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Edited by Kalim Deshmukh and Mayank Pandey

Nanostructured Materials for Energy Storage

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Edited by

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Volume 1

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Contents

Volume 4

Preface

The rapid increase in the development of advanced nanomaterials provides opportunities for designing unique and efficient energy storage devices with outstanding electrochemical performance. With the present technological developments, research on advanced electrode materials having enhanced power density, cyclic life, and operational safety has increased drastically. With the increasing demand for large-scale energy storage, nanostructured materials have grabbed significant attention, particularly in electric vehicles and next-generation wireless communication devices. The nanostructured energy storage devices can provide extensive power sources with high capacity, good efficiency, and longer cyclic stability. Nanostructured materials possess high specific surface areas, substantial porous structures, special physical and chemical properties, short transport length, higher reversible capacity, and longer cycle life, which make them very useful and value-added materials for energy storage applications. Additionally, the utilization of nanostructured materials in energy storage devices is advantageous because they exhibit a tunable structure with an interface in the nanometer range and they can be synthesized in various shapes, sizes, and topographies. Furthermore, nanomaterials exhibit a larger specific surface area, which is beneficial for enhancing the interaction between the energy devices and the interaction medium as compared with their bulk counterparts. Moreover, nanostructured materials help in advancing the functioning and development of long-life and durable energy storage devices by providing chemically and physically stable electrode materials. Over the last few decades, a library of nanomaterials having different compositions, tailorable properties, and controlled morphology has been studied as electrode (both anode and cathode) materials for lithium-ion batteries (LIBs) and supercapacitors (SCs). The ideal performance criteria for highly efficient energy storage devices are fast ion interchange, high conductivity, excellent electrode–electrolyte interface, good faradaic reactions, and good charging/discharging stability. Nanostructured materials provide significantly enhanced ionic transport and improved electronic conductivity in contrast to traditional materials used in batteries and SCs. Moreover, they also possess more intercalation sites, thereby enabling high specific capacities, fast ion diffusion, and the ability to tolerate high currents. These interesting features of nanostructured materials-based electrodes offer an efficient solution to high-energy and high-power energy storage systems. Thus, continuous efforts have been made by researchers to exploit the unique properties of nanostructured materials that are useful in developing and designing high-performance energy storage devices. However, the control synthesis and optimization of the synthesis processes of nanostructured materials are the keys to designing efficient electrodes as per specific application needs. Besides, it is essential to understand the energy storage behavior at the nanoscale, the relationship between the structure, morphology, and energy storage performance as well as the potential energy storage mechanisms of these nanostructured materials.

The book *Nanostructured Materials for Energy Storage* provides a comprehensive discussion of the recent advances in LIB and SC applications of nanostructured materials with diverse structures and improved properties that help enhance the performance of low-cost, rapid, and highly efficient LIBs and SCs. The book presents innovative concepts and breakthrough knowledge required for the development of nanostructured materials for LIBs and SCs. This book covers the fundamental principles of LIBs and SCs; provides a basic understanding of material selection, synthesis process, characterization, functionalization, design parameters, and development of nanostructured materials for LIBs and SCs applications; and discusses related mechanisms. The book comprises 43 chapters providing a detailed and in-depth discussion on the synthesis, characterizations, device fabrication, and energy storage performance of various nanostructured materials like graphene, hexagonal boron nitride (h-BN), MXenes, carbon nanotubes (CNTs), carbon nanofibers (CNFs), transition metal oxides (TMOs), layered transition metal dichalogenides (TMDs), metal–organic frameworks (MOFs), lithium titanates, lithium transition metal orthosilicates, silicon, molybdenum- and vanadium-based nanomaterials, gel polymer electrolytes, hydrogels, and conducting polymer nanocomposites. As a whole, this book provides a detailed discussion of the current knowledge on the synthesis of various nanostructured materials, their properties and characterizations, functionalization strategies, design and development of LIBs and SCs, and explores the key requirement areas for the development of efficient energy storage devices. A scientific book of this scale is highly needed to explore and comprehensively discuss the recent advances, emerging trends, and the technical challenges in using different nanostructured materials in LIBs and SCs-based energy storage devices. Overall, this book will be a valuable source of reference for all working in the fields of nanostructured materials, electrochemistry, and energy storage devices.

Finally, we highly appreciate the excellent cooperation and valuable contributions from numerous authors across the globe. Our sincere appreciation also goes to the Wiley-VCH team, especially Dr. Martin Preuss, Daniela Bez, and Chandra Sekar Monica, for their efforts and dedicated support during the publication of this book. Finally, we would like to thank Wiley-VCH for publishing this book.

Dr. Kalim Deshmukh
Dr. Mayank Pandey

1

Lithium-Ion Batteries: Fundamental Principles, Recent Trends, Nanostructured Electrode Materials, Electrolytes, Promises, Key Scientific and Technological Challenges, and Future Directions

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1.1 Introduction

Lithium-ion batteries (LIBs) nowadays have found their applications in various areas as portable electrical devices (mobile phones and tablets) and electrical and hybrid vehicles [1–3]. They offer some benefits like high power density, environmental friendliness, and suitable lifetime. Conventional LIBs include a graphite anode, a cathode with the general formula of $LiTMO_2$ (TM (transition metals): Ni, Mn, etc.), and an organic liquid electrolyte. The electrolyte is mostly based on some carbonate-based solvents like ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl carbonate (DMC), a conducting salt ($LiPF_6$), and some additive materials [4, 5]. There are many motivations for further research on LIBs, such as decreasing the battery degradation, increasing lifetime and energy density, using environmentally friendly and recyclable materials, and decreasing the cost. Therefore, a review of the types and preparation methods of LIBs, future trends, and key issues regarding lithium batteries is provided in this chapter.

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1.2 Lithium-Ion Batteries

1.2.1 Fundamental Principles

Researchers are now putting in a lot of time and effort to come up with better ways to store energy. For the commercialization of alternative energy and consequently the substitution of fossil fuels and existing energy sources, several strategies are essential. Because of their high energy density, extended service lifetime, minimal self-discharge, and low volumetric and weight losses, rechargeable LIBs have an essential role in this industry [6–13].

Furthermore, the LIBs act as energy storage with the highest efficiency for a variety of portable devices, including laptops, mobile phones, and digital electronics [14–19]. However, the use of LIBs in pure electric vehicles (PEVs), hybrid electric vehicles (HEVs), and plug-in HEVs (PHEVs) requires between two and five times the energy density than current lithium battery technology (150 Wh kg^{-1}) can provide. Increasing the lithium batteries' energy density may be accomplished by producing high-capacity cathode and anode electrode materials or by employing high-voltage cathode active substances as electrodes. The electrolyte breakdown that happens at more than 4.2 V vs. Li/Li^+ is one of the key obstacles to designing a high-voltage cathode in LIBs. In this regard, significant research is still underway to increase the efficiency of LIBs employing organic and inorganic-based materials [20–22].

The present concept of LIBs is based on the use of transition metal oxides or phosphates as active materials on the cathode side ($LiMn_2O_4$, $LiCoO_2$, $LiFePO_4$, $LiCo_{1/3}Mn_{1/3}Ni_{1/3}O_2$, and so on). On the other hand, the anode uses graphite as its active element. A polypropylene/polyethylene membrane filled with an electrolyte comprising lithium salts (like $LiPF_6$) in various percentages of organic carbonates, including ethylene propylene and DMCs, separates the anode and cathode. The separator keeps the electrodes from making electrical communication while enabling lithium ions to move from the cathode to the anode when charging and discharging. The passage of lithium ions from the anode to the cathode enables the transformation of the chemical into electrical energy, which is referred to as the second phenomenon.

Reversible capacity, long cycle life, strong electrical and ionic conductivity, the diffusion of lithium into active material at a high rate, demonstrated eco-compatibility, and low cost are all conditions for active materials to be deemed acceptable candidates for LIBs. $LiMn_2O_4$, $LiCoO_2$, and $LiFePO_4$ are cathode materials of the highest quality, while graphite is the most often utilized anode due to its superior properties such as low and flat working potential vs. Li, cheap cost, and long cycle life. Nevertheless, graphite permits just one Li ion with 6 carbon atoms to be intercalated (see Figure 1.1), giving a stoichiometry of LiC_6 and a 372 mAh g^{-1} reversible capacity. The penetration rate of lithium into materials containing carbon is between 10^{-12} and 10^{-6} cm^2 s^{-1} (ranging from 10^{-9} to 10^{-7} cm^2 s^{-1} for graphite), leading to low energy density. The replacement of graphite anodes with substances comprising greater energy, capacity, and power density is thus critical. Despite its enormous capacity (3860 mAh g^{-1}), lithium metal cannot be used as an anode in secondary

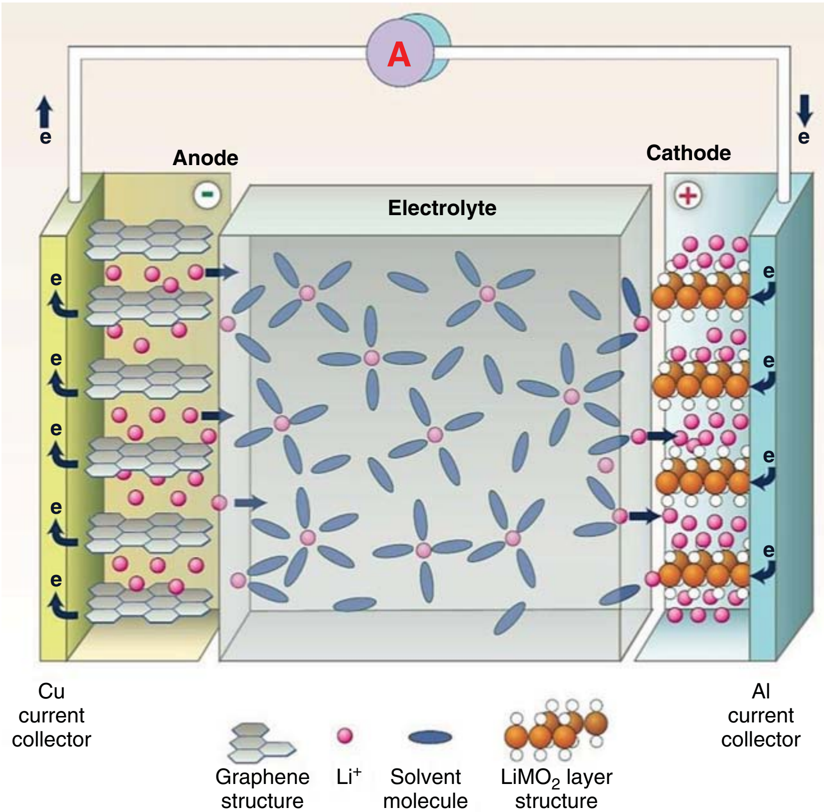

Figure 1.1 Schematic representation of lithium insertion/de-insertion mechanism for current rechargeable lithium battery. Source: Ref. [23], Copyright 2011. American Association for the Advancement of Science.

batteries due to health and safety considerations. A short circuit between the anode and the cathode may occur if tree growth occurs on lithium metal.

1.2.2 Recent Trends

Transportation systems and energy consumption may be accurately measured by population growth and the development of cities. LIBs were originally intended for use in electric vehicle (EV) transportation, residential energy storage, and, more widely, the elimination of community reliance on fossil fuels, among other applications. Because of its increasing acceptability and commercial diffusion by electric machines, LIBs technology is expected to be a major accomplishment in renewable energy sources. In reality, when it comes to energy and power production, LIBs outperform all other battery technologies. For this reason, battery technology that can alter the situation has been the primary focus of most studies so far. Historical evidence indicates that LIB technology is quite recent, having just been in a commercial application for around thirty years.

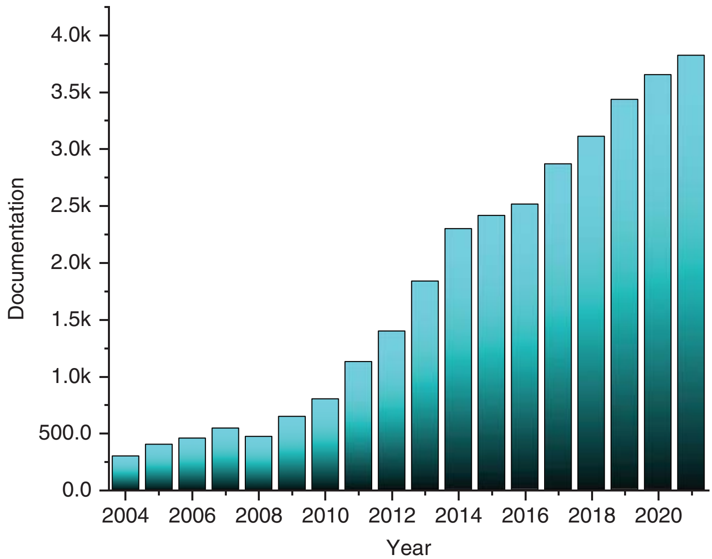

Figure 1.2 Number of publications related to LIB topics. Source: Scopus.

Since its debut commercialization by Sony in 1991, the LIBs' performance has continuously improved, allowing for these accomplishments. Improvements are made not only in terms of specific energy (Wh kg^{-1}) and energy density (Wh l^{-1}) but also in terms of safety, affordability, and charging rate [24, 25]. Nevertheless, further progress is required to accelerate the energy revolution that our contemporary civilization is experiencing.

Figure 1.2 displays the number of publications related to LIB topics. The growing number of relevant scientific articles from 2000 to 2019 demonstrates the dramatic increase in academic research on LIBs. During the same time period, almost 10,500 patents relating to LIBs were published (source: Google Patents). Consequently, the cars powered by batteries face an uphill battle against vehicles powered by internal combustion engine (ICE)-driven that are more than 150 years old. LIBs, electric machines, and other LIB-related products were mass-produced and commercialized as a result of the pledges and financial backing of the Central Financial Authority (CFA). Stanley Whittingham, Akira Yoshino, and John Goodno, three of the technology's pioneers, have been awarded the 2019 Nobel Prize in Chemistry by the Royal Swedish Academy of Sciences. It demonstrated that there had been a significant shift in research and development, as well as the influence of LIBs on our civilization. Nevertheless, it is anticipated that all essential operational parameters of LIB technology (such as energy, safety, power, and cost) will continue to improve. EVs such as HEVs, PHEVs, or all-electric EVs (BEVs) are projected to gain in popularity as time goes on. Because the automobile industry accounts for more than 60% of all LIB production globally, it is, in reality, the driving force behind these breakthroughs. It is crucial to remember that EVs accounted for "just" little more than 1% of total automotive sales globally in 2017 [26]. It is important to note that this percentage surpassed 4% in 2020, more than four years beyond the original forecast. People are encouraged to purchase BEVs and PHEVs by national authorities that supply subsidies (purchase credits) or tax advantages. There are plans to enhance these incentives in almost every EU member state, and several have already put limitations on the purchase of ICE vehicles (Figure 1.3).

Incentives have also been provided in the United States, Japan, and China. These framework initiatives have surely aided in the rise of worldwide EV registrations (Figure 1.4a) and cumulative sales (Figure 1.4b), both of which have shown excellent growth rates. It should be noted that, despite the fact that financial incentives for EVs in China and the United States were higher in 2020, resulting in a higher worldwide growth rate (37%), sales in both countries neared the previous year's level, while sales in Europe, for example, grew.

Customers may be put off by the high cost of a new EV compared to a conventional vehicle powered by an ICE. Battery costs are expected to fall over the next several years owing to increasing manufacturing and the usage of cheaper metals more costly than cobalt (Figure 1.5) [29]. But it is worth noting that the price per kilowatt-hour at the pack level decreased by nearly 85% between 2010 and 2018. The NEDO 2030 research and development targets for the future generation of batteries indicate that battery pack costs may reduce again (Figure 1.5) [29].

The LIBs, as previously stated, are likely to improve in all operational measurements. Therefore, security is of paramount importance. Fires and explosions produced by unintended combustion of volatile solvents used in LIBs are comparable to those caused by gasoline or diesel fuel, according to a National Highway Traffic Safety Administration (NHTSA) assessment on the danger of electrochemical failure. Figure 1.6 demonstrates the schematic representation of the electrolyte, anode, and cathode constituents utilized in battery research and development for EVs [29]. There is no doubt that safety can and should be improved, but major strides have already been made in this regard. It is also expected that in driving distances of 500 km (300 miles) or more, with charging times of 10–15 minutes or less, they will need refueling equal to that of ICE-powered cars. The employment of solid or liquid electrolytes, cathode materials without cobalt, increased understanding of interconnections, and the long-term usage of future LIBs are all techniques that are consistent with each other [29].

The importance of manufacturing and recycling facilities for the creation of raw materials and cells cannot be overestimated. The manufacture of LIBs is currently primarily concentrated in Asia, particularly in Korea, China, and Japan. Nevertheless, an increase in global manufacturing is required to fulfill the escalating demands of the automobile industry. While Tesla is expected to boost its cell output in the United States to 22 GWh per year, manufacturing over 300 GWh is now on the table in Europe. To fulfill the rising demand for electric cars, however, a major increase in manufacturing will be required in the near future. Figure 1.7 shows the selected most popular research trends in rechargeable Li and Li-ion battery fields for achieving high energy densities in future batteries [30].

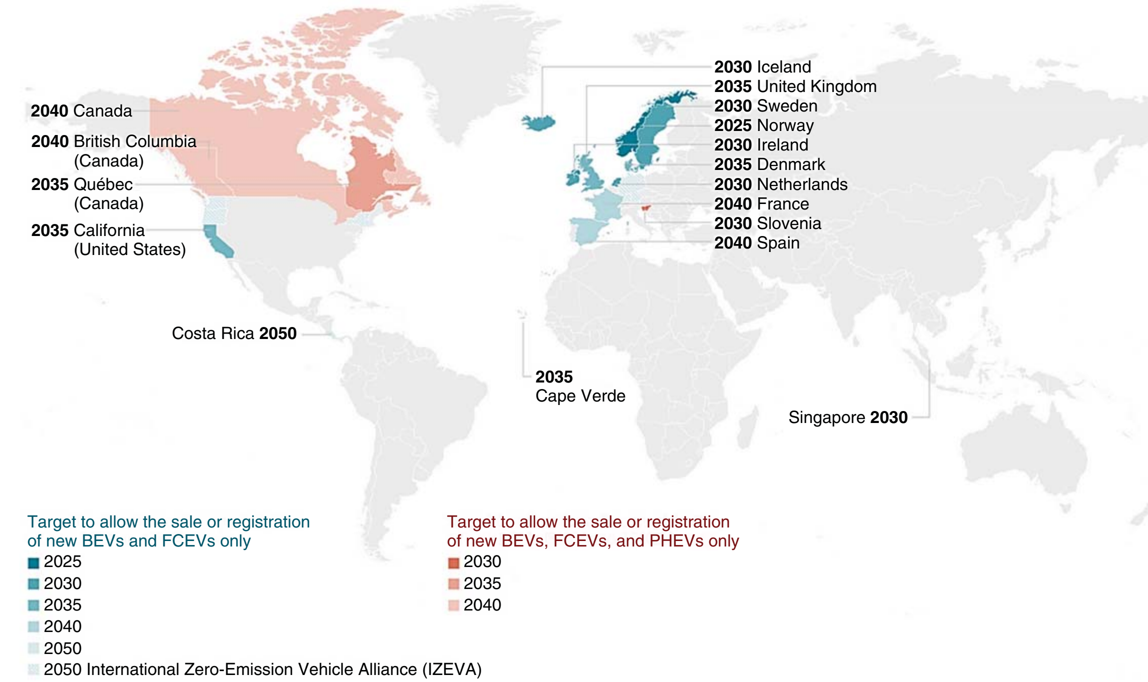

Figure 1.3 Plans to restrict the registration of automobiles that are (solely) fueled by gasoline (in years) for numerous world nations and an overview of incentives in place for purchasing EVs (marked by the green checkmark) (Please keep in mind that this list is not complete and Scotland has given a different date than the rest of the United Kingdom). Source: Ref. [27]. International Council on Clean Transportation.

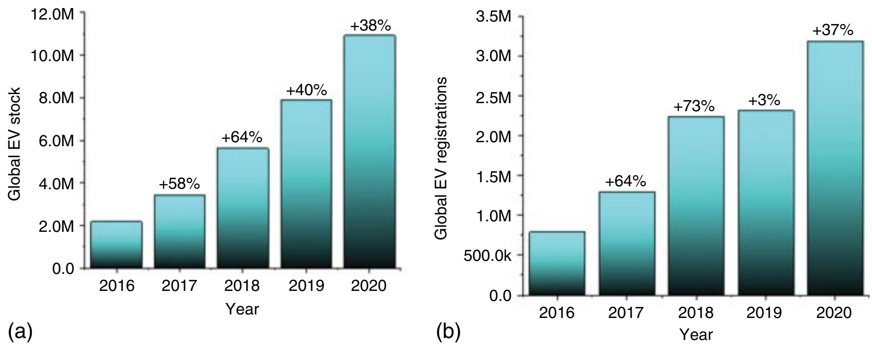

Figure 1.4 Worldwide annual statistics on electric machine stocks (a) and registrations (b), based on electrical dynamics. Source: Ref. [28], Zentrum für Sonnenenergie- und Wasserstoff.

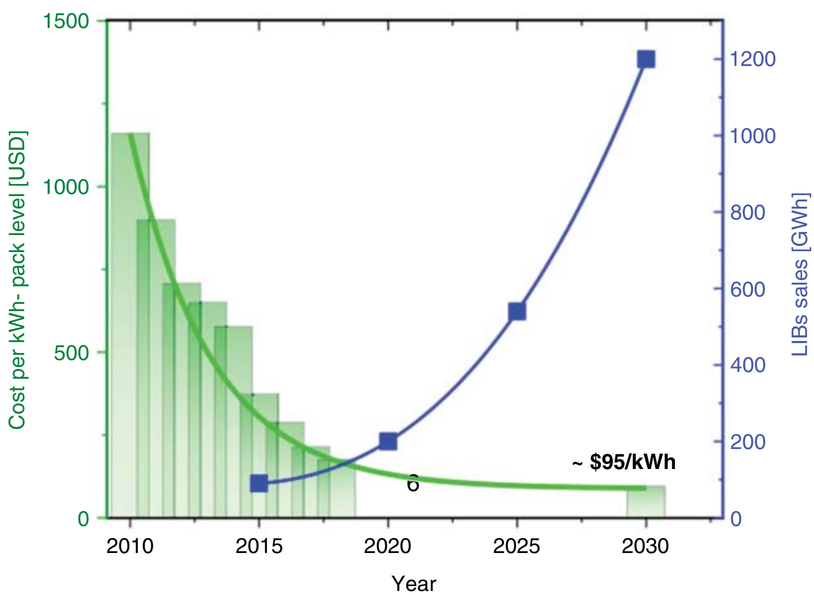

Figure 1.5 Pack-level lithium battery pricing (a portion of this diagram is derived from Bloomberg NEF's "Behind-the-scenes view at the expense of lithium-ion batteries" published by NEDO for 2030). Source: Ref. [29]. Copyright 2020. Reproduced with permission from Elsevier.

1.2.3 Which Options Are Available for Battery-Active Materials?

The energy density of the next generations of lithium and LIBs can be determined by the specific capacity and the voltage at which the active materials of the battery work. Studies, financial support, and efforts have been made in the field of the production of electrode materials for lithium-ion and lithium batteries. The advantages, disadvantages, and the most commonly used anode and cathode materials are reviewed in Figures 1.8, 1.9, and 1.10 [31–33].

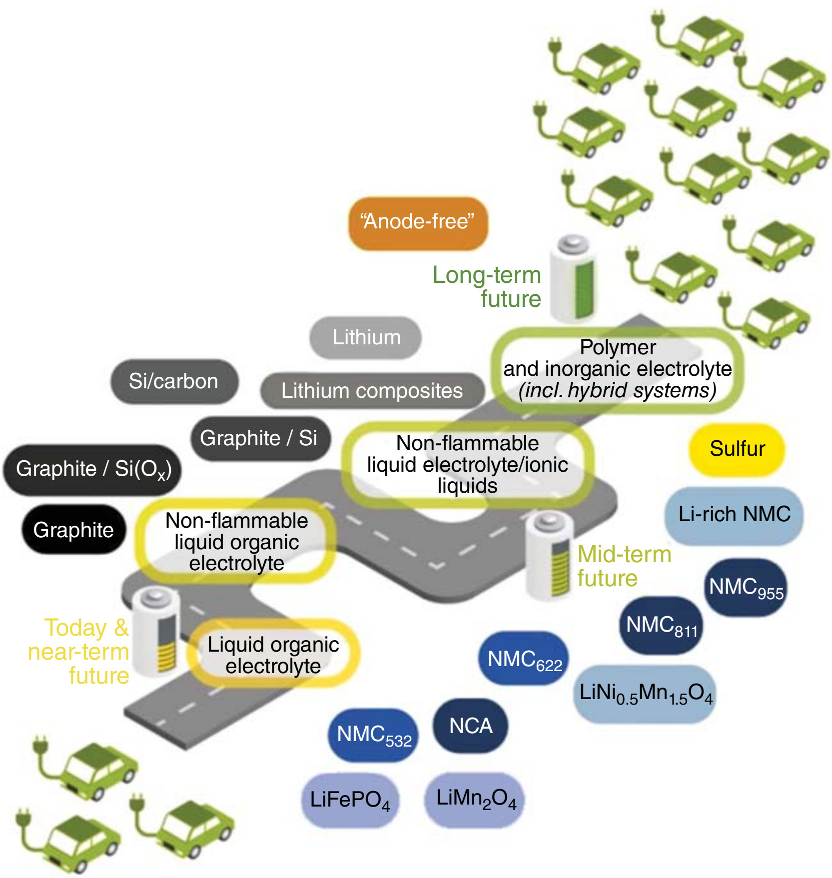

Figure 1.6 Schematic representation of the electrolyte, anode, and cathode constituents utilized in battery research and development for electric vehicles. Plan of R&D strategies for electrical machines based on the substances applied in anode, cathode, and electrolyte. Source: Ref. [29]. Copyright 2020. Reproduced with permission from Elsevier.

Figure 1.8 shows the growth of LIB operating electrodes. Generally, cathode materials should have a high voltage and anode materials should possess a low voltage, while every electrode material should benefit from a high specific capacity [31]. Materials that have the mentioned properties can lead to the improvement of Li-ion and Li batteries' energy densities and also result in the reduction of the size and weight of future batteries. On the other hand, ecological and economic factors such as production cost, benignity, and abundance should not be neglected. Figure 1.9 displays the voltage in contrast with the capacity chart of the function of anode and cathode materials for high-rate LIB [32]. Figure 1.10a demonstrates a graphical depiction of the engaged anode materials for the following generation of lithium batteries and illustrates the capability compression and potential (in contrast with Li/Li^+) [33]. Figure 1.10b represents a graphical depiction of

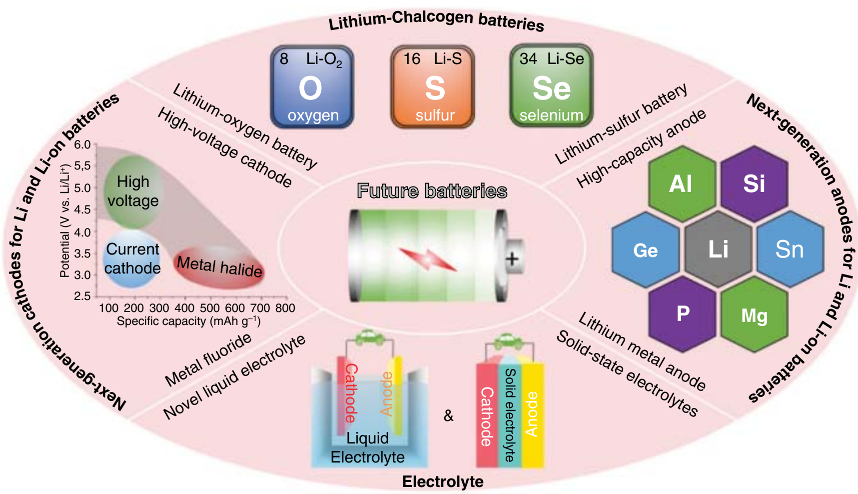

Figure 1.7 The selected most popular research trends in rechargeable Li and Li-ion battery fields for achieving high energy densities in future batteries. Source: Ref. [30]. Copyright 2020. Reproduced with permission from the Royal Society of Chemistry.

three various kinds of lithium storage anodes, along with their benefits and drawbacks [33].

1.2.3.1 High-Voltage Cathode Materials

The average work potential and the specific volume-weight capacities for many kinds of thick interlayer cathode materials, such as commercial and high-voltage cathodes, have been shown in Figure 1.11 which indicates that the crystal structure of $LiMO_2$ (M = Ni, Co, or Mn) and its derivatives have lots of lithium and manganese [30]. In Figure 1.11, it can be seen that the commercial cathodes of lithium manganese oxide (LMO, $LiMnO_2$), lithium cobalt oxide (LCO, $LiCoO_2$), and lithium iron phosphate (LFP, $LiFePO_4$) have low work potential (<3.8 V) and also low volume-weight capacities (<750 mAh cm^{-3} and <180 mAh g^{-1}) [30].

Great efforts have been made in the field of cell energy density progress, optimization, and research on the materials with better capacities and higher work potentials in the construction of the cathode (for example, >3.8 V and >200 mAh g^{-1}). Previous studies report that layered oxides containing high percentages of nickel, lithium, and manganese can be considered solutions for the near future. The group of layered oxides with high Ni contents ($LiNi_{1-x}M_xO_2$, M = Co, Mn, and Al) have improved gravimetric and volumetric specific capacities compared with other intercalation-type cathode materials that have been utilized in some of the commercial products. This group includes $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA, ~220 mAh g^{-1} and ~980 mAh cm^{-3}) and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811, ~200 mAh g^{-1} and ~932 mAh cm^{-3}). In addition, there are also substantial options

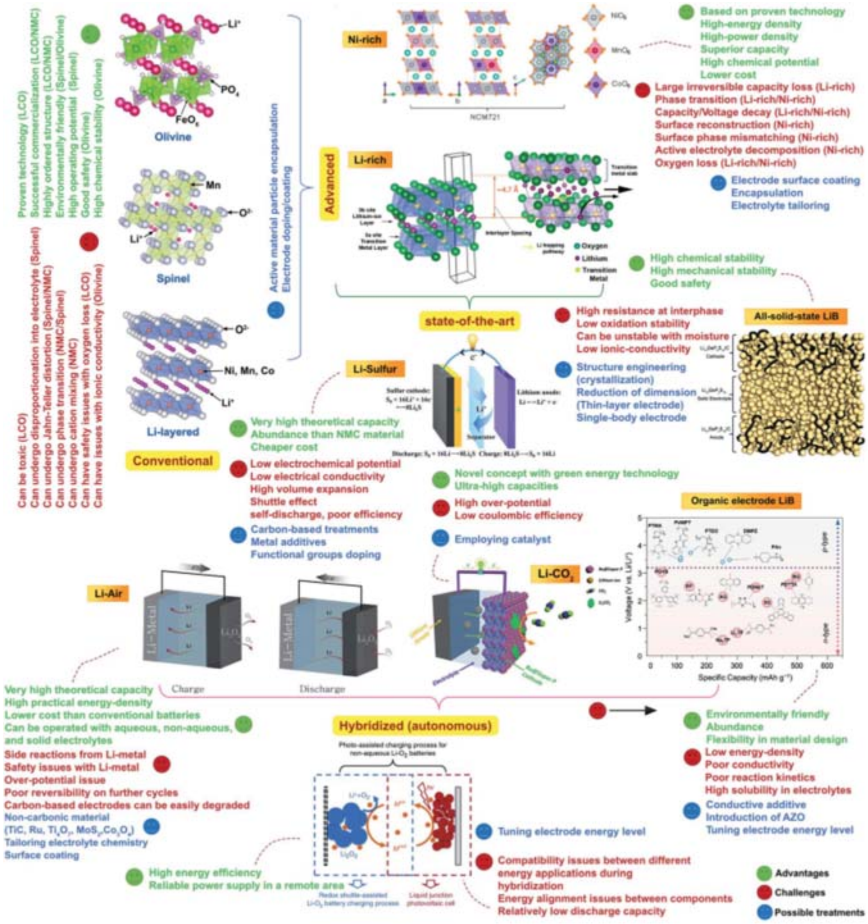

Figure 1.8 Depiction of the growth of lithium-ion battery operating electrodes. Source: Ref. [31]. Copyright 2019. Reproduced with permission from the Royal Society of Chemistry.

such as $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM333, ~150 mAh g^{-1}) and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622, ~170 mAh g^{-1}). The materials with high nickel content, such as $xLi_2MnO_{3-(1-x)}$ $LiMO_2$ or $Li_{1+x}M_{1-x}O_2$, M = Mn, Ni, Co, in comparison with the layered oxides with high values of nickel are more inexpensive and have better capacities (250–300 mAh g^{-1}). For example, the work potential, specific weight capacity, and specific volume capacity for the high-voltage spinel oxide $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) are 4.7 V, 147 mAh g^{-1}, and 626 mAh cm^{-3}, respectively. According to the reports of the previous study, the better work potential and specific gravity can result in high voltages using periodic LCO cathodes (high-voltage LCO: H-LCO) [34] of sulfates and phosphates (low specific capacity ~170 mAh g^{-1}) such as $LiNiSO_4F$ and Li_2NiPO_4F. They are polyanionic compounds and can produce good work potentials in the interval from 4.0 to 5.3 V.