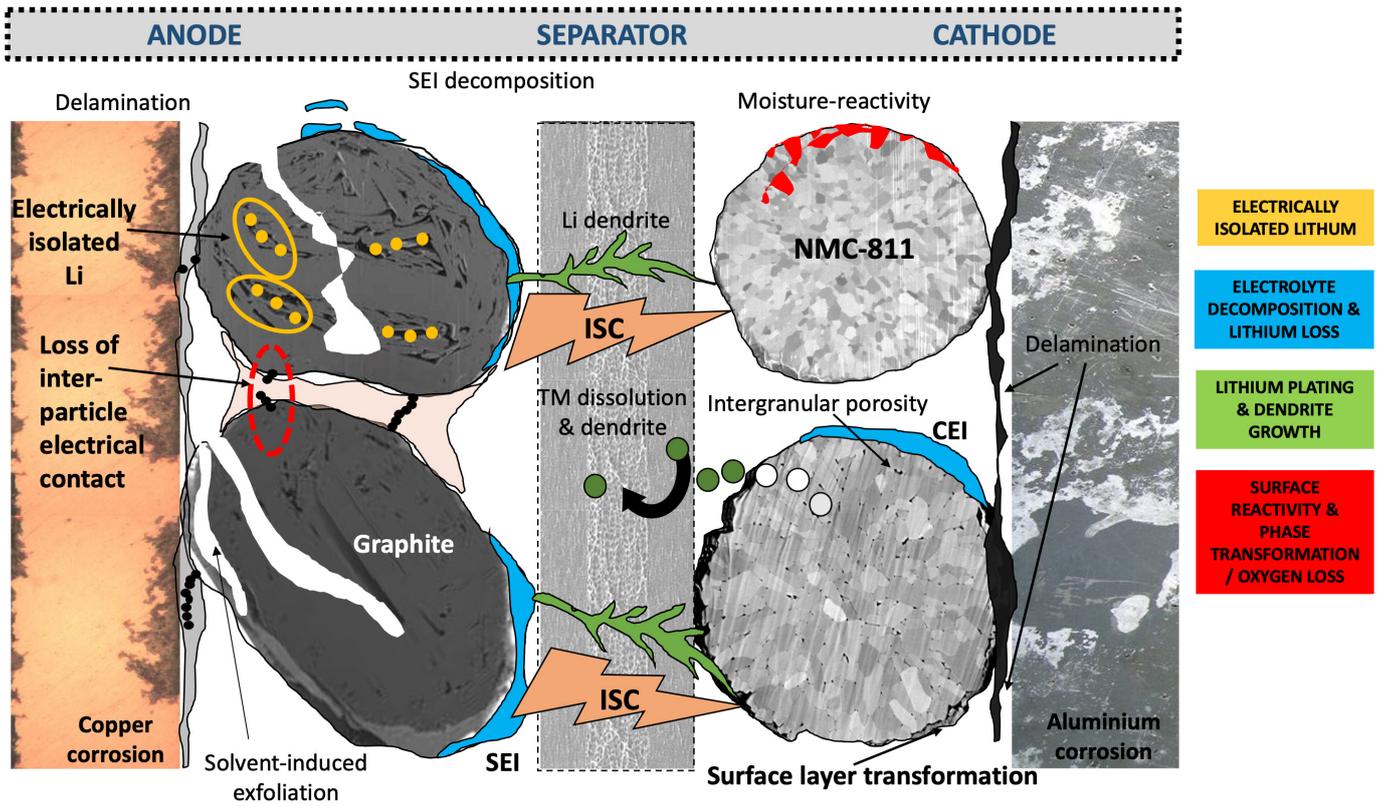
⁴ Grey, C.P. and Hall, D.S., Nature Communications, Prospects for lithium-ion batteries and beyond—a 2030 vision, Volume 11 (2020).

⁵ Intercalation is the inclusion of a molecule (or ion) into materials with layered structures.

⁶ A chemical process where the final product differs in chemistry to the initial materials.

⁷ A Wang, A., Kadam, S., Li, H., Shi, S. & Qi, Y., Review on the modelling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. npj Comput. Mater. 4, (2018).

Figure 2: Multiple degradation and failure modes in a simplified lithium-ion battery



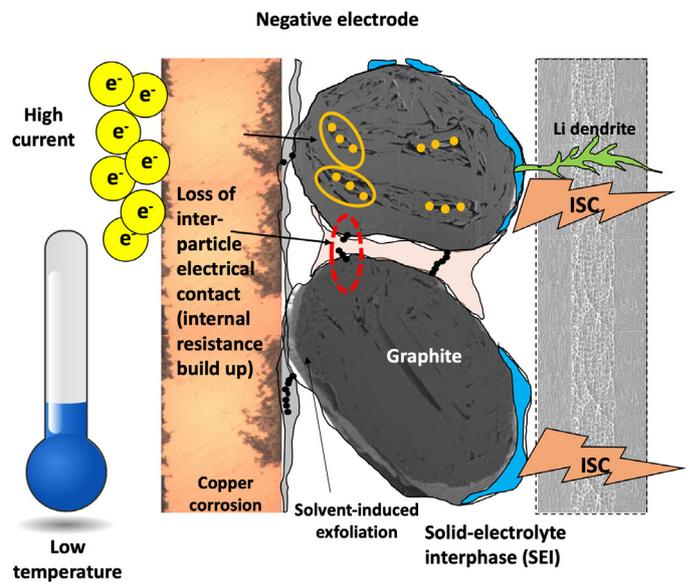
Operational Considerations

Batteries operate by having two electrodes, made of different materials, which have an electrical potential difference between them (expressed as a voltage). This difference relates to the amount of charge or power capacity that can be generated, stored and delivered. The charge and discharge are based on chemical changes or reactions – the reason why batteries are termed electrochemical devices. The anode takes in lithium ions (becomes active) at low voltages upon charging the battery and is thus termed the negative electrode. If the voltage becomes too low however, the lithium ions can turn into lithium metal and this has two downsides:

(i) The greater the extent to which the lithium metal grows or “plates out”, the fewer free lithium ions are available. Lithium is also irreversibly lost (chemically) when consumed by the growth of a **solid-electrolyte interphase (SEI)** layer on the negative electrode surface. Both modes of lithium loss reduce the charge “currency” or lithium inventory, and thus the battery’s capacity, because there will be a diminished amount of lithium freely available to convey charge between the positive and negative electrodes.

(ii) In a worst-case scenario, the metallic lithium can grow into branch-like structures called **dendrites**, which can protrude through the insulating separator and short-circuit the battery. This can cause a catastrophic failure mode, as has been seen in high-profile EV fires covered in the media. Figure 3 depicts the “perfect storm” conditions that are most likely to result in lithium plating or dendrite growth.

Figure 3: Lithium dendrite formation



Capacity Fade

Broadly speaking, capacity fade is caused by numerous modes of degradation that lead to an impaired ability of the battery to store power. It is generally underpinned by a combination of the following scenarios:

- The loss of the lithium ions in the electrode active materials,
- The electrode active materials becoming unavailable for participation in the active electrochemistry of the cell,
- The loss of electrolyte.



Li-ion Technology Performance Benchmarks

As LIBs are likely to remain the dominant technology that powers electrification in the near term, degradation research focuses on evolutionary advances rather than revolutionary step changes. To make such advances, researchers need to understand more deeply the complex spectrum of physical and chemical events that occur within a LIB across its entire life. Deeper knowledge of such events will provide manufacturers with the ability to make incremental changes to materials, components and processing approaches. The aim is to maximise capacity retention over the life of the battery and mitigate the rates of ageing and degradation.

Understanding Degradation and SOH will be Fundamental to Determining the Second Life of Repurposed Batteries

Electrochemistries that are being developed today are not likely to see the end of their first life until *circa* 2035, based on the typical automotive warranty and life cycle. In this timeframe, it is envisaged that electrochemistry, battery management systems and knowledge of how to minimise degradation will have moved on significantly. Therefore, in order to develop a viable business model around the repurposing of batteries for any second life application, it is critical that the state-of-health of cells and modules can be determined as quickly and accurately as possible. To compete against new 2035 technologies, a deep understanding of battery degradation is key to providing a trustable warranty for the sale of batteries for second life applications.

Ultimately, future energy storage applications will demand batteries that can be safely operated for significant periods (~ 20 years) with low costs per kWh/year. The unknowns are the extent and type of degradation that will have occurred by the end of first life for auto battery packs, and whether the batteries will indeed have, for example, five more years left in them for a second life application.

Safety Considerations Relating to Degradation Modes

To maximise the safety of batteries, the failure modes and rates of all degradation processes must be minimised. This can only be achieved by understanding the fundamental landscape of degradation processes across multiple scales, from atoms to systems, and how they inter-relate.

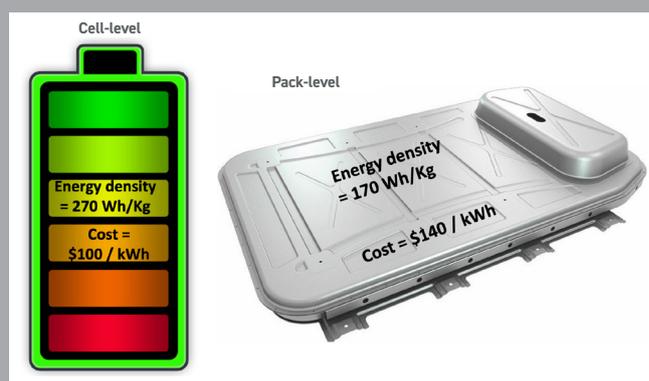
Box 1: Performance of existing Li-ion technologies

The current performance benchmarks are outlined below for battery EV cells and packs.

For high volume applications such as standard passenger cars or portable electronics, the primary metrics considered are usually cost (\$/kWh), energy density (Wh/kg or Wh/l, which determines EV range) and life (the number of cycles before a LIB reaches 80% of initial capacity, at which point the battery/EV is generally considered to have reached the end of its first life).

For more performance-orientated products, for example a high-performance road or racing car, power density (W/kg or W/litre) becomes more critical, but there is always a trade-off between energy and cost.

Existing performance benchmarks for high volume automotive cells⁸



The growth of automotive electrification has now increased the number of pouch and prismatic cell formats available with a variety of electrode chemistries. Within the existing LIB chemistries, the cylindrical cell format⁹ leads the evolution in performance and is the place where new electrochemistry developments are tried first.

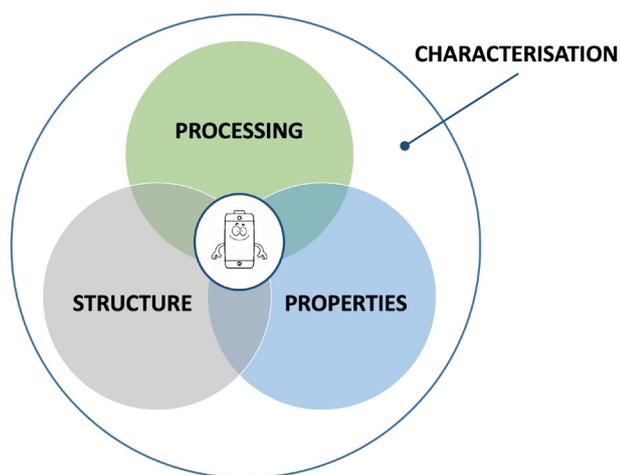
⁸ Lithium-ion cells are referred to here as batteries even though this is technically incorrect (batteries are collectives of cells).

⁹ The cylindrical cell format emerged from portable electronics. The 18650 (18mm diameter x 65mm long) cell was initially popular as a standard but has recently been overtaken by 21700 cells, driven by a need for reduced complexity due to its increased capacity. Use of 21700 cells also improves energy density at a cell and pack level. 21700 is likely to be superseded itself in the near future, which was been well publicised via the Tesla battery day in September 2020.

Specifically, such understanding requires the highly resolved characterisation of physical and chemical dynamics, and their interactive consequences. It is only by this correlation of degradation events and root-causes – across many length-scales – that researchers can better fill the knowledge gaps around performance influencers.

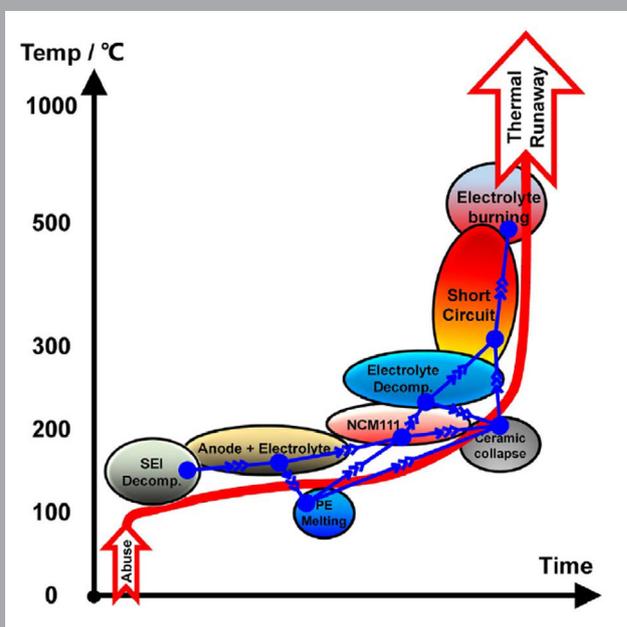
Figure 4 applies a central paradigm of material science to the components of a LIB. It highlights how material properties, structure and processing parameters will all influence how it will function. All these factors have a mutual interdependence and need holistic consideration when developing new battery materials. This is highly appropriate to LIB technology, as the effective, joined-up characterisation from the atom to the application, is what lies at the heart of technical advances. Such knowledge will inform and accelerate improvement in materials and battery component stability, through design, manufacturing and testing feedback loops. This will ultimately drive improvements in battery safety through deeper understanding of complex relationships.

Figure 4: Key inter-relationships driving LIB performance



Box 2: Implications of battery degradation on safety

One of the most critical safety concerns with LIB is battery fire. While incidents of fires in devices with LIBs are relatively rare, ensuring LIB safety is critical for businesses, consumer confidence, and legislative compliance. This results in significant rounds of expensive and time-consuming validation and test work. Notably, many of the thermal events that can lead to cell failure and LIB fires occur within LIBs that have undergone degradation. These are often initiated by component deterioration and are propagated by the combustion of flammable organic solvents in the electrolyte. Additional oxygen release from the cathode materials (transition metal oxides) can serve to further propagate combustion. The sequence is illustrated below.¹⁰



Research into battery degradation extends beyond improving battery performance. It also presents an opportunity to advance battery safety.

Challenges to Further LIB Improvements: Evolution Rather than Revolution

The goals of future battery research remain the same as those faced by the battery pioneers of the 70s and 80s: higher levels of energy and power, longer lifespans, reductions in cost and increases in safety.

Step changes in battery performance by new technologies, such as solid-state batteries and lithium-sulfur, are expected. However, commercialisation and mass manufacture of these types of batteries could be a decade or more away, so incremental improvements to the materials and components within current LIBs will be needed to improve EV performance in the near-term. Examples of the scientific breakthroughs and advances in engineering that are

¹⁰ Feng, X et al, Thermal runaway mechanism of lithium-ion battery for electric vehicles: a review, Energy Storage Materials, Volume, 10, pp. 246-267 (2018).

and operating limitations are explained by an electrochemical principle termed the "diffusion-limited C-rate (DLC)"¹¹ for LIBs (see Figure 7). Understanding this fundamental compromise, and the associated practical limits of LIB components, is critical for pushing forward performance limits.

One of the design challenges for improving the architecture of battery electrodes is establishing how to maintain stability and minimise the lithium ion losses. This centres on the complex set of physical and chemical processes previously outlined in Figure 2 that occur during battery operation.¹²

Technology Road Map

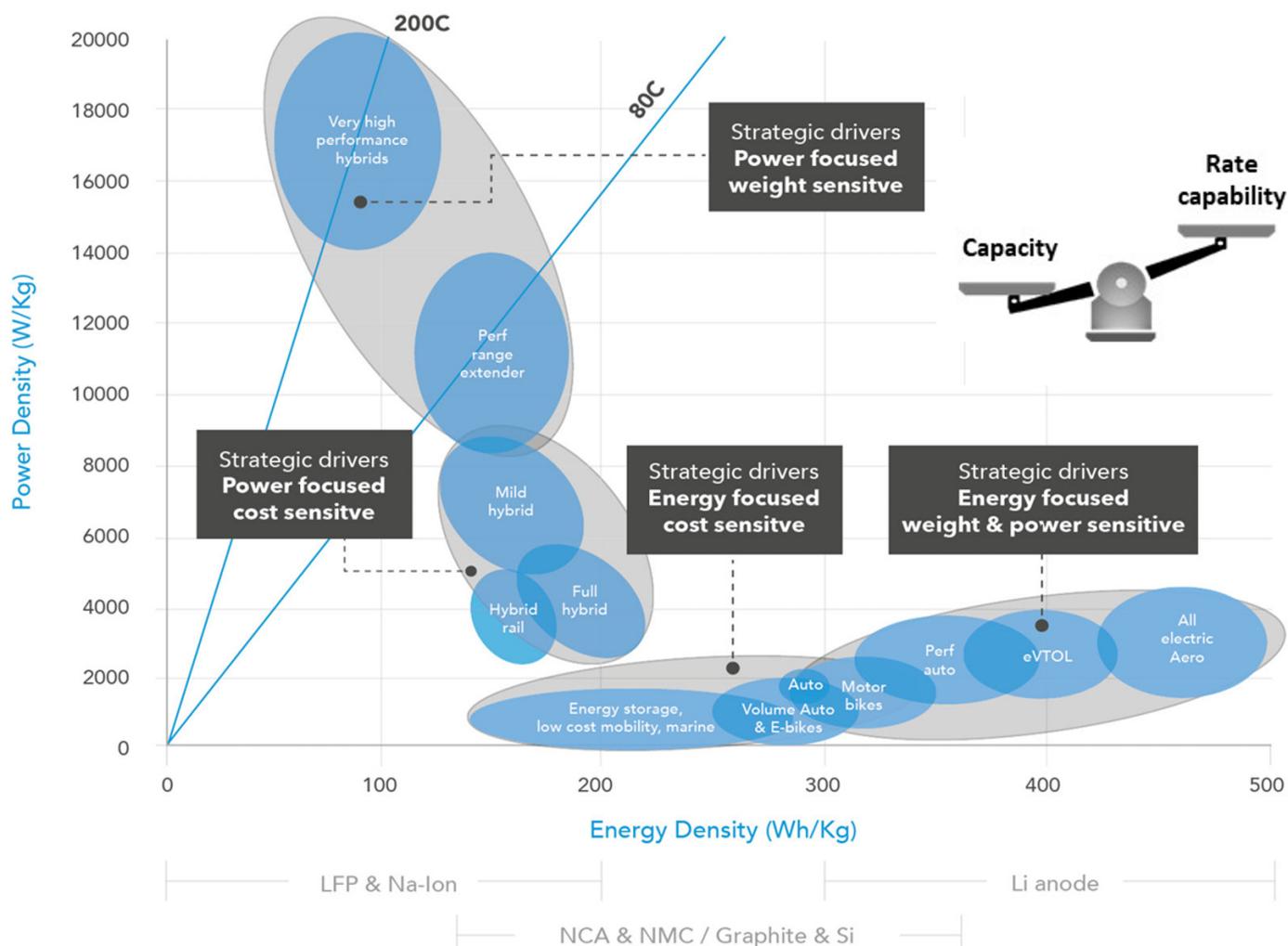
Energy storage is diversifying - from static energy storage to aerospace, from high-performance hybridisation¹³ to low-cost mobility, and from marine to mining. These different applications can be broadly categorised by energy, power, cost and weight requirements and can be grouped into the following clusters (see Figure 7):

- Power focused and weight sensitive. Applications that are mostly very high-performance hybrids where the rate of energy transfer and the system mass are critical. An example of this is a Formula 1 KERS cell (Kinetic Energy Recovery System).
- Power focused and cost sensitive (hybrid EVs). Applications in automotive hybridisation where system performance must be balanced with cost to make an affordable business case.
- Energy focused and cost sensitive (EVs, grid storage, marine). This cluster is the largest and is currently being led by the increasing annual production volume in EVs. Even with significant progress on cost reduction, this cluster is still very cost-sensitive requiring further reductions in cell costs.
- Energy focused, weight and power sensitive (aerospace). These applications require more revolution in performance than evolution, needing both improvements in energy density, power handling (charge and discharge) and safety.

For a more comprehensive explanation around cross-sector requirements, refer to Reference 14.

Figure 7: Future energy storage requirements 2025-2030

(courtesy of the APC, WMG)



¹¹ C. Heubner, M. Schneider and A. Michaelis, Diffusion-limited C-Rate: A Fundamental Principle Quantifying the Intrinsic Limits of Li-Ion Batteries, *Adv. Energy Mater.*, 1902523 (2019).

¹² Ma, D., Cao, Z. & Hu, A. Si-Based Anode Materials for Li-Ion Batteries: A Mini Review. *Nano-Micro Lett.* 6, 347-358 (2014).

¹³ M Dowson, From Research and Manufacturing to Application and End of Life - Enabling Electrification Across Sectors.

¹⁴ From "Research and Manufacturing to Application and End of Life - Enabling Electrification Across Sectors" Battery Targets and Priorities Across Sectors, 2020 to 2035, October 2020.

All these diverse requirements drive the need for a greater understanding of degradation mechanisms, control and mitigation strategies.

For energy-focused applications, knowledge of degradation will benefit EV owners by reducing warranty costs and minimising degradation performance and range losses over their car's lifetime. Confidence in the state-of-health of the battery will also improve residual values, reducing the total cost of ownership. There are likely to be a range of degradation mechanisms within this segment, balancing the effects of both calendar ageing and use (or energy throughput). For example, the use case of a passenger car covering 10,000 miles a year over 15 years is very different to that of a commercial vehicle covering the same distance in two. For heavy goods vehicles, buses, and rail, requirements are likely to be both very long calendar life (greater than 20 years) and higher energy throughput.

For power-sensitive applications, the key focus is likely to be around minimising performance variability throughout a battery's life. This would potentially minimise weight and cost by eliminating the need to carry excess capability at the beginning of the battery's life. This becomes even more critical for aerospace applications, which are highly weight-sensitive but also require safety-critical battery management systems that can determine the true state of charge, health and performance of a battery throughout its life.

Going forward, the short-term focus will centre on the optimisation of existing lithium-ion battery cell and pack technologies to meet performance targets. This requires overcoming the challenges within manufacturing, i.e. the incremental fine-tuning of the chemical compositions of electrodes and electrolytes in parallel with managing the state-of-health of these batteries. These developments are underpinned by an evolution in the understanding of the degradation methods of LIBs.

Conclusion

In this Insight, we have explored the operation of LIBs and mapped out the key degradation modes that lead to capacity fade. We have outlined how an understanding of degradation mechanisms is critical for the design of next-generation LIBs with improved components. However, to achieve deeper understanding of degradation mechanisms, effective characterisation (from microscopic to macroscopic scales) is key and there is still room for improvement. This will benefit technical usage needs; an example of this would be a widening of the usable 'state of charge' window, which is presently restricted to protect the battery. Enabling a widening of these limits during use would, for example, enable an increase in EV range whilst maintaining lifetime for a low-cost automotive cell.

To repurpose LIBs in a second life application, effective characterisation will also be required to assess the battery's SoH. For meaningful re-deployment, this will need to resolve features, timescales and underlying causes of degradation as accurately as possible.

There are also opportunities in developing techniques for the early detection of degradation 'signatures' in real world applications outside of a lab environment i.e., during deployment. Innovation is still required in the field to support both the evolution of existing lithium-ion chemistries and the emergence of novel chemistries.

This Insight considers present and future performance benchmarks and what is required at component level to meet these targets. As the world continues to electrify, we will continue to see a diversification of energy density and power needs and the development of batteries tailored to meet those needs. A deeper understanding of the battery degradation signatures of each of these battery types, facilitated by continued high quality research and innovation, will be required to ensure their successful deployment in commercial applications.

Glossary of Terms

Term / Acronym	Description
Alloying	An alloy is a metallic substance composed of two or more elements, as either a compound or a solution. The components of alloys are ordinarily themselves metals, though carbon, a non-metal, can be present.
Anode	The battery community commonly refers to the negative electrode in a rechargeable battery as the anode, regardless of whether the battery is being charged or discharged. This convention is used throughout this document.
Battery ageing	Ageing of a lithium-ion cell generally means a decrease in its energy density and power capability, caused by the loss of capacity and the increase of impedance. Early-stage ageing tends to be linear with respect to capacity fade with time, before entering a "roll-over" accelerated capacity fade. Generic ageing mechanisms can be described as (i) calendar ageing (degradation caused during storage); (ii) cycle ageing (degradation events occurring during charge-discharge cycles).
Battery degradation	Battery degradation occurs due to ageing mechanisms in its components and increases in internal resistance. It is collectively under-pinned by irreversible chemical and structural changes in battery components.
Capacity fade	Capacity fade is a gradual decrease in the amount of charge a battery can hold and occurs with repeated use as the battery ages.
Cathode	The battery community commonly refers to the positive electrode in a rechargeable battery as the cathode, regardless of whether the battery is being charged or discharged. This convention is used throughout this document.
CEI	Cathode-electrolyte interphase. A layer that forms on the cathode's active particles in contact with electrolyte.
Conversion chemistry	Conversion reaction materials react during lithiation to form entirely new products, often with dramatically changed structure and chemistry.
Current collector	A metal that distributes current flowing in or out of the electrode, connecting it to the external circuit.
Delamination	Delamination (or disbondment) is the loss of adhesion between electrode coatings and current collector foils. The resulting areas of detached coating contribute to resistance increases.
Dendrites	Dendrites are microscopic tree-like structures that can grow on anode surfaces under certain conditions.
DLC	Diffusion-limited C-rate. This is the diffusion-limited current density adapted for porous Li-ion insertion electrodes and originates from diffusion-limitations in the electrolyte. It is the fastest theoretical rate at which current can be drawn from a LIB without significant capacity decline and is a trade-off between energy and power density.
Electrolyte	The electrolyte in a LIB is a combination of organic solvents containing a dissolved lithium salt. The solvents are most commonly carbonates.
eVTOL	Electric vertical take-off and landing. This is a type of aircraft that uses electric power to hover, take off, and land vertically.
Intercalation	Intercalation is the reversible insertion of a molecule or ion into a material with a layered structure.
Intergranular porosity	Some cathode materials have aggregate-type structures, called secondary particles. These are composed of primary particles or grains. Spaces or voids between these are known as intergranular porosity.
ISC	An internal short circuit occurs when the two electrodes in a battery cell become electronically connected. The resulting high current density can give rise to localised temperature increases, and in certain circumstances a thermal runaway.
LFP	Lithium iron phosphate (LiFePO_4) is a cathode material used in LIBs. LFP is typically used for low cost, low performance applications.
NCA	Lithium nickel cobalt aluminium oxide is a class of cathode active material used in LIBs. NCA batteries are used in several high cost, high performance EVs.
NMC	Lithium nickel manganese cobalt oxide is a class of cathode active material used in LIBs. NMC is often the battery chemistry of choice for current-generation EVs.
SEI / SEI decomposition	The solid-electrolyte interphase; a layer that forms on the anode's active particles in contact with electrolyte. It is a product of partial electrolyte decomposition and serves to passivate the underlying graphite from further reaction. Stable SEI layers are critical for long-term performance. Thermal events can destabilise the SEI and cause it to decompose and compromise the battery's safety.
Separator	An electrically insulating porous layer in a LIB that prevents the anode and cathode touching, which would cause a short circuit.
SOH	State-of-health is a measure of the condition of a battery, compared to its ideal condition. Typically, a battery's SoH will be 100% at the time of manufacture and will decrease over time and use.
TM	Transition metal. In LIBs, typically nickel, manganese and cobalt.
Solvent-induced exfoliation	The separation of layers in a layered material. Solvent-induced exfoliation of graphite occurs when small molecules can insert themselves between layers to expand and eventually separate them.
Voltage limitation	Organic liquid electrolytes have a voltage range in which they remain non-degraded and functional. This is their stability window and defines their voltage limitations. Different chemistries have differing voltage limitations.

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