

Present and future lithium-ion battery materials

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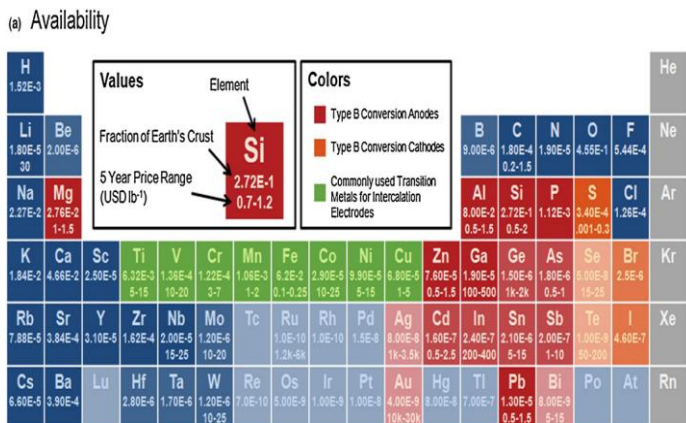
Abstract

Key technical and scientific breakthroughs and problems for a wide variety of Li-ion battery electrodes are discussed in this paper. Suitable materials may be compared using the periodic table and potential/capacity charts. Intercalation materials such as lithium cobalt oxide (LCO), lithium nickel cobalt manganese oxide (NCM), lithium nickel cobalt aluminium oxide (NCA), lithium iron phosphate (LFP), lithium titanium oxide (LTO), and others have their performance characteristics, current limitations, and recent breakthroughs compared to those of conversion materials such as alloying anodes (Si, Ge, Sn etc.), chalcogenides (F, Cl, Br, I). Polyanion cathode materials are also explored in this paper. Electrode materials are detailed in detail, including their cost and availability as well as their ability to conduct electricity, their ability to expand, and their ability to dissolve. Strategies for dealing with the present difficulties are classed into general and particular ones.

Introduction

Portable devices, power tools, and hybrid/fully electric vehicles all rely on Li-ion batteries because of their unbeatable combination of high energy and power density [1]. Electric vehicles (EVs) may cut greenhouse gas emissions by up to 80% if they take the place of gasoline-powered cars in the transportation mix [2]. Li ion batteries' high energy efficiency may also allow them to be used in various electric grid applications, such as improving the quality of energy harvested from wind, solar, geo-thermal, and other renewable sources, thus contributing to their greater use and building an energy-sustainable economy. As a result, both private sector and public funding organisations have devoted considerable attention to Li-ion battery development in the last several years. Despite this, there are those who believe that Li-ion batteries will not be able to meet the world's energy storage demands in the long term. A limited life span of Li and several transition metals now utilised in Li-ion batteries may one day become a concern in various applications (such as transportation and the grid) [3]. Li-ion batteries, on the other hand, offer a number of basic benefits over other chemistries. There are a number of advantages to using lithium ion batteries, including the lowest reduction potential of any element. As an added bonus, Li is the third-lightest element and possesses one of the most compact charged ions' ionic radiuses of any single charged ion. Li-ion batteries benefit from their high gravimetric and volumetric capacitance and power density as a result of these features. Finally, increased charge capacity per ion is possible with multivalent cations, but the extra charge limits their mobility significantly. Developing such alternative chemistries will be very difficult, because of the fact that ionic diffusion in solid electrodes is frequently the rate-limiting element for battery power performance Li will not be in low supply very soon [4,5]. Similar assertions have been made regarding the peaking of oil, but as prices rise and new exploration and mining methods are developed, the world's oil reserves and resources have yet to materialise. The quantity of Li in the Earth's crust is sufficient to power the whole world's automotive fleet in absolute terms [6]. Increasing costs, on the other hand, might be an issue for Li-ion batteries, since the high cost of these batteries is

preventing them from being widely used in alternative energy sources. It's worth noting that Li isn't a huge role in



battery costs at the moment. Li is employed in the

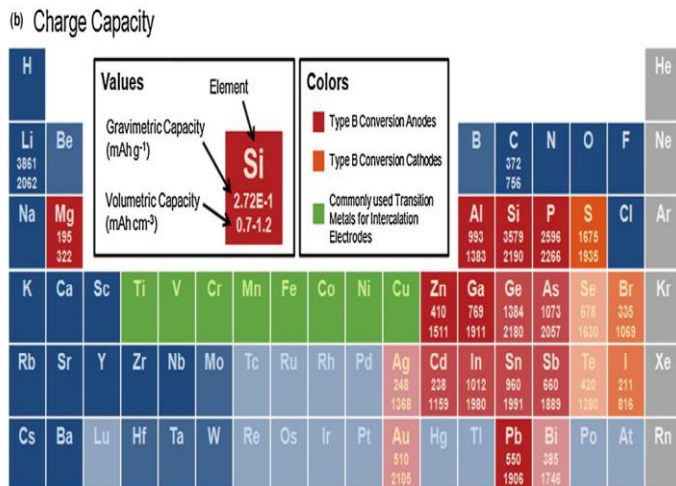
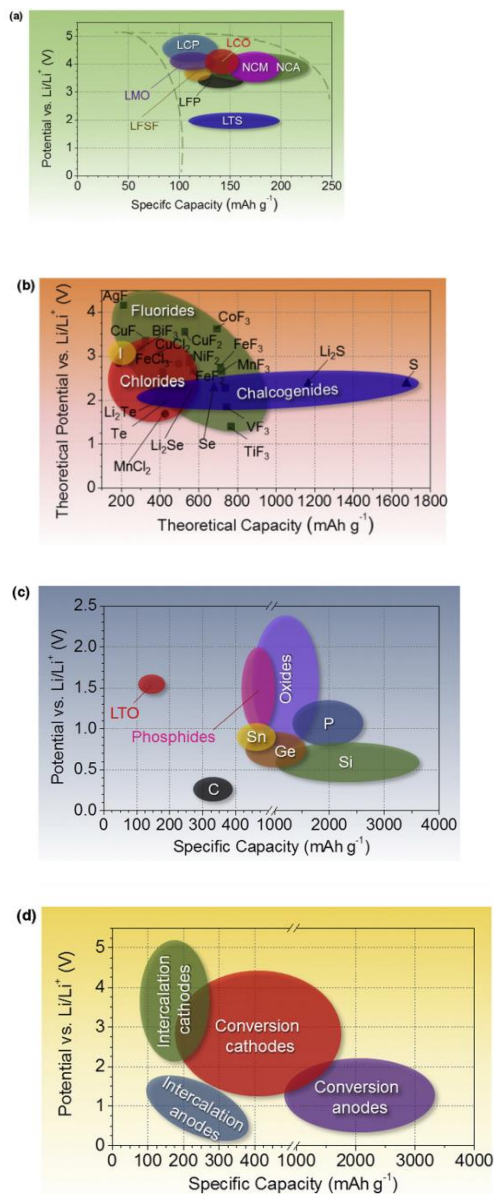


FIGURE 1 availability and capacity of elements that may host lithium as electrodes. Element abundances below 10⁻⁵ are mildly faded, while elements below 10⁻⁷ are faded much worse. Pricing are based on averages over the last five years for most metals (except for Ge, which has a three-year price range) [10–13], carbon in the form of 80–100 mesh natural graphite [14], and sulphur in the form of Vancouver/USGS prices [13,15]. Based on delithiated mass and volume, gravimetric and volumetric capacities are estimated. cathode and electrolyte, which make up just a minor fraction of the entire cost Processing costs and the cost of cobalt in cathodes are the two biggest determinants in these components [8]. Li-ion batteries are likely to continue to dominate portable electrochemical energy storage for many years to come because of their inherent advantages. As the primary source of portable electrochemical energy storage, enhancing the cost and performance of Li-ion batteries has the potential to dramatically extend their uses and allow new technologies that rely on energy storage. Electrode materials have been the focus of a significant amount of Li-ion battery research to date. Li batteries' energy and power densities may be increased and their size and cost decreased by using electrodes with better rate capability, more charge capacity, and (for cathodes) a high enough voltage. As long as the material isn't extremely costly or scarce, this is a reasonable assumption. For example, in Figure 1a, you can see the wholesale price for different metals and their abundances as a proportion of the Earth's crust [9]. Relative variations in pricing may be seen even when the electrodes are not made out of pure metal. The cost difference in cathode materials derived from Mn and Co may be explained by the fact that Mn is cheaper than Co. The fact that there are so many components means that the element isn't as readily available as it

might be. While supply and demand have a role in the genuine availability of a product, this chart highlights the benefits of certain components. P and S, for example, are much more common than the more conductive elements I which are scarce.

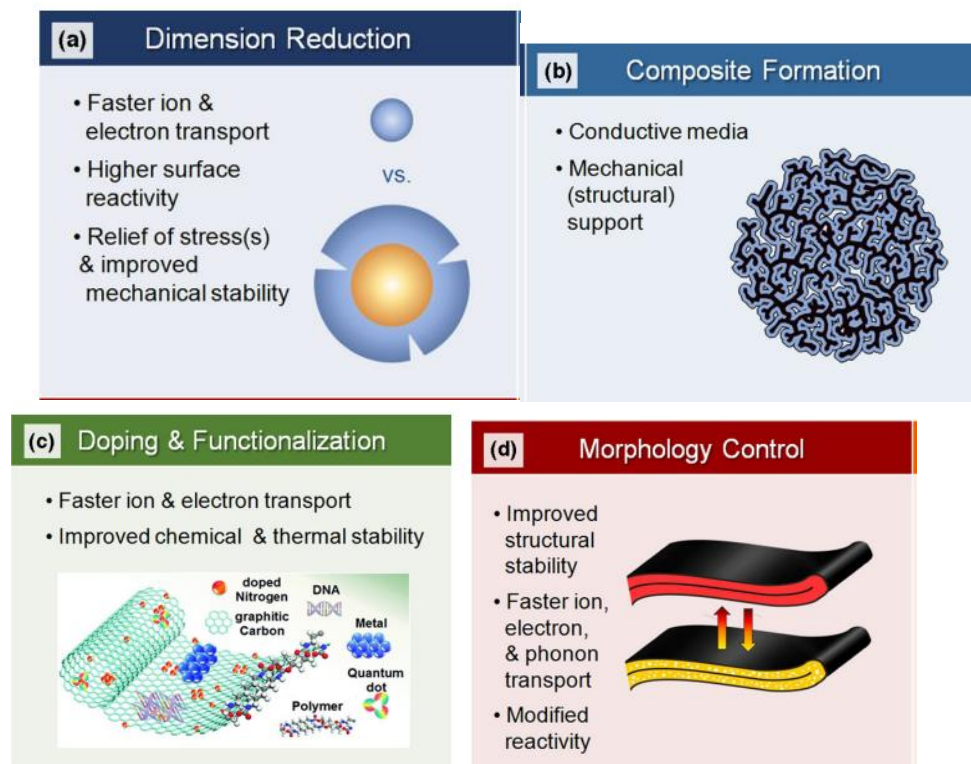


Some of the most often used (a) intercalation-type cathodes (experimental), (b) conversion cathodes (the theoretical), (c) conversion anodes (experimental), and an overview of the average discharge potentials and specific capacities for all kinds of electrodes Groups V, VI, respectively.. Figure 1b shows the theoretical specific and volumetric capabilities of the components involved in conversion reactions with Li. Since most cathode materials are compounds, they cannot be included in a periodic table. For anodes, intercalation cathodes, and converter cathodes, Figure 2 is a pretty complete version of a popular chart depicting average electrode potential versus empirically accessible or theoretical capacity. Anode and cathode combinations and their theoretical cell volt ages, capacities, and energy densities may be evaluated by the reader in this way. Use the chart to discover compatible electrolytes, additives and collector materials for the electrode materials of your choice. For the intercalation

materials (Fig. 2a), the acronyms for the following elements are used: LCO for "lithium cobalt oxide," LMO for "lithium manganese oxide," NCM for "nickel cobalt manganese oxide," NCA for "nickel cobalt aluminium oxide," LCP for "lithium cobalt phosphate," LFP for "lithium iron phosphate," LFSF for "lithium ironfluorosulfate," and LTS. Various methods have been used to facilitate the use of novel electrode materials. According to Fig. 3, many of these techniques may be applied to any kind of material or crystal structure. We'll cover a wide variety of cathode and anode materials, from commercially accessible and presently utilised materials to promising new materials that might be employed in the future. The most recent developments in anode and cathode material research, as well as their fundamental characteristics, prospects, and problems, will be reviewed. Despite the current surge in interest in flexible batteries, this review will exclude them in favour of citing other sources [16–21].

Cathodes

Materials for intercalation cathodes It is possible to store guest ions in intercalation cathodes, which are solid host networks. A reversible process allows the guest ions to be added and deleted from the network. Metal chalcogenides, transition metal oxides, and polyanion compounds are the host network compounds in a lithium-ion battery. The crystal structures of these intercalation compounds may be separated into layered, spinel, olivine, and tavorite (Fig. 4). Li-ion batteries' cathode materials' intercalation compounds first took on a layered structure. A long time ago, the intercalating cathode materials of metal chalcogenides, as TiS_3 and $NbSe_3$, were explored. In contrast to TiS_3 , $NbSe_3$ showed reversible electrochemical activity owing to the irreversible structural shift from trigonal prismatic to octahedral coordination on lithiation. Among the numerous



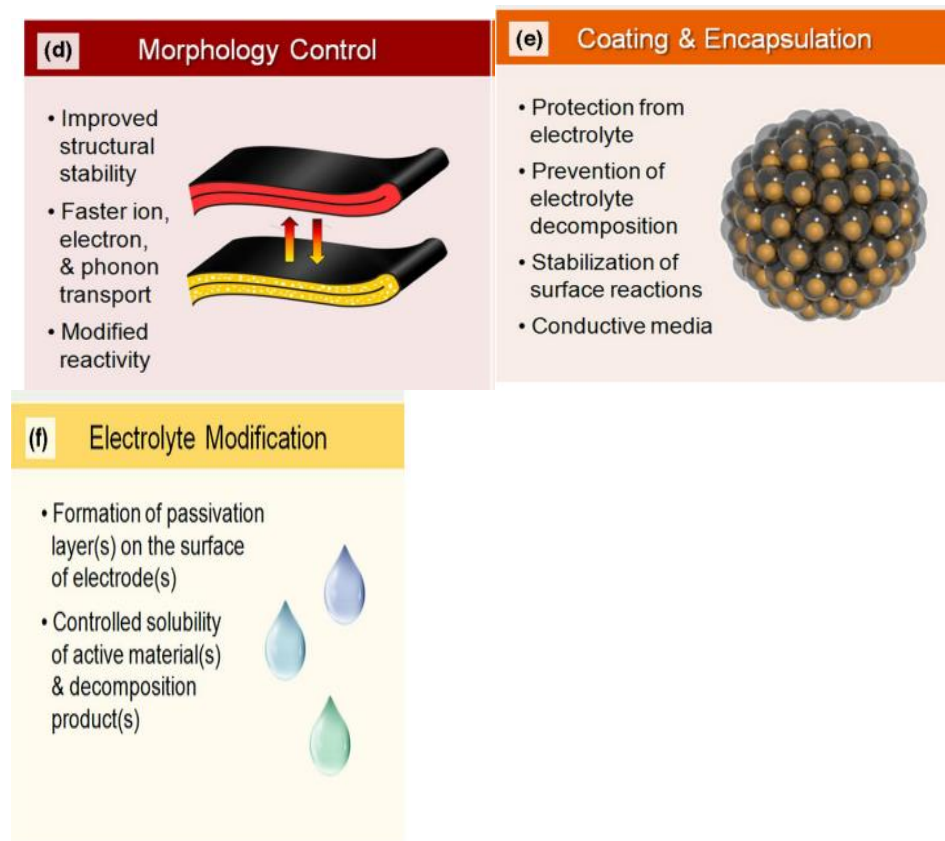


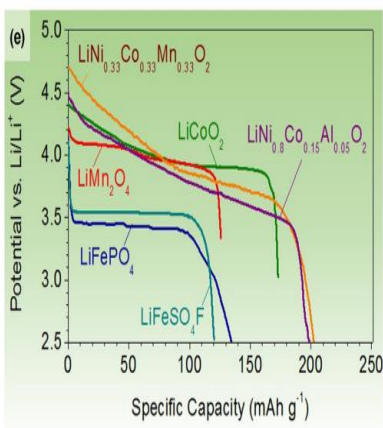
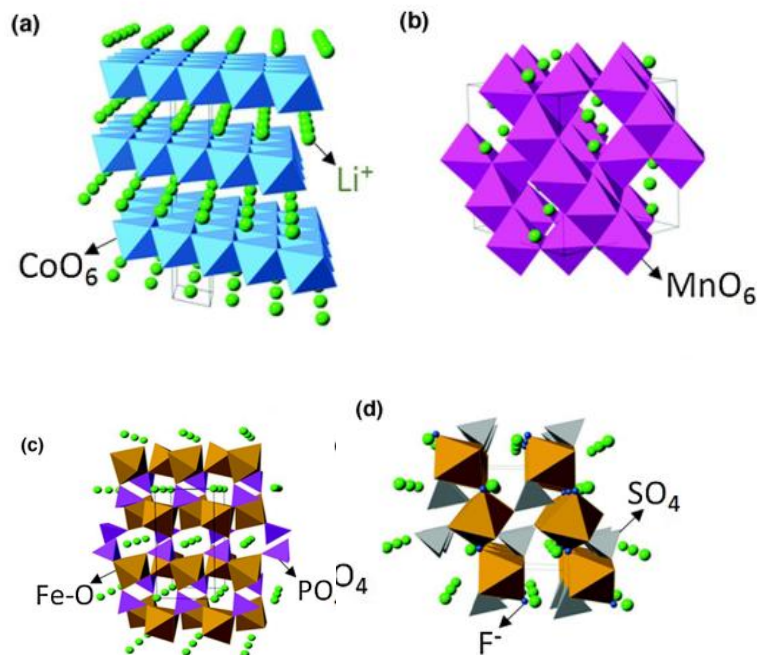
FIGURE 3(a) reduction in active material dimensions, (b) construction of composites, (c) doping and functionalization, (d) adjusting particle shape, (e) formation of coatings or shells around active materials, (f) alteration of electrolyte. Figures (c) and (e) are reprinted with permission from the Royal Society of Chemistry [22] and Nature Publishing Group [23], respectively, for use in this article.

Because of its high gravimetric energy density and extended cycle life (1000+ cycles) compared to other chalcogenides, LiTiS_2 (LTS) was extensively investigated and subsequently commercialised by Exxon [25,26]. Due to their higher operating voltage and greater energy storage capacity, transition metal oxide and polyanion compounds are the focus of most current intercalation cathode research. Intercalation cathodes typically have a specific capacity of 100–200 mAh/g and an average voltage of 3–5 V compared to Li/Li^+ . Table 1 (Fig. 4e, e) shows that

Transition metal oxide

First and most commercially effective layered transition metal oxide cathodes are LiCoO_2 (LCO) invented by Goodenough [46]. Since SONY was the first company to commercialise this material, it continues to be found in the vast majority of commercial Li-ion batteries on the market today. Alternating layers include Co and Li, which produce a hexagonal symmetry (Fig. 4a). Due to LCO's high theoretical specific capacity of 274 mAh/g, high theoretical volumetric capacity of 1363 mAh/cm³, low self-discharge, high discharge voltage, and strong cycling behaviour [47–48], it is a highly desirable cathode material. Cost, thermal stability and capacity decline at high current rates or deep cycling are the main drawbacks. Because of the high price of Co, LCO cathodes are pricy (Fig. 1). Lithium metal oxide cathodes with low thermal stability leak oxygen when heated over a specific threshold, leading to an exothermic process that might cause the cell to explode [49]. Since thermal runaway is a serious risk when using Li-ion batteries, all Boeing 787 flights were forced to be grounded in 2013 [50]. Among commercial cathode materials, LCO has the lowest thermal stability of any transition metal oxide intercalation cathode. LCO

generally develops thermal runaway above 200°C owing to an exothermic interaction between released oxygen and organic molecules. Lattice deformation from hexagonal to monoclinic symmetry (delithiation over 4.2 V, suggesting about 50% or more Li extraction) deteriorates cycle performance [52]. There have been several studies on dopants and partial replacements for Co, including Mn, Al, Fe, and Cr [53–56], with promising but limited results. When it comes to improving LCO stability and performance characteristics even during deep cycling, the mechanically and chemically stable oxide material (Al₂O₃, B₂O₃, TiO₂, ZrO₂) was more successful since it could prevent structural change in LCO and side reactions with electrolyte. With a theoretical specific capacity of 275 mAh g⁻¹, LNO has the same crystal structure as LiCoO₂. Research is fueled by its high energy density and inexpensive cost compared to Co-based materials. In the process of synthesis and delithiation, the Ni²⁺ ions tend to substitute for Li⁺ sites in pure LNO cathodes, preventing Li diffusion [59]. Because LNO is so much more thermally efficient than



The crystal structures and discharge profiles of four example intercalation cathodes are shown in Figure 4: layered (LiCoO₂), spinel (LiMn₂O₄), olivine (LiFePO₄), and tavorite (LiFeSO₄F). intercalation cathodes [27–33], as well as typical discharge patterns (e).

Because Ni^{3+} is more easily reduced than Co^{3+} , LCO is more unstable than LCO. Cationic disorder may be reduced by substituting a portion of Ni with Co [61]. Adding a tiny quantity of Al may increase both thermal stability and electrochemical performance [63]. This has led to widespread commercial adoption of the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode, such as the Panasonic battery for Tesla EVs. Co-based oxide cathodes have lower useful discharge capacity and longer storage calendar life than NCA. Due to SEI development and micro-crack propagation at grain boundaries, it has been found that capacity fading may be significant at extreme temperatures (40–70°C). $LiMnO_2$ (LMO) may potentially be a viable option since Mn is significantly less poisonous than Co or Ni, making it more cost-effective. There have been improvements in LMO preparation procedures over the last two decades that have resulted in anhydrous and stoichiometric LMO that is free of impurities, differing stoichiometries, poor crystallinity, and undesired structural change during cycle. Although the layered structure has a propensity to transform into a spinel structure during Li ion extraction [67] and since Mn leaks out of LMO during cycling [31], the cycling performance of LMO was still not sufficient. Observed in all metal cathodes, Mn dissolution occurs as the disproportionation reaction between the ionised Mn^{3+} and the resulting Mn^{2+} or Mn^{4+} ions. To stabilise the anode SEI, Mn^{2+} is assumed to dissolve in the electrolyte. For cathodes containing Mn, the concentration of Mn in the electrolyte and anode SEI has been shown to rise with age [68–71]. Anode impedance rises with Mn dissolution on carbon anodes [70], but not with LTO [72]. [70, 72] (which has a negligible SEI). LMO's low cycle stability (particularly at rising temperatures) has stifled broad commercialization of cationic doping, despite the fact that this method has been tested both experimentally and conceptually. As a consequence of a constant endeavour to find a cathode material less costly than LCO, the NMO cathode was developed. Because it can employ less expensive transition metals while yet maintaining a comparable energy density as LCO, NMO has the potential to be an appealing material. Higher Li extraction capacities are possible because of the presence of Ni. Cation mixing, on the other hand, may result in poor Li diffusivity and an undesirable rate capability. High rate capability in layered cathodes may be achieved by the use of low valence transition metal cations (Ni^{2+}), according to recent ab initio computational modelling. Ion exchange technique NMO recently synthesised revealed a very low concentration of faults in NMO and a capacity of 180 mAh g⁻¹ even at a very high rate of 6 C. Researchers discovered that adding Co atoms in $Li(Ni_{0.5}Mn_{0.5})O_2$ significantly improved structural stability [77]. In comparison to LCO, $LiNi_xCo_yMn_zO_2$ (NCM, or NMC) has a comparable or greater attainable specific capacity and a similar working voltage, but at a cheaper cost, since the Co content is decreased. The most common type of NMC is $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$, which is extensively utilised in the battery industry. Reversible specific capacity of 234 mAh g⁻¹ and excellent cycle stability even at 50°C were shown by recent efforts, such as the production of macroporous NMC [78]. Large voltage operation (4.5–3.0 V) may also lead to high capacity (>200 mAh g⁻¹) in Li_2MnO_3 stabilised $LiMO_2$ (where M = Mn, Ni, or Co). During the first cycle, the Li_2MnO_3 is activated, releasing Li_2O [80], which offers an additional supply of Li^+ . It is possible to use the residual Li_2MnO_3 as a Li reservoir and to aid in the diffusion of Li. Because it contains more Li ions than a typical layered oxide compound, this substance is referred to as a lithium-rich layered oxide compound. Cathode material with an average composition of $LiNi_{0.68}Co_{0.18}Mn_{0.21}O_2$ was published recently [81]. Each particle has a bulk material surrounding an outer layer of concentration gradient material. Nickel-rich layered oxide ($LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$) is used as the bulk material while the outer layer is Mn and Co-substituted NMC ($LiNi_{0.46}Co_{0.23}Mn_{0.31}O_2$) is used as the outer layer for enhanced cycle life and safety. The gas evolution caused

by the interaction between Ni ion and electrolyte is delayed because of the presence of stable Mn⁴⁺ in the surface

Characteristics of representative intercalation cathode compounds; crystal structure, theoretical/experimental/commercial gravimetric and volumetric capacities, average potentials, and level of development.

Crystal structure	Compound	Specific capacity (mAh g ⁻¹) (theoretical/experimental/typical in commercial cells)	Volumetric capacity (mAh cm ⁻³) (theoretical/typical in commercial cells)	Average voltage (V) [34]	Level of development
Layered	LiTi ₂ S ₂	225/210 [35]	697	1.9	Commercialized
	LiCoO ₂	274/148 [36]/145	1363/550	3.8	Commercialized
	LiNiO ₂	275/150 [37]	1280	3.8	Research
	LiMnO ₂	285/140 [38]	1148	3.3	Research
	LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂	280/160 [32]/170	1333/600	3.7	Commercialized
	LiNi _{0.4} Co _{0.15} Al _{0.05} O ₂	279/199 [33]/200	1284/700	3.7	Commercialized
	Li ₂ MnO ₃	458/180 [39]	1708	3.8	Research
Spinel	LiMn ₂ O ₄	148/120 [40]	596	4.1	Commercialized
	LiCo ₂ O ₄	142/84 [41]	704	4.0	Research
Olivine	LiFePO ₄	170/165 [42]	589	3.4	Commercialized
	LiMnPO ₄	171/168 [43]	567	3.8	Research
	LiCoPO ₄	167/125 [44]	510	4.2	Research
Tavorite	LiFeSO ₄ F	151/120 [30]	487	3.7	Research
	LiVPO ₄ F	156/129 [45]	484	4.2	Research

layer, it is hypothesised.

There is a lot of Mn in spinel Li₂Mn₂O₄ (often referred to as LMO) [82], which makes it an excellent material for making LMO. In a ccp array of oxygen anions, Li is found in tetrahedral 8a sites, whereas Mn is found in octahedral 16d sites (Fig. 4b). Li⁺ may diffuse via the three-dimensional structure's unoccupied tetrahedral and octahedral interstitial spaces. Because of irreversible side reactions with electrolyte, oxygen loss from the delithiated LiMn₂O₄, Mn dissolution, and the production of tetragonal Li₂MnO₄ at the surface at rapid c-rates, inadequate long-term cyclability is considered to be caused by these factors. As a result of reduced Li⁺ diffusion lengths and increased electronic transport via nanoparticles, the rate performance may be considerably enhanced LMO nanowires and mesoporous LMO have been synthesised by several different groups [85–89]. As a result of shortened diffusion lengths, dissolution may be suppressed by the use of ZnO on the cathode surface, layered structure, metal doping, oxygen stoichiometry, metal doping, and blending with other materials. When compared to bulk spinel, a new ordered mesoporous lithium rich Li_{1.12}Mn_{1.88}O₄ spinel has been found [96].

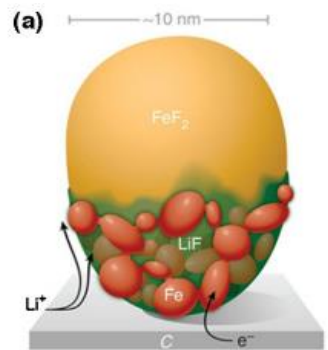
Polyanion compounds

Polyanions are a novel family of chemicals that researchers have discovered while looking for new cathode materials. Cathode redox potential is increased and the structure is stabilised by large (XO₄)³⁻ polyanions (X = S; P; Si; As; Mo; W). Olivine (LFP) is the olivine structure's best-known representative material, noted for its thermal stability and high power capabilities. Octahedral Li⁺ and Fe²⁺ sites in LFP are filled by tetrahedral P in a distorted hexagonal close-packed (HCP) oxygen array that is somewhat deformed (Fig. 4c). Table 1 shows that the LiFePO₄ cathode has a lower average potential (Fig. 4e) than other cathodes, as well as poor electrical and ionic conductivity. Since LFP's inception, researchers have worked tirelessly to increase its performance and mechanistic understanding. The rate performance may be improved by combining particle size reduction with carbon coating [98] and cationic doping [99]. If particles are uniformly nano-sized and conductive nanocarbons are employed in the cathodes, high electrochemical performance may be obtained without a carbon covering [100]. For instance, a virus-templated amorphous anhydrous FP/CNT composite showed encouraging results [101]. Redox reactions in non-conducting LFP were found to be very facile because of the [0 1 0] direction of lithium diffusion in the nonconducting LFP [102]. However, the low density of nanostructured LFP electrodes and their low average voltage restrict the energy density of LFP cells. An alluaudite non-olivine LFP that displayed fundamentally different electrochemical behaviour from that of an olivine LFP was recently discovered and described. For greater specific energy, but at the penalty of lesser conductivity, LiMnPO₄ (LMP) is another olivine structure that provides 0.4 V more average voltage than olivine LFP (Table 1) (104). A number of other materials have been studied in the hopes of achieving better performance, stability, and energy density, such as LiNiCoPO₄ and LiMn_{0.33}Fe_{0.33}Co_{0.33}PO₄ (also known as LCP and NCP), but more work is still needed [105–107]. New Li₃V₂(PO₄)₃ (LVP),

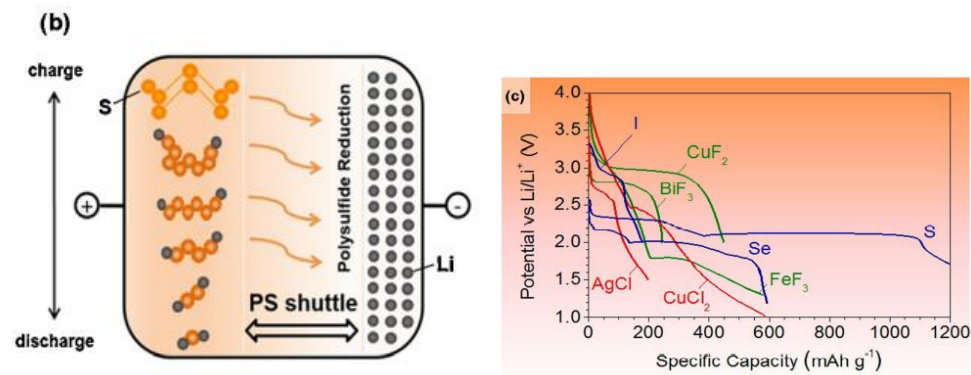
which has an operational voltage (4.0 V) and excellent capacity (197 mAh/g) [108], has been developed. Despite LVP's poor electrical conductivity, the LVP/C nanocomposites showed a theoretical capacity of 95% at a high rate of 5 C. (similar with LFP). In addition to its high cell voltage and good specific capacity (151 mAh g⁻¹), LiFeSO₄F (LFSF) is an intriguing cathode material. Due to its superior ionic/electrical conductivity, LiFeSO₄F does not need carbon coating or nanoparticles. In addition to being cost-effective, LiFeSO₄F may be made using a wide variety of readily available materials. Two Fe₂O₄F₂ oxyfluoride octahedra, somewhat deformed, are joined by F vertices in the trans position, producing chains that are aligned with the c-axis, and the Li⁺ are positioned along the (1 0 0), (0 1 0), and (1 0 1) directions, respectively (Fig. 4d). The fluorosulfate and fluorophosphate families of compounds were found to be the most promising after simulated evaluation of tavorite-structured cathode materials. Polyanions are a novel family of chemicals that researchers have discovered while looking for new cathode materials. Cathode redox potential is increased and the structure is stabilised by large (XO₄)₃ polyanions (X = S; P; Si; As; Mo; W). For the olivine structure, LiFePO₄ (LFP) serves as an excellent example of a thermally stable, high-power material. Octahedral Li⁺ and Fe²⁺ sites in LFP are filled by tetrahedral P in a distorted hexagonal close-packed (HCP) oxygen array that is somewhat deformed (Fig. 4c). Table 1 shows that the LiFePO₄ cathode has a lower average potential (Fig. 4e) than other cathodes, as well as poor electrical and ionic conductivity. Since LFP's inception, researchers have worked tirelessly to increase its performance and mechanistic understanding. The rate performance may be improved by combining particle size reduction with carbon coating [98] and cationic doping [99]. If particles are uniformly nano-sized and conductive nanocarbons are employed in the cathodes, high electrochemical performance may be obtained without a carbon covering [100]. For instance, a virus-templated amorphous anhydrous FP/CNT composite showed encouraging results [101]. Redox reactions in non-conducting LFP were found to be very facile because of the [0 1 0] direction of lithium diffusion in the nonconducting LFP [102]. However, the low density of nanostructured LFP electrodes and their low average voltage restrict the energy density of LFP cells. An alluaudite non-olivine LFP that displayed fundamentally different electrochemical behaviour from that of an olivine LFP was recently discovered and described. For greater specific energy, but at the penalty of lesser conductivity, LiMnPO₄ (LMP) is another olivine structure that provides 0.4 V more average voltage than olivine LFP (Table 1) (104). A number of other materials have been studied in the hopes of achieving better performance, stability, and energy density, such as LiNiCoPO₄ and LiMn_{0.33}Fe_{0.33}Co_{0.33}PO₄ (also known as LCP and NCP), but more work is still needed [105–107]. New Li₃V₂(PO₄)₃ (LVP), which has an operational voltage (4.0 V) and excellent capacity (197 mAh/g) [108], has been developed. Even though LVP has a poor electrical conductivity, the LVP/C nanocomposites showed 95 percent theoretical capacity at a rate of 5 C. (similar with LFP). Cathode material LFSF has a high cell voltage and good specific capacity (151 mg⁻¹ g⁻¹) [109] making it an attractive option. Because of LiFeSO₄F's superior ionic/electronic conductivity, no carbon coating or nanoparticles are required. LiFeSO₄F is also cost-effective due to the abundance of minerals used in its production. Octahedral chains are formed by the transposition of F vertices in the transpositional position of the Fe₂O₄F₂ O₄F₂ oxyfluoride. The Li⁺ are placed at (1 0 0), (0 1 0), and (1 0 1) points along the C-axis (Fig. 4d). The fluorosulfate and fluorophosphate families of compounds were found to be the most promising, whereas the oxysulfate family was shown to be the least promising [110]. Fe(SO₄)F and V(PO₄)F may be charged and discharged at rates equivalent to those found in tiny olivine Fe(PO₄) particles in tavorite structured materials with 1D diffusion channels that have low activation energies. LiV PO₄F, a vanadium-containing material, cycles well and has high voltage and capacity [45,111], but its toxicity and environmental effect are a worry. Li⁺ can be intercalated at 1.8 V, making it useful as an anode (Li_{1+x}VPO₄ where x = 0–1) and cathode (Li_{1-x}VPO₄ where x = 0–1). Further information on synthesis methods, chemical characteristics and mechanisms may be found elsewhere [112,113].

Conversion cathode materials

During the lithiation/delithiation process, conversion electrodes go through a solid-state redox reaction in which the crystalline structure changes and chemical bonds are broken and recombined. Generally speaking, the reversible electrochemical reaction for conversion electrode materials is: A Type AMX_zLi (1) If you use type B, you get the following output: (2) When using metal halides as cathodes, Type A (Eq. (1)) contains metal halides with two or more high-valence metal ions in order to achieve greater theoretical capacitances. For FeF₂ particles, this process is



shown in Figure 5a [114]. Ionized fluorine, which has



A lithiation reaction front propagating through a single FeF_2 particle [114] is shown in Figure 5 (reproduced with permission copyright (2014) from Nature Publishing Group); a polysulfides shuttle is shown in Figure 5 (reproduced with permission copyright (2014) from Nature Publishing Group); and (c) discharge profiles typical of conversion cathodes are shown in Figure 5 (reproduced with permission copyright (2014) from Nature Publishing Group). LiF forms as a result of the greater mobility, which diffuses out of the FeF_2 and forms LiF behind it [115]. This results in a 'sea' of LiF ($\text{Li}(y/z)\text{X}$ from Eq. (1)) containing metal nanoparticles. Even though certain Type A active materials have an intermediary Li insertion phase, the same process may be seen for all. The Type B reaction (Eq. (2)) is followed by S, Se, Te, and I. As a result of its high theoretical specific capacity (1675 mAh g^{-1}), cheap price point, and abundance in the Earth's crust, S has been investigated the most. Type B cathodes in lithium air batteries also employ oxygen as a Type B cathode, but the technical barriers are fundamentally different due to the fact that oxygen is gas. At a systems level, attempts to utilise ambient air aggravate the situation. This assessment does not include lithium air batteries. It is shown in Figure 5b that intermediate polysulfides soluble in organic electrolytes are used in the entire S conversion procedure. Cathode discharge trends are shown in Figure 5c. The discharge characteristics of BiF_3 [116] and CuF_2 [117] seem promising, with high voltage plateaus. However, Li_2S [118], S [119] and Se [120] similarly display flat and extended voltage plateaus, showing excellent kinetics of the interaction between solids.

Fluorine and chlorine compounds

Due to intermediate voltages and high theoretical specific and volumetric capacities, metal fluorides (MF) and chlorides (MCl) have become more popular. Poor conductivity, excessive voltage hysteresis, volume expansion, undesired side reactions, and dissolution of active material are all common problems with MF and MCl (Table 2). The huge band gap caused by the highly ionic quality of the metal halogen bond makes most MF, particularly FeF_3 and FeF_2 , renowned for their poor electrical conductivity. They may, nonetheless, facilitate strong ionic conduction because of their open architectures [126,127]. Similarly, chlorides have low electrical conductivity because of this. Due to factors such as low electronic conductivity and low ion mobility (Table 2) [128], all of the MF and MCl materials studied exhibit very high voltage hysteresis. Metal nanoparticles are also formed by Type A conversion

materials after they have been completely lithiated. Catalyzing the breakdown of cyclic carbonates at relatively high voltages using BiF₃ and FeF₂ has been observed to reduce cycle life [116,129]. Cu nanoparticles, on the other hand, may be electrochemically transformed to Cu¹⁺, which subsequently dissolves into the electrolyte. The voltage hysteresis may be exacerbated even if these undesired side reactions do not occur, since metal nanoparticles may agglomerate across several cycles [131]. Many ionic chemicals, including certain fluorides, may be dissolved in polar liquids [135]. LiCl and other metal chlorides are more sensitive to dissolving in a variety of solvents, including those used in Li battery electrolytes. There are some minor changes in the volume expansions of MF and MCl based on the room temperature densities of compounds before and after lithiation [155] (Table 2). Volume increases of 2–25% have been seen in the most extensively investigated MF and MCl materials. Even while the risk of fracture and electrical contact loss is lower than with Type B conversion cathode materials and conversion/alloying anode materials (which will be covered in the next sections), it is nevertheless conceivable.

TABLE 2

Challenges including conductivity, volume expansion, voltage hysteresis and cathode dissolution of conversion cathodes.

Materials	Electronic conductivity (S m ⁻¹)	Theoretical potential (V)	Volume expansion fraction (%)	Voltage hysteresis V (vs. Li)	Qualitative solubility in organic electrolytes
FeF ₂	Insulator [132]	2.66	16.7	0.7-1 [115,132]	-
FeF ₃	Insulator [126]	2.74	25.6	0.8-1.6 [124,126,133,134]	-
CoF ₂	Poor [126]	2.85	21	0.8-1.2 [135]	Soluble [135]
CuF ₂	Insulator [117,126,127]	3.55	11.6	0.8 [136]	-
NiF ₂	Poor [126]	2.96	28.3	0.8-2 [137,138]	-
BiF ₃	Poor [126]	3.18	1.76	0.5-0.7 [116,129]	-
FeCl ₃	Poor	2.83	22.6	-	Soluble
FeCl ₂	Poor	2.41	19.9	-	Soluble
CoCl ₂	Poor	2.59	23	1 [139]	Soluble
NiCl ₂	Poor	2.64	30.3	-	Soluble
CuCl ₂	Poor	3.07	21.1	1.2 [123]	Soluble
AgCl	Poor	2.85	19.4	0.25 [123]	Insoluble [123]
LiCl	Poor	-	-	-	Soluble
S	Insulator 5×10^{-20} [140]	2.38	79	0.12-0.40 [119,140,141]	Soluble Intermediates
Li ₂ S	Insulator [142,143]	2.38	-	0.12-0.4 [144-147]	Soluble Intermediates
Se	Semiconductor 10^{-5} [148]	2.28	82.5	0.2-2.0 [120,125,149-152]	Soluble Intermediates
Li ₂ Se	Poor	2.28	-	-	Soluble Intermediates
Te	Semiconductor 2×10^2 [153]	1.96	104.7	0.3 [153]	-
I	Poor	3.01	49.3	0.2 [122]	Soluble [122]
LiI	Poor	3.01	-	-	Soluble [122]

Nanoparticles of conversion materials must be synthesised in order to overcome their poor conductivities and shorten the route for electrons and ions. It is common practise to spread or wrap active components in conductive matrix materials for MF and MCl composites in order to increase their conductivity, such as FeF₃/CNT [156], FeF₃/graphene (157,158), AgCl/acetylene black (123), and BiF₃/MoS₂/CNT (129). In order to prevent undesirable interactions between the electrolyte and active material at various phases of charge and discharge, electrolyte changes are also necessary [116].

Sulfur and lithiumsulfide

Due to sulfur's inexpensive cost and copious supply in the Earth's crust, it has a theoretical capacity of 1675 mAh g⁻¹. As a result, the electrolyte dissolution of intermediate reaction products (polysulfides) as well as S loss during vacuum drying are all problems with S-based cathodes compared to Li/Li⁺ electrodes with higher potential, lower electrical conductivity, and no dissolution of polysulfides in the electrolyte. Because sulfur's volume changes by 80 percent, it may damage the electrical contact in typical carbon composite electrodes [160]. Encapsulation in a hollow structure with surplus internal void space may reduce the effects of both dissolution and volume expansion. Sulfur has been infiltrated and chemically precipitated into polyvinyl pyrrolidone polymer [161], carbon [162], and titanium dioxide [163] capsules. These materials have cycle lives approaching 1000 cycles when tested in half cells with thin electrode designs. Li₂S electrodes have also been developed to avoid expansion-related problems, eliminate S evaporation during drying, and create entire cells with Li-free (and hence safer) anodes [142,144,145,147,164–171]. Because Li₂S has a significantly higher melting point than S, it is more difficult to penetrate a host than S. As a result of the excellent solubility of Li₂S in ethanol and other ecologically friendly solvents (such as acetone), different Li₂S-based nanocomposites may be formed, such as Li₂S nanoparticles embedded in conductive carbon [144]. blank gaps are unnecessary since the completely lithiated Li₂S does not expand. After 400 charge/discharge cycles, carbon-coated Li₂S exhibited no change in morphology [147]. Polysulfide dissolution is frequently mitigated with the use of electrolyte alteration (Fig. 3f). As a result, polysulfide

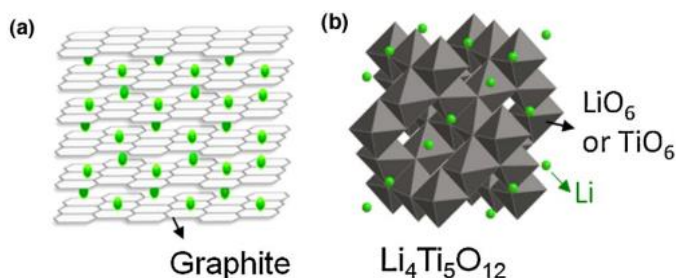
precipitation was prevented on the surface of Li metal by the use of LiNO₃ (172) and P2S₅ (173) additives. As an alternative, lithium polysulfides may be added to temporarily reduce cathode dissolution. Polysulfide solubility was similarly reduced in many works using higher molarity electrolytes [175,145,176]. Finally, solid state electrolytes may minimise polysulfide dissolving while simultaneously enhancing cell safety by preventing Li dendrite short circuiting [167,177–179]. Solid state electrolytes

Selenium and tellurium

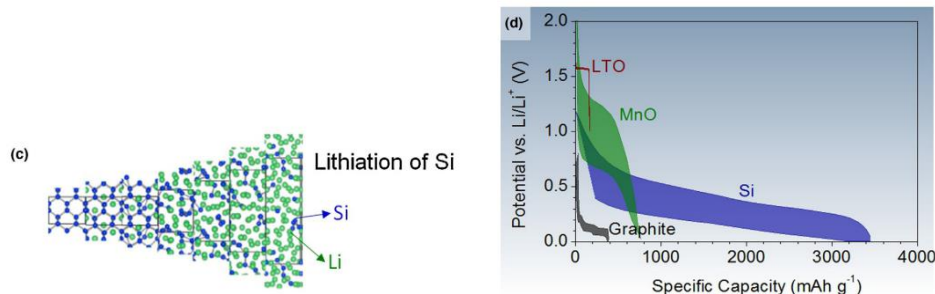
Recent attention has been paid to Se and Te because of their stronger electrical conductivities than S and their large theoretical volumetric capacities of 1630 mAh cm³ and 1280 mAh cm³ in the completely lithiated form, respectively Se and Te are more efficient at using active materials and have a greater rate capability than S because of their higher electronic conductivity. Similar to S, high-order polyselenides dissolve in Se-based cathodes, causing rapid capacity loss, poor cycle performance, and low coulombic efficiency. Se-based cathodes. Polytelluride dissolution has not been documented to date. Significant volume changes are also evident in Se and Te, as seen in Table 2. Se and Te, on the other hand, have the same melting point as S. To enhance their performance, both materials have been infiltrated into different porous carbon hosts (120,153,180) and disseminated or wrapped in conductive matrices (125,149) Te, on the other hand, is too costly for most purposes. Se and Te, on the other hand, are not likely to be employed in large-scale manufacturing because of their abundance (Fig. 1). Volume 18, Number Iodine in Materials Today Because of its high energy density and low self-discharge rate, the lithium-iodine main battery is an essential power source for implanted cardiac pacemakers. I₃ and I are formed during discharge from cathodic I, which is subsequently converted back into I during storage [122]. For most other uses of this chemical, however, its limited power capability makes it a problem. Iodine, triiodide, and lithium iodide all dissolve in organic electrolytes [122]. Iodine ions have been proposed as an alternative to LiI in lithium-flow batteries because of LiI's great solubility in organic solvents. Due to the low melting point of I, iodine has recently been injected into the pores of porous carbon (1138C). Iodine–conductive carbon black composite demonstrated a high discharge voltage plateau, strong cycle performance and a high rate capability attributable to improved electronic conductivity and inhibited active material dissolution [122]. [122]

graphitic and hard carbons

Carbon anodes have been the anode material of choice for Li-ion batteries for more than 20 years, and they remain so today. Electrochemical activity in carbon is caused by Li intercalation between graphene planes, which provides strong 2D mechanical stability, electrical conductivity and Li transport. Li intercalation (Fig. 6a). This method can store up to 1 Li atom every 6 C. Compared to lithium, carbon has low delithiation potential, high Li diffusivity, strong electrical conductivity, and minimal volume change during lithiation/delithiation lithiation/delithiation processes (Table 3). Because of its cheap cost, availability, moderate energy density, power density and cycle life compared to any other intercalation-type anode materials, carbon is a suitable choice. However, the volumetric capacity of commercial graphite electrodes (330–430 mAh cm³) is relatively limited compared to other cathode



materials (Fig. 2).



CLARIFICATION 6: Crystal structures of lithiated graphite, lithium titanate, and silicon during lithiation (reproduced with permission copyright (2014) American Chemical Society) and charge–discharge profiles at low charge/discharge rates, showing voltage hysteresis [191– 193]. (reproduced with permission copyright (2014) American Chemical Society).

There are two main kinds of commercial carbon anodes. Carbons with large graphite grains, such as graphitic carbons, may obtain near to theoretical charge capacity. Propylene carbonate (PC) is the ideal electrolyte because to its low melting point and rapid Li transfer, although graphitic carbons do not mix well with PC. This causes the graphite to exfoliate and lose its capacity because PC intercalates with Li⁺ between the graphitic surfaces. Li intercalation occurs in the basal planes even without solvent intercalation, hence the SEI is also selectively

TABLE 3

Properties of some commonly studied anode materials.

Material	Lithiation potential (V)	Delithiation potential (V)	D (cm ² s ⁻¹)	Volume change
Graphite [182,193–198]	0.07, 0.10, 0.19	0.1, 0.14, 0.23	10 ⁻¹¹ –10 ⁻¹³	10%
LTO [199–203]	1.55	1.58	10 ⁻¹² –10 ⁻¹¹	0.20%
Si [34,191,204–209]	0.05, 0.21	0.31, 0.47	10 ⁻¹³ –10 ⁻¹¹	270%
Ge [34,209–212]	0.2, 0.3, 0.5	0.5, 0.62	10 ⁻¹² –10 ⁻¹⁰	240%
Sn [34,209,213–215]	0.4, 0.57, 0.69	0.58, 0.7, 0.78	10 ⁻¹⁶ –10 ⁻¹³	255%
Li ₂ O [216] (amorphous)	N/A	N/A	5 × 10 ⁻¹² –5 × 10 ⁻¹⁰	N/A

[218] There are other formations on these planes. Uniaxial 10% strain is applied to edge planes during Li intercalation of single crystalline graphite [197,198]. A cell's cycle life may be shortened if the SEI is damaged by the high strain. These days, amorphous carbon has been applied on graphitic carbon to shield the sensitive edge planes from electrolyte and increase coulombic efficiency [219, 220]. Small graphitic grains with disorganised orientation make hard carbons less vulnerable to exfoliation than soft carbons, which contain larger graphitic grains. As a consequence, the volume growth of these grains is more uniformly distributed. Excess gravimetric capacity is also provided by nanovoids and flaws [182,221–223], giving a capacity more than the theoretical 372 mAh g⁻¹. Hard carbons are a high-capacity, high-cycle-life material because of their combination of these qualities. As a result, the coulombic efficiency is reduced in the initial few cycles due to the large percentage of exposed edge planes. Li-ion batteries have a severe capacity limitation due to the restricted Li supply that may be found in a fully charged cell. In addition, the vacant regions greatly decrease the particle density and hence limit the capacity of the volumetric capacity further. Finally, in carbon-based anodes, impurities like hydrogen atoms can also provide additional capacity [224]. Because of their increased voltage hysteresis, more irreversible capacity loss and lower volumetric capacities, such electrodes are unlikely to be marketed [223–223]. Oxide of lithium-titanium (Li₄Ti₅O₁₂/LTO) To far, despite the greater cost of Ti, lower cell voltage, and decreased volumetric capacity, LTO has been widely used because of its better thermal stability [51], high rate, and long cycle life (175 mAh g⁻¹ & 600 mAh cm³ theoretical). A "zero strain" intercalation process with a high lithiation potential lead to a high rate and stability. Due to lithiation/delithiation, LTO is deemed to have "zero strain" since it barely changes volume by 0.2% [201–203]. The charge–discharge graph shows a modest volt age hysteresis electrochemically (Fig. 6d). Anode SEI development and growth, which may impede liquid insertion and cause Li losses in graphite anodes, can be minimised because to the LTO's high equilibrium potential (1.55 V vs. Li/Li⁺) (Table 3). Stability is enhanced by

the absence of volume change even when an SEI is generated. Using LTO nanoparticles, like intercalation cathode material, results in greater rate performance at the price of decreased volumetric capacity [225,226]. The high potential of LTO inhibits Li dendrite growth even at high rates, making it exceedingly safe. Li-ion batteries with high power and long cycle life may benefit from LTO despite its reduced Li diffusivity and electrical conductivity. LTO anodes, however, do not totally prevent surface reactions. The organic electrolyte reacts violently with the LTO active ingredient, causing significant gassing in LTO [227]. It is possible to prevent this process from occurring by covering the electrode with carbon. However, carbon may also catalyse and speed up the disintegration and creation of an SEI, particularly at high temperatures. In spite of this, LTO anodes have an advantage over other anode materials in high power applications since they can endure for tens of thousands of cycles. Amalgamated materials, or alloying materials (Type B) Electrochemical alloying materials (i.e. Type B conversion materials as in Eq. (2)) at a low potential are referred to as 'alloying materials' in this context (preferably below 1 V). In spite of their great volumetric and gravimetric capacities, alloying materials are well known for their gigantic volume expansion during lithiation (Fig. 6c illustrates how this occurs for Si). This may lead to the loss of electrical contact between particles [232]. The SEI protective layer on anodes may be destroyed by volume change, leading in continual electrolyte breakdown, loss of lithium inventory, and increased cell impedance. For this reason, alloying anodes, particularly at high mass loadings, have a limited cycle life owing to the loss of active material [233] and rising cell impedance [234]. Carbon composites with alloying material particles that are tiny enough for mechanical stability, electron transport, and Li transport are often the most effective technique. This strategy also maintains Li diffusion routes inside the electrode. (which commonly requires a hierarchical structure such as Fig. 2b [235]). The active material may be encased in a carbon shell with enough empty space to allow for volume expansion to stabilise the SEI (Fig. 2e) [236–241]. This might theoretically help to stabilise the SEI and prevent smaller particles from sintering into bigger ones, resulting in longer cycle times even at higher mass loadings [23]. To further stabilise SEI and extend cycle life [242–244], electrolyte additives can be used, and binders with high stiffness and swell minimally can be used to provide additional mechanical stability when no carbon shell is used [245–249]. Binders that bond to the active material and have high stiffness can also be used to provide mechanical stability. There is yet no evidence that high mass loading electrodes with high volumetric capacity and long cycle life (103 or more cycles) in complete Li-ion battery cells can be produced. For this reason, the first few cycles of nanoparticle cycling result in significant SEI development and permanent capacity loss due to the particles' high surface areas. Because of its availability, low average delithiation potential, high gravimetric and volumetric capacity, low cost, chemical stability, and non-toxicity, silicon (Si) has garnered the most attention of all alloying materials. Due to its comparable features, such as lower gravimetric capacity and somewhat lower cell voltage, but better electrical conductivity, Sn has also attracted considerable attention. Even when particle sizes are reduced to the 10 nm range [250], Sn seems to be easily breaking (Fig. 2a). In spite of the fact that it is prohibitively costly for the majority of practical applications, Ge does not fracture even at greater particle sizes [251,252]. (Fig. 1a). [253] The fact that Ga is a liquid at ambient temperature is also noteworthy, but it's pricey. Although Zn, Cd, and Pb have excellent volumetric capacity, they have poor gravimetric capacity among the cost-effective Li alloying metals. In situ transmission electron microscopy (TEM) confirms that even with nano dimensions, Al suffers from severe fracture. Recent years have seen some attention paid to P and Sb. By simply ball milling the material with carbon, excellent electrodes may be made with both elements' high capacity [255,256]. The problem is that both of these elements are poisonous, have strong delithiation potentials, and Sb is also not particularly useful in the production of metal.

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Conclusion

This battery has distinct benefits and decades of development that have made it the high energy density, long cycle life, and efficient battery it is today. Despite this, new electrode materials are being developed to push the limits of cost, energy density, power density, cycle life, and safety, among other parameters. Other than their restricted electrical conductivity, sluggish Li transport, dissolution or other undesirable interactions with the electrolyte and low thermal stability and excessive volume expansion, many potential anode and cathode materials are also brittle in the mechanical sense of the word. Fig. 3 summarises the many strategies that have been used to solve these difficulties. Intercalation cathodes have been put on the market and conversion material technology is moving toward general commercialization. Li ion battery electrode materials research has been interesting in the past several

decades. Li-ion batteries will very sure have a bigger influence on our lives in the years to come as new materials and techniques are discovered.

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