Future Material Developments for Electric Vehicle Battery Cells Answering Growing Demands from an End-User Perspective

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Abstract: Nowadays, batteries for electric vehicles are expected to have a high energy density, allow fast charging and maintain long cycle life, while providing affordable traction, and complying with stringent safety and environmental standards. Extensive research on novel materials at cell level is hence needed for the continuous improvement of the batteries coupled towards achieving these requirements. This article firstly delves into future developments in electric vehicles from a technology perspective, and the perspective of changing end-user demands. After these end-user needs are defined, their translation into future battery requirements is described. A detailed review of expected material developments follows, to address these dynamic and changing needs. Developments on anodes, cathodes, electrolyte and cell level will be discussed. Finally, a special section will discuss the safety aspects with these increasing end-user demands and how to overcome these issues.

Keywords: electric vehicle; battery material; anode; cathode; electrolyte; battery safety; end-user demands

1. Introduction

Nowadays, batteries have become an essential part of everyday life. With products and devices becoming increasingly electrified, battery usage has grown heavily over the past decade. Currently, they are mainly used in portable electronics, mobility applications and stationary storage. Mobility applications, comprising different categories of electric vehicles (EVs), represent the biggest share of the global battery market and are expected to continue growing, following the expected increase in electromobility [1]. EVs are projected to demand 90–95% of the total production of Li-ion batteries (LIBs) by 2030 with most predictions indicating around 150 million EVs on the roads by that time. Because of the dominating share on the battery market, the demands of the electrification of vehicles and their end-user expectations have been the primary drivers for the development of advanced battery technologies over the past decade. In the automotive industry, the end-user is demanding batteries that should be safe, sustainable and have affordable traction combined with high volumetric and gravimetric energy density and power, excellent electric

performance and durability in a wide ambient temperature range, low self-discharge and long shelf-life. In addition, the ability to sustain fast charging with a minimal impact on cell ageing is becoming increasingly important as electromobility is rolling out in increasing numbers to a wider circle of users and locations [2,3].

A variety of different materials have been thoroughly analysed and tested on battery components, aiming to meet and balance all these requirements while ensuring complementarity and stability when combined in a battery cell. Up until now, LIBs have proven to be the most robust technology enabler for the development of EVs. Different chemistries have been demonstrated to be more suitable for different applications, as shown in Figure 1. Incremental improvements over time and the Ni-rich cell chemistries currently available on the market have made LIBs even more suitable by improving aspects such as their specific energy and power among others. However, the quest for even higher energy density and specific energy as well as fast-charging capabilities remains a priority for the industry. At the same time, the demands from the end-users change with time as the mobility applications evolve and new usage patterns and behaviours are established. This accentuates the need for further improvements and has accelerated the need for development of novel battery materials that can meet the needs of future generations of EVs. Several articles have reviewed different novel battery materials and their influence on the different parameters of the battery in terms of performance, safety, cost etc. However, most articles make this review from a technology push perspective and do not take into account the future end-user demands. Therefore, this article will look at upcoming and changing future end-user demands and how these influence battery requirements. The analysis of novel material developments will be made coming from this end-user perspective and will highlight the technology pull perspective. Special focus is placed on the safety requirements of cells and batteries made from these novel materials.

Type	Chemistry	Performance						Main Applications						
		Energy	Power	Calendar Life	Cycle Life	Safety/Stability	Cost	Consumer Electronics	Power Tools	Light Duty Vehicles	Cars	Trucks/ Commercial Vehicles	Buses	Grid
LFP (Lithium Iron Phosphate)	LiFePO$_4$	++	++	++	++	+++	+	•	•	•	•	•	•	•
NCA (Lithium Nickel Cobalt Aluminium Oxide)	LiNiCoAlO$_2$	+++	+++	++	++	+	+	•		•	•			•
LMO (Lithium Manganese Oxide)	LiMn$_2$O$_4$	+	+++	-	++	++	++	•	•	•	•			•
LCO (Lithium Cobalt Oxide)	LiCoO$_2$	++	++	+	+	+	+	•						
LTO (Lithium Titanate Oxide)	Li$_4$Ti$_5$O$_{12}$	-	+++	+	+++	+++	-				•		•	•
NMC (Lithium Nickel Manganese Cobalt Oxide)	LiNi$_x$Co$_x$Mn$_x$O$_2$	+++	++	++	++	++	++	•	•	•	•	•	•	•
HE-NMC (High Energy Lithium Nickel Manganese Cobalt Oxide)	LiNi$_x$Co$_x$Mn$_x$O$_2$	++++	++	+	+	-	++	•	•	•	•	•	•	•
HVS (High Voltage Spinel) *	LiMn$_{1.5}$Ni$_{0.5}$O$_4$	++++	++	+	+	-	+	•	•	•	•	•	•	•
Solid State **		++++	++	++	-	+++	++	•	•	•	•	•	•	•

* currently at TRL6-7
** currently at TRL4-5

Figure 1. Li-ion battery overview (TRL = technology readiness level).

2. Projected Demand from End-User Side

Looking from the side of the end-users, in addition to the need for affordable and safe EVs, one of the main drivers is "range anxiety", caused by a combination of limited EV driving range and relatively long charging times plus an underdeveloped charging infrastructure [2,3].

All things remaining the same, increasing the battery energy density will translate into longer driving ranges in vehicles, as there will be more energy available for propulsion per battery unit. If the added energy comes with improved fast charging capability, this would be even better, as it would reduce the refuelling time, and further enhance freedom

to move with minimum inconvenience [4]. In the interest of sustainability, the combination of high energy density with fast charging capability opens another possibility, namely, to reduce the battery size and to rely on frequent, fast charging events to accumulate mileage. The latter option has the potential to significantly reduce the cost of the traction battery as well as decrease the material resources and energy consumption needed to produce the battery. However, it would also require batteries with improved cycle life to ensure that the total lifetime of the battery is not shortened. The traction battery currently represents up to 30–50% of the total cost to produce a battery-powered vehicle, depending on the level of electrification [5]. By reducing the battery size, the current cost gap between conventional internal combustion engine vehicles and EVs can potentially be closed and make them more affordable and achievable to a wider customer base [6,7].

Climatisation, of both the traction battery and the occupant compartment, is a notable load on the battery even today [8]. Owners of battery-powered vehicles who live in climate zones with seasonal variations will note a decline in the driving range per charge during sub-zero temperature periods, as the battery needs to be warmed for optimal electric performance. In warm climates, the battery needs cooling in order to prevent accelerated ageing at higher temperatures [9]. Hence, new battery systems with electrical and durability performances that are less affected by operating temperatures would have many advantages and free up battery energy for other uses on the vehicle, such as extending the driving range.

However, there are two parallel technology developments emerging alongside with electrification which are closely associated with the sustainability transition of the transport sector. These are autonomous (self-driving) cars and connected services. The gradual introduction of these technologies will likely have a major impact on the energy demand and usage of available energy in the battery in future EVs [10]. The energy demand from powering these applications is provided by the same battery that is also used for traction, which means that the total packed energy must be split between different loads. Autonomous driving requires 360° sensors, monitoring and online data processing to detect and manoeuvre obstacles, as well as to respond to the activities of all surrounding road users. The processors needed to manage these operations with sufficient speed and safety represent a significant energy load on the battery. In dense urban traffic, the energy consumption of these processors is typically of the same order of magnitude as the energy required to propel the vehicle. Under these conditions, future EV batteries would need to have double the energy density in order to retain the same driving range per charge cycle as they do today [11].

The energy consumption related to connected services depends on the nature of the over the air information exchange with the vehicle and how the systems are designed. For example, extensive use of the infotainment system and apps offering streaming services will have an impact on the amount of energy available for propulsion [12]. This technology is still very much in development, and it is not unlikely that the EVs will experience an evolution as the technology develops and matures, similar to the one we have witnessed in, e.g., mobile phones over the last two decades. The first mobile phones were very limited in what they could do and the smartphones currently on the market are a far cry from what we dreamed was even possible from the start. However, as with all other functions and features on the vehicle, the connected services will be powered by the traction battery and this will have an impact on the energy demand. The following section of this paper will show how the foreseen energy demand increase will be supplied by new battery technology with higher energy density as the research on novel components evolves and matures.

Ultimately, it is the driver and other vehicle occupants who will decide how the available energy in the EV battery is used, for example maximising driving range or accepting a shorter driving range to enjoy the freedom of a self-driving car and the on-board infotainment system. In addition to the on-board energy consuming functions discussed above, the future role of the EV batteries as energy storage support to the smart grids discussed in the context of the electrification transition should also be considered [13,14].

Making the traction battery available to vehicle-to-grid (V2G) applications will result in an increased total energy throughput over the battery lifetime [15]. This increase in battery usage yields a faster battery degradation. Preliminary studies show that over five years driving-related degradation accounts for 1–2.5% of capacity loss, V2G degradation is in the range of 1–2% and calendar ageing brings around 6% of the total capacity fade in a passenger car [16,17]. It is unlikely that vehicle owners will accept a trade-off that involves negative impacts on the durability performance of the battery in the vehicle [18,19]. Hence, improved cycle life and capability to retain long-term electric capacity with higher total energy throughput is also likely to emerge as increasingly important to meet the expectations and needs of the market and society. End-users' priorities regarding long-range or affordability are also going to be an important factor [3]. As the access to charging infrastructure improves, not only in city centres but also in more remote areas, the demand for affordable vehicles with smaller batteries is likely to increase, especially if the fast charging capability improves compared to now. Future batteries with higher energy densities would support these possible user trends, as well as other development directions that become possible as new technology advances in autonomous cars and connected services are made available and become mainstream. An overview of current demands and the corresponding battery requirements is provided in Table 1 in light of the end-user needs.

Table 1. End-user needs overview.

Demand	Battery Requirements
Reducing range anxiety.	Increasing energy density.
Convenience of charging.	Fast charging.
Sustainable EV.	Reduce size of battery by higher density + fast charging. Reduction of critical raw materials (Novel active materials that do not rely on critical elements and materials). Increase the recycling potential of the components.
Climatisation.	Wider operating temperature window.
Autonomous driving.	Increase energy density to maintain same range performance or higher energy throughput (cycle life).
Connected vehicles.	
Comfort and infotainment.	
Temporary energy storage applications, e.g., vehicle-to-grid, vehicle-to-vehicle.	Energy throughput not reflected by mileage and calendar life (cycle life).
Reduced cost.	Reduction of critical raw materials use, reduction of battery size.
Increased safety.	Non-flammable materials, high stability of components.

Finally, it is also worth mentioning that there are ongoing regulatory developments that are likely to affect how batteries can be designed and used in electrified vehicles. Two examples are the Global Technical Regulation (GTR) on in-use battery durability within the UN ECE Vehicle Regulations framework [20] and the European Commission's proposal for a new Battery Regulation [21]. Both regulations are expected to be adopted during 2021 and they incorporate mandatory electrical performance and durability requirements on batteries. The proposed Battery Regulation also includes sustainability requirements for repair, remanufacturing, repurposing, recyclability and use of recovered substances in new cells and batteries, which may limit the cell chemistries, battery systems' design options and vehicle usage patterns that will be possible in the EU internal market. It is important to be watchful that these regulations and similar global initiatives do not introduce unintended technology restrictions, which create unsurmountable obstacles to developing batteries capable of meeting the demands and expectations of future applications.

3. Projected Improvements on Component and Cell Level

The continuous increase in demand from the end-user side and the anticipated changes in end-user expectations will require further improvement of the battery and its components. Further development of the materials used for the battery components will be one of the main focus areas for research to meet new requirements.

Commercial LIBs are based on intercalation materials and have energy density <600 Wh· L^{-1} and specific energy <300 Wh·kg^{-1} at cell level [22], cycling performance <1000 cycles and C-rate capability <2C [23]. Additionally, there are still concerns regarding their safety, cost and sustainability that should be addressed by the next-generation battery systems for future automotive applications. Considering the current and future end-user needs mentioned above, increasing energy density, cycle life, and enabling fast charging capabilities are the main aspects to be improved in future battery cells. The driving range of the best performing current EVs is set at 600 km. This range can be directly correlated to the specific energy at the cell level among other parameters. Therefore, next-generation LIBs are expected to reach 700 Wh·L^{-1} and 350 Wh·kg^{-1} with outstanding cycling performance of 2000 cycles and higher current response $\geq$ 3C to satisfy user demands. To achieve this, a large spectrum of (electro)chemical and physical improvements are expected (and required) for all components, from the materials up to the cell level optimisation and design. These are presented and discussed in the following sections: anode, cathode, electrolyte, together with cell considerations and alternative battery systems. Equally important to performance are the end-user needs related to the cost, safety and sustainability aspects of future LIBs. Certain chemicals/metals have limited resources, are highly toxic, present ethical issues related to their sourcing or are expensive. All these aspects should be evaluated as a whole to achieve an innovative LIB technology for the next generation of EVs.

3.1. Anodes

The first LIBs commercialised by Sony back in 1991 consisted of coke carbon as the active material in the negative electrode [24,25]. Around 1995, graphite was introduced when it was understood how the surface of the graphite could be protected to prevent exfoliation [26]. Twenty-five years later and despite considerable research efforts to find higher performant substitutes, most of the commercially available Li-ion cells still include graphite in their anode formulation [27,28]. Thus, one could expect negligible advances in the development of novel materials for this electrode. The most pursued feature in the search of electrode active materials is the specific capacity, i.e., the capacity of the material to accommodate Li in its atomic structure [29]. A higher specific capacity implies a lower volume of material necessary to store a certain amount of Li and, at the end of the game, a clear advantage towards other candidates. In addition, from an electrochemical point of view, it is preferable for an anode material to have a reduction potential close to that of Li/Li$^+$ ($-$3.04 V vs. Normalised Hydrogen Electrode, NHE). The closer the potential of the material is from this value, the higher will be the voltage of the final cell [29]. The combination of a high specific capacity and a working potential close to $-$3.04 V vs. NHE would result in an anode appropriate for high energy density applications, such as EVs [30–32].

Furthermore, it is necessary to maintain these characteristics upon repetitive discharge and charge cycles [33,34]. Thus, a third significant feature of ideal anode material is high reversibility towards the storage of Li. In this regard, the formation of a stable solid electrolyte interphase (SEI) plays a key role in the cycling stability of these materials. This SEI, identified for the first time by Prof. Peled back in 1979 [35], is a passivation layer formed on the anode surface by the reaction of some electrolyte with the fresh electrode [36]. This layer prevents the continuous reaction of electrolyte at the anode and it is mainly formed during the first galvanostatic cycle(s) of the battery [32,33]. It is permeable for Li$^+$ diffusion while it is not for the rest of the electrolyte components [37,38]. Interestingly, it is a crucial component of the battery and it represents an industrial bottleneck for battery manufacturers, which try to optimise the SEI formation protocol [39,40]. Last but not least,

safety, cost, and environmental aspects also influence the selection of the negative electrode material [41].

The most widely studied anode materials can be classified in two main groups depending on the mechanism followed to store Li: (i) insertion/intercalation materials and (ii) conversion materials. The former accommodate Li-ions in their structure, while the latter, also known as alloying materials, form compound phases [42].

3.1.1. Insertion/Intercalation Materials

Graphite

Graphite is the dominating anode active material in Li-ion technology. Its theoretical capacity is 372 mAh·g^{-1} between 0.25 and 0 V vs. Li/Li$^+$ [43,44]. This carbonaceous material presents planar structure with hexagonal rings [45] and can accommodate one Li-ion per hexagon, in-between graphene planes, as the fully lithiated graphite structure is defined as LiC$_6$ [44,46]. This material shows good 2D mechanical stability, electric conductivity, and Li$^+$ transport. In addition, it has high electrical conductivity, and electrodes based on this material do not need significant fractions of conductive additives [42,47]. Furthermore, it is cheap and abundant, and even though it can be obtained directly from mining (natural graphite), it can also be manufactured (artificial graphite). However, the former is in the Critical Raw Materials (CRM) list [48].

Nevertheless, this excellent material also has some disadvantages that prompt researchers and battery manufacturers to find alternatives. On the one hand, its operation potential can be too close to Li/Li$^+$ reduction potential: under high currents Li transport might not be fast enough to allow successful intercalation of Li-ions [49,50]. This creates limitations on fast charge capability and induces the safety issue known as Li plating, which consists of the deposition of metallic Li at the surface of the graphite electrode [51,52]. Moreover, this can also occur when there is a shift in the working potential of the electrode and it approximates to (or overpasses) 0 V vs. Li/Li$^+$ [53].

On the other hand, the necessary SEI formation can also be troublesome depending on the electrolyte used [41,43]. The volumetric expansion of graphite is not high—roughly 10% for the fully lithiated LiC$_6$ phase—but the continuous expansion and contraction of this component leads to a gradual cracking of the SEI and exposure of fresh graphite to the electrolyte [41,54,55]. Thus, it is important to build up a mechanically stable SEI and minimise the electrode cracking. For that aim, selecting the adequate additives and cell formation protocol defined for each electrode–electrolyte combination is key [39–41,56,57].

Lithium Titanate Oxide

Lithium titanate oxide (Li$_4$Ti$_5$O$_{12}$, LTO) is nowadays the main alternative to graphite in commercial Li-ion cells. Interestingly, many of the disadvantages of graphite can be overcome by this material. Nevertheless, its output is lower compared with graphite in some other respects. The main advantage of this oxide is that it is considered as a "zero strain Li host", meaning that it does not undergo volumetric expansion upon lithiation [58–60]. Thus, the SEI formed is not fractured during cycling and allows an extended cycle life compared to graphite, even at high C-rates [61,62]. This makes LTO a good candidate for high power applications [63,64]. However, the formation of this SEI is accompanied by prominent gassing, particularly at high temperatures [59]. Another significant disadvantage compared to graphite is its low capacity (175 mAh·g^{-1}) and its working potential (1.55 V vs. Li$^+$/Li), which hinders the implementation of this material in high energy Li-ion cells. Yet, the latter can also entail an advantage due to the impossibility of Li plating. Its poor electric conductivity requires conductive additives in the anode formulation [41,62]. The energy density is, therefore, further diminished due to the addition of inactive components to LTO electrodes. In addition, it does not permit a particularly high Li$^+$ diffusion and is more costly than graphite [42,62]. All in all, even though it has been implemented in some EV models, such as the Honda Fit [24], due to its excellent response to high C-rates, high safety

and cycle life, it has more widely been adopted as an anode material for low energy density applications.

Other Alternatives

New rock salt type anode lithium-vanadium oxide ($Li_3V_2O_5$) can reversibly cycle two Li-ions at an average voltage of about 0.6 V vs. Li/Li^+, providing a capacity of 260 mAh$\cdot g^{-1}$, fast charging (up to 40% of the capacity in 20 s), as well as over 6000 stable cycles [65]. The start-up Tyfast was spun out to commercialise this technology, with a focus on electric buses and power tools.

3.1.2. Conversion/Alloying Materials

Silicon (Si)

Silicon has been explored as a strong candidate for high energy Li-ion cells due to its enormous theoretical capacity: 4200 and 3579 mAh$\cdot g^{-1}$ based on the formation of $Li_{4.4}Si$ and $Li_{3.75}Si$, respectively [66,67], and low working potential (0.4 V vs. Li/Li^+) [68]. However, this significant ability to store Li is associated with a ~400% volume expansion that jeopardises the mechanical integrity of the SEI formed at the electrode surface [69,70]. Indeed, the most significant drawback of this material is associated with the expansion-contraction of Si during the lithiation-delithiation cycles. The SEI is fractured continuously during the cell cycling: when the fresh Si surface is exposed to electrolyte, the latter further reacts forming new SEI, as previously discussed for graphite [71–73]. The electrolyte consumption, however, is much higher for Si due to the forty-fold higher volumetric expansion. In addition, the volume variation upon cycling also promotes the formation of void spaces in the electrode structure. This change of morphology is usually associated with a decrease in the electric conductivity of the electrode [70]. Furthermore, the mechanical stress induced by the expansion-contraction cycles leads to the pulverisation of Si particles, which lose contact with the rest of the electrode [70]. This last disadvantage has been faced by tailoring the Si material size: it was determined that there is a critical particle size, 150 μm for crystalline Si, below which pulverisation is significantly mitigated [74]. Indeed, several groups have focused their research on obtaining innovative Si nano-structures to limit the difficulties associated with the volumetric expansion [75,76]. Nevertheless, incorporating micron-sized particles is unequivocally more cost-effective for processing real Li-ion anodes [77]. Furthermore, Si requires fluoroethylene carbonate (FEC) as an additive in the electrolyte to form a stable SEI, which further increases the cost of the cell [71,78]. Some more realistic research fields attempting the adoption of Si as a regular anode material have been associated with the development of novel binders to minimise the impact of the volumetric expansion [69,79] or the prelithiation of Si-based electrodes to mitigate the capacity losses during the first cycles [75,80,81]. In any case, Si is usually added as an additive, blended with graphite, in the anode formulation [75,77,81] as the aforementioned difficulties associated with its volume change limit its use as the sole active material. In the last years, the development of Si-carbon composites has been widely promoted due to the industrial interest of Si [82–85]. In most of them, carbonaceous structures are used to buffer the volume expansion and reduce the particle and SEI fractures. Finally, apart from the electrochemical characteristics of the material, the possibility of using Si from metallurgical waste is a plus point in favour of this material as well as silicon oxide, which will be discussed in the following lines [84].

Silicon Oxide (SiO_x)

The addition of silicon oxide (SiO_x) has been adopted by the industry as an intermediate step previous to the definitive implementation of Si. SiO_x has lower specific capacity than Si (1200 mAh$\cdot g^{-1}$ [86]) but its volumetric expansion is accordingly lower (~118% for the full lithiation of SiO_x) [68,74]. Furthermore, Si-O bonds in the oxide structure are stronger than Si-Si bonds, and particle pulverisation is, therefore, minimised [68,87]. However, the main disadvantage of this material is the presence of oxygen radicals at the SiO_x

particle surface, which enhances the reaction with the electrolyte leading to an enhanced irreversible capacity loss in the first cycle [41,88]. Even blended in small fraction with graphite, this last parameter complicates the widespread implementation of the material in high concentrations for commercial LIBs [24,41,86]. However, it has been confirmed to be an anode component in Tesla's batteries [76,89].

Other Alternatives

Metal (principally iron and manganese) sulphides can provide remarkable capacities above 650 mAh·g^{-1} and can be obtained from side-products of some industrial activities, which is in favour of the circular economy [90,91]. However, their capacity retention and cycle life are low [92,93]. Many efforts related to these materials have been associated with the development of sulphide-carbon composites to enhance their cycling stability [93–95]. Nevertheless, to our knowledge they have not yet been implemented in industrial Li-ion cell prototypes.

Recently, black phosphorous has been claimed as an extraordinarily high capacity material (2596 mAh·g^{-1}) [96]. Nevertheless, phosphorous is toxic and can be dangerous due to phosphine formation [42]. On the other hand, germanium, an element from the same group as Si, has a high capacity [97] and does not fracture [76], but it might be too expensive for practical devices [42]. In addition, a recent publication [98] reported the use of iron-doped zinc oxide ($Zn_{0.9}Fe_{0.1}O$) as an alternative to graphite due to its superior specific capacity and rate capability. It is a promising material that improves the output of traditional metal oxides, but its voltage hysteresis is still too high and needs further research before upscaling from laboratory-scale cells to more realistic systems.

Finally, Table 2 has been included to sum up the characteristics of the different anode materials and make a direct comparison between them.

Table 2. Characteristics and evaluation of the different anode materials described. The minimum grade is 1 and the maximum is 5. Env. Friend. refers to environmental friendliness.

Material	Energy Density	Cycle Life	Power Capability	Cost	Safety	Env. Friend.	Readiness
Graphite	3	5	4	5	5	4	5
LTO	2	5	5	3	4	4	5
$Li_3V_2O_5$	3	4	3	3	3	4	2
Si	5	2	2	3	5	5	3
SiO_x	4	3	3	4	5	5	4
Sulphides	4	2	2	2	3	5	2
P	4	2	2	3	1	1	2
Ge	4	2	2	1	4	3	1
$Zn_{0.9}Fe_{0.1}O$	3	3	1	4	4	4	1

3.2. Cathodes

Currently, several materials are investigated as potential cathode for next-generation LIBs. In this section, two candidates are mainly discussed in-depth due to their high theoretical capacity to store energy: Ni-rich and Li-rich oxides. Even though $LiMn_2O_4$ and $LiFePO_4$ have interesting (and critical) properties for the automotive industry, such as being Co-free, low cost and presenting high C-rate performance for rapid battery charging, they are not considered in this manuscript due to their lower theoretical capacity <200 mAh·g^{-1}. Other reviews can be considered for these materials [42,99].

3.2.1. Nickel-Rich Cathodes

Layered oxides for LIBs have the α-NaFeO$_2$-type structure and are composed of alternate layers of M and Li (where M is a metal) between oxygen atoms. During charge, layered oxides undergo structural transitions to an irreversible phase which limits the capacity of the electrode. This irreversible transformation is much dependent on material stoichiometry [100] as well as electrode cycling conditions [101] and the operational voltage for these materials must be carefully adjusted between 4–4.4 V to avoid cation reorganisation and oxygen loss [102]. For instance, an irreversible phase transformation occurs in Li$_x$CoO$_2$ at x = 0.5 (or 4.2 V) where x corresponds to Li stoichiometry [103]. This induces fracture of particles and particle isolation from the electrically conductive network, so its capacity is limited to 140 mAh·g^{-1} to avoid irreversible capacity loss together with an increased cell polarisation. To maximise discharge capacity, LiNiO$_2$ was investigated [104] and early studies demonstrated that the material can deliver >150 mAh·g^{-1} depending on synthesis conditions [105]. Besides, Ni is readily available, cheaper and less toxic than Co. From these considerations, and because LiNiO$_2$ is a complex oxide difficult to prepare in large amounts [104,105], efforts were re-directed to Ni-rich compositions [106]. The LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811) compound is mainly considered as a potential candidate for next-generation LIBs. It delivers a high capacity $\geq$200 mAh·g^{-1} but suffers from low ionic diffusivity and poor cycling [107,108]. If the Ni content is decreased, e.g., NCM622 or NCM523, compositions store less energy but their capacity retention, as well as kinetics, improve significantly [106]. NCM622 and NCM523 are indeed commercially available and represent current state-of-the-art layered materials for LIBs. Other interesting compositions are LiNi$_x$Co$_y$Al$_z$O$_2$ (NCA) or LiNi$_x$Co$_y$Mg$_z$O$_2$ (NCMg). The first, i.e., LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$, [109] is promising but it also suffers from rapid structural degradation on cycling as in NCM811 requiring coating strategies to optimise performance [106,110]. Mg-doped compositions deliver a high capacity of 228 mAh·g^{-1} at moderate rates and remarkable capacity retention after 300 cycles [111]. A more recent approach to improve cycling performance of Ni-rich oxides is to fabricate core-shell structures; a Ni-rich core encapsulated with a stable concentration-gradient layer that has reduced Ni content. This approach is interesting but challenging from the material up-scaling point of view. An example of a concentration gradient structure is GC-LiNi$_{0.83}$Co$_{0.07}$Mn$_{0.10}$O$_2$ which exhibits a higher discharge capacity of 213 mAh·g^{-1} with improved thermal and cycling stability compared to the bare oxide [112]. In brief, layered compositions with Ni content beyond 80% are promising, with suitable dopants to replace cobalt and new coating strategies to improve cycling performances and electrode kinetics. In addition, aqueous-based electrode formulations would be preferred for improved processing sustainability, and the surface reactivity of these materials should also be addressed.

3.2.2. Lithium-Rich Oxides

Li-rich oxides are another class of materials that are currently investigated for mobility applications. Li-rich oxides with the formula Li$_{1+X}$M$_{1-X}$O$_2$ integrate two structurally compatible components, LiMO$_2$ and Li$_2$MO$_3$, and they are often referred to as composite oxides. Both structures are analogues, hence Li$_2$MO$_3$ can be described in layered notation with Li/M cation ordering in the M layer, i.e., Li[Li$_{1/3}$M$_{2/3}$]O$_2$ [113]. The use of composite oxides (1 − x)Li$_2$MO$_3$·xLiMO$_2$ [114,115] is appealing because it allows the electrochemically active LiMO$_2$ structure to be stabilised, which, in turn, improves the cycling performance of the electrode e.g., NCM811-Li$_2$MnO$_3$ [116]. However, the main challenges of Li-rich oxides remain unresolved. Li-rich oxides can theoretically store a large capacity >400 mAh·g^{-1} if two Li are considered active per Li$_2$MO$_3$ formula unit but, in reality, the electrodes deliver lower capacity and in the range of 200–300 mAh·g^{-1} [117–119] due to irreversible electrochemical (de)intercalation of Li ions. Additionally, Li-rich based electrodes show limited capacity retention, poor efficiencies and sluggish kinetics [120]. This gap in terms of material performance was first discussed for Li$_2$MnO$_3$ [121]. Several mechanisms were considered at charging voltages $\geq$ 4.5 V vs. Li/Li$^+$, from oxide

decomposition via oxygen evolution [122] to phase transformation [123,124] and oxidation of the non-aqueous electrolyte [125]. Recent reports demonstrate that a reversible and stable anionic capacity is feasible for the oxides [126] requiring fine-tuning of the chemical compositions, in addition to stable electrolytes at high voltages. Several approaches have been discussed in the literature to improve cycling performances of Li-rich oxides, and the most promising results have been obtained by material doping. For instance, a Na-doped Li-rich cathode material delivers 281 mAh·g^{-1} at 0.1C and good rate capacity up to 5C by reducing the Li(Na)/Mn cation mixing in the structure [127]. Al-doped samples show superior cycling performances and lower voltage decay than parent composition, since it appears that the dopant reduces the transition rate to the spinel phase [128]. The higher electronegativity of Sn^{4+} with respect to Mn^{4+} leads to stronger structural bonds which improve cycling performance of the material with respect to parent LNMO [129] (Figure 2). Other interesting approaches are particle encapsulation using a conductive layer [130] or surface modification [131,132]. Both approaches have shown improved kinetics and cycling performances with respect to bare materials. In general, Co-free Li-rich materials are promising cathodes for next-generation LIBs due to the high experimental capacities reported, but significant improvements on cycling performance and rate-capability are still needed. Fine-tuned compositions are expected in the near-term, together with electrolytes with stable operation at $\geq$4.5 V vs. Li/Li$^+$.
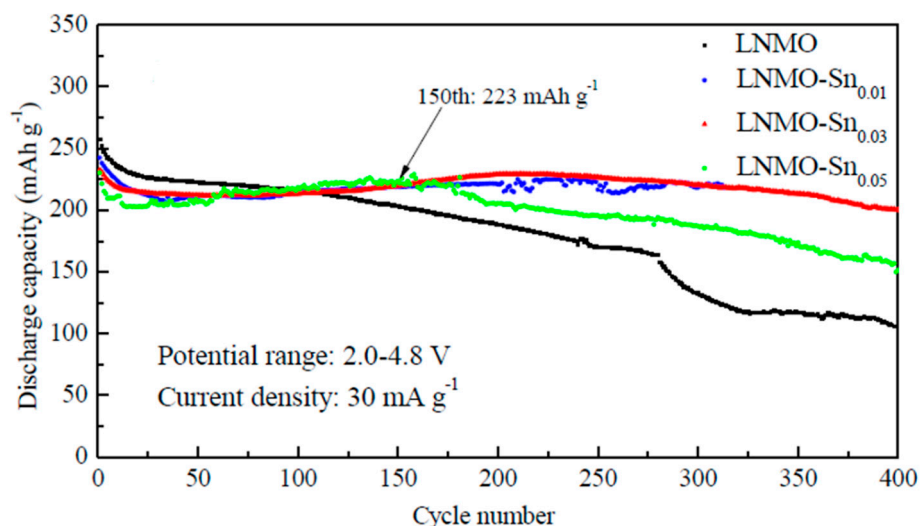

Figure 2. Cycling performance of LNMO, LNMO-Sn$_{0.01}$, LNMO-Sn$_{0.03}$, and LNMO-Sn$_{0.05}$ samples at 30 mA·g^{-1}. Republished with permission of The Royal Society of Chemistry from [129]; permission conveyed through Copyright Clearance Center, Inc.

Table 3 summarises the characteristics of the different cathode materials and makes a direct comparison between them.

Table 3. Characteristics and evaluation of the different cathode materials presented. The minimum grade is indicated with 1 and the maximum with 4. Env. Friend. refers to Environmental Friendliness.

Material	Energy Density	Cycle Life	Power Capability	Cost	Safety	Env. Friend.	Readiness
LiFePO$_4$	2	4	4	4	4	4	4
LiMn$_2$O$_4$	3	3	3	4	3	4	3
NCM811	3	2	3	2	3	1	2
Li$_{1+x}$(Mn, Ni)$_{1-x}$O$_2$	4	1	2	3	2	3	1

3.3. Electrolytes

Besides the electrodes, the electrolyte is another vital component of the battery and it also contributes to the energy density, cycle life, power, cost, and safety. The main function of an electrolyte in LIBs is to conduct Li^+ ions between the positive and negative electrodes and the key technological parameters linked to increasing the performance and demands are related to having high ionic conductivity (to obtain high performance), low electronic conductivity (to avoid self-discharge), wide electrochemical window (to be used with high- and low-voltage electrodes), high chemical stability (to avoid side reactions), and high thermal stability (to enhance safety).

The state-of-the-art electrolyte in LIBs since market introduction is composed of $LiPF_6$ salt dissolved in carbonate-based solvents. Although many researchers have only focused on the components, the amount of electrolyte is also important and is often disregarded, especially when considering the cell level [133]. Below the optimal electrolyte volume, the cell resistance increases, resulting in a higher capacity fade, while further increasing the electrolyte volume does not improve the cyclability significantly [134]. As the electrolyte will contribute to the weight of the battery, the electrolyte volume should be optimised to maximise the cell performance and energy density. There are several factors to consider when calculating the amount of electrolyte. It should fill the pores in the electrodes and the separator and it is consumed to form passivating layers on the surface of the electrodes to, ideally, prevent further electrolyte decomposition [134,135].

The electrolyte components; salt, solvents and additives, have been developed to meet the increasing demands in batteries mainly in terms of performance but also of sustainability and safety.

3.3.1. Lithium Salts

The archetypical $LiPF_6$ salt provides good ionic conductivity, solubility, cycling performance and sufficient electrochemical stability for current cathode materials. However, the drawback of $LiPF_6$ its its low thermal and chemical stability, which involves the release of hydrogen fluoride (HF) in the presence of trace amounts of water. Although it is beneficial for passivating the aluminium current collector [136], HF is highly toxic and can react further with other electrolyte components to form other toxic compounds such as fluorophosphonates [137]. Therefore, it is a safety hazard during the manufacturing and recycling processes [138]. While other fluorinated salts, such as LiTFSI and LiFSI have shown higher solubility, conductivity and thermal stability than $LiPF_6$-based electrolytes [139], and good electrochemical performance in high-energy-density batteries [140], they fail to passivate the aluminium and, in the case of LiFSI, it contains labile F atoms susceptible to hydrolysis [141]. Therefore, efforts should be made to find alternative fluorine-free salts that will make LIBs safer and more sustainable. The most popular one is LiBOB. which has slightly lower solubility and conductivity in conventional carbonate solvents, but features good electrochemical performance below 4.2 V vs. Li/Li^+ [141]. Examples of LiBOB-based electrolytes in high-energy-density LIBs (Si-graphite and NCM111) have been reported featuring improved performance to that of $LiPF_6$-based electrolytes at low current rates (85% capacity retention after 200 cycles at C/10) but still limited at high current rates (60% capacity retention after 300 cycles at C/2) [142]. Despite the general belief that the utmost requirement of the solid electrolyte interphase (SEI) is to be fluorinated [143], it has also been proven that an O-rich SEI is also able to passivate a silicon-graphite composite anode and provide good electrochemical performance in full cells with NMC111. Overall, more efforts should be made to understand the role of fluorine in the SEI and how it can be replaced by other fluorine-free alternatives.

3.3.2. Solvents

Electrolyte's solvents used nowadays in LIBs combine cyclic carbonates, ethylene carbonate (EC), and linear carbonates, ethyl methyl carbonate or diethyl carbonate. This combination leads to good salt solubility, high ion mobility and low viscosity. However, the

main limitation of EC, in particular, is its high anodic reactivity, which makes it unsuitable when using high-voltage cathode materials [144]. Different strategies have been developed to overcome this issue, such as including additives to passivate the cathode and to replace EC with other solvents. Alternative solvents to carbonates are sulfones, which can operate with high-voltage cathodes but require the incorporation of additives to form a stable SEI and allow graphite operation [140]. This points out that the best electrolyte composition for the anode might not be the best for the cathode, thus full cell tests should be carried out to investigate the feasibility of an electrolyte to provide good performance at the cell level. This is particularly important when using, for example, high-energy-density Si in the anode, as it is known to consume active Li from the cathode due to continuous electrolyte degradation [145–147]. Nevertheless, the aforementioned solvents are still volatile and flammable which compromise the safety and recyclability of the battery. To overcome these issues, room temperature ionic liquids could be used as alternative solvents as they have wide electrochemical stability, low flammability, low volatility and high thermal stability [148,149]. An electrolyte based on 1-ethyl-3-methyl imidazolium-TFSI with LiTFSI as salt used with Li-rich layered oxide ($Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$) in half-cell configurations has shown an initial capacity of 200 mAh·g^{-1} and 70% capacity retention after 50 cycles at C/10 and 30 °C [150]. Ionic liquids have also been used in full cells with LNMO-LTO [151] but, to the best of our knowledge, in these cases, graphite has not been used as an anode.

3.3.3. Additives

Due to the overall good electrochemical performance of $LiPF_6$ in carbonate-based solvents, they remain the state-of-the-art electrolyte composition. However, the new electrode materials with higher capacity and cell voltage introduced in LIBs operate beyond the thermodynamic stability limits of electrolytes. Inevitably nowadays, this leads to the formation of passivating layers (SEI and CEI) from the decomposition of the electrolyte. To circumvent this issue, sacrificial additives are included in the electrolyte formulation, mainly to form stable passivating layers on the electrodes prior to the bulk electrolyte components (salt and solvent). Each additive has its own reaction mechanism depending on its chemical structure as well as the interface where the reaction occurs. Therefore, additives should be designed to target specific properties of the interphases, such as the surface where they will react (cathode or anode), the voltage at which it will happen, the composition, thickness, conductivity and resistance (Figure 3). Developing high-energy-density active materials entails that they will be highly reactive and impose tougher requirements for the passivating layers and the electrolyte. In general, electrolyte additives for anode materials should be able to be reduced before the electrolyte and should form a stable and thin passivating layer that remains stable throughout battery operation. For materials suffering from high volume changes, such as Si and Sn, the formed SEI should also be flexible and mechanically strong. Examples of successful additives are FEC and VC, where the former can form a dense F-rich layer composed primarily of LiF and both additives can form a polymeric flexible layer [152,153]. In the case of the cathodes, the main challenges are the transition metal dissolution (especially manganese), interfacial reaction and contact loss of the components. To form a stable cathode electrolyte interphase (CEI) the additive should oxidise before the electrolyte and cover the electrode's surface to avoid further decomposition of the electrolyte and prevent the degradation of the active material. In addition, the presence of active sites on the cathode decreases the electrochemical stability window of the electrolyte [154]. Therefore, an accurate determination of the electrochemical stability window of the electrolyte should be carried out with the active material in the intended chemical system rather than with only the current collector or other surfaces [155]. Promising additives targeting the cathode electrode to lower cell are, for example, methylene methanedisulfonate and tris(trimethlysilyl)phosphite for NCM [156,157], 1,3-propane sultone are used for Li-rich cathode materials to prevent metal dissolution and electrode structural changes [158,159], and tris(trimethylsilyl)phosphate

for Li-rich and spinel $LiMn_2O_4$ to improve the rate capability, metal dissolution and allow high-temperature storage [160–162].
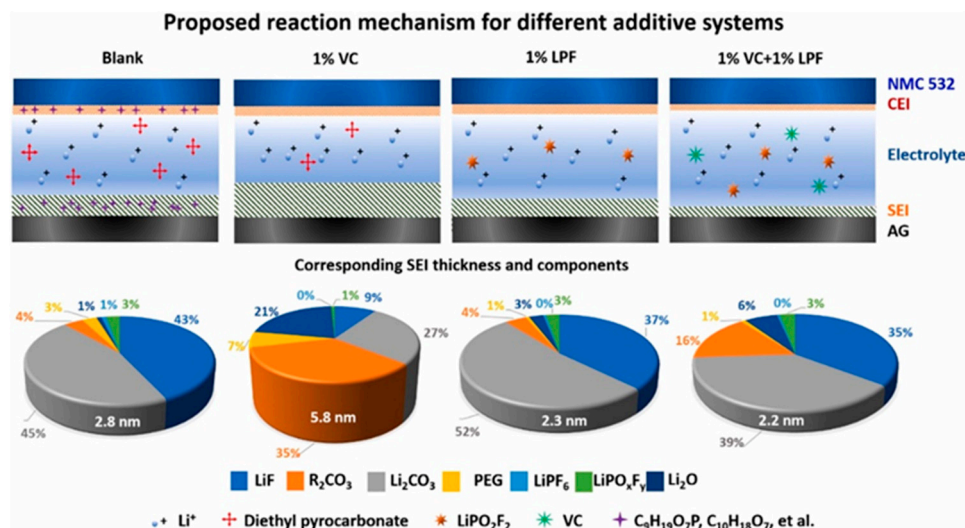

Figure 3. Proposed reaction mechanism of different additives on the passivating layers of NMC523/graphite cells and the specific atomic ratio of the SEI components on the anode. Reprinted from [163], with permission from Elsevier.

Another parameter to optimise is the number of additives. Ideally, it should be kept to the minimum and still be able to form thin SEI and CEI with low resistance. Above the optimum amount, it could have a negative effect on the battery performance with a continuous electrolyte decomposition and, consequently, faster battery ageing. Interphases have been investigated for several decades and they are still the most elusive and least understood components in batteries [143], while electrolyte additives have become a billion-dollar industry [163]. As one single additive unfortunately does not solve all the issues, especially in the full cell configuration, a combination of additives is preferred to provide a cooperative effect on the performance of the battery [154,164]. Attaining the "right" interphases and interfaces in batteries is key to achieving successful high-performance long-life batteries.

3.3.4. Solid-State Electrolytes

Liquid electrolytes present some limitations, not only regarding safety but also their inability to be used with other high-energy-density active materials such as Li metal. It is not surprising that Li metal with the highest capacity and energy density would be the most reactive component in LIBs. That is what has limited its application in LIBs. One way to overcome these challenges is to use solid-state electrolytes, which can be summarised into ceramic (garnet structure oxides, halides, phosphosulphides, etc.) [165] and polymeric (poly(ethylene oxide), polycarbonates, polyesters, polynitriles, etc.) [166,167]. While they feature different properties, common benefits over liquid electrolytes include battery safety, chemical stability, functionality with high-energy-density electrodes and low cost. Additionally, solid electrolytes will allow the voltage of Li-ion cells to extend beyond 5 V, as expected for oxide- and phosphate-based solid electrolytes [168]. These developments, together with the use of Li metal as an anode, will effectively increase the specific and volumetric energy of the cells [22]. However, state-of-the-art solid electrolytes still possess low ionic conductivity and poor electrode wetting, which limits their performance at room temperature but could be an advantage for applications at elevated temperatures [169].

3.4. Cell Considerations

Electrode fabrication is another critical step in order to increase the energy density at the cell level. In brief, electrodes are fabricated by coating the slurries (with a given active material, carbon and binder weight %) on a current collector (CC). Depending on the active material physical and chemical properties, the amount of carbon and binder are adjusted to optimise the conductivity and mechanical integrity of the electrode, respectively. State-of-the-art materials are conductive carbons able to withstand high operation voltages to improve the energy density of cells [170], water-soluble binders to process both anode and cathode electrodes in a greener and cost-effective way, e.g., Carboxymethyl cellulose (CMC) [171], and new functional membrane separators for safer and smarter Li-ion batteries [172]. However, the tendency is to reduce the weight % of inactive components as much as possible by using new active materials with higher conductivities and better mechanical properties. State-of-the-art LIBs contain electrodes with areal loadings in the range of 2–3 mAh·cm^{-2} to maximise discharge capacity, cycle life and rate capability at cell level. Electrode loadings for next-generation LIBs are expected to reach ≥4 mAh·cm^{-2} but this has consequences on the electrode thickness and porosity. High mass loading means highly compacted electrodes with reduced porosity which can result in a lower cell performance. Another important factor is the capacity ratio of negative to positive electrodes, called the N/P ratio which dictates battery discharge capacity and cycle life [133]. It is generally set to 1.10–1.15 for LIBs to offset Li lost at the anode (graphite) [22] but new electrode combinations will require optimised N/P values to achieve good performances. Regarding slurry toxicity and cost, alternatives to 1-Methyl-2-pyrrolidinone (NMP) as processing solvent are needed. Water works well as a processing solvent for the anodes, but it reacts with most cathodes leading to chemical leaching of the transition metals, e.g., Ni-rich oxides [173], leading to performance loss. Equally important are the thickness, structure, composition and coating layers of the CCs. Carbon-coated CCs are currently used in the mass production of LIBs because of their high performance and low cost. However, thinner CCs will help to increase energy density, and 3D CCs will improve the current response and cycle life at the cell level [174]. Cell production considering electrodes, separator and electrolyte have mainly two bottlenecks: electrolyte filling and battery formation. Electrolyte filling aims to dose the necessary amount of electrolyte into the battery. It is an expensive and time-consuming process that involves many steps [175], especially for highly compacted electrodes. The amount of electrolyte in a cell can be expressed as the ratio of electrolyte weight to cell capacity E/C, gA·h^{-1}) and it is usually in the range 1–2 gA·h^{-1} for commercial Li-ion cells. E/C < 1 will help to increase energy density at the cell level. The second bottleneck in cell production is the initial battery formation cycles. Specific current and voltage profiles are applied to enable safe and high-quality cell activation; they can take up to 20 h for LIBs [176]. Therefore, shorter cell activations are necessary to reduce cell production cost. Overall, developments discussed at the cell level are expected to contribute, together with the materials discussed in sections above, to an increased energy density for the Li-ion technology.

3.5. Alternatives to LIB: Lithium-Sulfur and Potassium-Ion as an Alternative for Li-Ion

In spite of the rapid development of LIBs over the past years to catch up with the necessities of the automotive industry, there are still uncertainties regarding cost, sustainability, extended driving range, fast charging as well as safety for the Li-ion technology. The lithium-sulphur (Li-S) technology can address some of these drawbacks but commercial Li-S cells are not yet available. Li-S batteries are promising because of their high theoretical energy density 2800 Wh·L^{-1}, low price and improved sustainability and safety with respect to LIBs. In brief, Li-S batteries do not operate in the same way as intercalation batteries do. S reacts with Li via a conversion mechanism forming new (and soluble) products during battery operation which need to be contained at the cathode. Over the past years, efforts have been made to design new cathodes to avoid the so-called "shuttle-effect" [177,178], separators with better efficiency [179], and suitable liquid electrolytes together with ad-

ditives to improve Li anode stability and safety [180]. An example of high-performance cathodes are 2D-organic layered materials containing atomically dispersed cations that deliver discharge capacities up to 1540 mAh·g^{-1} at 0.1C while retaining 496.5 mAh·g^{-1} after 2600 cycles at 3C with a decay rate as low as 0.013% per cycle [181]. Up-to-date results for Li-S are indeed promising but have been only demonstrated at lab-scale level [182] or as prototype cells by OXIS with an energy density 471 Wh·kg^{-1} [183].

Potassium-ion (K-ion) batteries have also started gaining attention, promising to address the Li scarcity issue. In comparison, K is more abundant. Research on K-ion batteries is still in its infancy, although existing work has shown promising results. K-based cathodes have exhibited energy densities close to 500 Wh·kg^{-1}, provide fast ionic conductivity in electrolyte, and high operating voltage. In addition, potassium has significantly lower cost than lithium, which could result in a lower cost per kWh for a battery system. Nevertheless, work is still needed to improve stability and address safety issues, as mentioned in the next section.

4. Safety Considerations

As mentioned in the previous sections, demands related to the electrochemical performance are becoming more challenging. Section 3.2 explained that LIBs are currently the most suitable for meeting these demands and that researchers are continuously developing new methods for improving their performance and enhancing their safety [184] by strongly focusing on cell material research. Table 4 demonstrates the safety of LIB and the influences of different anodes, cathodes, electrolytes and separators. However, with rising energy content, the safety risks increase [185]. The typical safety concerns associated with liquid battery technologies are leaking electrolyte, smoke, fire, and explosion as a result of thermal runaway (although most cells are designed to preclude the possibility of explosion) [186]. Usually, these safety concerns are caused due to excessive temperature at a significant state of charge (SOC). Cell failure and abusive conditions are the causes of excessive temperatures, which arise due to mechanisms on different levels: (a) electrical e.g., short-circuit and overcharge, (b) mechanical/physical, e.g., crush and shock, (c) environmental, e.g., overheating. To avoid the repetition of the text, authors would suggest readers to refer [186,187] for a detailed description (battery failure mechanism and processes along with battery standards and regulations) about these levels. Measures to improve safety are taken at the cell material level in parallel to optimisation with respect to energy content. This includes electrode materials, advanced separators and electrolytes as well as additives to further improve their properties. In addition, "external" measures such as sensor surveillance and battery management systems (BMS) are applied and constantly improved [188]. However, traditional liquid electrolyte LIBs are reaching their theoretical limits. In such a context, other emerging liquid battery technologies such as K-ion and Li-S are being intensively studied.

K-ion batteries have recently gained significant attention due to their low cost, fast ionic conductivity in an electrolyte, and high operating voltage. Similarly, Li-S batteries are becoming popular for their low cost and higher energy density. However, safety is the most critical factor when it comes to the regular usage and commercialisation of such battery technologies. As mentioned in Section 3.5, Li-S cells can lead to an improved state of safety. However, investigations on K-ion batteries show different results. For example, compared to the commercial Li-graphite anodes, thermal runaway studies of K-ion batteries show an inherent threat due to the poor heat dissipation, and thermal runaway (100 °C versus 150 °C), but generate less heat (395 J·g^{-1} versus 1048 J·g^{-1}) [189]. This is the main issue causing safety concerns, i.e., K has a lower melting point and more reactive characteristics compared to Li [185]. The three major possible ways that could address the safety concerns of K-ion batteries are, (a) thermally stable and low-cost separators with high melting points, (b) solid electrolytes and quasi-solid electrolytes such as polymer-based electrolytes, which will lower the risks of internal short circuits and thermal explosions, and (c) liquid

electrolytes or electrode materials with flame retardants as additives to increase the thermal activation temperature [185].

Similarly, the safety enhancement of Li-S batteries can be achieved by modifying metal anodes [190,191], optimising cathode materials [192,193], designing new separators [194–196], selecting suitable electrolyte [197–199], and adding additives [200,201]. The detailed safety aspects of Li-S batteries along with the scientific issues for its industrial application are elaborated in [202].

Li-ion batteries consist of liquid or gel electrolyte which are flammable, toxic, and the cells can experience short circuit due to accidents or internal faults, which could lead to thermal runaway and fire propagation. In contrast to this issue, solid electrolytes are considered a safer alternative to mitigate such risks because the electrolyte is mostly non-flammable [203] and shows improved mechanical properties. Moreover, as discussed in Section 3.3.4 the use of solid electrolytes can lead to further improvements not only regarding performance but also safety, thus, solid-state batteries have attained growing interest from authorities as well as vehicle manufacturers [186]. Cell producers claim that they "can achieve more than two times the energy density of conventional LIBs and significantly improve safety" [184]. This can be achieved by replacing the liquid electrolyte with a solid electrolyte which would also suppress dendrite growth [184], i.e., one of the major concerns for cell failure of LIBs. While solid electrolytes tend to show enhanced safety levels in this respect, a major drawback compared to common technologies is the reduced ion diffusivity. When comparing liquid electrolytes to their solid counterparts, a difference in conductivity of the order of 10^{-2} S·cm^{-1} can be noticed [184]. The ion conductivity of solid electrolytes is thermally dependent and increases with temperature, meaning that they are well suited for high-temperature applications. However Table 4 presents the list of advantages and challenges of Li-ion versus solid-state batteries for a better understanding of both technologies.

Table 4. Advantages and challenges of Li-ion battery versus solid-state battery [204].

Li-Ion Liquid Battery		Solid-State Battery	
Advantages	Challenges	Advantages	Challenges
Low processing cost.	Shelf time is reduced by self-discharge.	High thermal stability.	Ceramic and glass separators are brittle and break due to pressure/stress.
Flexible separators can withstand high mechanical stress.	Flammable electrolyte causes a safety concern.	Less self-discharge.	Ceramic and glass are harder to manufacture in large quantities. Manufacturing process may emit toxic gases.
High ionic conductivity at room temperature.	Solid-electrolyte Interfacial Layer impacts the life cycle.	High ionic conductivity over a broad range of temperature.	
	Limited choice of cathode material due to liquid electrolyte reaction.	Non-volatile electrolyte	
	Poor thermal stability.	Safer and non-flammable electrolyte options available	
	Overcharge sensitivity issue.	High energy density and tolerance.	

Overall, it can be said that one of the potential solutions at the cell material level to overcome the challenges of liquid batteries is the solid-state battery. This technology has its own challenges, but it certainly has more advantages compared to its counterpart. Solid electrolytes improve battery safety due to their superior mechanical, electrochemical, and thermal stability when compared to liquid electrolytes, and are considered a promising solution for increasing battery capacity while enhancing battery safety [184]. It should

be mentioned that additional measures can be applied to enhance the overall system's safety. These might include battery packaging design (such as material choice, crashworthiness), positioning of cells inside the battery and the battery itself inside the vehicle, threat detection mechanisms (sensors, BMS), contingency measures such as extinguishing systems or non-flammable shielding and warning and signalling strategies. Although these measures are targeted to damage limitation, they play a key role in enhancing the safety of future battery systems, since none of the aforementioned cell improvement efforts can guarantee the complete absence of hazardous situations.

Recognising the safety challenges of the LIB, in particular in light of ever-increasing volumetric energy densities, development of thermal runaway and thermal propagation detection methods have been seeing intensified interest from the industry and research communities [205–212]. Battery safety is increasingly becoming a matter of system safety, rather than an inherent cell safety question. As the knowledge about the battery systems increases, the BMS algorithms and functionalities are becoming more advanced and able to identify faulty cell behaviour and intervene to prevent or mitigate safety incidents. Different types of detectors are being evaluated and implemented into EV batteries to provide or enable early detection of cells at risk. Gas detection, pressure sensors, strain gauge and force sensors show promise as their response time is faster than temperature sensors [206]. Pressure sensors and gas detection are quite similar, since they are activated by gas emissions from the cells, whereas the pressure sensor is monitoring the forces between cells and how these are affected by cell swelling, and the strain gauge measures cell deformation and excessive swelling. There are also examples of more advanced detection principles based on acoustic signals, e.g., ultrasonic methods, and predictive models incorporated into the BMS, which use data from the battery, e.g., cell voltages, temperatures and currents, to detect inconsistencies [213,214]. Commercial systems based on these principles are appearing on the market. The acoustic detection systems monitor changes in the cell active materials. Predictive models monitor electrochemical performance and monitor deviations compared to expected behaviour. Impedance monitoring is another example of detection technology which monitors and responds to changes in the electrochemical performance that are associated with abnormal cells [212].

The UN ECE Global Technical Regulation on Electric Vehicle Safety (GTR 20) [215] adopted 2018, requires that new EVs registered in 2023 have technology installed which can detect the occurrence of a thermal event in case of a single-cell thermal runaway, which can lead to thermal propagation within the battery. The vehicle must also provide a timely warning to allow safe evacuation of vehicle occupants prior to hazardous conditions occur inside the passenger compartment. Furthermore, GTR 20 does not specify a test to assess thermal propagation safety, but assumes a functional safety approach and requires the vehicle manufacturer to provide evidence of appropriate risk reduction management and verification of the effectiveness of the implemented safety measures to satisfy the safety requirements.

5. Conclusions and Outlook

Future developments within EVs and their use have an impact on the end-user requirements. As a result, user-driven demands will require battery densities surpassing currently used batteries with 300 Wh·kg^{-1} and 600 Wh·L^{-1} to address range anxiety as well as accommodate the incorporation of novel technologies and usage patterns that will consume a significant part of the battery's energy on non-traction-related activities, such as autonomous driving, as well as connected vehicles, comfort and infotainment. At the same time, higher energy throughput will support the additional energy-consuming activities while maintaining or improving cycle life. Improving cycle life will be crucial for the adoption of V2G applications. Fast charging capabilities ($\geq$3C) will ensure that charging an EV will become more convenient and therefore increase EV adoption, while it would contribute to improving EV sustainability by reducing the size of the battery. Gravimetric and volumetric energy densities of 350 Wh·kg^{-1} and 700 Wh·L^{-1} with exceptional cycling

performances of 2000 cycles and higher current response ≥3C are the key targets in the short-term. Increasing the operating temperature range of battery cells will avoid the use of energy towards climatisation and hence would contribute to increasing range and/or reducing the size of the battery.

Looking at how the different components and their materials will need to evolve in the future to answer these changing requirements, following future research is expected per component.

1. Anodes. Although graphite is the dominating active anode material in Li-ion technologies, its energy and power density limitations in combination with natural graphite being in the critical raw material list have raised the need for researching new compositions such as Si-based and other metal sulphides, which can provide capacities above 650 mAh·g^{-1} and could be recycled from other products, contributing to a circular economy.
2. Cathodes. Ni-rich and Li-rich oxides are gaining attention, showing that Co-free Li-rich materials bring improved kinetics and cycling performances. However, these still need further research to improve cycling performance and rate capability.
3. Electrolytes. The impact of electrolyte composition on the battery's energy density, cycle-life, power, cost and safety has shifted the industry's attention to improving all its components—salts, solvents and additives—looking at a considerable number of diverse compositions. Solid-state electrolytes are currently thought to be a promising alternative as they increase safety, chemical stability and energy density with the possibility to use Li metal, while reducing costs.
4. Further considerations for safety enhancement. From the authors' knowledge, there is no literature available that compares the exact characteristics of solid-state battery to liquid-state battery under abuse conditions, henceforth this area can be researched further. Nonetheless, based on this research it can be said that the solid-state solutions can be combined with a good packing design, positioning of cells and the battery within the vehicle, inclusion of contingency measures and signalling strategies to ensure optimal safety standards.

Research efforts are ongoing in parallel, for the various battery materials and components. An added challenge is that such components will need to be combined in a stable and well performing battery cell; in many cases, individual materials could perform well in low TRLs, but poorly when combined with other materials in cell environments. Several initiatives that look into finding the best combination of such materials in a stable cell environment are ongoing, such as the COBRA H2020 project.

All of the above-mentioned expected future material developments for battery components will finally not only meet the changing end-user demands but also contribute to Europe's holistic sustainability objectives while ensuring affordability of EVs, making them accessible to a wider audience and therefore, exponentially increasing the impact of these vehicles.

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References

1. Tsiropoulos, I.; Tarvydas, D.; Lebedeva, N. Li-ion batteries for mobility and stationary storage applications. *Publ. Off. Eur. Union Luxemb.* **2018**, 1–72. [CrossRef]
2. Helmbrecht, M.; Olaverri-Monreal, C.; Bengler, K.; Vilimek, R.; Keinath, A. How electric vehicles affect driving behavioral patterns. *IEEE Intell. Transp. Syst. Mag.* **2014**, *6*, 22–32. [CrossRef]
3. Sun, X.H.; Yamamoto, T.; Morikawa, T. Fast-charging station choice behavior among battery electric vehicle users. *Transp. Res. Part D Transp. Environ.* **2016**, *46*, 26–39. [CrossRef]
4. Christensen, L.; Nørrelund, A.V.; Olsen, A. Travel behaviour of potential Electric Vehicle drivers. The need for changing A contribution to the Edison project. In Proceedings of the European Transport Conference 2010, Glasgow, UK, 11–13 October 2010.
5. Battery Pack Prices Cited below $100/kWh for the First Time in 2020, While Market Average Sits at $137/kWh. Available online: https://about.bnef.com/blog/battery-pack-prices-cited-below-100-kwh-for-the-first-time-in-2020-while-market-average-sits-at-137-kwh/ (accessed on 3 March 2021).
6. Interactive Map: Affordability of Electric Cars, Correlation between Market Uptake and GDP in the EU. Available online: https://www.acea.be/news/article/interactive-map-affordability-of-electric-cars-correlation-between-market-u (accessed on 3 March 2021).
7. *Electrification of the Transport System—Expert Group Report*; European Commision: Brussels, Belgium, 2017.
8. Zhang, Z.; Wang, D.; Zhang, C.; Chen, J. Electric vehicle range extension strategies based on improved AC system in cold climate—A review. *Int. J. Refrig.* **2018**, *88*, 141–150. [CrossRef]
9. Yuksel, T.; Michalek, J.J. Effects of Regional Temperature on Electric Vehicle Efficiency, Range, and Emissions in the United States. *Environ. Sci. Technol.* **2015**, *49*, 5. [CrossRef]
10. Autonomous Cars' Big Problem: The Energy Consumption of Edge Processing Reduces a Car's Mileage with up to 30%. Available online: https://medium.com/@teraki/energy-consumption-required-by-edge-computing-reduces-a-autonomous-cars-mileage-with-up-to-30-46b6764ea1b7 (accessed on 4 March 2021).
11. Baxter, J.A.; Merced, D.A.; Costinett, D.J.; Tolbert, L.M.; Ozpineci, B. Review of Electrical Architectures and Power Requirements for Automated Vehicles. In Proceedings of the 2018 IEEE Transportation and Electrification Conference and Expo (ITEC 2018), Long Beach, CA, USA, 13–15 June 2018; pp. 102–107.
12. Islam, E.S.; Moawad, A.; Kim, N.; Rousseau, A. Vehicle Electrification Impacts on Energy Consumption for Different Connected-Autonomous Vehicle Scenario Runs. *World Electr. Veh. J.* **2019**, *11*, 9. [CrossRef]
13. Hardy, K.; Krasenbrink, A. *EV-Smart Grid Interoperability Centers in Europe and the U.S.*; Argonne National Laboratory: Lemont, IL, USA, 2011.
14. *Supporting Innovative Solutions for Smart Grids and Storage, Innovation and Networks Executive Agency INEA*; European Commission: Brussels, Belgium, 2018.
15. Uddin, K.; Dubarry, M.; Glick, M.B. The viability of vehicle-to-grid operations from a battery technology and policy perspective. *Energy Policy* **2018**, *113*, 342–347. [CrossRef]
16. Peterson, S.B.; Apt, J.; Whitacre, J.F. Lithium-ion battery cell degradation resulting from realistic vehicle and vehicle-to-grid utilization. *J. Power Sources* **2010**, *195*, 2385–2392. [CrossRef]
17. Thingvad, A.; Marinelli, M. Influence of V2G Frequency Services and Driving on Electric Vehicles Battery Degradation in the Nordic Countries. In Proceedings of the EVS 31 & EVTeC 2018, Kobe, Japan, 1–3 October 2018; p. 20189132.
18. van Heuveln, K.; Ghotge, R.; Annema, J.A.; van Bergen, E.; van Wee, B.; Pesch, U. Factors influencing consumer acceptance of vehicle-to-grid by electric vehicle drivers in the Netherlands. *Travel Behav. Soc.* **2021**, *24*, 34–45. [CrossRef]
19. Geske, J.; Schumann, D. Willing to participate in vehicle-to-grid (V2G)? Why not! *Energy Policy* **2018**, *120*, 392–401. [CrossRef]
20. *COM(2020) 798/3 Proposal for a New UN GTR on In-Vehicle Battery Durability for Electrified Vehicles*; ECE-TRANS-WP.29-GRPE-2021-18e; UNECE: Geneva, Switzerland, 2021.
21. *Proposal for a Regulation of the European Parliament and of the Council Concerning Batteries and Waste Batteries, Repealing Directive 2006/66/EC and Amending Regulation (EU) No 2019/1020*; European Commission: Brussels, Belgium, 2020.
22. Betz, J.; Bieker, G.; Meister, P.; Placke, T.; Winter, M.; Schmuch, R. Theoretical versus Practical Energy: A Plea for More Transparency in the Energy Calculation of Different Rechargeable Battery Systems. *Adv. Energy Mater.* **2019**, *9*. [CrossRef]
23. Li, J.; Murphy, E.; Winnick, J.; Kohl, P.A. Studies on the cycle life of commercial lithium ion batteries during rapid charge-discharge cycling. *J. Power Sources* **2001**, *102*, 294–301. [CrossRef]
24. Li, M.; Lu, J.; Chen, Z.; Amine, K. 30 Years of Lithium-Ion Batteries. *Adv. Mater.* **2018**, *30*, 1800561. [CrossRef]

25. Zhang, H.; Li, C.; Eshetu, G.G.; Laruelle, S.; Grugeon, S.; Zaghib, K.; Mauger, A.; Guyomard, D.; Rojo, T.; Gisbert-trejo, N.; et al. From solid solution electrodes and the rocking-chair concept to today's batteries. *Angew. Chem. Int. Ed.* **2020**, *59*, 534–538. [CrossRef]

26. Dahn, J.R.; Zheng, T.; Liu, Y.; Xue, J.S. Mechanisms for lithium insertion in carbonaceous materials. *Science* **1995**, *270*, 590–593. [CrossRef]

27. Lain, M.J.; Brandon, J.; Kendrick, E. Design strategies for high power vs. High energy lithium ion cells. *Batteries* **2019**, *5*, 64. [CrossRef]

28. Raccichini, R.; Amores, M.; Hinds, G. Critical Review of the Use of Reference Electrodes in Li-Ion Batteries: A Diagnostic Perspective. *Batteries* **2019**, *5*, 12. [CrossRef]

29. Linden, D.; Reddy, T.B. *Handbook of Batteries*, 3rd ed.; McGraw Hill Professional: New York, NY, USA, 2002; ISBN 9780470402528.

30. International Energy Agency. *Global EV Outlook 2020*; OECD: Paris, France, 2020. [CrossRef]

31. McKerracher, C.; Izadi-Najafabadi, A.; Soulopoulos, N.; Doherty, D.; Frith, J.T.; Albanese, N.; Grant, A.; Berryman, I. *Electric Vehicle Outlook 2019*; IEA: Paris, France, 2019. Available online: https://www.iea.org/reports/global-ev-outlook-2019 (accessed on 3 March 2021).

32. Logan, E.R.; Dahn, J.R. Electrolyte Design for Fast-Charging Li-Ion Batteries. *Trends Chem.* **2020**, *2*, 354–366. [CrossRef]

33. Xu, C.; Märker, K.; Lee, J.; Mahadevegowda, A.; Reeves, P.J.; Day, S.J.; Groh, M.F.; Emge, S.P.; Ducati, C.; Layla Mehdi, B.; et al. Bulk fatigue induced by surface reconstruction in layered Ni-rich cathodes for Li-ion batteries. *Nat. Mater.* **2021**, *20*, 84–92. [CrossRef]

34. Goriparti, S.; Miele, E.; De Angelis, F.; Di Fabrizio, E.; Zaccaria, R.P.; Capiglia, C. Review on recent progress of nanostructured anode materials for Li-ion batteries. *J. Power Sources* **2014**. [CrossRef]

35. Peled, E. The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems—The Solid Electrolyte Interphase Model. *J. Electrochem. Soc.* **1979**, *126*, 2047–2051. [CrossRef]

36. Peled, E.; Menkin, S. Review-SEI: Past, present and future. *J. Electrochem. Soc.* **2017**, *164*, A1703–A1719. [CrossRef]

37. Zhou, Y.; Su, M.; Yu, X.; Zhang, Y.; Wang, J.G.; Ren, X.; Cao, R.; Xu, W.; Baer, D.R.; Du, Y.; et al. Real-time mass spectrometric characterization of the solid–electrolyte interphase of a lithium-ion battery. *Nat. Nanotechnol.* **2020**, *15*, 224–230. [CrossRef] [PubMed]

38. Wu, J.J.; Bennett, W.R. Fundamental Investigation of Si Anode in Li-Ion Cells. In Proceedings of the 2012 IEEE Energytech, Cleveland, OH, USA, 29–31 May 2012; pp. 1–5.

39. Moretti, A.; Sharova, V.; Carvalho, D.V.; Boulineau, A.; Porcher, W.; de Meatza, I.; Passerini, S. A Comparison of Formation Methods for Graphite//LiFePO4 Cells. *Batter. Supercaps* **2019**, *2*, 240–247. [CrossRef]

40. An, S.J.; Li, J.; Du, Z.; Daniel, C.; Wood, D.L. Fast formation cycling for lithium ion batteries. *J. Power Sources* **2017**, *342*, 846–852. [CrossRef]

41. Armand, M.; Axmann, P.; Bresser, D.; Copley, M.; Edström, K.; Ekberg, C.; Guyomard, D.; Lestriez, B.; Novák, P.; Petranikova, M.; et al. Lithium-ion batteries—Current state of the art and anticipated developments. *J. Power Sources* **2020**, *479*. [CrossRef]

42. Nitta, N.; Wu, F.; Lee, J.T.; Yushin, G. Li-ion battery materials: Present and future. *Mater. Today* **2015**, *18*, 252–264. [CrossRef]

43. Winter, M.; Barnett, B.; Xu, K. Before Li Ion Batteries. *Chem. Rev.* **2018**, *118*, 11433–11456. [CrossRef]

44. Levi, M.D.; Aurbach, D. The mechanism of lithium intercalation in graphite film electrodes in aprotic media. Part 1. High resolution slow scan rate cyclic voltammetric studies and modeling. *J. Electroanal. Chem.* **1997**, *421*, 79–88. [CrossRef]

45. Sengupta, R.; Bhattacharya, M.; Bandyopadhyay, S.; Bhowmick, A.K. A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites. *Prog. Polym. Sci.* **2011**, *36*, 638–670. [CrossRef]

46. Fuller, T.F.; Doyle, M.; Newman, J. Simulation and Optimization of the Dual Lithium Ion Insertion Cell. *J. Electrochem. Soc.* **1994**, *141*, 1–10. [CrossRef]

47. Wetjen, M.; Pritzl, D.; Jung, R.; Solchenbach, S.; Ghadimi, R.; Gasteiger, H.A. Differentiating the Degradation Phenomena in Silicon-Graphite Electrodes for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2017**, *164*, A2840–A2852. [CrossRef]

48. *Study on the Review of the List of Critical Raw Materials*; European Commission: Brussels, Belgium, 2017; ISBN 978-92-79-47937-3. [CrossRef]

49. Liu, Q.; Du, C.; Shen, B.; Zuo, P.; Cheng, X.; Ma, Y.; Yin, G.; Gao, Y. Understanding of Undesirable Anode Lithium Plating Issues in Lithium-Ion Batteries. *RSC Adv.* **2016**, *6*, 88683–88700. [CrossRef]

50. Tanim, T.R.; Dufek, E.J.; Dickerson, C.C.; Wood, S.M. Electrochemical quantification of lithium plating: Challenges and considerations. *J. Electrochem. Soc.* **2019**, *166*, A2689–A2696. [CrossRef]

51. Cannarella, J.; Arnold, C.B. The Effects of Defects on Localized Plating in Lithium-Ion Batteries. *J. Electrochem. Soc.* **2015**, *162*, A1365–A1373. [CrossRef]

52. Harper, G.; Sommerville, R.; Kendrick, E.; Driscoll, L.; Slater, P.; Stolkin, R.; Walton, A.; Christensen, P.; Heidrich, O.; Lambert, S.; et al. Recycling lithium-ion batteries from electric vehicles. *Nature* **2019**, *575*, 75–86. [CrossRef]

53. Campbell, I.D.; Marzook, M.; Marinescu, M.; Offer, G.J. How observable is lithium plating? Differential voltage analysis to identify and quantify lithium plating following fast charging of cold lithium-ion batteries. *J. Electrochem. Soc.* **2019**, *166*, A725–A739. [CrossRef]

54. Landa-Medrano, I.; Eguia-Barrio, A.; Sananes-Israel, S.; Lijó-Pando, S.; Boyano, I.; Alcaide, F.; Urdampilleta, I.; De Meatza, I. In Situ Analysis of NMC|Graphite Li-Ion Batteries by Means of Complementary Electrochemical Methods. *J. Electrochem. Soc.* **2020**, *167*, 090528. [CrossRef]

55. Attia, P.M.; Das, S.; Harris, S.J.; Bazant, M.Z.; Chueh, W.C. Electrochemical kinetics of sei growth on Carbon Black: Part I. experiments. *J. Electrochem. Soc.* **2019**, *166*, E97–E106. [CrossRef]

56. Wood, D.L.; Li, J.; An, S.J. Formation Challenges of Lithium-Ion Battery Manufacturing. *Joule* **2019**, *3*, 2884–2888. [CrossRef]

57. Mao, C.; An, S.J.; Meyer, H.M.; Li, J.; Wood, M.; Ruther, R.E.; Wood, D.L. Balancing formation time and electrochemical performance of high energy lithium-ion batteries. *J. Power Sources* **2018**, *402*, 107–115. [CrossRef]

58. Ma, R.; Shao, L.; Wu, K.; Shui, M.; Wang, D.; Pan, J.; Long, N.; Ren, Y.; Shu, J. Comparison of LiVPO4F to Li4Ti5O12 as anode materials for lithium-ion batteries. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8615–8627. [CrossRef]

59. Chen, Z.; Belharouak, I.; Sun, Y.-K.; Amine, K. Titanium-Based Anode Materials for Safe Lithium-Ion Batteries. *Adv. Funct. Mater.* **2013**, *23*, 959–969. [CrossRef]

60. Wang, J.; Zhao, H.; Wen, Y.; Xie, J.; Xia, Q.; Zhang, T.; Zeng, Z.; Du, X. High performance Li4Ti5O12 material as anode for lithium-ion batteries. *Electrochim. Acta* **2013**, *113*, 679–685. [CrossRef]

61. Vujković, M.; Stojković, I.; Mitrić, M.; Mentus, S.; Cvjetićanin, N. Hydrothermal synthesis of Li4Ti5O12/C nanostructured composites: Morphology and electrochemical performance. *Mater. Res. Bull.* **2013**, *48*, 218–223. [CrossRef]

62. Fu, R.; Zhou, X.; Fan, H.; Blaisdell, D.; Jagadale, A.; Zhang, X.; Xiong, R. Comparison of lithium-ion anode materials using an experimentally verified physics-based electrochemical model. *Energies* **2017**, *10*, 2174. [CrossRef]

63. Zheng, J.; Xiao, J.; Nie, Z.; Zhang, J.-G. Lattice Mn^{3+} Behaviors in Li$_4$Ti$_5$O$_{12}$/LiNi0.5Mn$_{1.5}$O$_4$ Full Cells. *J. Electrochem. Soc.* **2013**, *160*, A1264–A1268. [CrossRef]

64. Zhang, Q.; Li, X. High Rate Capability of Nd-Doped Li$_4$Ti$_5$O$_{12}$ as an Effective Anode Material for Lithium-Ion Battery. *Int. J. Electrochem. Sci.* **2013**, *8*, 7816–7824.

65. Liu, H.; Zhu, Z.; Yan, Q.; Yu, S.; He, X.; Chen, Y.; Zhang, R.; Ma, L.; Liu, T.; Li, M.; et al. A disordered rock salt anode for fast-charging lithium-ion batteries. *Nature* **2020**, *585*, 63–67. [CrossRef] [PubMed]

66. Schnabel, M.; Harvey, S.P.; Arca, E.; Stetson, C.; Teeter, G.; Ban, C.; Stradins, P. Surface SiO$_2$ thickness controls uniform-to-localized transition in lithiation of silicon anodes for lithiumion batteries. *ACS Appl. Mater. Interfaces* **2020**. [CrossRef]

67. Swamy, T.; Chiang, Y.-M. Electrochemical Charge Transfer Reaction Kinetics at the Silicon-Liquid Electrolyte Interface. *J. Electrochem. Soc.* **2015**, *162*, A7129–A7134. [CrossRef]

68. Li, P.; Zhao, G.; Zheng, X.; Xu, X.; Yao, C.; Sun, W.; Dou, S.X. Recent progress on silicon-based anode materials for practical lithium-ion battery applications. *Energy Storage Mater.* **2018**, *15*, 422–446. [CrossRef]

69. Wang, L.; Liu, T.; Peng, X.; Zeng, W.; Jin, Z.; Tian, W.; Gao, B.; Zhou, Y.; Chu, P.K.; Huo, K. Highly Stretchable Conductive Glue for High-Performance Silicon Anodes in Advanced Lithium-Ion Batteries. *Adv. Funct. Mater.* **2018**, *28*, 1704858. [CrossRef]

70. Casimir, A.; Zhang, H.; Ogoke, O.; Amine, J.C.; Lu, J.; Wu, G. Silicon-based anodes for lithium-ion batteries: Effectiveness of materials synthesis and electrode preparation. *Nano Energy* **2016**, *27*, 359–376. [CrossRef]

71. Jung, R.; Metzger, M.; Haering, D.; Solchenbach, S.; Marino, C.; Tsiouvaras, N.; Stinner, C.; Gasteiger, H.A. Consumption of Fluoroethylene Carbonate (FEC) on Si-C Composite Electrodes for Li-Ion Batteries. *J. Electrochem. Soc.* **2016**, *163*, A1705–A1716. [CrossRef]

72. Alaboina, P.K.; Cho, J.S.; Uddin, M.J.; Cho, S.-J. Mechanically prelithiated silicon nano alloy as highly engineered anode material. *Electrochim. Acta* **2017**, *258*, 623–630. [CrossRef]

73. Li, X.; Colclasure, A.M.; Finegan, D.P.; Ren, D.; Shi, Y.; Feng, X.; Cao, L.; Yang, Y.; Smith, K. Degradation mechanisms of high capacity 18650 cells containing Si-graphite anode and nickel-rich NMC cathode. *Electrochim. Acta* **2019**, *297*, 1109–1120. [CrossRef]

74. Pan, K.; Zou, F.; Canova, M.; Zhu, Y.; Kim, J.H. Systematic electrochemical characterizations of Si and SiO anodes for high-capacity Li-Ion batteries. *J. Power Sources* **2019**, *413*, 20–28. [CrossRef]

75. Chae, S.; Choi, S.-H.; Namhyung, K.; Sung, J.; Cho, J. Integration of Graphite and Silicon Anodes for the Commercialization of High-Energy Lithium-Ion Batteries. *Angew. Chem.* **2019**, *59*, 110–135. [CrossRef]

76. Feng, K.; Li, M.; Liu, W.; Kashkooli, A.G.; Xiao, X.; Cai, M.; Chen, Z. Silicon-Based Anodes for Lithium-Ion Batteries: From Fundamentals to Practical Applications. *Small* **2018**, *14*. [CrossRef]

77. Andersson, R.; Hernández, G.; Edström, K.; Mindemark, J. Micro versus Nano: Impact of Particle Size on the Flow Characteristics of Silicon Anode Slurries. *Energy Technol.* **2020**, *8*, 2000056. [CrossRef]

78. Jaumann, T.; Balach, J.; Langklotz, U.; Sauchuk, V.; Fritsch, M.; Michaelis, A.; Teltevskij, V.; Mikhailova, D.; Oswald, S.; Klose, M.; et al. Lifetime vs. rate capability: Understanding the role of FEC and VC in high-energy Li-ion batteries with nano-silicon anodes. *Energy Storage Mater.* **2017**, *6*, 26–35. [CrossRef]

79. Mazouzi, D.; Karkar, Z.; Hernandez, C.R.; Manero, P.J.; Guyomard, D.; Roué, L.; Lestriez, B. Critical roles of binders and formulation at multiscales of silicon-based composite electrodes. *J. Power Sources* **2015**, *280*, 533–549. [CrossRef]

80. Chae, S.; Ko, M.; Kim, K.; Ahn, K.; Cho, J. Confronting Issues of the Practical Implementation of Si Anode in High-Energy Lithium-Ion Batteries. *Joule* **2017**, *1*, 47–60. [CrossRef]

81. Ryu, J.; Bok, T.; Kim, S.; Park, S. Fundamental Understanding of Nanostructured Si Electrodes: Preparation and Characterization. *ChemNanoMat* **2018**, *4*, 319–337. [CrossRef]

82. Zhao, S.; Xu, Y.; Xian, X.; Liu, N.; Li, W. Fabrication of Porous Si@C Composites with Core-Shell Structure and Their Electrochemical Performance for Li-ion Batteries. *Batteries* **2019**, *5*, 27. [CrossRef]

83. Louli, A.J.; Li, J.; Trussler, S.; Fell, C.R.; Dahn, J.R. Volume, Pressure and Thickness Evolution of Li-Ion Pouch Cells with Silicon-Composite Negative Electrodes. *J. Electrochem. Soc.* **2017**, *164*, A2689–A2696. [CrossRef]

84. Wu, H.; Zheng, L.; Zhan, J.; Du, N.; Liu, W.; Ma, J.; Su, L.; Wang, L. Recycling silicon-based industrial waste as sustainable sources of Si/SiO$_2$ composites for high-performance Li-ion battery anodes. *J. Power Sources* **2019**. [CrossRef]

85. Ashuri, M.; He, Q.; Liu, Y.; Emani, S.; Shaw, L.L. Synthesis and performance of nanostructured silicon/graphite composites with a thin carbon shell and engineered voids. *Electrochim. Acta* **2017**, *258*, 274–283. [CrossRef]

86. Suh, S.S.; Yoon, W.Y.; Kim, D.H.; Kwon, S.U.; Kim, J.H.; Kim, Y.U.; Jeong, C.U.; Chan, Y.Y.; Kang, S.H.; Lee, J.K. Electrochemical behavior of SiOx anodes with variation of oxygen ratio for Li-ion batteries. *Electrochim. Acta* **2014**, *148*, 111–117. [CrossRef]

87. Wang, J.; Bao, W.; Ma, L.; Tan, G.; Su, Y.; Chen, S.; Wu, F.; Lu, J.; Amine, K. Scalable Preparation of Ternary Hierarchical Silicon Oxide-Nickel-Graphite Composites for Lithium-Ion Batteries. *ChemSusChem* **2015**, *8*, 4073–4080. [CrossRef]

88. Tan, T.; Lee, P.-K.; Yu, D.Y.W. Probing the Reversibility of Silicon Monoxide Electrodes for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2018**, *166*, A5210–A5214. [CrossRef]

89. Nguyen, T.T.D.; Abada, S.; Lecocq, A.; Bernard, J.; Petit, M.; Marlair, G.; Grugeon, S.; Laruelle, S. Understanding the thermal runaway of ni-rich lithium-ion batteries. *World Electr. Veh. J.* **2019**, *10*, 79. [CrossRef]

90. Horwitz, N.E.; Shevchenko, E.V.; Park, J.; Lee, E.; Xie, J.; Chen, B.; Zhong, Y.; Filatov, A.S.; Anderson, J.S. Synthesis, modular composition, and electrochemical properties of lamellar iron sulfides. *J. Mater. Chem. A* **2020**, *8*, 15834–15844. [CrossRef]

91. Sun, D.; Wang, L.; Li, Y.; Yang, Y.; Zhou, X.; Ma, G.; Lei, Z. Confined Metal Sulfides Nanoparticles into Porous Carbon Nanosheets with Surface-Controlled Reactions for Fast and Stable Lithium-Ion Batteries. *ChemElectroChem* **2019**, *6*, 4464–4470. [CrossRef]

92. Wang, J.; He, H.; Wu, Z.; Liang, J.; Han, L.; Xin, H.L.; Guo, X.; Zhu, Y.; Wang, D. Controllable construction of flower-like FeS/Fe$_2$O3 composite for lithium storage. *J. Power Sources* **2018**, *392*, 193–199. [CrossRef]

93. Lv, J.; Du, J.; Jia, H.; Ma, J.; Zheng, S.; Nie, Y.; Song, K.; Bai, L. Hierarchical carbon-coated Fe1-xS/mesocarbon microbeads composite as high-performance lithium-ion batteries anode. *Ceram. Int.* **2020**, *46*, 9485–9491. [CrossRef]

94. Fei, L.; Williams, B.P.; Yoo, S.H.; Carlin, J.M.; Joo, Y.L. A general approach to fabricate free-standing metal sulfide@carbon nanofiber networks as lithium ion battery anodes. *Chem. Commun.* **2016**, *52*, 1501–1504. [CrossRef]

95. Li, L.; Gao, C.; Kovalchuk, A.; Peng, Z.; Ruan, G.; Yang, Y.; Fei, H.; Zhong, Q.; Li, Y.; Tour, J.M. Sandwich structured graphene-wrapped FeS-graphene nanoribbons with improved cycling stability for lithium ion batteries. *Nano Res.* **2016**, *9*, 2904–2911. [CrossRef]

96. Jin, H.; Xin, S.; Chuang, C.; Li, W.; Wang, H.; Zhu, J.; Xie, H.; Zhang, T.; Wan, Y.; Qi, Z.; et al. Black phosphorus composites with engineered interfaces for high-rate high-capacity lithium storage. *Science* **2020**, *370*, 192–197. [CrossRef]

97. Tokur, M.; Aydin, A.; Cetinkaya, T.; Akbulut, H. Shoring Up the Lithium Ion Batteries with Multi-Component Silicon Yolk-Shell Anodes for Grid-Scale Storage Systems: Experimental and Computational Mechanical Studies. *J. Electrochem. Soc.* **2017**, *164*, A2238–A2250. [CrossRef]

98. Asenbauer, J.; Hoefling, A.; Indris, S.; Tübke, J.; Passerini, S.; Bresser, D. Mechanistic Insights into the Lithiation and Delithiation of Iron-Doped Zinc Oxide: The Nucleation Site Model. *ACS Appl. Mater. Interfaces* **2020**, *12*, 8206–8218. [CrossRef]

99. Hu, M.; Pang, X.; Zhou, Z. Review Recent progress in high-voltage lithium ion batteries. *J. Power Sources* **2013**, *237*, 229–242. [CrossRef]

100. Xu, C.; Reeves, P.J.; Jacquet, Q.; Grey, C.P. Phase Behavior during Electrochemical Cycling of Ni-Rich Cathode Materials for Li-Ion Batteries. *Adv. Energy Mater.* **2020**, *11*, 2003404. [CrossRef]

101. Feng, Y.; Xu, H.; Wang, B.; Tuo, K.; Wang, P.; Wang, S.; Liang, W.; Lu, H.; Li, S. Structural evolution of nickel-rich layered cathode material LiNi$_{0.8}$Co0.1Mn$_{0.1}$O$_2$ at different current rates. *Ionics (Kiel)* **2021**, *27*, 517–526. [CrossRef]

102. Wu, Y.; Li, M.; Wahyudi, W.; Sheng, G.; Miao, X.; Anthopoulos, T.D.; Huang, K.W.; Li, Y.; Lai, Z. Performance and Stability Improvement of Layered NCM Lithium-Ion Batteries at High Voltage by a Microporous Al$_2$O$_3$ Sol-Gel Coating. *ACS Omega* **2019**, *4*, 13972–13980. [CrossRef] [PubMed]

103. Dong, B.; Biendicho, J.J.; Hull, S.; Smith, R.I.; West, A.R. In-Situ Neutron Studies of Electrodes for Li-Ion Batteries Using a Deuterated Electrolyte: LiCoO$_2$ as a Case Study. *J. Electrochem. Soc.* **2018**, *165*, A793–A801. [CrossRef]

104. Whittingham, M.S. Lithium Batteries and Cathode Materials. *Chem. Rev.* **2004**, *104*, 4271–4302. [CrossRef]

105. Shaari, H.R.; Sethuprakhash, V. Review of electrochemical performance of LINIO2 and their derivatives as cathode material for lithium-ion batteries. *J. Teknol. Sci. Eng.* **2014**, *70*, 7–13. [CrossRef]

106. Julien, C.M.; Mauger, A. *Lithium-Ion Batteries*; Springer International Publishing: Berlin/Heidelberg, Germany, 2020. [CrossRef]

107. Wang, X.; Ding, Y.L.; Deng, Y.P.; Chen, Z. Ni-Rich/Co-Poor Layered Cathode for Automotive Li-Ion Batteries: Promises and Challenges. *Adv. Energy Mater.* **2020**, *10*, 1–28. [CrossRef]

108. Zou, Y.; Yang, X.; Lv, C.; Liu, T.; Xia, Y.; Shang, L.; Waterhouse, G.I.N.; Yang, D.; Zhang, T. Multishelled Ni-Rich Li(NixCoyMnz)O2 Hollow Fibers with Low Cation Mixing as High-Performance Cathode Materials for Li-Ion Batteries. *Adv. Sci.* **2017**, *4*, 1–8. [CrossRef]

109. Park, K.J.; Hwang, J.Y.; Ryu, H.H.; Maglia, F.; Kim, S.J.; Lamp, P.; Yoon, C.S.; Sun, Y.K. Degradation Mechanism of Ni-Enriched NCA Cathode for Lithium Batteries: Are Microcracks Really Critical? *ACS Energy Lett.* **2019**, *4*, 1394–1400. [CrossRef]

110. Takanashi, S.; Abe, Y. Improvement of the electrochemical performance of an NCA positive-electrode material of lithium ion battery by forming an Al-rich surface layer. *Ceram. Int.* **2017**, *43*, 9246–9252. [CrossRef]

111. Li, H.; Zhou, P.; Liu, F.; Li, H.; Cheng, F.; Chen, J. Stabilizing nickel-rich layered oxide cathodes by magnesium doping for rechargeable lithium-ion batteries. *Chem. Sci.* **2019**, *10*, 1374–1379. [CrossRef]

112. Sun, Y.K.; Lee, B.R.; Noh, H.J.; Wu, H.; Myung, S.T.; Amine, K. A novel concentration-gradient Li[Ni0.83Co0.07Mn$_{0.10}$]O$_2$ cathode material for high-energy lithium-ion batteries. *J. Mater. Chem.* **2011**, *21*, 10108–10112. [CrossRef]

113. Boulineau, A.; Croguennec, L.; Delmas, C.; Weill, F. Structure of Li$_2$MnO$_3$ with different degrees of defects. *Solid State Ion.* **2010**, *180*, 1652–1659. [CrossRef]

114. Thackeray, M.M.; Kang, S.H.; Johnson, C.S.; Vaughey, J.T.; Benedek, R.; Hackney, S.A. Li$_2$MnO$_3$-stabilized LiMO$_2$ (M = Mn, Ni, Co) electrodes for lithium-ion batteries. *J. Mater. Chem.* **2007**, *17*, 3112–3125. [CrossRef]

115. Thackeray, M.M.; Kang, S.H.; Johnson, C.S.; Vaughey, J.T.; Hackney, S.A. Comments on the structural complexity of lithium-rich Li1+xM1−xO2 electrodes (M = Mn, Ni, Co) for lithium batteries. *Electrochem. Commun.* **2006**, *8*, 1531–1538. [CrossRef]

116. Yang, J.; Hou, M.; Haller, S.; Wang, Y.; Wang, C.; Xia, Y. Improving the Cycling Performance of the Layered Ni-Rich Oxide Cathode by Introducing Low-Content Li$_2$MnO$_3$. *Electrochim. Acta* **2016**, *189*, 101–110. [CrossRef]

117. Johnson, C.S.; Kim, J.S.; Lefief, C.; Li, N.; Vaughey, J.T.; Thackeray, M.M. The significance of the Li$_2$MnO$_3$ component in "composite" xLi 2MnO$_3$·(1-x)LiMn 0.5Ni 0.5O$_2$ electrodes. *Electrochem. Commun.* **2004**, *6*, 1085–1091. [CrossRef]

118. Yan, J.; Liu, X.; Li, B. Recent progress in Li-rich layered oxides as cathode materials for Li-ion batteries. *RSC Adv.* **2014**, *4*, 63268–63284. [CrossRef]

119. Lu, Z.; Beaulieu, L.Y.; Donaberger, R.A.; Thomas, C.L.; Dahn, J.R. Synthesis, Structure, and Electrochemical Behavior of Li[Ni[sub x]Li[sub 1/3−2x/3]Mn[sub 2/3−x/3]]O[sub 2]. *J. Electrochem. Soc.* **2002**, *149*, A778. [CrossRef]

120. Yu, X.; Lyu, Y.; Gu, L.; Wu, H.; Bak, S.M.; Zhou, Y.; Amine, K.; Ehrlich, S.N.; Li, H.; Nam, K.W.; et al. Understanding the rate capability of high-energy-density Li-rich layered Li$_{1.2}$Ni$_{0.15}$Co$_{0.1}$Mn$_{0.55}$O$_2$ cathode materials. *Adv. Energy Mater.* **2014**, *4*, 1–11. [CrossRef]

121. Johnson, C.S.; Korte, S.D.; Vaughey, J.T.; Thackeray, M.M.; Bofinger, T.E.; Shao-Horn, Y.; Hackney, S.A. Structural and electrochemical analysis of layered compounds from Li$_2$MnO$_3$. *J. Power Sources* **1999**, *81–82*, 491–495. [CrossRef]

122. Armstrong, A.R.; Holzapfel, M.; Novák, P.; Johnson, C.S.; Kang, S.H.; Thackeray, M.M.; Bruce, P.G. Demonstrating oxygen loss and associated structural reorganization in the lithium battery cathode Li[Ni0.2Li0.2Mn0.6]O2. *J. Am. Chem. Soc.* **2006**, *128*, 8694–8698. [CrossRef] [PubMed]

123. Li, J.; Xing, L.; Wang, Z.; Tu, W.; Yang, X.; Lin, Y.; Liao, Y.; Xu, M.; Li, W. Insight into the capacity fading of layered lithium-rich oxides and its suppression: Via a film-forming electrolyte additive. *RSC Adv.* **2018**, *8*, 25794–25801. [CrossRef]

124. Kim, D.; Croy, J.R.; Thackeray, M.M. Comments on stabilizing layered manganese oxide electrodes for Li batteries. *Electrochem. Commun.* **2013**, *36*, 103–106. [CrossRef]

125. Armstrong, A.R.; Robertson, A.D.; Bruce, P.G. Overcharging manganese oxides: Extracting lithium beyond Mn^{4+}. *J. Power Sources* **2005**, *146*, 275–280. [CrossRef]

126. Assat, G.; Tarascon, J.M. Fundamental understanding and practical challenges of anionic redox activity in Li-ion batteries. *Nat. Energy* **2018**, *3*, 373–386. [CrossRef]

127. Zhang, P.; Zhai, X.; Huang, H.; Zhou, J.; Li, X.; He, Y.; Guo, Z. Suppression of structural phase transformation of Li-rich Mn-based layered cathode materials with Na ion substitution strategy. *Electrochim. Acta* **2020**, *349*, 136402. [CrossRef]

128. Guo, H.; Xia, Y.; Zhao, H.; Yin, C.; Jia, K.; Zhao, F.; Liu, Z. Stabilization effects of Al doping for enhanced cycling performances of Li-rich layered oxides. *Ceram. Int.* **2017**, *43*, 13845–13852. [CrossRef]

129. Qiao, Q.Q.; Qin, L.; Li, G.R.; Wang, Y.L.; Gao, X.P. Sn-stabilized Li-rich layered Li(Li0.17Ni0.25Mn$_{0.58}$)O$_2$ oxide as a cathode for advanced lithium-ion batteries. *J. Mater. Chem. A* **2015**, *3*, 17627–17634. [CrossRef]

130. Park, K.; Kim, J.; Park, J.H.; Hwang, Y.; Han, D. Synchronous phase transition and carbon coating on the surface of Li-rich layered oxide cathode materials for rechargeable Li-ion batteries. *J. Power Sources* **2018**, 105–110. [CrossRef]

131. Lei, Y.; Ni, J.; Hu, Z.; Wang, Z.; Gui, F.; Li, B.; Ming, P.; Zhang, C.; Elias, Y.; Aurbach, D.; et al. Surface Modification of Li-Rich Mn-Based Layered Oxide Cathodes: Challenges, Materials, Methods, and Characterization. *Adv. Energy Mater.* **2020**, *10*, 1–27. [CrossRef]

132. Kang, S.H.; Thackeray, M.M. Enhancing the rate capability of high capacity xLi$_2$MnO$_3$ (1-x)LiMO$_2$ (M = Mn, Ni, Co) electrodes by Li-Ni-PO$_4$ treatment. *Electrochem. Commun.* **2009**, *11*, 748–751. [CrossRef]

133. Ue, M.; Sakaushi, K.; Uosaki, K. Basic knowledge in battery research bridging the gap between academia and industry. *Mater. Horiz.* **2020**. [CrossRef]

134. An, S.J.; Li, J.; Mohanty, D.; Daniel, C.; Polzin, B.J.; Croy, J.R.; Trask, S.E.; Wood, D.L. Correlation of Electrolyte Volume and Electrochemical Performance in Lithium-Ion Pouch Cells with Graphite Anodes and NMC532 Cathodes. *J. Electrochem. Soc.* **2017**, *164*, A1195–A1202. [CrossRef]

135. An, S.J.; Li, J.; Daniel, C.; Meyer, H.M.; Trask, S.E.; Polzin, B.J.; Wood, D.L. Electrolyte Volume Effects on Electrochemical Performance and Solid Electrolyte Interphase in Si-Graphite/NMC Lithium-Ion Pouch Cells. *ACS Appl. Mater. Interfaces* **2017**, *9*, 18799–18808. [CrossRef] [PubMed]

136. Morita, M.; Shibata, T.; Yoshimoto, N.; Ishikawa, M. Anodic behavior of aluminum in organic solutions with different electrolytic salts for lithium ion batteries. *Electrochim. Acta* **2002**, *47*, 2787–2793. [CrossRef]

137. Solchenbach, S.; Metzger, M.; Egawa, M.; Beyer, H.; Gasteiger, H.A. Quantification of PF 5 and POF 3 from Side Reactions of LiPF 6 in Li-Ion Batteries. *J. Electrochem. Soc.* **2018**, *165*, A3022–A3028. [CrossRef]

138. Brückner, L.; Frank, J.; Elwert, T. Industrial recycling of lithium-ion batteries—A critical review of metallurgical process routes. *Metals* **2020**, *10*, 1107. [CrossRef]

139. Li, L.; Zhou, S.; Han, H.; Li, H.; Nie, J.; Armand, M.; Zhou, Z.; Huang, X. Transport and Electrochemical Properties and Spectral Features of Non-Aqueous Electrolytes Containing LiFSI in Linear Carbonate Solvents. *J. Electrochem. Soc.* **2011**, *158*, A74. [CrossRef]

140. Alvarado, J.; Schroeder, M.A.; Zhang, M.; Borodin, O.; Gobrogge, E.; Olguin, M.; Ding, M.S.; Gobet, M.; Greenbaum, S.; Meng, Y.S.; et al. A carbonate-free, sulfone-based electrolyte for high-voltage Li-ion batteries. *Mater. Today* **2018**, *21*, 341–353. [CrossRef]

141. Xu, K. Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.* **2014**, *114*, 11503–11618. [CrossRef]

142. Hernández, G.; Naylor, A.J.; Chien, Y.C.; Brandell, D.; Mindemark, J.; Edström, K. Elimination of fluorination: The influence of fluorine-free electrolytes on the performance of LiNi1/3Mn1/3Co1/3O2/silicon-graphite li-ion battery cells. *ACS Sustain. Chem. Eng.* **2020**, *8*, 10041–10052. [CrossRef]

143. Wang, C.; Meng, Y.S.; Xu, K. Perspective—Fluorinating Interphases. *J. Electrochem. Soc.* **2019**, *166*, A5184–A5186. [CrossRef]

144. Xia, J.; Petibon, R.; Xiong, D.; Ma, L.; Dahn, J.R. Enabling linear alkyl carbonate electrolytes for high voltage Li-ion cells. *J. Power Sources* **2016**, *328*, 124–135. [CrossRef]

145. Klett, M.; Gilbert, J.A.; Trask, S.E.; Polzin, B.J.; Jansen, A.N.; Dees, D.W.; Abraham, D.P. Electrode Behavior RE-Visited: Monitoring Potential Windows, Capacity Loss, and Impedance Changes in $Li_{1.03}(Ni0.5Co0.2Mn_{0.3})_{0.97}O_2$ /Silicon-Graphite Full Cells. *J. Electrochem. Soc.* **2016**, *163*, A875–A887. [CrossRef]

146. Dupré, N.; Moreau, P.; De Vito, E.; Quazuguel, L.; Boniface, M.; Bordes, A.; Rudisch, C.; Bayle-Guillemaud, P.; Guyomard, D. Multiprobe Study of the Solid Electrolyte Interphase on Silicon-Based Electrodes in Full-Cell Configuration. *Chem. Mater.* **2016**, *28*, 2557–2572. [CrossRef]

147. Delpuech, N.; Dupre, N.; Moreau, P.; Bridel, J.S.; Gaubicher, J.; Lestriez, B.; Guyomard, D. Mechanism of Silicon Electrode Aging upon Cycling in Full Lithium-Ion Batteries. *ChemSusChem* **2016**, *9*, 841–848. [CrossRef]

148. Lewandowski, A.; Świderska-Mocek, A. Ionic liquids as electrolytes for Li-ion batteries-An overview of electrochemical studies. *J. Power Sources* **2009**, *194*, 601–609. [CrossRef]

149. Balducci, A.; Jeong, S.S.; Kim, G.T.; Passerini, S.; Winter, M.; Schmuck, M.; Appetecchi, G.B.; Marcilla, R.; Mecerreyes, D.; Barsukov, V.; et al. Development of safe, green and high performance ionic liquids-based batteries (ILLIBATT project). *J. Power Sources* **2011**, *196*, 9719–9730. [CrossRef]

150. Brutti, S.; Simonetti, E.; De Francesco, M.; Sarra, A.; Paolone, A.; Palumbo, O.; Fantini, S.; Lin, R.; Falgayrat, A.; Choi, H.; et al. Ionic liquid electrolytes for high-voltage, lithium-ion batteries. *J. Power Sources* **2020**, *479*, 228791. [CrossRef]

151. Cao, X.; He, X.; Wang, J.; Liu, H.; Röser, S.; Rad, B.R.; Evertz, M.; Streipert, B.; Li, J.; Wagner, R.; et al. High Voltage $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ Lithium Ion Cells at Elevated Temperatures: Carbonate-versus Ionic Liquid-Based Electrolytes. *ACS Appl. Mater. Interfaces* **2016**, *8*, 25971–25978. [CrossRef]

152. Choi, N.S.; Yew, K.H.; Lee, K.Y.; Sung, M.; Kim, H.; Kim, S.S. Effect of fluoroethylene carbonate additive on interfacial properties of silicon thin-film electrode. *J. Power Sources* **2006**, *161*, 1254–1259. [CrossRef]

153. Jin, Y.; Kneusels, N.J.H.; Marbella, L.E.; Castillo-Martínez, E.; Magusin, P.C.M.M.; Weatherup, R.S.; Jónsson, E.; Liu, T.; Paul, S.; Grey, C.P. Understanding Fluoroethylene Carbonate and Vinylene Carbonate Based Electrolytes for Si Anodes in Lithium Ion Batteries with NMR Spectroscopy. *J. Am. Chem. Soc.* **2018**, *140*, 9854–9867. [CrossRef]

154. Haregewoin, A.M.; Wotango, A.S.; Hwang, B.J. Electrolyte additives for lithium ion battery electrodes: Progress and perspectives. *Energy Environ. Sci.* **2016**, *9*, 1955–1988. [CrossRef]

155. Xu, K.; Ding, S.P.; Jow, T.R. Toward Reliable Values of Electrochemical Stability Limits for Electrolytes. *J. Electrochem. Soc.* **1999**, *146*, 4172–4178. [CrossRef]

156. Xia, J.; Sinha, N.N.; Chen, L.P.; Kim, G.Y.; Xiong, D.J.; Dahn, J.R. Study of Methylene Methanedisulfonate as an Additive for Li-Ion Cells. *J. Electrochem. Soc.* **2014**, *161*, A84–A88. [CrossRef]

157. Sinha, N.N.; Burns, J.C.; Dahn, J.R. Comparative Study of Tris(trimethylsilyl) Phosphate and Tris(trimethylsilyl) Phosphite as Electrolyte Additives for Li-Ion Cells. *J. Electrochem. Soc.* **2014**, *161*, A1084–A1089. [CrossRef]

158. Yim, T.; Kim, S.H.; Woo, S.G.; Lee, K.; Song, J.H.; Cho, W.; Kim, K.J.; Kim, J.S.; Kim, Y.J. 1,3-Propanesultone as an effective functional additive to enhance the electrochemical performance of over-lithiated layered oxides. *RSC Adv.* **2014**, *4*, 19172–19176. [CrossRef]

159. Pires, J.; Timperman, L.; Castets, A.; Peña, J.S.; Dumont, E.; Levasseur, S.; Dedryvère, R.; Tessier, C.; Anouti, M. Role of propane sultone as an additive to improve the performance of a lithium-rich cathode material at a high potential. *RSC Adv.* **2015**, *5*, 42088–42094. [CrossRef]

160. Zhang, J.; Wang, J.; Yang, J.; Nuli, Y. Artificial Interface Deriving from Sacrificial Tris(trimethylsilyl) phosphate Additive for Lithium Rich Cathode Materials. *Electrochim. Acta* **2014**, *117*, 99–104. [CrossRef]

161. Rong, H.; Xu, M.; Xing, L.; Li, W. Enhanced cyclability of $LiNi0.5Mn_{1.5}O_4$ cathode in carbonate based electrolyte with incorporation of tris(trimethylsilyl)phosphate (TMSP). *J. Power Sources* **2014**, *261*, 148–155. [CrossRef]

162. Guéguen, A.; Bolli, C.; Mendez, M.A.; Berg, E.J. Elucidating the Reactivity of Tris(trimethylsilyl)phosphite and Tris(trimethylsilyl)phosphate Additives in Carbonate Electrolytes—A Comparative Online Electrochemical Mass Spectrometry Study. *ACS Appl. Energy Mater.* **2020**, *3*, 290–299. [CrossRef]

163. Qian, Y.; Hu, S.; Zou, X.; Deng, Z.; Xu, Y.; Cao, Z.; Kang, Y.; Deng, Y.; Shi, Q.; Xu, K.; et al. How electrolyte additives work in Li-ion batteries. *Energy Storage Mater.* **2019**, *20*, 208–215. [CrossRef]

164. Ma, L.; Xia, J.; Dahn, J.R. Ternary Electrolyte Additive Mixtures for Li-Ion Cells that Promote Long Lifetime and Less Reactivity with Charged Electrodes at Elevated Temperatures. *J. Electrochem. Soc.* **2015**, *162*, A1170–A1174. [CrossRef]

165. Tan, D.H.S.; Banerjee, A.; Chen, Z.; Meng, Y.S. From nanoscale interface characterization to sustainable energy storage using all-solid-state batteries. *Nat. Nanotechnol.* **2020**, *15*, 170–180. [CrossRef]

166. Mindemark, J.; Lacey, M.J.; Bowden, T.; Brandell, D. Beyond PEO—Alternative host materials for Li+ -conducting solid polymer electrolytes. *Prog. Polym. Sci.* **2018**, *81*, 114–143. [CrossRef]

167. Long, L.; Wang, S.; Xiao, M.; Meng, Y. Polymer electrolytes for lithium polymer batteries. *J. Mater. Chem. A* **2016**, *4*, 10038–10039. [CrossRef]

168. Li, J.; Ma, C.; Chi, M.; Liang, C.; Dudney, N.J. Solid electrolyte: The key for high-voltage lithium batteries. *Adv. Energy Mater.* **2015**, *5*, 1–6. [CrossRef]

169. Manthiram, A.; Yu, X.; Wang, S. Lithium battery chemistries enabled by solid-state electrolytes. *Nat. Rev. Mater.* **2017**, *2*, 1–16. [CrossRef]

170. Ko, S.; Yamada, Y.; Lander, L.; Yamada, A. Stability of conductive carbon additives in 5 V-class Li-ion batteries. *Carbon N. Y.* **2020**, *158*, 766–771. [CrossRef]

171. Bresser, D.; Buchholz, D.; Moretti, A.; Varzi, A.; Passerini, S. Alternative binders for sustainable electrochemical energy storage-the transition to aqueous electrode processing and bio-derived polymers. *Energy Environ. Sci.* **2018**, *11*, 3096–3127. [CrossRef]

172. Pan, Y.; Chou, S.; Liu, H.K.; Dou, S.X. Functional membrane separators for next-generation high-energy rechargeable batteries. *Natl. Sci. Rev.* **2017**, *4*, 917–933. [CrossRef]

173. Wood, M.; Li, J.; Ruther, R.E.; Du, Z.; Self, E.C.; Meyer, H.M.; Daniel, C.; Belharouak, I.; Wood, D.L. Chemical stability and long-term cell performance of low-cobalt, Ni-Rich cathodes prepared by aqueous processing for high-energy Li-Ion batteries. *Energy Storage Mater.* **2020**, *24*, 188–197. [CrossRef]

174. Yamada, M.; Watanabe, T.; Gunji, T.; Wu, J.; Matsumoto, F. Review of the Design of Current Collectors for Improving the Battery Performance in Lithium-Ion and Post-Lithium-Ion Batteries. *Electrochem* **2020**, *1*, 124–159. [CrossRef]

175. Knoche, T.; Reinhart, G. Electrolyte Filling of Large-Scale Lithium-Ion Batteries: Challenges for Production Technology and Possible Approaches. *Appl. Mech. Mater.* **2015**, *794*, 11–18. [CrossRef]

176. Pathan, T.S.; Rashid, M.; Walker, M.; Widanage, W.D.; Kendrick, E. Active formation of Li-ion batteries and its effect on cycle life. *J. Phys. Energy* **2019**, *1*, 044003. [CrossRef]

177. Yang, D.; Zhang, C.; Biendicho, J.J.; Han, X.; Liang, Z.; Du, R.; Li, M.; Li, J.; Arbiol, J.; Llorca, J.; et al. ZnSe/N-doped carbon nanoreactor with multiple adsorption sites for stable lithium-sulfur batteries. *ACS Nano* **2020**, *14*, 15492–15504. [CrossRef]

178. Zhang, C.; Biendicho, J.J.; Zhang, T.; Du, R.; Li, J.; Yang, X.; Arbiol, J.; Zhou, Y.; Morante, J.R.; Cabot, A. Combined High Catalytic Activity and Efficient Polar Tubular Nanostructure in Urchin-Like Metallic NiCo$_2$Se$_4$ for High-Performance Lithium-Sulfur Batteries. *Adv. Funct. Mater.* **2019**, *29*, 1–11. [CrossRef]

179. Liu, H.; Lai, W.H.; Yang, H.L.; Zhu, Y.F.; Lei, Y.J.; Zhao, L.; Peng, J.; Wang, Y.X.; Chou, S.L.; Liu, H.K. Efficient separators with fast Li-ion transfer and high polysulfide entrapment for superior lithium-sulfur batteries. *Chem. Eng. J.* **2021**, *408*, 127348. [CrossRef]

180. Wang, Q.; Wang, H.; Wu, J.; Zhou, M.; Liu, W.; Zhou, H. Advanced electrolyte design for stable lithium metal anode: From liquid to solid. *Nano Energy* **2021**, *80*, 105516. [CrossRef]

181. Liang, Z.; Yang, D.; Tang, P.; Zhang, C.; Jacas Biendicho, J.; Zhang, Y.; Llorca, J.; Wang, X.; Li, J.; Heggen, M.; et al. Atomically dispersed Fe in a C2N Based Catalyst as a Sulfur Host for Efficient Lithium–Sulfur Batteries. *Adv. Energy Mater.* **2020**, *11*, 2003507. [CrossRef]

182. Zhu, K.; Wang, C.; Chi, Z.; Ke, F.; Yang, Y.; Wang, A.; Wang, W.; Miao, L. How Far Away Are Lithium-Sulfur Batteries from Commercialization? *Front. Energy Res.* **2019**, *7*. [CrossRef]

183. Oxis January 2020. OXIS Energy Is Close to Achieving 500 Wh/kg and Is Targeting 600 Wh/kg with Solid State Lithium Sulfur Technology. [Press Release]. Available online: https://oxisenergy.com/https-oxisenergy-com-wp-content-uploads-2020-01-500-and-600-whkg-pressor-pdf/ (accessed on 29 March 2021).

184. Solid-State Lithium Ion Batteries—The Challenges. Available online: https://www.intertek.com/blog/2019-05-21-lion/ (accessed on 29 March 2021).

185. Zhang, W.; Liu, Y.; Guo, Z. Approaching high-performance potassium-ion batteries via advanced design strategies and engineering. *Sci. Adv.* **2019**, *5*, 7412–7422. [CrossRef]

186. McDowall, J.; Biensan, P.; Broussely, M. Industrial lithium ion battery safety—What are the tradeoffs? In Proceedings of the International Telecommunications Energy Conference (INTELEC), Rome, Italy, 30 September–4 October 2007; pp. 701–707.

187. Ruiz, V.; Pfrang, A.; Kriston, A.; Omar, N.; Van den Bossche, P.; Boon-Brett, L. A review of international abuse testing standards and regulations for lithium ion batteries in electric and hybrid electric vehicles. *Renew. Sustain. Energy Rev.* **2018**, *81*, 1427–1452. [CrossRef]

188. Liu, K.; Liu, Y.; Lin, D.; Pei, A.; Cui, Y. Materials for lithium-ion battery safety. *Sci. Adv.* **2018**, *4*, eaas9820. [CrossRef]

189. Adams, R.A.; Varma, A.; Pol, V.G. Mechanistic elucidation of thermal runaway in potassium-ion batteries. *J. Power Sources* **2018**, *375*, 131–137. [CrossRef]

190. Lin, D.; Liu, Y.; Cui, Y. Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotechnol.* **2017**, *12*, 194–206. [CrossRef]

191. Xu, W.; Wang, J.; Ding, F.; Chen, X.; Nasybulin, E.; Zhang, Y.; Zhang, J.G. Lithium metal anodes for rechargeable batteries. *Energy Environ. Sci.* **2014**, *7*, 513–537. [CrossRef]

192. Wang, C.; Wang, X.; Wang, Y.; Chen, J.; Zhou, H.; Huang, Y. Macroporous free-standing nano-sulfur/reduced graphene oxide paper as stable cathode for lithium-sulfur battery. *Nano Energy* **2015**, *11*, 678–686. [CrossRef]

193. Cleaver, T.; Kovacik, P.; Marinescu, M.; Zhang, T.; Offer, G. Perspective—Commercializing Lithium Sulfur Batteries: Are We Doing the Right Research? *J. Electrochem. Soc.* **2018**, *165*, A6029–A6033. [CrossRef]

194. Chung, S.-H.; Han, P.; Singhal, R.; Kalra, V.; Manthiram, A. Electrochemically Stable Rechargeable Lithium-Sulfur Batteries with a Microporous Carbon Nanofiber Filter for Polysulfide. *Adv. Energy Mater.* **2015**, *5*, 1500738. [CrossRef]

195. Ma, G.; Huang, F.; Wen, Z.; Wang, Q.; Hong, X.; Jin, J.; Wu, X. Enhanced performance of lithium sulfur batteries with conductive polymer modified separators. *J. Mater. Chem. A* **2016**, *4*, 16968–16974. [CrossRef]

196. Wang, Y.; He, J.; Zhang, Z.; Liu, Z.; Huang, C.; Jin, Y. Graphdiyne-Modified Polyimide Separator: A Polysulfide-Immobilizing Net Hinders the Shuttling of Polysulfides in Lithium-Sulfur Battery. *ACS Appl. Mater. Interfaces* **2019**, *11*, 35738–35745. [CrossRef] [PubMed]

197. Pang, Q.; Liang, X.; Kwok, C.Y.; Nazar, L.F. Advances in lithium-sulfur batteries based on multifunctional cathodes and electrolytes. *Nat. Energy* **2016**, *1*, 1–11. [CrossRef]

198. Judez, X.; Zhang, H.; Li, C.; González-Marcos, J.A.; Zhou, Z.; Armand, M.; Rodriguez-Martinez, L.M. Lithium Bis(fluorosulfonyl) imide/Poly(ethylene oxide) Polymer Electrolyte for All Solid-State Li-S Cell. *J. Phys. Chem. Lett.* **2017**, *8*, 1956–1960. [CrossRef] [PubMed]

199. Liu, X.; Li, X.; Li, H.; Wu, H. Bin Recent Progress of Hybrid Solid-State Electrolytes for Lithium Batteries. *Chem. A Eur. J.* **2018**, *24*, 18293–18306. [CrossRef]

200. Zeng, W.; Cheng, M.M.C.; Ng, S.K.Y. Effects of transition metal cation additives on the passivation of lithium metal anode in Li-S batteries. *Electrochim. Acta* **2019**, *319*, 511–517. [CrossRef]

201. Liu, S.; Li, G.R.; Gao, X.P. Lanthanum Nitrate As Electrolyte Additive To Stabilize the Surface Morphology of Lithium Anode for Lithium-Sulfur Battery. *ACS Appl. Mater. Interfaces* **2016**, *8*, 7783–7789. [CrossRef] [PubMed]

202. Liu, B.; Fang, R.; Xie, D.; Zhang, W.; Huang, H.; Xia, Y.; Wang, X.; Xia, X.; Tu, J. Revisiting Scientific Issues for Industrial Applications of Lithium-Sulfur Batteries. *Energy Environ. Mater.* **2018**, *1*, 196–208. [CrossRef]

203. Professor John Kilner: Solid State Batteries Are Essential for a Safe—MSE Supplies LLC. Available online: https://www.msesupplies.com/blogs/news/professor-john-kilner-solid-state-batteries-are-essential-for-a-safe-energy-storage-system (accessed on 29 March 2021).

204. Solid-State Batteries-FutureBridge. Available online: https://www.futurebridge.com/blog/solid-state-batteries/ (accessed on 29 March 2021).

205. Liao, Z.; Zhang, S.; Li, K.; Zhang, G.; Habetler, T.G. A survey of methods for monitoring and detecting thermal runaway of lithium-ion batteries. *J. Power Sources* **2019**, *436*, 226879. [CrossRef]

206. Koch, S.; Birke, K.; Kuhn, R. Fast Thermal Runaway Detection for Lithium-Ion Cells in Large Scale Traction Batteries. *Batteries* **2018**, *4*, 16. [CrossRef]

207. Cai, T.; Stefanopoulou, A.G.; Siegel, J.B. Early Detection for Li-Ion Batteries Thermal Runaway Based on Gas Sensing. *ECS Trans.* **2019**, *89*, 85–97. [CrossRef]

208. Parekh, M.H.; Li, B.; Palanisamy, M.; Adams, T.E.; Tomar, V.; Pol, V.G. In Situ Thermal Runaway Detection in Lithium-Ion Batteries with an Integrated Internal Sensor. *ACS Appl. Energy Mater.* **2020**, *3*, 7997–8008. [CrossRef]

209. Wu, Y.; Wang, Y.; Yung, W.K.C.; Pecht, M. Ultrasonic Health Monitoring of Lithium-Ion Batteries. *Electronics* **2019**, *8*, 751. [CrossRef]

210. Raijmakers, L.H.J.; Danilov, D.L.; Van Lammeren, J.P.M.; Lammers, M.J.G.; Notten, P.H.L. Sensorless battery temperature measurements based on electrochemical impedance spectroscopy. *J. Power Sources* **2014**, *247*, 539–544. [CrossRef]

211. Srinivasan, R.; Demirev, P.A.; Carkhuff, B.G. Rapid monitoring of impedance phase shifts in lithium-ion batteries for hazard prevention. *J. Power Sources* **2018**, *405*, 30–36. [CrossRef]

212. Carkhuff, B.G.; Demirev, P.A.; Srinivasan, R. Impedance-Based Battery Management System for Safety Monitoring of Lithium-Ion Batteries. *IEEE Trans. Ind. Electron.* **2018**, *65*, 6497–6504. [CrossRef]

213. Robinson, J.B.; Owen, R.E.; Kok, M.D.R.; Maier, M.; Majasan, J.; Braglia, M.; Stocker, R.; Amietszajew, T.; Roberts, A.J.; Bhagat, R.; et al. Identifying Defects in Li-Ion Cells Using Ultrasound Acoustic Measurements. *J. Electrochem. Soc.* **2020**, *167*, 120530. [CrossRef]

214. Klink, J.; Grabow, J.; Orazov, N.; Benger, R.; Börger, A.; Ahlberg Tidblad, A.; Wenzl, H.; Beck, H.P. Thermal fault detection by changes in electrical behaviour in lithium-ion cells. *J. Power Sources* **2021**, *490*, 229572. [CrossRef]

215. UNECE. *Global Technical Regulation No. 20 Electric Vehicle Safety (EVS)*; UNECE: Geneva, Switzerland, 2018.