Automotive Li-Ion Batteries: Current Status and Future Perspectives

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Lithium ion batteries (LIBs) are currently the most suitable energy storage device for powering electric vehicles (EVs) owing to their attractive properties including high energy efficiency, lack of memory effect, long cycle life, high energy density and high power density. These advantages allow them to be smaller and lighter than other conventional rechargeable batteries such as lead-acid batteries, nickel-cadmium batteries (Ni-Cd), and nickel-metal hydride batteries (Ni-MH). Modern EVs, however, still suffer from performance barriers (range, charging rate, lifetime, etc.) and technological barriers (high cost, safety, reliability, etc.), limiting their widespread adoption. Given these facts, this review sets the extensive market penetration of LIB-powered EVs as an ultimate objective and then discusses recent advances and challenges of electric automobiles, mainly focusing on critical element resources, present and future EV markets, and the cost and performance of LIBs. Finally, novel battery chemistries and technologies including high-energy electrode materials and all-solid-state batteries are also evaluated for their potential capabilities in next-generation long-range EVs.

1. Introduction

Transportation industries play an important role in the worldwide economy and social development. Unfortunately, they bring some negative effects as well, such as large depletion of fossil fuels and environmental pollution. Currently, almost one quarter of global energy-related greenhouse gas (GHG) emissions are contributed by transport vehicles.[1] To mitigate these problems, developing green, sustainable energy together with alternative-fuel vehicles, particularly battery-powered vehicles, has become a promising alternative in the automotive industry.

Although electric vehicles (EVs) have only recently gained widespread attention, they are not a new technology. In contrast to internal combustion engine (ICE)-powered vehicles (ICEVs), battery electric vehicles (BEVs) which were first built by Robert Anderson (Scotland) in 1834 have a longer history.[2] At that time, the battery had to be replaced after discharge owing to the shortage of rechargeable batteries. It was not until 1859, with the invention of the rechargeable lead-acid battery by Gaston Plante (France),[3] that electric cars became more practical. Until the dawn of the 20th century, BEVs became the dominant type of automobiles. However, with the invention of gasoline-powered vehicles in 1910,[4] electric automobiles were gradually replaced from the market due to their relatively high cost, limited range (40 miles) and speed (45 miles per hour). Since then, a clear majority of people have driven gasoline-fueled vehicles instead of BEVs. During the 1970s, electric automobiles were revived again because the oil embargo and energy crisis in

1973 resulted in a rapid rise in the price of gasoline.[5,6] During the next several decades, the EV market was covered by lead-acid batteries (the first generation, General Motors (GM)'s EV1,[7,8] range: 80-100 miles) and nickel-metal hydride (Ni-MH) batteries (the second generation,[9,10] range: 100-140 miles) in succession. Owing to poor sales and limited competitiveness with conventional ICEVs, GM ultimately cancelled its leasing program.

In 1991, the successful commercialization of rechargeable lithium ion batteries (LIBs) led to the reduction of market shares of conventional Ni-MH batteries and nickel-cadmium (Ni-Cd) batteries.[11-13] To date, LIBs have dominated the major market of consumer electronics & devices. Among various commercialized automotive batteries including lead-acid batteries (energy density: 40-60 Wh kg^{-1}), Ni-MH batteries (energy density: 40-110 Wh kg^{-1}), and LIBs (energy density > 150 Wh kg^{-1}),[14] LIBs are the most suitable technology to fulfill the requirements of next-generation EVs owing to their flexibility, higher energy and power densities, lower cost, relatively less pollution, and smaller and lighter cell designs.[15,12,16] Meanwhile, the continuous improvement of LIB performance and cost has also facilitated their adoption in the automotive industry. Moreover, with the signing of the Paris Agreement in 2016 for reducing global GHG emissions,[17-19] global carmakers are speeding up the pace of LIB-powered EV development. Compared to conventional ICEVs, however, EVs propelled by LIBs still suffer from some barriers (such as range,[20,21,8] charging rate,[22] lifetime,[23] high cost,[24-26] safety,[27] reliability,[28] limited charging infrastructures,[29-31] etc.), thus impeding their widespread adoption.

Battery performance and cost are the two most important factors for battery-powered EVs. The former largely determines the driving distance of EVs while the latter dictates if EVs are cost-competitive with ICEVs and can become affordable in the future. According to the United States Department of Energy (DOE) 2022 target, a further increase in battery energy density is mandatory to meet future driving range requirements (at least 300 miles per charge) and battery costs need to be reduced to $125/kWh.[32] Besides range and cost, some other crucial factors that influence the extensive market penetration of electric automobiles require further improvement including battery lifetime (at least 10 years), safety, and reliability, and charging infrastructure. Besides the required improvement of battery technology, the mass adoption of electric automobiles also depends on government incentives[33] (such as registration tax exemption) and consumer attitudes and behaviors[34]. To achieve this goal, all participants in various areas including government, material manufacturers, battery industries, automotive industries, and electronics will have a unique role to play in such a great challenge. On the government aspects, many countries have provided strong support in the development of electric cars. For example, the United States pledged $2.4 billion in federal grants to support the development of batteries and next-generation EVs.[35] The European Union has collectively invested EUR 43 billion (including public and private investments) into EV-related research (EVUE 2012), which is expected to increase to EUR 225 billion across all 28 member countries.[36] China is investing US$15 billion in the electric automotive industry.[37] Moreover, in 2015 China became the largest EV market in the world.[38] Recently, based on the state grid corporation of China, the charging infrastructure investments for EVs will reach RMB 200 million (US$29 billion) in 2020, which includes installing 29,000 charging poles by 2017 and 120,000 charging poles by 2020.[39]

On the aspects of carmakers, more and more auto companies have devoted greater effort to develop electric cars. Recently, three major German carmakers (Volkswagen, Daimler, and BMW Groups) committed investments of over EUR 50 billion to develop electric automobiles in 2017. Moreover, Volkswagen Group has declared its intent of being the largest EV maker by 2025, aiming to overtake rival Renault-Nissan. Mercedes Benz, a division of Daimler, plans to invest EUR 10 billion in electrification.[40] On the battery industry aspect, Tesla is building new battery factories marketed as "Gigafactory" in Nevada of the United States in order to enhance production yield of battery packs. Upon the completion of "Gigafactory", the projected capacity would be 150 GWh/year (associated production volume of electric cars of 1.5 million units per year).[41,42] At that time, the production cost of battery packs for EVs will reduce by 30%, expected by Tesla.[43] Therefore, LIB production is rapidly expanding to the transportation industry, where along with grid and industrial energy storage, they have a bigger future market than the consumer electronics & devices (Figure 1).

Herein, we present a comprehensive review of the latest advances and challenges of LIB-powered EVs. First, we provide a comprehensive analysis of automotive LIBs in terms of market, cost, and critical element resources. Then, the current state-of-the-art automotive Li-ion chemistries including $LiMn_2O_4$ (LMO), $LiFePO_4$ (LFP), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), and layered $LiNi_{1-x-y}Mn_yCo_zO_2$ (NMC) have been discussed and the barriers to widespread adoption of electric cars are also summarized. Finally, considering theoretical energy limitations of current Li-ion chemistries (lithium transition oxide cathode and graphite anode: 350 Wh kg^{-1} at the cell level) for automotive industries,[44] new high-energy and high-capacity battery materials including Ni-rich NMC cathode materials, silicon-based anode materials, and innovative battery chemistries including all-solid-state batteries (SSBs) are evaluated and discussed for next-generation EV applications in the short and long terms.

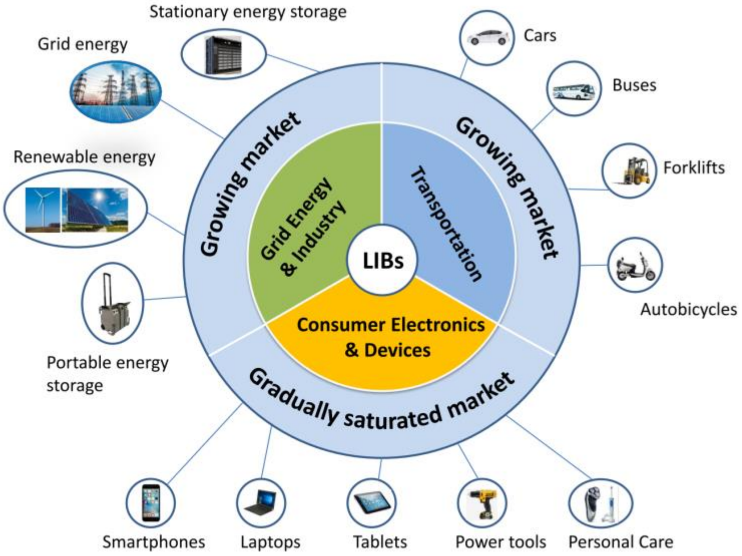

Figure 1. The applications of LIBs in the three main fields including consumer electronics & devices, transportation, and grid energy & industry.

2. Market, cost, and critical material analyses for automotive batteries

2.1 Automotive battery market

Over the past decade (2006-2016), the six-fold increase in the total produced LIB capacity (from 11 GWh in 2006 to 78 GWh in 2016) reveals the rapid development of this technology, especially for the automotive market (Figure 2a).[45] Global demand growth has approximately doubled every 5 years, and it is predicted that global LIB capacities will reach 125 GWh (2020), 220 GWh (2025), and 390 GWh (2030), respectively.[46] Although automotive LIBs have shown rapid development, the total market share of electric cars within new cars sold is still very low. As shown in Figure 2b, the global market share of new plug-in EVs (PEVs) was 0.86% in 2016, up from 0.62% in 2015 and 0.38% in 2014.[1]

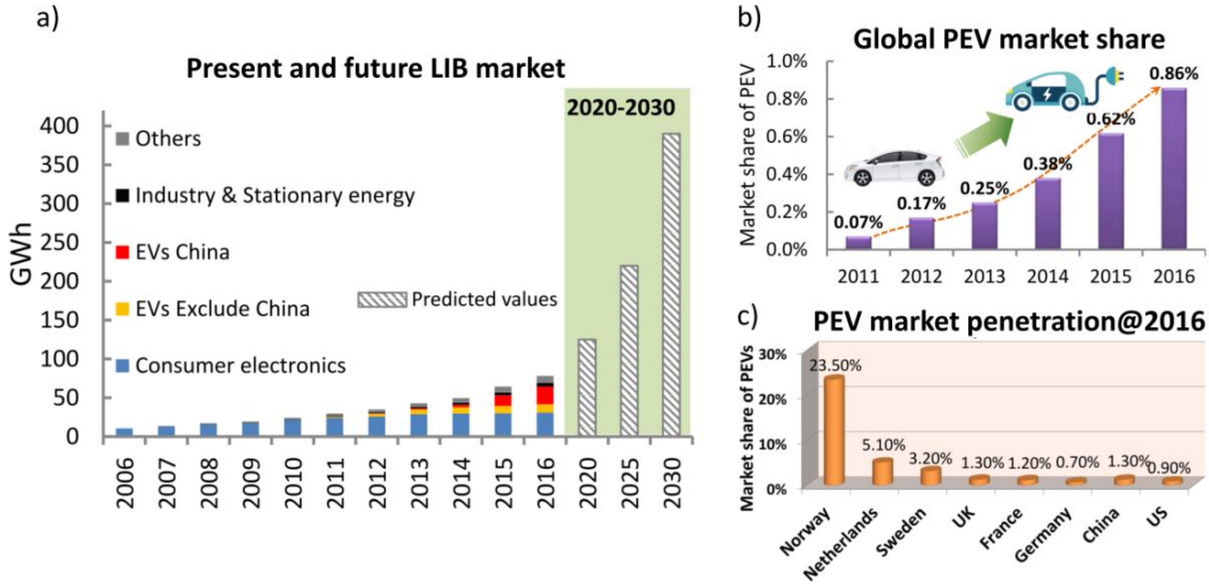

Figure 2. a) The present (2006-2016) and future (predicted values in 2020-2030)[46] LIB market including consumer electronics, EVs, industry & stationary energy, and

others, b) the market share of PEV annual sales in the global new car sales in recent 5 years, c) the PEV market penetration of different countries in the total its domestic light vehicles sold in 2016.

Besides the efforts of carmakers, some governments have also initiated incentive policies for pushing EV development. For instance, the European Union (EU) has been relatively aggressively driving its electric transportation industry by facilitating a competitive approach to their adoption. The British government gave Nissan a £20.7 million (US$32.5 million) grant to develop a new plant that will serve as the manufacturing base of the Nissan Leaf for all of Europe.[47] Toyota has already sold more than 6 million of its flagship Prius models, roughly 10% of which were in Europe. Therefore, signs of a shift toward fully electrified powertrains are becoming apparent. However, even in Europe, the market shares of EVs within total new car sales in each country in 2016 were less than 5% (except Norway (23.5%) and the Netherlands (5.1%)) (Figure 2c),[48] indicating the overall nascent stage of EV adoption. Other countries hold EV market penetration percentages of 3.2% (Sweden), 1.3% (UK), 1.2% (France), 0.7% (Germany), 0.9% (US) and 1.3% (China), respectively.

According to Navigant research, the global market for automotive LIBs is expected to grow from $7.8 billion in 2015 to $30.6 billion in 2024.[49] Different countries and research institutes have given optimistic opinions and forecasts for the future EV market, largely pinned by falling battery prices and increasing EV ranges.

Dutch Bank ING forecasted that all new cars sold in Europe could be electric by 2035, further stating that fully electric cars would become the rational choice for European consumers between 2017 and 2024.[50] UK's National Grid said that 90% of new cars in Britain would be expected to be electric by 2050. By 2024, the cost of ownership (including buying and fueling) of EVs in Germany is predicted to be the same as conventional ICEVs. Consumers' concerns over "range anxiety" should evaporate in the 2020s, although this is dependent on the expectation that EV driving distance per one charge will increase from 100-150 miles for most models today to 400 miles and above in the next decade. In addition, by the end of the next decade, carmakers will begin focusing solely on electric models. Swedish firm Volvo has marked the beginning of this trend, indicating that it would only develop hybrid, plug-in hybrid or fully electric cars from 2019.[50]

Although the above projections optimistically predict huge market growth of electric automobiles, current EV production is still in its infancy and many future factors are not certain. Various energy storage technologies needed to enable long-range EVs are either not mature enough to be cost-competitive with internal combustion engine technologies, or are still in the early stages of research and development. Therefore, they require additional attention before their potential can be fully achieved. Governments could play an important role in accelerating the development and deployment of energy storage technologies by supporting targeted demonstration projects for promising storage technologies and by eliminating price distortions that prevent storage technologies from being compensated for the suite of services they provide. To date, there are still many challenges and technological barriers for limiting EV widespread adoption. Thus, developing electric automobiles requires government, industry, academia and financial stakeholders to work together to overcome existing various barriers.

2.2. Battery costs for EVs

While the speed of electric automobile adoption can be hastened by regulation and government subsides, it will also depend on the total of cost ownership relative to ICEVs, where the price of the battery packs is a critical factor. Even if all of the other performance criteria are achieved, too high of a cost will seriously impede EV commercial success. To enable EVs that are cost-competitive with ICEVs, the cost of battery packs needs to fall below $125/kWh, which is also a target set by the US DOE for 2022.[24] In this regard, pursuing continuous cost reduction as well as simultaneously continuing to improve performance is an ultimate goal for propelling commercial application of EVs. This section will mainly focus on the analysis of current and future battery costs for automotive applications.

From 2010 to 2016, LIB costs gradually decreased at a rate of almost 20% per year (Figure 3b).[24] Many methodologies or models have been used to calculate and predict LIB battery costs, all of which heavily depend on production volume assumptions. Learning curves show the development of production cost as a function of cumulative production and have been considered as the most objective method to project cost of technology in the future. Experience curves describe the production price development to account for cost factors including R&D and depreciation which are also important to project future cost. Schmidt et al. analyzed the future cost of electrical energy storage based on experience curves,[25] revealing that regardless of the specific battery technology, capital costs are on a trajectory towards about $340/kWh for installed stationary systems and about $175/kWh for battery packs once 1 TWh of capacity is deployed.[25] Cumulative investments of $175-510 billion would be required for any technology to reach 1 TWh deployment, which could be achieved by 2027-2040 based on market growth projection. Worldwide investment in clean energy has a compound annual growth rate (CAGR) of 15.5% (2004-2015) and reached $349 billion in 2015, of which 78% was spent on wind energy and solar energy while only 3% was spent on electrical energy storage ($10 billion).[51,52] To achieve the cumulative investment of $175-510 billion identified to result in 1 TWh cumulative installed capacity, 0.9-2.5% of annual clean energy investment must be spent on each energy storage technology.

Recently, many automotive original equipment manufacturers (OEMs) have enlarged or plan to enlarge their battery production scale for pushing the rapid market penetration of electric cars. A typical example is Tesla Corporation. To enlarge production capacity, Tesla has built its own battery factory- Gigafactory in Nevada of the US. This Gigafactory began mass production of cells in January 2017, and is claimed to help reduce the production cost for their EV batteries by 30%.[53] Its projected capacity for 2018 is 50 GWh/year and its final capacity upon completion of the whole factory is planned to be 150 GWh/year. Tesla expects to achieve a cost target for battery packs under $100/kWh by 2020. Besides the Gigafactory in Nevada, Tesla plans to build other Gigafactories in New York and Europe.[54] With the continuous increase of production capacity of batteries, battery costs will be further reduced, which is very favorable for future market penetration of EVs.

Besides production volume, other solutions including optimizing cell fabrication (e.g. 18650 cylindrical cell is converted to 21700 cylindrical cell with a 35% increase of energy density).[55], reducing manufacturing costs, and enhancing pack assembly efficiency are able to be used to lower the battery cost (Figure 3c). In general, the entire battery costs for EVs consist of the cell, module and pack (including battery management systems, sensors, cooling system, etc.). Cell costs are composed of the cathode, anode, electrolyte, separator, and other materials (including Al foil, Cu foil, binder and conducting agents), as well as cell manufacturing (labor, energy, utilities, R&D, overheads, warranty, margin, etc.). As for cell costs, raw material cost accounts for 50-70% of the total cost while cathode materials alone possess the highest occupancy of 22%.[45] Thus, lowering raw material cost or developing new low-cost and high-energy battery chemistries would be very favorable for the reduction of battery costs in the future.

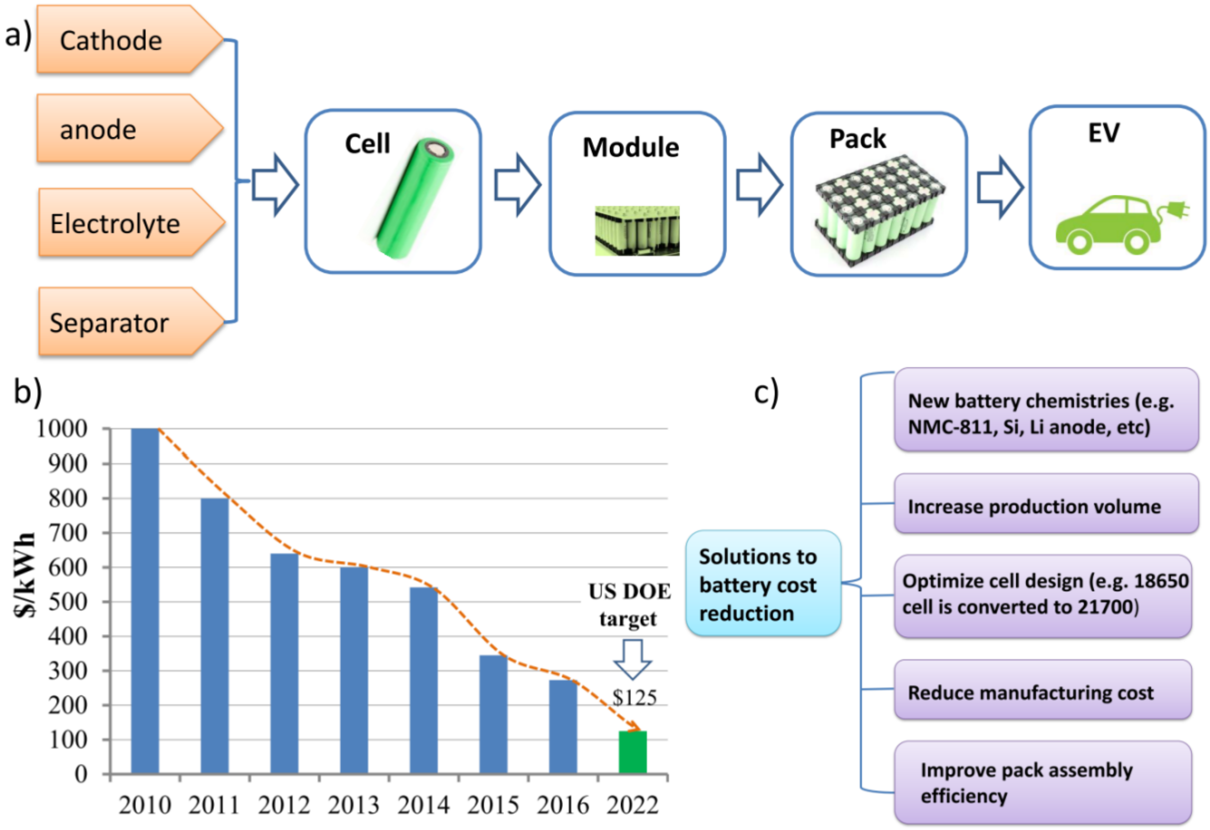

Figure 3. a) The schematic diagram of the manufacturing process of battery packs for EVs, b) cost evolution trend of LIB from 2010 to 2016 (Date source: Bloomberg New Energy Finance)[56], c) The potential solutions to battery cost reduction.

2.3 Critical element resource analyses

Many elements are used in LIBs including lithium, cobalt, nickel, manganese, graphite, aluminum, copper, carbon, titanium, and silicon. These elements are harvested from natural mines in the earth's crust or recovered from brine. As discussed previously, automotive application of LIBs will rapidly increase in the coming years, which will directly incur high production of raw materials including lithium, cobalt, nickel and manganese. Nickel, manganese, graphite, aluminum, and copper already have sufficient production volumes established for other industries and have no detectable supply concerns.[57] As such, several critical raw materials (e.g. lithium, cobalt) should be evaluated through the use of a scenario-based supply and demand analysis owing to their limited resources (lithium reserves: 12-14 million tons (Mts) based Li metal equivalent; cobalt reserves: 7.1 Mts), restricted extracting technology, and high demand from growing automotive industries and large-scale grid energy storage.[58]

Lithium resources

Lithium is usually present in trace amount in minerals/ores, brines, clays and sea water. However, the extracting lithium from brines and ores is only economically feasible at the moment. Thus, the majority of lithium is currently from brines. According to the estimates of the USGS in 2011, the total lithium resources are around 29 Mts. The largest resources are mainly in Bolivia (9 Mts), Chile (>7.5 Mts), China (5.4 Mts), and Argentina (2.6 Mts).[59]

As far as lithium is concerned, until recently it was used for a variety of industrial purposes (ceramic/glass, lubricants, aluminum production, catalysts for rubber production) instead of batteries (which were <5% in the whole lithium market).[60] However, the current major use of lithium is for batteries, accounting for 39% of the global lithium market (ceramic/glass: 24%; lubricants: 12%, medical: 5%, other: 20%) in 2015.[61] In 2025, the battery market will demand almost two times the entire lithium market in 2015, representing 70% of the global lithium market, including 38% for automotive applications. In general, lithium demand for BEVs (8-15 kg Li for 50-100 kWh EV battery pack) is far higher than those of portable electronics (smartphones: ~2 g Li; tablets: 2-6 g Li; laptop PC: 15-20 g Li).[62] Thus, lithium consumption will be mainly driven by EVs.

To predict lithium demand in the short term (2016-2025) and in the long term (2016-2035), lithium consumption and supply are roughly calculated by two scenarios: low-growth scenario (15% CAGR) and high-growth scenario (30% CAGR), since the CAGR of total battery production capacity (GWh) was between 15% and 30% during 2011-2016.[45] The total market for LIBs in 2016 was ~78 GWh[45] and the average required lithium amount for LIBs is assumed to be 151 g/kWh.[59] Using these figures, the cumulative total amount of lithium demand by 2025 is calculated to be 0.24 Mts (with 15% CAGR) and 0.50 Mts (with 30% CAGR). Given the average lithium supply]of 50,000 tons in 2017,[59] the corresponding total lithium supply is calculated to be 3.5 Mts (assuming 15% CAGR) during 2016-2025 (Figure 4a). If it is assumed that half of all lithium production is used for batteries, these results clearly indicate that global lithium production capability can easily fulfill the corresponding demand in the short term (2016-2025). To further examine if LIBs suffer from lithium supply risks in the long term until 2035, the lithium demand and production were also calculated based on the above two scenarios. As displayed in Figure 4a, the cumulative lithium demands are 1.20 Mts (15% CAGR) and 7.40 Mts (30% CAGR), respectively. Although the cumulative lithium demand with the high scenario during 2016-2035 is still less than that of available lithium reserves (12-14 Mts), it surpasses the predicted cumulative lithium production (5.12 Mts with 15% CAGR). Therefore, improving the lithium supply capacity and extracting technology will be necessary if a high EV sales growth rate occurs in the long term. However, it is very difficult to give an accurate prediction for lithium demand and supply because it largely depends on many factors, such as battery production volume, growth rate, geopolitics, the number of new plants for extracting lithium, or changing technical factors for lithium refinement. In this regard, developing recycling programs to recover lithium from used batteries may be a necessary solution for mitigating potentially unsustainable lithium consumption problems.

Cobalt resources

Besides lithium, cobalt is also a critical element in cathode materials because it enables increased energy density and structural stability but also brings some drawbacks such as toxicity, high price, and limited production. Moreover, 50% of cobalt reserves and production are concentrated in the Democratic Republic of the Congo and Zambia.[57] In general, cobalt has been used in many industrial areas such as batteries, superalloys,[63] catalysts,[64,65] and magnets.[66] Among them, the battery industry accounted for 50% of the total cobalt industrial application (Figure 4d) in 2017.[62] Currently, the identified global cobalt resources are around 25 Mts while the economically extractable cobalt reserves were estimated to be 7.1 Mts in 2016. The total world production of cobalt amounted to 0.12 Mts in 2016.[67]

Among the state-of-the-art Li-ion chemistries, only LCO, NCA and NMC use cobalt as active components. Owing to the relatively low amount of cobalt (10 atom%) in NCA, NMC and LCO are used to estimate the cobalt demand in this evaluation. For LCO, the lithium demand will be assumed to have a 0% CAGR in the future since it has gradually reached saturation in the market from 2011-2016 without an evident future growth. The market shares of NMC in the whole LIB market are 26% (2016) and 41% (prediction for 2025).[45] To be relatively accurate in calculating cobalt demand, the average NMC market share (33.5%) is used. For simplification, only NMC-111 is employed to calculate the cobalt consumption although Ni-rich and Co-less NMC chemistries will be developed in the future. As shown in Figure 5b, the cobalt demand during 2016-2025 is roughly estimated to be from 0.44 Mts (15% CAGR) to 0.72 Mts (30% CAGR) while the projected production is 2.44 Mts (15% CAGR), revealing good matching between cobalt supply and demand in the short term. In the long term (2016-2035), total cobalt demand is calculated to range from 1.50 Mts (15% CAGR) to 7.47 Mts (30% CAGR). While the projected cobalt production (12.30 Mts with 15% CAGR) would meet this demand, the cobalt demand with 30% CAGR would outpace the economically available cobalt reserves (7.1 Mts), leading to a serious cobalt supply risk in the following 20 years. Thus, improving the extraction technology of cobalt mines to increase feasible cobalt reserves is an important future objective for making cobalt supplies respond efficiently to demand changes. Without significant improvements in this regard, the continuously increased cobalt demand and resultant supply risk could require battery producers to decrease its use in batteries. At present, however, the use of cobalt is still highly necessary for cathode materials owing to its stabilizing effect in layered transition metal oxides and high energy density. As such, developing Co-lean (e.g. NMC-622, NMC-811) cathodes for replacing present NMC-111 is a main task in the near future. In the long run, cobalt-free materials will be more attractive and cost-competitive. On the other hand, similarly to lithium, recycling of cobalt could play a critical role in mitigating a demand and supply matching problem in the future.

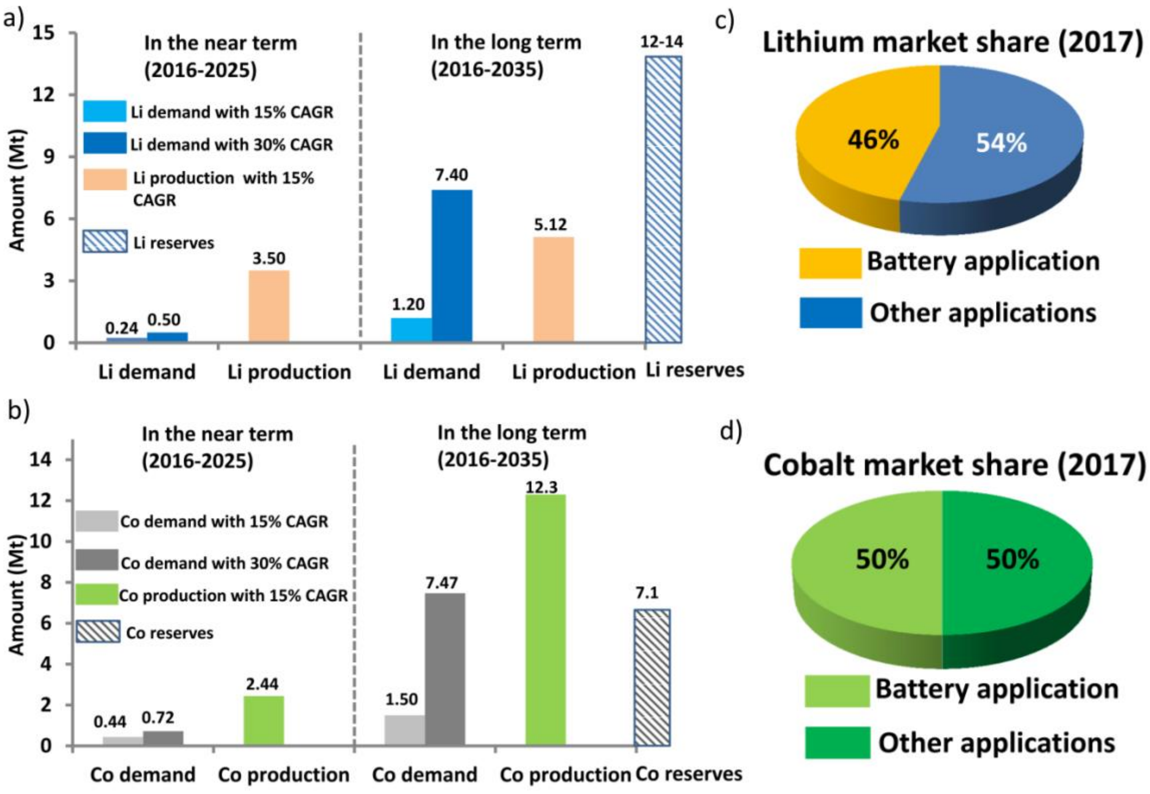

Figure 4. The estimated demand and production for a) lithium and b) cobalt in the short term (2016-2025) and in the long term (2016-2035). Note that only the demand of the battery industry for lithium is analyzed. The estimated demands for lithium and

cobalt are based on the actual total annual capacity (78 GWh) in 2016 and the productions for lithium and cobalt are based on their respective actural production for lithium (0.05 Mts in 2017) and cobalt (0.12 Mts in 2016).[46] The calculations are based on two scenarios with 15% and 30% CAGR for lithium and cobalt. For cobalt, it is only used for LCO, NMC and NCA chemistries in which LCO keeps negligible growth while NCA contains only 10 atom% Co. Thus, the cobalt demand is roughly calculated based on LCO with 0% CAGR and NMC with 15% and 30% CAGR. For simplification, only NMC-111 was used to calculate the cobalt demand although Ni-rich and Co-less NMC chemistries will be developed in the future. c, d) the current market share of lithium and cobalt in the total industry applications in 2017.

3. The state-of-the-art Li-ion chemistries for automotive batteries

LIBs comprise a family of battery chemistries that use various combinations of cathode and anode materials. Each combination has distinct advantages and disadvantages in terms of performance, cost, safety, and other parameters. Currently, the most prevalent battery technology for consumer electronics is lithium cobalt oxide (LCO). However, this chemistry is not suitable for automotive applications owing to its intrinsically structural instability in the over-delithiated state, leading to safety risks.[68] Moreover, the limited resources and high cost of cobalt is a significant barrier to its widespread application for electric automobiles. Compared to LCO, other cathode materials including spinel LMO, NCA, NMC and LFP have become the most prominent battery chemistries for EVs because they not only possess more stable crystal structures but also have much more abundant resources and lower cost, thus showing large application potential for EVs. All automotive battery chemistries require elaborate monitoring, balancing, and cooling systems to control the chemical release of energy, prevent thermal runaway, and ensure safety and a long lifespan. On the technical side, competing LIB technology can be compared across five aspects: energy density, power density, safety, cost and life span (Figure 5). On the business side, battery cost is one of the major barriers because high price will impede the widespread adoption of EVs. In the near future, automotive manufacturers will aim to reduce battery costs by various favorable solutions such as developing low cost battery materials, increasing production volume, decreasing manufacturing cost, optimizing cell design, etc. (this will be further discussed in the following sections).

To date, LMO, LFP, NCA, and NMC battery technologies have been successfully adopted by many carmakers such as Tesla, BMW, BYD, Chevrolet, Mercedes Benz-Daimler, Volkswagen, Nissan, etc. With ever-increasing demand of electric cars for mitigating oil consumption and reducing GHG emissions, the production volume of the major four battery cathode materials has correspondingly increased. The yield of the cathode materials reached over 180,000 tons in 2016, and could grow to over 400,000 tons in 2025.[45] In 2016, NMC, LFP and LCO accounted for 83% of the whole market share, which are mainly used for EV application except LCO (LCO is mainly used for electronic devices including smartphones, tablets, and laptops). By 2025, NMC battery technology is expected to increase its market share from 26% to 41% owing to its higher energy density than LFP while NCA and LMO will maintain stable occupancies of the total market.[1] NCA technology is mainly used by Tesla, while most other automakers use LFP, NMC and LMO or blended NMC and LMO technology. Given their relatively mature technologies, such battery technologies will still dominate the EV market in the foreseeable future before new types of battery chemistries become mature enough for automotive application.

Table 1 gives an overview of various cell chemistries (LFP, LMO, NCA, NMC and their blended systems) for automotive applications. With the rapid development of EV industries, specific energy of LIB has also undergone a fast increase in recent years. Until now, the achieved highest gravimetric and volumetric energy densities at the cell level are 250 Wh kg^{-1} and 670 Wh L^{-1} (based on 18650-type cells), respectively.[69] The current energy content of EVs has continuously increased to 100 kWh and above, and longer driving ranges (over 300 km).

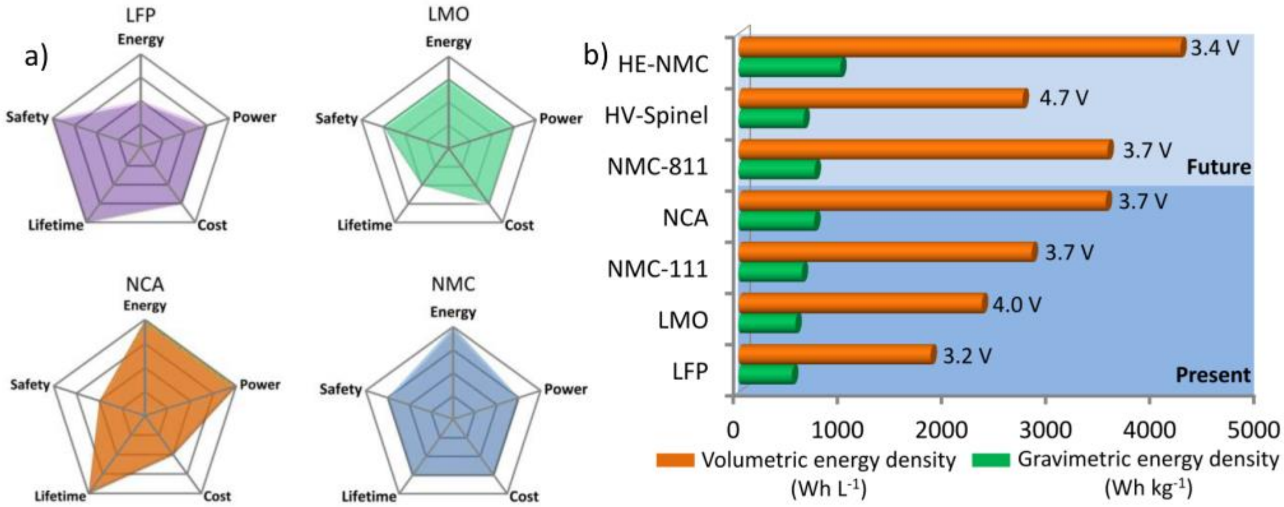

Figure 5. a) Key-performance parameters of four current battery chemistries (LFP, LMO, NCA, and NMC) for EVs. The inside and outside represent a low and high value, respectively. b) Volumetric energy densities and gravimetric energy densities of various electrode materials at a material level. NMC-811, HV-Spinel and HE-NMC represent $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, spinel $LiNi_{0.5}Mn_{1.5}O_4$ and $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M=Ni, Mn, Co), respectively.

3.1 LFP technology for EVs

In 1996, JB Goodenough et al. developed lithium iron phosphate (LFP) as a potential cathode alternative to replace structurally unstable LCO upon overcharge.[70] Since then, LFP has attracted a large amount of attention owing to excellent thermal stability, long cycle life, enhanced safety and tolerance if abused. Importantly, LFP is more tolerant to full charge conditions and is less stressed than other lithium-ion systems if kept at high voltage for a prolonged time, leading to superior structural stability and cycling performance.[71] Unfortunately, such material possesses low electronic conductivity (~ 10^{-9} S cm^{-1}) compared to lithium metal oxides. To enhance structural and surface conductivity, metal doping and conductive agent coating onto LFP electrodes are two efficient solutions,[72] leading to a remarkable increase of the achievable capacity at an acceptable charge/discharge current density. In addition, nanoscale materials can effectively shorten electronic and ionic transport lengths,[73] thus contributing to enhanced electrochemical performance. To date, carbon-coated nano-LFP materials have been successfully commercialized by many battery manufactures including A123 and BYD.[74,75] Up to now, LFP technology has been widely used in many electric cars, such as BMW Active Hybrid 3 and 5 series, Chevrolet Spark, and BYD (e6).[76,77] Among them, the BYD group mainly uses LFP as its power drivetrains for EVs including e-cars, e-buses, and e-forklifts.[78]

As a trade-off, LFP's lower nominal voltage of 3.3 V/cell reduces the specific energy below those of cobalt-based battery chemistries. With most batteries, cold temperature reduces performance and elevated storage temperature shortens the service life, and LFP is no exception. LFP has a higher self-discharge than other Li-ion batteries, which can cause balancing issues with aging. This can be mitigated by employing high quality cells and/or using sophisticated control electronics, both of which increase the cost of the pack.[79,80]

Despite these solutions, LFP technology for automotive applications still faces a limited energy density of ~120 Wh kg^{-1} at a cell level, close to the maximum limitation (~ 170 Wh kg^{-1}). This is much lower than the requirement of energy density

(> 250 Wh kg^{-1} at a cell level in 2025) for next-generation EVs.[76] Furthermore, owing to its low volumetric energy density (220 Wh L^{-1}), LFP is suitable for heavy-duty applications (e.g. buses, trucks) than for portable electronics and e-cars since volumetric specific energy is more critical than gravimetric specific energy. Due to this drawback, layered NMC, NCA and their blends of NMC/NCA and LMO/NMC will likely become the main targets of OEMs owing to their relatively higher specific energy. Besides automotive applications, LFP still has a large potential market in power supply systems owing to its low cost and long cycle life.

Table 1. Various LIB cell chemistries for EVs.

Cell chemistry (cathode/anode)		Cells						Battery packs		EV Model
		Producer	Type	Capacity (Ah)	Voltage (V)	Energy density (Wh kg^{-1})	Energy density (Wh L^{-1})	Energy (kWh)	Range (km)	
LFP	LFP/C	A123	Pouch	20	3.3	131	247	21	130	Chevrolet spark EV (2012)
	LFP	BYD	Prismatic	-	3.3	120	220	61	300	BYD e6 (2010)
NCA	NCA/C	Panasonic	Cylindrical	3.2	3.6	236	673	60-100	330-500	Tesla S (2012)
	NCA/Si-C NCA/SiO-C	Panasonic	Cylindrical	3.4	3.6	236	673	60-100	330-500	Tesla X (2015)
	NCA/Si-C	Panasonic	Cylindrical	4.75	3.6	260	683	75-100	350-500	Tesla 3 (2017)
NMC	NMC/C	Panasonic/Sanyo	Prismatic	25	3.7	130	215	24	190	VW eGolf (2015)
	NMC/LTO	Toshiba	Prismatic	20	2.3	89	200	20	130	Honda Fit EV (2013)
	NMC/C	Li-Tec	Pouch	52	3.65	152	316	17	145	Smart Fortwo EV (2013)
	NMC/C	SK Innovation	Pouch	38	3.7	-	-	27	145	Kia Soul EV (2014)
	NMC/C	LG Chem	Pouch	56	3.65	186	393	60	383	Chevrolet Bolt (2016)
	NMC/C	LG Chem	Pouch	59	3.7	241	466	41	400	Renault Zoe (2017)
Blended chemistries	NMC-LMO/C	Li energy Japan	Prismatic	50	3.7	109	218	16	160	Mitsubishi i-MIEV (2008)
	NMC-LMO/C	Samsung SDI	Prismatic	63	3.65	172	312	24	140	Fiat 500e (2013)
	NMC-LMO/C	LG Chem	Pouch	16	3.7	-	-	35.5	160	Ford Focus EV (2012)
	NMC-LMO/C	LG Chem	Pouch	36	3.75	157	275	26	150	Renault Zoe (2012)
	LMO-NCA/C	AESC	Pouch	33	3.75	155	309	24	135	Nissan Leaf (2010)
	LMO-NCA/C	AESC	Pouch	40	3.75	167	375	30	172	Nissan Leaf (2015)

C: graphite; LTO: $Li_4Ti_5O_{12}$; Si: silicon; LFP: $LiFePO_4$; LMO: $LiMn_2O_4$; NCA: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$; NMC: $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. Data are from references.[81-83]

3.2 LMO technology for EVs

Spinel LMO was first reported by M. Thackeray and co-workers in 1983.[84] In 1996, Moli Energy commercialized such materials as cathodes for LIBs. Compared to LCO, LMO possesses a more stable spinel structure, lower cost, non-toxicity, and three-dimensional Li^+ diffusion pathways. Particularly, Li^+ ions can occupy the interstitial spaces defined by $[Mn_2O_4]$ polyhedral frameworks, thus providing better rate capability compared to materials with two-dimensional frameworks for Li^+ diffusion.

One main disadvantage of LMO is its low capacity (theoretical capacity: 148 mAh g^{-1}). In addition, it suffers from poor high-temperature performance because of its instability in the electrolyte, leading to Mn dissolution (disproportionation reaction of Mn^{3+} ions into Mn^{2+} and Mn^{4+}) and capacity loss.[85,86] Among the four major Li-ion chemistries, LMO shows moderate safety and relatively low specific energy. Despite the drawbacks of LMO, it possesses a cost-competitive advantage with the lowest price (< 10 \$ kg^{-1}) among various electrode materials, which is very crucial for pushing EV commercial applications. As such, most LMO batteries blend with NMC (to be discussed in the following section) to synergistically improve the specific energy and prolong the lifetime for EV application.[87] This combination brings out the best in each system, and the LMO/NMC combination has been employed for most EVs such as the Nissan Leaf, Chevy Volt, BMW i3, etc. LMO, which typically constitutes 30% in the LMO /NMC composites, provides high current boost on acceleration while the remaining NMC part offers the long driving range. Thus, in the future, the LMO demand will be mostly driven by LMO/NMC blended composites in EVs. Such composite cathodes could replace LFP in China for the application of electric cars and electric buses.

3.3 NCA technology for EVs

As an alternative to LCO, layered lithium nickel oxide ($LiNiO_2$: LNO) has been proposed and researched owing to its high theoretical capacity of 275 mAh g^{-1} and relatively lower cost (Ni is much cheaper than Co).[88] Unfortunately, stoichiometric LNO with a Li/Ni ratio of 1:1 is difficult to synthesize because it often results in Li-deficient $Li_{1-x}Ni_{1+x}O_2$ with part of the Ni^{2+} ions in the Li layer,[89] due to the similar ionic radii of Li^+ (0.76 Å) and Ni^{2+} (0.69 Å). Moreover, the synthesis of LNO requires the introduction of O_2 atmosphere.[90] To enhance the cycle stability of LNO and simultaneously mitigate its synthesis problems, heteroatom doping has been proved as an effective solution by forming the $LiNi_{1-x}M_xO_2$ (M=Co, Mn, Al, etc) phase.[91-93]

Lithium nickel cobalt aluminum oxide (NCA: $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) can be prepared by dual doping of Co and Al into the LNO structure. The major reason for doping of these two elements together is as follows. Al incorporation into $LiNiO_2$ can minimize detrimental phase transition and improve the thermal stability of $LiNiO_2$.[94] Upon repeated Li extraction/insertion process, Al^{3+} can keep the crystal structural stable. Moreover, the presence of Al^{3+} can increase operation voltage owing to weakening of the Ni-O bond by the stronger Al-O bond through the inductive effect.[95,96] Co substitution at the Ni sites can reduce cation mixing and also stabilize the layered structure, and the formation of Ni^{2+} can be effectively hindered by Co^{3+} incorporation.[97,98] In addition, compared to LNO, the $LiNi_{1-x}Co_xO_2$ phase is easily prepared without the necessity to use oxygen atmosphere. Co^{3+} is also electrochemically active, which can compensate the capacity in NCA. Finally, the double doping of trivalent Co and Al in the transition metal layer can further reduce cation mixing, resulting in superior structural stability and electrochemical performance. As for the doping amount of heteroatoms in LNO, a higher level of Al^{3+} in the transition metal layer interrupts facile expansion and contraction of the crystal structure during repeated Li^+ extraction and insertion. It has been demonstrated that 5% Al^{3+} is empirically sufficient to stabilize the layer structure. Meanwhile, considering that Al is electrochemically inactive and Co is expensive, NCA with Co (15 mol%) and Al (5 mol%) is the optimized result.[99] Such material delivers a high discharge capacity of approximately 200 mAh g^{-1}, which is the highest specific capacity among the currently mature Li-ion technologies. Furthermore, such material exhibits excellent cycling stability not only at room temperature but also at elevated temperature (60 ^{o}C).[100]

Compared to spinel LMO, NCA is more expensive but has advantages of higher specific capacity (200 mAh g^{-1} at the material level), high energy density (> 200 Wh kg^{-1} at the cell level) and long life (calendar life: > 15 years). By 2025, the energy density for NCA is expected to reach 300 Wh kg^{-1} and 700 Wh L^{-1} at a cell level.[101]

To date, NCA technology has been successfully employed in electric cars such as Tesla products (Model X, Model S, Model 3).

3.4 NMC technology for EVs

In the automotive battery industry, one of the most successful Li-ion chemistries is the cathode combination of nickel manganese cobalt oxide (NMC). $LiNi_{1-x-y}Mn_xCo_yO_2$ (NMC) has similar or higher specific capacity than LCO and similar operating voltage while having lower cost since the Co content is reduced. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC-111) is the most common form of NMC and is widely used in the battery market.[102] Another successful combination of NMC is $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC-532).[103] Other combinations using various amounts of metals are possible. For NMC, nickel is known for its high energy density but poor stability. Manganese has the benefit of forming a spinel structure to achieve low internal resistance, but gives a low specific energy. Combing the two metal elements can improve each other's merits. NMC-based battery technology is also well-suited for EV applications due to having the lowest self-heating rate.

There is a move towards NMC-blended Li-ion chemistry as the system can be built economically and it achieves good overall performance. The three active components of nickel, manganese and cobalt can easily be blended to suit a wide range of applications for automotive and energy storage systems (EES) that need frequent cycling. NMC-111, NMC-442 and NMC-532 are currently the-state-of-the-art cathode materials for LIBs. In the near future, Ni-rich NMC cathode materials (NMC-811, NMC-622) under development will likely be adopted in the automotive industry owing to their higher specific energy and lower cost. However, although Ni-rich NMC can efficiently enhance the specific energy, it is very hard to exceed its theoretical limitation (350 Wh kg^{-1} at a cell level).

In the long term, high-voltage spinel $LiNi_{0.5}Mn_{1.5}O_4$ (HV-spinel) could be a promising alternative as a next-generation high-energy cathode material for EVs (Figure 5-6). HV-spinel possesses a high operating voltage at 4.7 V and a specific capacity of 130 mAh g^{-1},[104] which leads to a specific energy of around 580 Wh kg^{-1} that can be obtained at the cathode-level. Although it shows a modest energy improvement, HV-spinel also has a large attraction due to facile synthesis, low cost, environmental friendliness, good safety and excellent rate capability owing to both high electron and ionic (Li^+) conductivity. In particular, the rate capability of disordered HV-spinel phase (space group *Fd-3m*) is several orders of magnitude higher than that of the ordered one (space group $P4_332$).[105] However, such material suffers from some drawbacks such as severe capacity fading at elevated temperature (60 °C) and the electrolyte decomposition owing to higher operating voltage.[106] Therefore, a high-voltage electrolyte needs to be developed for developing HV-spinel applications in the future.

High-energy NMC (HE-NMC) layered-layered composite materials, with the general formula $xLi_2MnO_3\bullet(1-x)LiMO_2$ (M=Ni, Mn, Co), are another alternative cathode which may become practical in the longer term (Figure 5-6). During the past several years, HE-NMC materials have attracted a large amount of attention and have raised considerable interest for the automotive industry because they exhibit the highest specific energy (~900 Wh kg^{-1}) among all the cathode materials.[107,108] HE-NMC materials are composed of $LiMO_2$ (M=Ni, Mn, Co) and Li_2MnO_3. In such a composite structure, the layered $LiMO_2$ component can be stabilized by the structurally compatible Li_2MnO_3 component. This allows a much larger degree of delithiation than that normally possible with pure layer LCO ($Li_{1-x}CoO_2$, x(max)=0.5). In the cutoff voltage range of 2.0-4.4 V vs. Li^+/Li, $LiMO_2$ is the only electrochemically active component, since Li_2MnO_3 is inactive as the manganese ions are already tetravalent and cannot be further oxidized.[76] In this regard, the main function of Li_2MnO_3 is to stabilize the $LiMO_2$ layered structure by providing Li^+ ions to the active $LiMO_2$ component. However, when the voltage is increased to 4.4-4.6 V, Li_2MnO_3 becomes active and capacities above 250 mAh g^{-1} can be theoretically obtained.[109] In the higher voltage range, the electrochemically active MnO_2 phase will be generated owing to the removal of Li_2O from Li_2MnO_3. Despite the favorably high capacity, HE-NMC still suffers from poor cycling stability, seriously limiting its practical application in the EV industry. This is mainly attributed to the extensive removal of Li_2O from Li_2MnO_3, resulting in damage to the electrode surface and increased impedance, especially at high current densities. The severe voltage fading is probably ascribed to the transition towards a spinel phase when cycling at a cutoff window of 2.0 and 4.6 V. Besides cycling performance, low electronic conductivities and low tap densities need to be enhanced before HE-NMC could be considered as a potential battery technology for next-generation EV applications.[76]

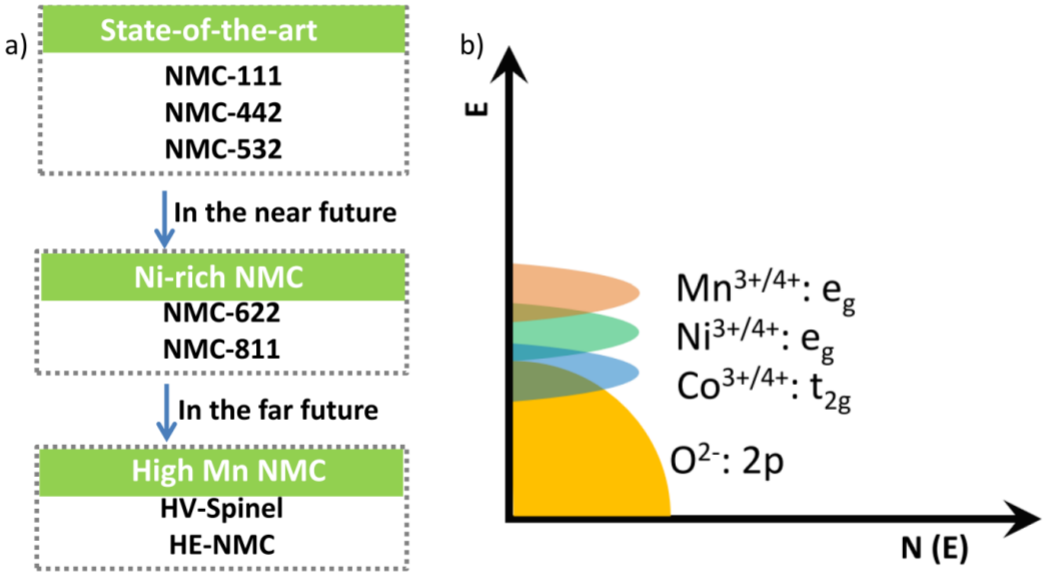

Figure 6. a) The state-of-the-art NMC cathode materials, near-future NMC materials and far-future NMC series materials, b) Schematic diagram of the positions of the various redox couples relative to the top of the oxygen: 2p band.

3.5 Nickel-rich NMC chemistries for near-future automotive batteries

As previously discussed, LMO, NCA, NMC and LFP are currently the major Li-ion technologies for automotive applications. Each of these cathode materials has its own advantages and disadvantages. In general, the layered structures (NCA, NMC) can give the highest specific capacities up to 200 mAh g^{-1}, but suffer from structural and/or chemical instabilities during repeated cycling, which is related to chemical composition and state of charge. The structural instability is attributed to a migration of transition metal ions from the octahedral sites of the transition metal layers to the octahedral site of the lithium layer by a neighboring tetrahedral site.

Among the ions of the three elements of Ni, Co, and Mn, Mn^{3+} has the lowest octahedral site stabilization energy (OSSE, i.e., a small difference between the crystal field stabilization energies in the octahedral and tetrahedral sites), and easily migrates and suffers from a structural transition from layered phase to spinel upon cycling.[110] In contrast, Co^{3+} possesses the highest OSSE and thus exhibits excellent structural stability, but it suffers from poor chemical stability upon the extraction of Li^+ ions over 50%, which is mainly due to an overlap of the t_{2g} band of low-spin $Co^{3+/4+}$ with the top of the 2p band of O^{2-} (Figure 6b). Compared to Co, Mn provides better chemical stability because the e_g band of $Mn^{3+/4+}$ is further above the top of the 2p band of the O^{2-}. In contrast to Mn and Co, Ni shows a moderate structural and chemical stability since it has a higher OSSE than Mn^{3+}, and the e_g band of low-spin $Ni^{3+/4+}$ barely touches the top of the 2p band of the O^{2-}. On another note, Co is the most expensive and toxic, Mn is the least expensive toxic while Ni is in between them for both factors. Meanwhile, Ni can exhibit a higher operating voltage, which is very useful for higher energy density. Based on the balance of these considerations, the automotive industry has shown preference to Ni-rich NMC battery technologies (such as NMC-622, NMC-811, and NCA) to achieve the best optimized performance and cost among these chemistries for future automotive applications.

Although the two Ni-rich cathode materials (NCA and NMC-811) exhibit similar chemical compositions and capacities, Al and Mn dopants show different effects on the structure. Compared to NCA, NMC-811 shows some favorable merits. The presence of Mn offers higher thermal stability because it elevates the onset exothermic reaction up to 220 ^{o}C,[111] relative to Al-doped NCA (180 ^{o}C).[112] Moreover, NMC-811 delivers the more uniform chemical composition owing to the introduction of Mn by a coprecipitation method compared to NCA with a facile heat treatment for introducing Al element. On the other hand, Al^{3+} is lighter, facilitates fast Li^{+} diffusion, and is able to replace mostly Ni^{3+} while Mn^{4+} will induce more Ni^{2+} in the structure, allows higher capacities, but results in a higher degree of cation mixing.[113] Therefore, simultaneously using Mn and Al as dopants in the layered metal oxides would be an ideal choice that has been recently demonstrated.[114]

4. Next-generation Li-based automotive batteries

To achieve driving ranges well beyond 300 miles in the future, the specific energy of today's LIBs need be further increased to 300 Wh kg^{-1} and above. As previously discussed, layered lithium transition metal oxides (NMC) have become the most popular cathodes for automotive battery technologies. As for the future generation of cathode materials, some of the most promising candidates in the NMC family will benefit from further optimization because the related battery technology is relatively mature. In this regard, by adjusting the content ratios of Ni, Mn and Co in the NMC compound, improved performance can be obtained such as the NMC-811 battery chemistry with higher specific energy and reduced battery cost. Considering the limited theoretical capacity of NMC compounds, however, NMC-811 may only be a transitional Li-ion technology. In the long term, to achieve energy densities of ~500 Wh kg^{-1} (or volumetric energy densities of ~1000 Wh L^{-1}) and above, new high-energy battery chemistry systems (all-solid-state batteries, Li-air batteries, Li-S batteries, etc.) need to be developed.

4.1. Ni-rich NMC battery chemistry for near-term EVs

Although NMC possesses a high theoretical capacity of around 275 mAh g^{-1}, Li^+ ions in the NMC compound cannot be completely extracted upon charging owing to structural instabilities occurring at a high state of charge. Thus, the accessible capacity is usually 160 mAh g^{-1} for NMC-111, which his much lower than its theoretical value. When charged up to 4.3 V vs. Li^+/Li, this is insufficient to meet the required specific energy targets. In this regard, increasing Ni content achieves a higher energy density; in particular, 25% of higher reversible capacity up to 200 mAh g^{-1} was reported for NMC-811 at the same upper cutoff voltage. By increasing Ni content to 80% and reducing Co content to 10%, NMC-811 possesses a specific capacity of 200 mAh g^{-1}, or 25% higher than that of NMC-111 (163 mAh g^{-1}). Moreover, the rate capability of NMC-811 is also improved owing to higher electronic conductivity (2.8×10^{-5} S cm^{-1}) and higher ionic diffusivity (10^{-8} to 10^{-9} cm^2 S^{-1}) compared to NMC-111 (electronic conductivity: 5.2×10^{-8} S cm^{-1}; ionic diffusivity: 10^{-11} to 10^{-12} cm^2 S^{-1}).[115]

Besides the contribution of the specific energy by using NMC-811, battery cost will be significantly decreased owing to the reduction of the expensive Co element in the NMC-811 (10 at.%) in contrast to NMC-111 (33.3 at.%). Therefore, recalling that the prices of cobalt, nickel and manganese are USD 61,499/ton, USD 11,701/ton, and USD 2,000/ton,[116] NMC-811 battery technology will represent lower costs than current mainstream battery technology. By 2021, the Co amount in NMC-811 will decrease by 69% in contrast to that of NMC-111. Recently, many battery manufactures such as LG Chem and SK innovation have announced that they will start the production of new NMC-811 battery materials in the near future. In addition, BMW also expects to use NMC-811 battery cells in its new BMW i5 in 2021. Meanwhile, the anode of future cells will be prepared by mixing graphite and a small amount of silicon (refer to Section 5.3 for further discussion), further contributing to a higher energy density by matching the NMC-811 cathode energy, as illustrated in Figure 7.

One major drawback of NMC-811 is its increased surface reactivity. Similar to NCA, such compound suffers from thermal instability due to oxygen release during the highly delithiated $Li_{1-\delta}Ni_{1-x-y}Mn_xCo_yO_2$. The reactive and unstable Ni^{4+} ions in the delithiated component tend to form more a more thermodynamically stable $Li_xNi_{1-x}O$ phase (NaCl structure), resulting in increased interfacial impedance and poor cycling life.[101] Furthermore, high pH values for NMC-811 cause additional difficulties for the cell manufacturing. Thus, mitigating surface reactivity of the Ni-rich NMC-811 cathode is an important issue in the near future.

Ma et al. systematically investigated the reactivity of NMC series cathode materials at the different state of charge and elevated temperature by using accelerating rate calorimetry (ARC).[117] The ARC results revealed that the upper cut-off potential and NMC composition strongly affect the thermal stability of various NMC materials when traditional carbonate-based electrolyte was employed. All of NMC series samples including NMC-111, NMC-442, NMC-532, NMC-622 and NMC-811 exhibit a continuously increased capacity with the increase of cut-off potential from 4.2 to 4.7 V. Moreover, the higher the Ni content in the compound is, the higher the specific capacity of NMC cathode is. In particular, NMC-811 delivers the highest specific capacities of 215 mAh g^{-1} (charged to 4.2 V), 234 mAh g^{-1} (charged to 4.4 V), 239 mAh g^{-1} (charged to 4.5 V) and 260 mAh g^{-1} (charged to 4.7 V). Although NMC-811 exhibits the best electrochemical performance among these NMC series cathode materials, it also shows the highest reactivity with the electrolyte at the delithiated state, indicating that increasing the cut-off potential does not influence the exothermic behavior of delithiated NMC-811. However, the self-heating rate increases at 120 ^{o}C, indicating structural instability. Apart from NMC-811, the reactivity of other NMC materials with electrolyte is affected by the upper cut-off voltage. As the upper cut-off potential increases, the self-heating rate increases, especially at a high potential of 4.7 V, revealing a trade-off between high energy density and safety. In addition, the chemical composition of NMC influences the thermal stability at different cut-off voltages. The amount of Mn^{4+} dominates the thermal stability of NMC compounds because it is not electrochemically active and can stabilize the oxide structure, especially at a highly delithiated state. Thus, higher Ni content and lower Mn/Co content result in a higher self-heating rate and lower onset temperature for exothermic reactions. Therefore, Ni-rich NMC-811 needs to be protected on the surface in order to avoid or mitigate the undesirable reaction between electrode and electrolyte.

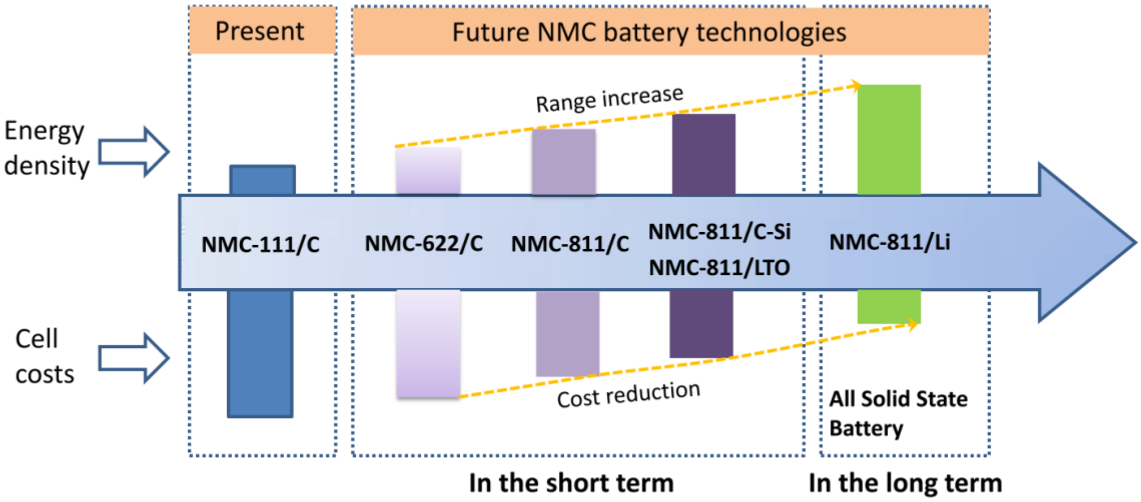

Figure 7. The roadmap of the present and future NMC-based battery technologies.

To mitigate or solve the instability issues of Ni-rich MNC-811 cathode materials, Sun et al. proposed the design and construction of a NMC-811@Li[$Ni_{0.5}Mn_{0.5}$]O_2 core-shell structure by using NMC-811 and Li[$Ni_{0.5}Mn_{0.5}$]O_2 as core and shell materials,[118] respectively. The former provided high capacity and high energy while the latter guaranteed the structural and thermal stability, exhibiting excellent cycling performance. Several years later, Sun et al. designed a concentration-gradient NMC cathode material like a core-shell structure, as displayed in Figure 8. In this unique structure, the core is Ni-rich NMC-811 while the shell is Mn-rich $Li(Ni_{0.46}Mn_{0.31}Co_{0.23})O_2$.[119] The former exhibits high capacity for meeting the requirements of high power and high energy for EVs while the latter enhances the thermal stability, since the Mn-rich compound is much more stable in contact with the electrolyte than the Ni-rich core. The electrochemical performance of pure NMC-811, $Li[Ni_{0.46}Mn_{0.31}Co_{0.23}]O_2$, and concentration-gradient $Li[Ni_{0.64}Mn_{0.18}Co_{0.18}]O_2$ were evaluated by charge and discharge tests. Such core-shell nanostructure shows that the concentration-gradient $Li[Ni_{0.64}Mn_{0.18}Co_{0.18}]O_2$ delivers a discharge capacity of 209 mAh g^{-1}, only slightly lower than that of pure NMC-811 (212 mAh g^{-1}). When evaluated for cycling stability at 55 ^oC, bulk NMC-811 shows a capacity retention of only 67% after 50 cycles while concentration-gradient $Li[Ni_{0.64}Mn_{0.18}Co_{0.18}]O_2$ retains a capacity retention as high as 96% during the same cycling period, which is similar to the cell based on the surface composition ($Li[Ni_{0.46}Mn_{0.31}Co_{0.23}]O_2$). Such findings indicate that the unique nanostructures built from concentration-gradient components can provide not only high capacity but also long cycle life at high temperature and high cut-off voltage. Besides half-cell tests, Sun et al. further examined the cycling performance of the designed concentration-gradient electrode materials by using an Al-pouch full cell with graphite as the anode. As displayed in Figure 13d, the concentration-gradient material exhibited a capacity retention of over 96.5% after 500 cycles, much higher than that of pure NMC-811 (80.4%). The poor cycling performance of pure NMC-811 is attributed to a structural transformation at the particle surface owing to the high reactivity of Ni^{4+} with electrolyte, leading to the increase of charge-transfer resistance between cathode and electrolyte during repeated cycling. In contrast, excellent cycling performance delivered by the as-prepared concentration-gradient electrode materials is mainly due to the engineering of surface composition with reduced Ni concentration and increased Mn concentration, thus restricting its reactivity with the electrolyte. In addition, the concentration gradient within the particle can impede the formation of microcracks and segregation that can occur at the interface between the bulk and outer shell layer of conventional core-shell structures.

To demonstrate the thermal stability and safety of the as-prepared concentration-gradient cathode materials, Sun et al. carried out differential scanning calorimetry trace measurements.[119] As shown in Figure 13e, the concentration-gradient material (blue line) charged to 4.3 V shows the onset exothermic reaction temperature at 270 ^{o}C, which is evidently lower than that of bulk NMC-811 (180 ^{o}C), indicating the better thermal stability of the concentration-gradient cathode at the charged state. Furthermore, by using nail penetration test, the cell based on NMC-811 shows a major thermal runaway with explosion and fire while the cell using the concentration-gradient material has no thermal event, further corroborating the thermal stability and safety of the designed concentration-gradient NMC cathode.

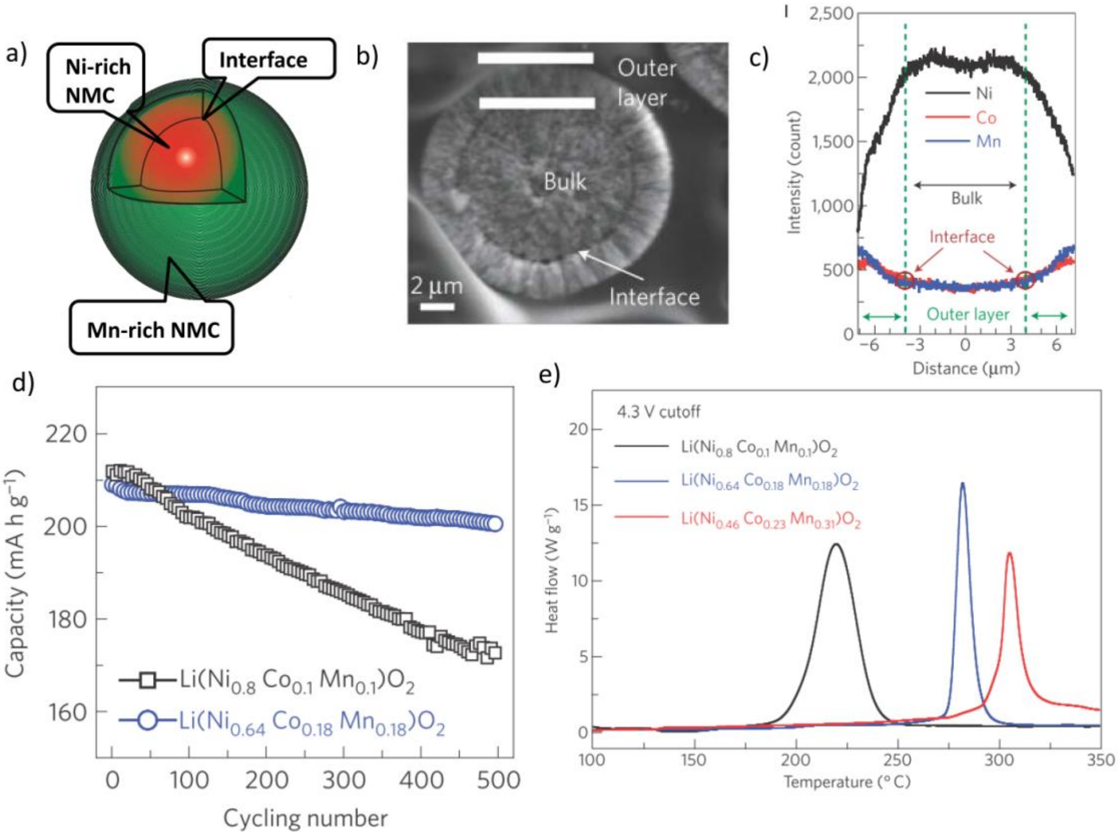

Figure 8. a) Schematic diagram of cathode materials with core-shelled NMC cathode materials with different compositions in the core (NMC-811), shell ($Li(Ni_{0.46}Mn_{0.31}Co_{0.23})O_2$) and the interlayer. Ni-rich NMC-811 core surrounded by concentration-gradient outer layer, b) SEM image and c) EPMA line scan of the final lithiated oxide $Li[Ni_{0.64}Mn_{0.18}Co_{0.18}]O_2$. In both cases, the gradual concentration changes of Ni, Mn, Co in the interlayer are clearly evident, d) cycling performance at 1 C rate (75 mA corresponds to 190 mA g^{-1}) of laminated–type lithium ion batteries with an Al-pouch full cell (75 mAh) using mesocarbon microbead graphite as the anode and either NMC-811 or concentration-gradient material as cathode (upper cut-off voltage of 4.2 V), e) Differential scanning calorimetry traces showing heat flow from the reaction of the electrolyte with $Li_{1-\delta}[Ni_{0.8}Mn_{0.1}Co_{0.1}]O_2$, concentration-gradient material $Li_{1-\delta}[Ni_{0.64}Mn_{0.18}Co_{0.18}]O_2$ and $Li_{1-\delta}[Ni_{0.46}Mn_{0.31}Co_{0.28}]O_2$ charged to 4.3 V.[119]

4.2 LTO technology for near-term EVs

Conventional graphite anodes suffer from poor rate capability and lithium dendrite problems upon overcharging, leading to internal short circuits and safety concerns, including fire or explosion owing to its flammable nature. Moreover, the formed SEI on the graphite surface results in a low Coulombic efficiency and an irreversible capacity loss. As far as automotive batteries are concerned, fast charge/discharge capability and safety are always two key factors that influence their market penetration.

Lithium titanate (LTO) is a promising candidate for replacing graphite in lithium-ion battery anodes because of its unique advantages for EV applications.[120] First, LTO possesses a stable spinel structure with "zero strain" feature upon lithiation/deliation (Figure 9), enabling fast charging/discharging capability.[121] Second, it has a high working potential at 1.55 V (vs. Li/Li^+) which helps to avoid the formation of lithium dendrites and SEI on the electrode surface, leading to superior safety performance. The high working potential also allows LTO anodes to use low-cost aluminum foil as their current collector, avoiding the formation of Li-Al alloy, which is very beneficial for large-scale EV applications. Third, LTO has a ultralong cycle lifetime up to 20,000 cycles, which is 10 times higher than that of graphite;[122] Finally, LTO can work at high-temperature and low-temperature conditions (-30~60 ^oC); 80% of full capacity can be obtained even at -30 ^oC. Such benefits could greatly improve conventional LIBs for automotive application in the near future.

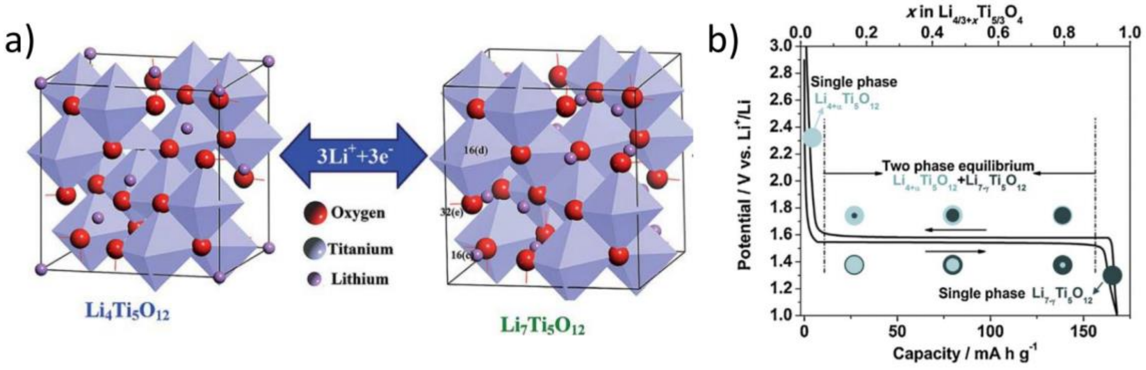

Figure 9. a) The schematic diagram of lithium insertion process of $Li_4Ti_5O_{12}$ crystal structure, b) the typical discharge and charge profiles of $Li_4Ti_5O_{12}$.

However, several challenges for LTO anodes to succeed in EV applications still exist. The first challenge is enhancing high-power performance for realizing rapid charging/discharging demands for automotive batteries.[123] LTO has some intrinsic kinetic problems owing to its low electric conductivity (~10^{-8} S cm^{-1}) and limited lithium diffusion coefficient (10^{-9}-10^{-16} cm^2 s^{-1}), thus limiting its high-rate capability. To this end, various strategies including nanostructuring, surface coating and doping have been employed to improve electrochemical properties of LTO. In recent years, nanosized LTO materials have been successfully commercialized and used for LIBs. The second challenge is gassing of the LTO electrode upon cycling (and even in the storage state) owing to significant interfacial reactions between LTO and electrolyte, seriously impeding its practical application for EVs. The third challenge is limited energy density of the LTO anode within a full cell. The specific energy of LIBs is associated with specific capacity and working voltage between cathode and anode.

For LTO batteries, it possess a limited specific capacity of 175 mAh g^{-1} ($Li_4Ti_5O_{12}+3e^-+3Li^+ \rightarrow Li_7Ti_5O_{12}$) and a high lithium insertion potential at 1.55 V (vs. Li/Li^+). When matching conventional LIB cathodes, the working voltages of full cells are usually 2.5 V (LCO/LTO), 2.5 V (LMO/LTO), 1.9 V (LFP/LTO), 2.5 V (NCA/LTO), and 2.5 V (NMC/LTO), which are evidently lower than the respective pairs with a graphite anode, leading to a lower energy density. Since energy density of a battery is directly proportional to its cell voltage, high-voltage cathode materials should be developed for matching the high potential of the LTO anode, such as $LiNi_{0.5}Mn_{1.5}O_4$ (4.7 V).[124] Such high-voltage cathodes, however, suffer from instability of electrolyte upon charging to high potentials of over 5 V. Therefore, it is highly desirable to develop highly stable electrolytes and solvents (e.g. solid electrolyte, ionic liquid) for future high-potential LTO-based full cells.

4.3 Silicon technology for near-term EVs

Silicon (Si), a typical alloying anode, has long been regarded as one of the most promising anode materials for replacing graphite. Si has the highest known theoretical specific capacity for lithium of ~4200 mAh g^{-1},[125] which is more than ten times that of graphite anodes (theoretical capacity: 372 mAh g^{-1}), and is also higher than other alloying anodes (e.g. Sn, Sb, Al) and conversion reaction-based anodes (e.g. metal oxides, metal sulfides, metal nitrides, metal phosphide). Additionally, Si anodes deliver a relatively low potential at around 0.4 V vs. Li/Li^+, which is favorable for the achievement of high-voltage full cells. Another important advantage of silicon is its abundant resource availability on earth, which is very beneficial for the reduction of battery cost for next-generation EVs.

Si anodes, however, still suffer from some drawbacks and limitations. First, the very large volume expansion (>300%) of Si anodes upon lithiation cause significant structural strain, mechanical fracture, and loss of active components from the current collector, leading to poor cycling performance. Second, such a large volume expansion/contraction will unavoidably result in the repeated fracture/re-formation of SEI during charge/discharge cycles, which irreversibly consumes lithium from cathode materials, resulting in low Coulombic efficiency and capacity loss. Third, Si possesses a low electrical conductivity, which is not favorable for high-power LIBs. To address these problems, various strategies have been developed such as the utilization of nanoscale silicon, nanostructure designs including hollow, yolk-shell and hollow nanostructures, mesoporous structures, carbon coating, nanoconfinement design, and the use of polymer binders (alginate, carboxymethylcelluose, self-heal binder),[123] as shown in Figure 10. Through these solutions, Si-based battery performance has been greatly improved.

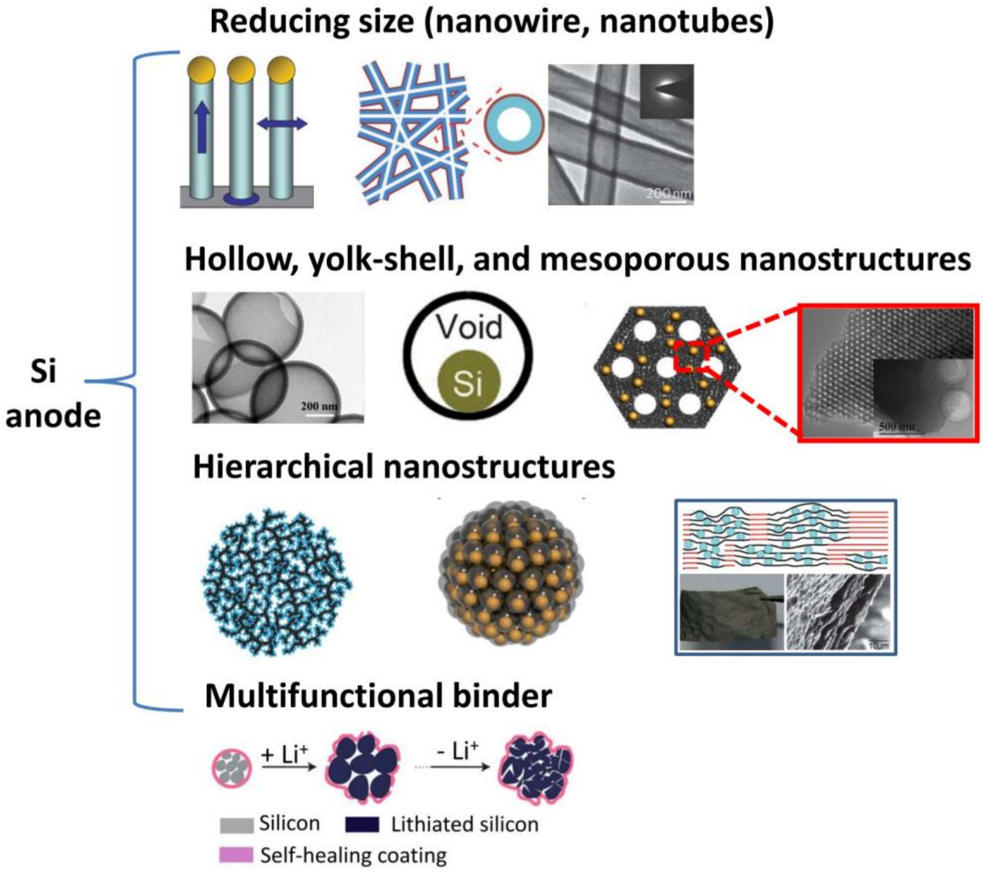

Figure 10. Schematic diagrams of various strategies for improving performance of Si anode.

Although these strategies have successfully enhanced the electrochemical performance of Si anodes, their practical application for EVs still suffers from many limitations in the short term such as high raw materials cost, high manufacturing costs and the difficulty of large-scale production. Therefore, using Si as a complete replacement for graphite is not realistic at present. However, Si/graphite or Si/carbon composite electrodes are a suitable choice in the near future. Such a partial replacement for graphite in battery anodes not only increases specific energy but also effectively overcomes the electrode expansion issues upon charge/discharge cycles.

For example, Cui and Cho et al. reported Si nanolayers embedded on graphite for high-energy LIBs,[126] as displayed in Figure 11. The obtained hybrids show a very high CE of 92% and a reversible capacity of 517 mAh g^{-1}, much higher than that of graphite.

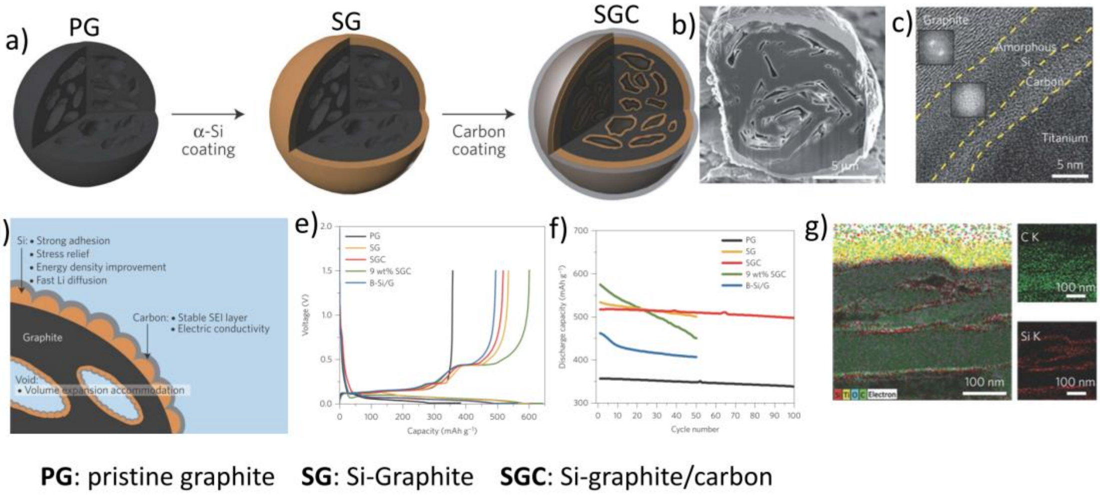

Figure 11. a) Schematic diagram of the fabrication process of the SGC hybrids, b) SEM image of cross-section SGC hybrids, c) HRTEM image at the interfacial region of the SGC hybrid with fast Fourier transform inset images, d) cross-sectional schematic view showing the detailed structural characteristic of a SGC particle, e) galvanostatic charge/discharge profles of PG, SG, and B-Si/G measured at 0.1 C, f) reversible discharge capacity versus cycle plot of PG, SG, SGC, 9 wt%-SGC, and B-Si/G cycled at 0.5 C for 100 cycles, g) SEEM images for element mapping by energy-dispersive spectroscopy.

4.4. New battery chemistries for next-generation EVs

Considering the limitations of conventional LIBs in terms of energy densities and element resources, developing new types of battery chemistries has become an important task for meeting the requirements of next-generation long-range EVs. At present, all-solid-state batteries (SSBs), lithium sulfur batteries, and lithium air batteries have received considerable attention owing to their higher specific energy and lower cost. In this review, SSBs are used a case for demonstrating their potentials for automotive applications in the future. Conventional LIBs usually use organic liquid electrolytes, which have some drawbacks such as complex reactions at the solid/liquid interface and thermal instability. In this regard, SSBs are a superior alternative owing to their nonflammable solid electrolyte and higher thermal stability.[127] Table 2 gives a summary of properties of common solid-state electrolyte materials. Currently, the main inorganic SSEs for all-solid-state LIBs are oxides and sulfides because of their high ionic conductivity (some of them show ionic conductivity comparable to or higher than those of liquid electrolyte). Compared to conventional LIBs, SSB would be safer and could also possess a longer cycle life, higher energy density and less requirements on packaging and state of charge monitoring circuits. Furthermore, the intrinsic solid electrolyte possesses some additional advantages for use in battery application. For instance, solid electrolytes act not only as an ionic transport support but also as a separator. The non-liquid nature of the electrolyte allows stacking of cells in a single package without ionic short circuit. Such a battery configuration effectively decreases the “dead volume” between single cells, leading to more compact space and higher specific energy for battery packs. This is very favorable for automotive application, as illustrated in Figure 12. Even so, the electrochemical performance of all-solid-state batteries is still inferior to that of commercial LIBs. The existing critical challenges need to be addressed such as large interfacial impedance, large charge-transfer resistance, volume change of electrode materials, and poor cycling stability. Poor cycling performance induced by the continuous development of the interfacial resistance layer at the electrode/electrolyte interface is one of the major barriers that need to be addressed before commercial application of SSBs is possible.[128] The electrochemical performance of SSBs is usually also impeded by low ionic conductivity of the electrolyte compared to liquid electrolyte. To solve such challenges, using interlayers such as gel polymers and solid polymers have been demonstrated as an effective solution to reduce the interfacial resistance and prevent undesirable side reactions between the SSE and electrode, especially for Li-metal anodes. Thus, this section will focus on two parts: non-Li metal-based SSBs and Li-metal-based SSBs.

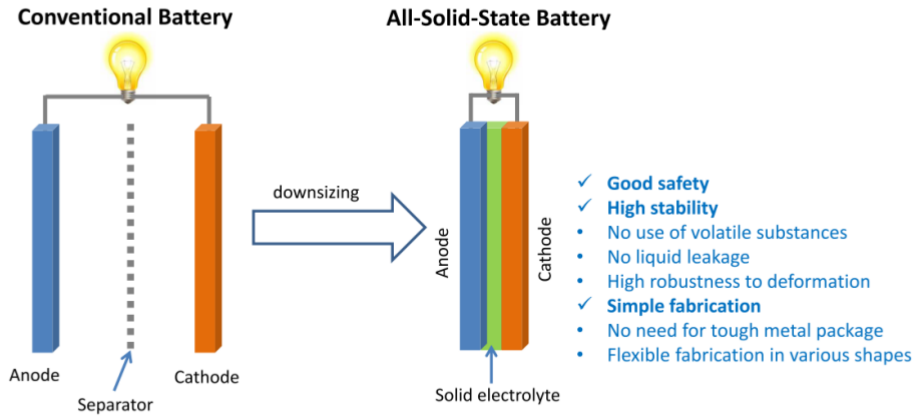

Figure 12. Schematic illustration of the conventional battery and all-solid-state battery.

Table 2. Comparison of room-temperature solid state electrolyte materials.

Classification	**Materials**	**Electronic conductivity (S cm^{-1})**	**Advantage**	**Disadvantages**
Thin film[129]	LiPON	6.4×10^{-6}	Stable with cathode and Li metal	Low conductivity; Expensive large-scale production
polymer[130]	PEO	10^{-4}	Stable with Li metal; Easy to produce a large-scale membrane; flexible	Limited thermal stability; Low oxidation voltage (< 4 V)
Oxide	NASICON[131] $LiTi_2(PO_4)_3$ Perovskite[132] $Li_{3.3}La_{0.56}TiO_3$ Garnet[133,130] $Li_7La_3Zr_2O_{12}$, $Li_7La_3Nb_2O_{12}$, $Li_5La_3Ta_2O_{12}$	10^{-5}-10^{-3}	High chemical and electrochemical stability; High oxidation voltage; High mechanical strength	Non-flexible; Expensive large-scale production
Sulfide	Li_2S-P_2S_5;[130] Li_2S-P_2S_5-MS_x;[130] β-Li_3PS_4[134]	10^{-7}-10^{-3}	High conductivity; Good mechanical strength and flexibility; Low grain boundary resistance	Low oxidation stability; Sensitive to moisture; Poor compatibility with cathode
Argyrodite	Li_6PS_5Cl[135]	4.6×10^{-3}	High ionic conductivity	Sensitive to air and water
	Li_6PO_5Cl[136]	1.0×10^{-9}	High oxidation voltage	

4.4.1. Non-Li metal anode based SSBs

SSEs composed of sulfides and thiophosphates typically react with metallic Li and generate an interphase. Thus, these compounds are only suitable for the application of non-Li metal SSBs. Kato et al. discovered that lithium superionic conductors, $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ and $Li_{9.6}P_3S_{12}$,[137] possessed the highest reported lithium ionic conductivity (Figure 13a) and high electrochemical stability. These materials were employed as SSEs for SSBs, showing extremely desirable electrochemical performance.

The authors demonstrated the above two SSEs via three solid-state cell designs (high-voltage cell, large-current cell and normal-type cell), as displayed in Figure 14d. The high-voltage cell requires a wide working potential to improve capacity and energy, resulting in the choice of a graphite anode and LCO as the anode and cathode, respectively. LTO was used as anode for the large-current-type SSB. The selection of a suitable electrolyte in the electrode composite is a key to enhancing the overall cell electrochemical properties. The best combination of cathode composite, anode composite, and SSE for each battery type are displayed in Figure 14d. In general, high-voltage SSB required an electrolyte with a wide working potential, and thus, $Li_{9.6}P_3S_{12}$, which has a high stability of ~0 V (vs. Li^+/Li), was employed as the anode composite. For the large-current-type SSB, high ionic conductivity is highly desirable and therefore, $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ was the best alternative owing to its best ionic conductivity.

As shown in Figure 14, all the solid-state cells exhibited superior electrochemical performance compared to conventional LIBs between -30 °C and 100 °C. Moreover, the electrochemical performance of the all-solid-state cells was further improved by using the developed SSEs. The all-solid-state cells showed superior rate capabilities with 150 C rate at 25 °C and 1500 C rate at 100 °C. Both large-current SSBs and normal-type SSBs exhibited excellent cycling performance at 100 °C using a high current density of 18 C (charge/discharge time: ~ 3 min). In contrast, conventional LIBs cannot work at this temperature due to thermal instability of liquid electrolyte and polymer separator. After 500 cycles, the all-solid-state cells can retain ~75% of the initial discharge capacity with 100% Coulombic efficiency.[137] Therefore, solid-state cells with $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ and $Li_{9.6}P_3S_{12}$ as SSEs exhibit excellent electrochemical performance owing to their superior ionic conductivity. Moreover, they provide high power density and ultrafast charging capability, revealing a promising prospect for future automotive applications.

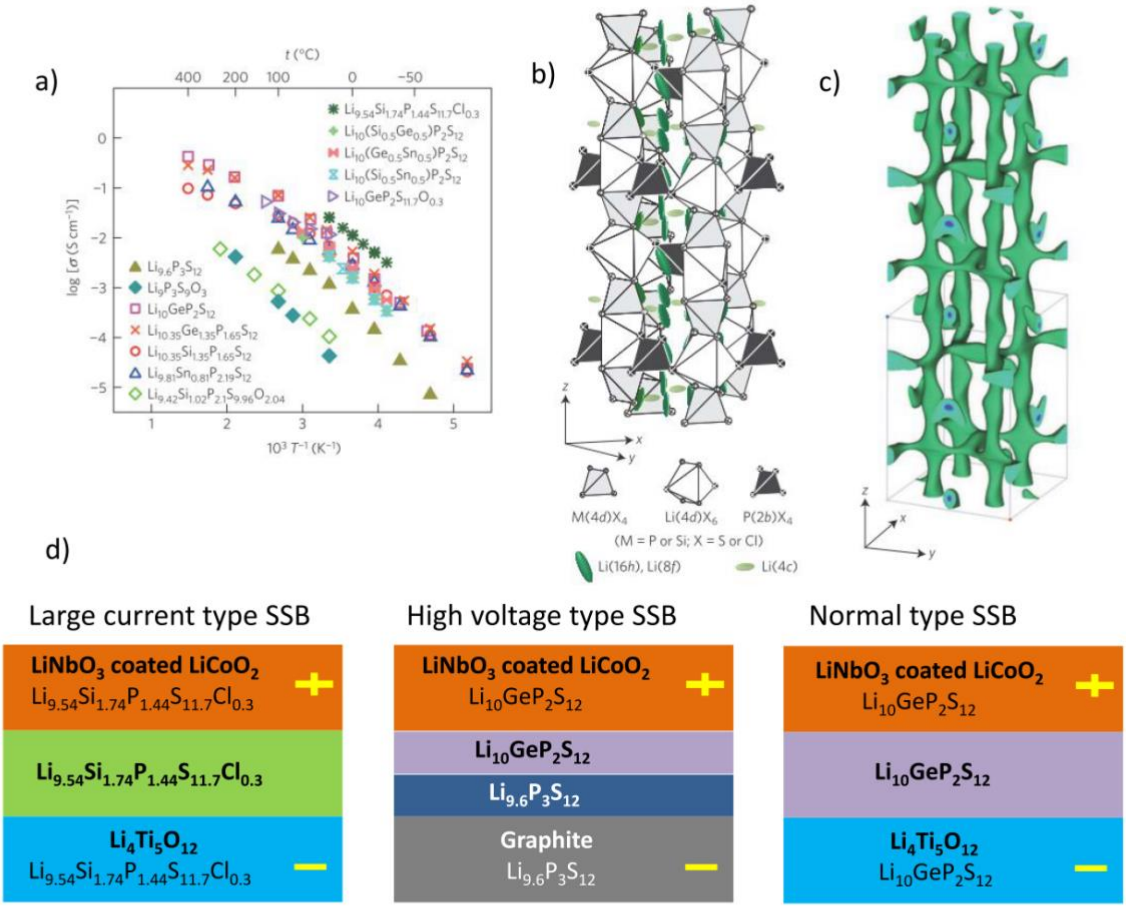

Figure 13. Ionic conductivity and crystal structure of $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$. a) Arrhenius conductivity plots for the LGPS and $Li_{9.6}P_3S_{12}$ and $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$, which were used as electrolytes in this study. b) Crystal structure of $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$. The thermal ellipsoids are drawn with a 50% probability. The framework structure consists of 1D polyhedral chains (edge-sharing $M(4d)X_4$ and $Li(4d)X_6$ connected by $P(2b)X_4$ tetrahedra. Conducting lithium is located on the interstitial site of Li(16h), Li(8f) and Li(4c). c) Nuclear distribution of Li atoms in $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ at 25 °C, calculated using the maximum entropy method at the iso-surface level of -0.06 fm $Å^{-3}$, d) Schematic illustrations of large-current-type SSB, high-voltage type SSB, and normal type SSB using different solid electrolytes as electrolyte and separator.[137]

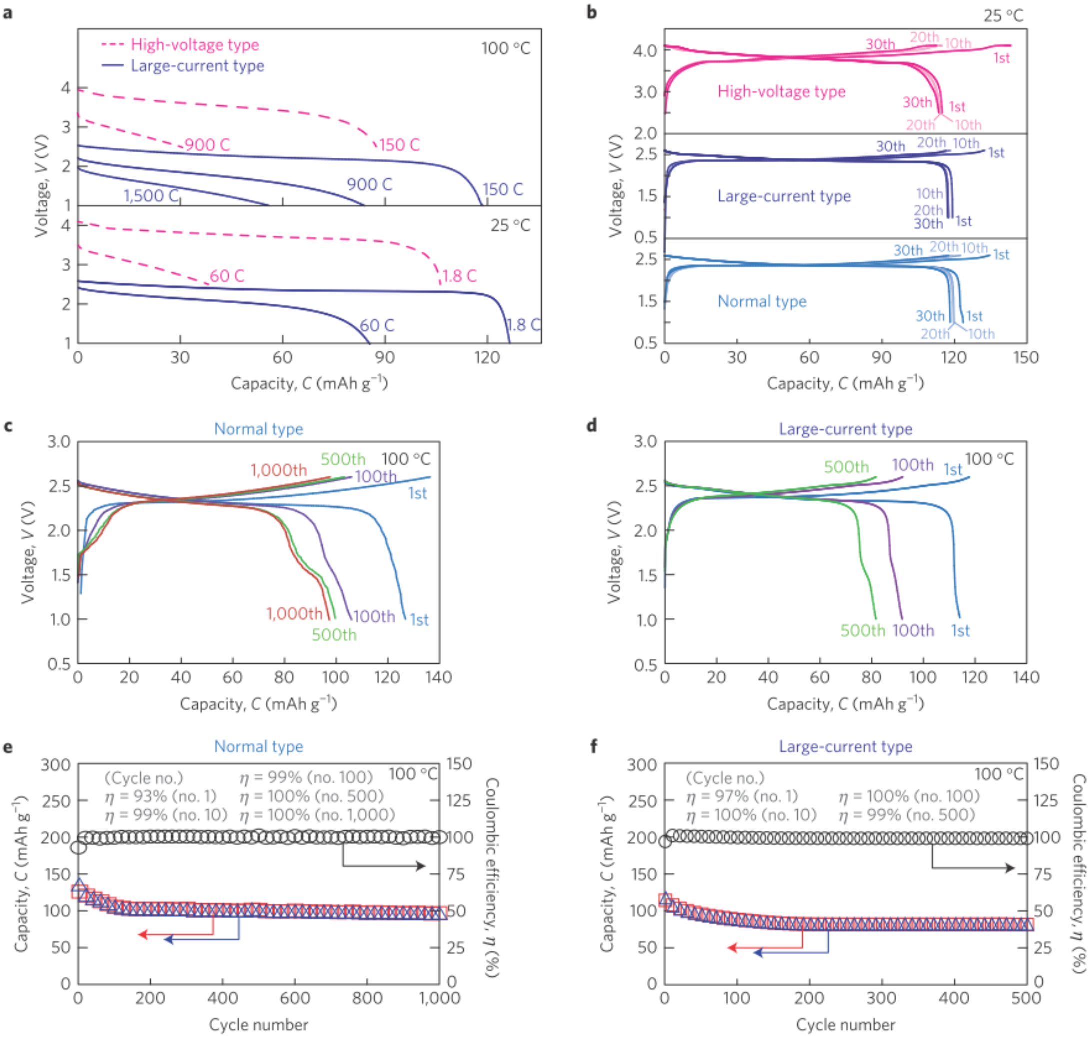

Figure 14. Electrochemical performance of all-solid-state cells. a) Discharge curves for the prepared all-solid-state energy devices. The rate nC corresponds to the full charge and discharge of the theoretical capacity of 0.667 mAh in 1/n h. b) Charge/discharge profiles for all-solid-state cells at a 0.1 C at 25 °C. c, d) The charge/discharge curves for the all-solid-state cells of the normal-type and large-current-type cell, respectively. at 100 °C (current density: 18 C). e, f) Cycling performance for the all-solid-state cells of the normal-type cell and large-current-type cell, respectively. The current density of 18 C corresponds to charge or discharge time of around 3 min (80% theoretical capacity). The specific capacity was calculated based on the weight of $LiNbO_3$ coated $LiCoO_2$.[137]

4.4.2. Li metal anode based SSBs

Li metal anodes possess a very high theoretical specific capacity (3860 mAh g^{-1}) and the lowest electrochemical potential (-3.04 V vs stand hydrogen electrode, SHE), both of which are very promising for future high-energy LIB application. Owing to these unique merits, the attention on Li metal has been revived recently, although it has also been considered as an unsafe anode many years ago.[138] Unfortunately, in conventional liquid electrolyte systems, metal Li still suffers some problems.[139] First, the formation and growth of Li dendrites caused by overly rapid electrochemical deposition on the Li metal surface can penetrate through the separator and give rise to internal short circuits. Dendritic Li can also detach from the current collector to form “dead Li”, leading to poor cycling performance. Just for this issue, the commercial application of rechargeable Li metal batteries has been negated since the 1970s. Another issue is the instable interface usually formed in organic electrolytes. Owing to high reactivity of metallic Li, corrosive reaction at the surface of Li metal often takes place, leading to the increase of interfacial resistance, reduction of Coulombic efficiency and poor lifetime. Finally, the large volume expansion of the electrode during repeated Li deposition/dissolution will seriously deteriorate the interfacial stability.

To mitigate or eliminate these problems, SSEs have become a superior alternative to replace conventional liquid electrolytes owing to the good mechanical rigidity leading to the prevention of Li dendrites and increased safety. The combination of high-energy Li metal anode and highly stable and safe SSEs would be a very promising solution to achieve high energy density for automotive industry applications. Figure 15b shows the ionic conductivities of various electrolytes including liquid electrolytes, polymer electrolytes, and inorganic SSEs. To push the application of SSEs in batteries, high ionic conductivity must be achieved. To date, sulfide/thiophosphate and oxide garnet-type electrolytes are two promising SSEs for SSBs with Li metal anodes. The former possesses higher room-temperature conductivities and the latter is advantageous for its chemical stability against metallic Li.

Figure 15c shows the schematic illustration of conventional LIBs and SSBs. When replacing liquid electrolyte with SSE while keeping the same anode material (graphite), the volumetric energy density will not be increased while the gravimetric energy density will decrease by 10% owing to the high density of solid materials compared to liquid materials. On the contrary, when the graphite anode is replaced by Li metal and SSE is used, the volumetric and gravimetric energy density will be increased by 70% and 40%, respectively.[69] Therefore, the combination of lithium metal anode and SSE is necessary to realize a large benefit for next-generation high-energy EVs. Despite these favorable advantages, metallic Li and SSEs still face severe challenges for practical applications, such as low ionic conductivity and limited chemical stability against metallic Li of SSEs, and large interface impedance between Li anode and SSEs.

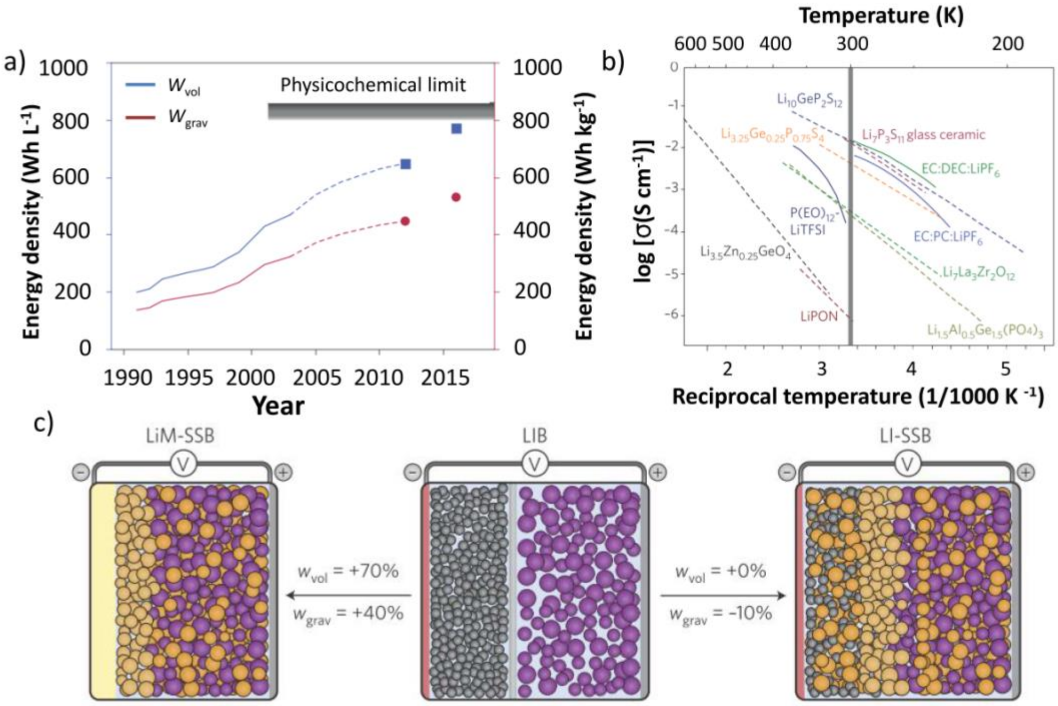

Figure 15. Energy density of LIBs and ionic conductivities of lithium electrolytes. a) Energy densities of the standard cylindrical 18650 LIB cells over the past 25 years are shown. b) Ionic conductivity of solid electrolyte are displayed in comparison to those of liquid electrolytes and polymers. c) Typical battery architectures for the conventional Li-ion and SSBs. The volumetric and gravimetric energy densities are represented by W_{vol} and W_{grav}, respectively.[69]

To date, various traditional cathode materials in LIBs have been matched with Li metal anodes for SSB applications. For example, Zhang et al. reported a $LiFePO_4$/Li SSB by using a composite electrolyte as SSE (Figure 16).[140] A PEO-based solid polymer electrolyte of PEO-1%-75% Li_2S 24% P_2S_5 1% P_2O_5 (LPOS) was coated on the surface of LAGP as composite electrolyte for the construction of an all-solid-state LFP/Li cell. Meanwhile, the LFP layer was also optimized by incorporating PEO-$LiClO_4$ into the LFP for preparing a composite cathode with a 3D continuous ionic and electronic network (PEO-LFP-$LiClO_4$). The LFP/Li SSB was assembled as illustrated in Figure 16a. The cell construction simultaneously leverages both the improvement of Li^+ ion conductivity in the cathode side and the reduction of the interfacial resistance at the electrode/electrolyte interface. Electrochemical tests show that such LFP/Li SSBs exhibit excellent electrochemical performance, showing a capacity retention of 96.6% after 1000 cycles at 1 C (Figure 16b). Although all-solid-state batteries provide a great possibility for application in EVs, there is still a long way to go for their practical implementation at the industrial level because it requires intensive and systemic efforts on the whole SSB systems including electrode materials, SSEs, electrode/electrolyte interface, and the cell configuration design.

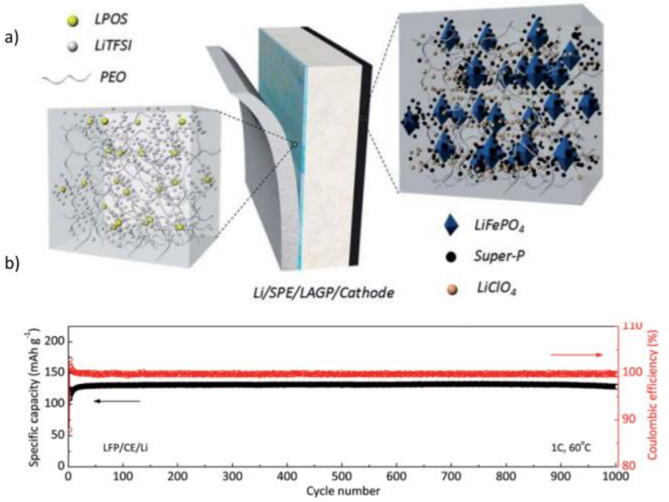

Figure 16. a) Schematic illustration of $LiFePO_4$/Li SSBs using PEO-Li_2S-P_2S_5 and LAGP as composite solid electrolyte, b) long-term cycling performance of LFP/CE/Li at 1 C.[140]

5. Conclusions and Outlook

This review article gives a comprehensive analysis and discussion for automotive LIBs in terms of market, battery cost, critical element analyses, currently state-of-art

Li-ion chemistries, and next-generation battery chemistries. Although the rapidly falling cost of battery packs and continuous improvement of performance in recent years are speeding up market penetration of electric automobiles, major breakthroughs in material chemistries are still required in order to fulfil the requirements of future EVs with longer range (at least 500 km) and lower cost (< $125/kWh). To steadily push the market penetration of EVs, two-step (short term and long term) strategic goals need be rationally set. In the period between 2016 and 2025 (short term), EVs are still required to depend on the relatively mature battery technologies including NMC, NCA, and LMO-NMC blended chemistries for developing new battery chemistries with high specific energy and lower cost such as Ni-rich NMC (e.g. NMC-811) and Si.

Considering its theoretical specific energy limitation (350-400 Wh kg^{-1}) of such battery systems, it is highly imperative for developing new higher-energy battery chemistries in the long term (beyond 2025) such as SSBs (e.g. NMC-811/SSE/Li, LNMO/SSE/Li), Li-S, Li-air batteries. In particular, solid-state Li-metal battery will bring new opportunities to EVs because metallic Li is likely the ultimate goal as high-performance anode for next-generation LIBs and SSEs can not only suppress side chemical reaction and Li dendrite problems caused by the conventional LIB systems, but also guarantee battery safety owing to their superior chemical and physical stability. In the meanwhile, SSEs can well address some challenges in the Li-air and Li-S batteries such as the dissolution of polysulfides.

Besides the concerns of energy density and cost for LIBs, element resources of battery materials, especially for critical elements such as Li and Co, have a significant effect on the market penetration of electric automobiles. In this review, Li and Co have been roughly evaluated in the short term (2016-2025) and in the long term (2016-2035) by two scenarios (high scenario: 30% CAGR; low scenario: 15% CAGR) based on the LIB annual production capacity, showing that there is no demand and supply risks for Li and Co regardless of high scenario and low scenario in the short term. But for the long term by 2035, Li demand outperforms its production while Co demand (7.47 Mt) exceeds its reserves (7.1 Mt) when facing a high growth rate (30%) for the LIB annual production capacity. Thus, improving lithium and cobalt extracting technology is highly desirable for fulfilling the rapid increase of LIB demands for transportation and grid energy systems in the future. Moreover, exploiting Co-free or Co-less battery chemistries and new battery systems with earth-abundant resources (e.g. sodium ion batteries) are both effective solutions to mitigate the huge consumption problems of Co and Li elements. In the meanwhile, developing LIB recycling is a very needful strategy to alleviate a demand and supply matching problem in the future.

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