Nanostructured Electrode Materials for Rechargeable Lithium-Ion Batteries

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ABSTRACT

Today, rechargeable lithium-ion batteries are an essential portion of modern daily life. As a promising alternative to traditional energy storage systems, they possess various advantages. This review attempts to provide the reader with an in-depth understanding of the working mechanisms, current technological progress, and scientific challenges for a wide variety of lithium-ion battery (LIB) electrode nanomaterials. Electrochemical thermodynamics and kinetics are the two main perspectives underlying our introduction, which aims to provide an informative foundation for the rational design of electrode materials. Moreover, both anode and cathode materials are clarified into several types, using some specific examples to demonstrate both their advantages and shortcomings, and some improvements are suggested as well. In addition, we summarize some recent research progress in the rational design and synthesis of nanostructured anode and cathode materials, together with their corresponding electrochemical performances. Based on all these discussions, potential directions for further development of LIBs are summarized and presented.

Keywords : Nanostructure, Lithium Ion Battery, Thermodynamics, Kinetics, Anode, Cathode

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1. Introduction

For many years, the non-renewable fossil fuels (e.g., coal, crude oil, and natural gas) have been the major energy resources powering the rapid development of the global economy and human civilization. With the large-scale consumption of these traditional fossil energies, a critical energy crisis, associated with the environmental impact of their combustion products, was triggered, resulting in global warming, and air and water pollution [1-3]. As a response to these problems, there is a growing demand for the development of alternative renewable and environmentally friendly energy supplies throughout the world [4,5]. In this regard, renewable energies, such as wind, sunlight, and tides, are the most promising energy sources to resolve these problems [6,7]. However, these energies sources suffer from large fluctuations, which limit their direct application in the grid

as a power supply and thus, necessitates highly efficient systems for energy storage and conversion on demand.

Typically, energy storage technologies, particularly for portable electronic devices, electric-powered vehicles, and even grid energy storage, make good use of the conversion of electricity and chemical potential, such as batteries [8], supercapacitors [9], and fuel cells [10]. Among many types of energy storage technologies, rechargeable battery systems are generally an important class, capable of converting chemical energy to electrical energy, and delivering the electrical energy by cycled charging/discharging processes [11,12]. Unlike traditional secondary batteries, including lead-acid, nickel-cadmium, and nickel metal hydride battery, which have a low energy capacity, heavy weight, and a short lifespan, lithium-ion batteries (LIBs) have been chosen as next-generation rechargeable batteries owing to their obvious advantages, such as a relatively high energy density (650 Wh L^{-1}), slow self-discharge, lighter weight, no memory effect, and longer cycle lifespan [11,13-15].

Since the first LIBs were commercialized by Sony

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Corporation in 1991, the last few decades have witnessed a revolution in the battery market and remarkable improvements in battery performance, in terms of the energy density (Wh L^{-1}), and the specific energy (Wh kg^{-1}) [16,17]. Today, LIBs occupy a dominant position among various high-energy applications, especially portable electronic devices, such as cell phones, laptops, and electric-powered automobiles, which includes hybrid electric vehicles (HEV), battery electric vehicles (BEV), or plug-in hybrid HEVs (PHEVs), and stationary energy storage as well [18-20]. However, the current LIBs are still not capable of providing a satisfactory supply for electric vehicles in terms of capacity, cost, and lifetime. Consequently, extensive efforts utilizing nanotechnology are required to develop strategies for further improving the battery performance [21].

In this review, we offer an overview of the advances in the latest electrode materials and focus on some of the state-of-the-art strategies for designing materials for high-performance LIBs as well. The first section presents a short review of the fundamental electrochemistry of LIBs and a deep treatment of the underlying battery reaction mechanisms for acquiring high-rate LIBs, from different perspectives, including thermodynamics and kinetics. Next, an overview of the current development of intrinsic nanostructured electrode materials with high performance in LIBs is presented, together with detailed classification schemes for both anodes and cathodes. Finally, a summary of the advantages and disadvantages of current electrode nanomaterials is presented, together with the future challenges and prospects regarding research on high-performance LIBs. We hope this review will serve as a basic guide for understanding and designing novel nanostructured electrode materials for application in high-rate LIBs.

2. Current status of electrodes for LIBs

LIBs occupy a dominant position among various energy storage technologies because of their unique advantages. Lithium is the third lightest element, and the lithium ion has one of the smallest ionic radii. Moreover, lithium possesses the lowest reduction potential, because of which lithium-based batteries have the highest possible cell potential. These properties enable LIBs to deliver the highest gravimetric and volumetric energy densities and the highest rate

capability in comparison with other battery chemistries. Moreover, to date, only LIBs have been successfully commercialized in the battery market, becoming an irreplaceable power source in comparison with other alkaline-ion batteries, such as Na-, and K-ion batteries [22-24]. Despite all these advantages, LIBs still suffer from poor kinetics of Coulombic reactions involved in ion diffusion, as well as electron transfer, in the anode and cathode [25]. Additionally, cost is still a major obstacle inhibiting their expansion into renewable energy applications in the long run. Therefore, it is necessary to improve the cost and performance of LIBs, which can significantly broaden their potential applications and facilitate novel technologies for energy storage.

To achieve breakthroughs toward high-performance LIBs, it is important to acquire a thorough understanding of the underlying mechanisms of battery reactions.

2.1 Fundamental configuration and working principles of LIBs

In general, the anode (negative electrode), cathode (positive electrode), electrolyte, and separator are the fundamental components of LIB configurations, as illustrated in Fig. 1 [26,27]. The cathode and anode are the most studied components because of their crucial impact on the battery performance. In principle, LIBs convert and store electrochemical energy through reversible electrochemical reactions. During charging, driven by an applied external voltage, lithium ions are extracted from the cathode and diffuse through the lithium-ion-conductive electrolyte, followed by insertion into the anode. Simultaneously, electrons are donated from the cathode and enter the anode through the external circuit, thus maintaining electric neutrality. During discharging, reverse reactions occur, along with the generation of electrons that flow to operate the external load. The lithium ions and electrons are generated from the following reactions:

The reversible electrochemical reaction occurring in LIBs demonstrates their charge-storage properties. As the diffusion of lithium ions and transfer of elec-

Fig. 1. Schematic of the operating mechanism of lithium-ion batteries. Reprinted with permission from Ref. 26. Copyright © 2014 The Royal Society of Chemistry.

trons are involved in the charging/discharging process, it is necessary to understand the transport pathways of lithium ions and electrons within battery systems [28,29].

In this section, analyses from both thermodynamic and kinetic perspectives are introduced to help readers acquire a basic familiarity with the correlation between structure and property of electrode materials.

2.2 Electrochemical thermodynamics

2.2.1 Band structure perspective

During the charging process, the lithium ion deintercalation together with the electron donation causes the redox reaction of the electrodes, leading to variations in the electronic structure of the redox centers, as depicted in Fig. 1. In general, the metal sites in lithium-based metal oxides, sulfides, and other compounds are considered as redox centers because the electrons in their d states are more active in comparison with those in the p states of anions [30]. By overlapping of the metal d states with the ligand p states, M-L bonds (M-transition metal; L-ligand) are formed, where the metal types, anions, and the formed crystal structure determine their bond characteristics, namely, ionic or covalent.

It is known that the fundamental principle of redox

Fig. 2. Schematic description of a slightly oxidized redox couple for different positions relative to the top of the anion p bands. (a) Itinerant versus polaronic character of hole states of a redox couple on the approach to the top of the anion p band, (b) pinned couple with predominantly anti-bonding (*a.b.*) anion p hole states and predominantly cation d bonding (*b.*) states, and (c) redox couple too far below the top of anion p band for significant cation d character in hole states. Reprinted with permission from Ref. 32. Copyright © 2009 American Chemical Society.

reactions can be explained with assistance of the band structure of both cations and anions. During discharging, the Fermi energy level (E_F) is the driving force for transporting electrons from a high energy level (anode) to a low energy level (cathode) within the band structure [31].

Considering insertion-type materials as an example, their charge/discharge reversibility in a battery system is influenced by the change in E_F of the transition metal (TM) ions. Because the electronic structure of the TM ions is 3d4s, the oxidation or reduction reaction of the metal elements occurs by the loss or gain of 3d-electrons, respectively, during the charging/discharging processes. Generally, the electrons hopping into the insertion-type materials can cause phase interface migration, and these electrons could be considered to be “small polarons” [31]. Consequently, some representative reaction mechanisms can be explained accordingly.

As depicted in Fig. 2, a good match between the energy level of the TM redox couple and the anion p-orbital is inevitable [32]. Obviously, as seen from Fig. 2(a)-(c), E_F drops gradually from $(d+p)^n/d^{n+1}$, which is close to the primarily TM cation d band, into the bottom of the combinational $(p+d)^n$ bonding, and even into the primarily anion p band. As indicated from Fig. 2(c), given that anions favor the electron loss, leading to oxidation, structural instability is caused during the intensive lithium ion deintercala-

tion. Therefore, the energy of the TM redox couple should be higher than that of the anion p-orbital, as depicted in Fig. 2(a), or close to the top of the p-orbital, resulting in the splitting of TM d-orbital into the bonding orbital $(d+p)^{n+1}$ and the anti-bonding orbital $(p+d)^n$, as depicted in Fig. 2(b). Because only the electrons from the orbital $(p+d)^n$ can be lost during charging, E_F can be pinned above the anion p-orbital. In summary, the energy level position of the p-orbital intrinsically restricts the voltage of electrodes [32].

Furthermore, whether or not E_F matches the lowest unoccupied molecular orbital (LUMO) of the electrolyte needs to be considered. As depicted in Fig. 3, the anode and cathode are the reductant and oxidant, respectively, and the energy separation E_g determines the energy window of the liquid electrolyte, which equals the difference between its LUMO and the highest occupied molecular orbital (HOMO). During discharging, electrons at E_F of the anode (μ_A) migrate through the external circuit to populate on the cathode (μ_C). If μ_A is above LUMO of the electrolyte, it undergoes a reducing reaction on the anode; and if μ_C is below HOMO of the electrolyte, it is oxidized on the cathode unless the electron transfer

energy across the interface reaches a kinetic stability. A passivation layer on the electrode materials is considered an effective strategy to prevent these reactions from occurring. Therefore, both μ_A and μ_C need to be located in the range of E_g to maintain thermodynamic stability, so that the open-circuit voltage (V_{OC}) of a battery is constrained according to the following equation:

$$eV_{OC} = \mu_A - \mu_C \leq E_g \quad (3)$$

with e being the electron charge. And the energy density of a battery is

$$E = QV_{OC} \quad (4)$$

where Q is the total charge transferred by the current per unit weight ($Ah\ g^{-1}$) on discharging or charging.

2.2.2 Gibbs free energy perspective

In addition to the electronic structural perspective, Gibbs free energy represents the minimum thermodynamic potential of a battery system at the chemical equilibrium state under a certain pressure and temperature. It equals the maximum electrical work generated by the electrochemical reaction, determined by the cell voltage (V) and electron charges:

$$\Delta G_r = -nFV \quad (5)$$

where ΔG_r represents the Gibbs free energy of the system, n is the number of transferred electrons, and F is the Faraday constant.

During charging/discharging, the Gibbs free energy variation in the battery system is expressed as:

$$G_r = \Delta H_r - T\Delta S_r = \Delta U_r + P\Delta V_r - T\Delta S_r \quad (6)$$

where P and T are the pressure and temperature, respectively. The $P\Delta V_r$ and $T\Delta S_r$ represent the volume change and the variation of the vibrational and configurational entropies during lithium ion intercalation/deintercalation, which is on the order of 10^{-5} and 10^{-2} eV, respectively. ΔU_r is the internal energy change, approximated as 2-3 eV. All these parameters are combined to evaluate the ΔG_r of the reaction [33,34].

According to the Nernst equation, the working voltage can be expressed by the chemical potential

Fig. 3. Schematic diagram for open-circuit energy of the electrolyte stability window E_g and the electrochemical potentials of anode (μ_A) and cathode (μ_C) in a system with a liquid electrolyte and solid electrodes. Φ_A and Φ_C are the anode and cathode work functions. Reprinted with permission from Ref. 32. Copyright © 2009 American Chemical Society.

Fig. 4. Voltage profile showing a linear correlation with the slope of the free energy of the electrode materials. (a) Formation of a solid solution between the electrode host material and Li as panel, (b) a smooth sloping voltage curve. (c) If Li insertion is accompanied by a first-order phase transformation from a Li-poor phase α , to Li-rich phase β , a free energy curve and (d) a plateau in the voltage curve are obtained. (e-f) Steps in the voltage profile demonstrate the existence of a stabilized intermediate phase. Reprinted with permission from Ref. 36. Copyright © 2012 American Chemical Society.

difference ($\mu_A - \mu_C$), also named as open-circuit voltage (V_{OC}) [35]:

$$V_{OC} = (\mu_A - \mu_C)/F \quad (7)$$

As depicted in Fig. 4, a significant picture of the voltage profile emerges from the measured voltage curve correlated with Gibbs free energy with varying lithium concentration [36]. Three main transformations are evident: the solid-solution reaction (Fig. 4(a-b)), first-order phase-transformation (Fig. 4(c-d)), and phase-separation reaction (Fig. 4(e-f)). Accordingly, the chemical potential, and thus, the battery voltage, are affected by Gibbs free energy. For instance, the chemical potential of oxygen plays a significant role in designing cathode materials with high voltage (>4.5 V) [37]. In general, a high oxygen chemical potential can be produced by a high voltage during charging. When the potential is above 0 eV, O_2 generated in the crystal lattices can be released from the cathode materials, making their structure unstable, thus making safety a consideration [38]. As a result, for developing high-voltage cathodes, a far higher negative oxygen chemical potential and improved thermal and structural stability are crucial for high-performance batteries with improved stability and safety.

In practice, if the electrolyte reduction/oxidation is self-limiting, many electrochemical cells can operate moderately beyond the electrochemical window (E_g) of the electrolyte. This requires the decomposition products to be ionically conductive for lithium-ion transportation, and electronically insulating as well to prevent further decomposition. Such passivation films, called the solid electrolyte interphase (SEI), can typically form below the reduction potential of the electrolyte, and are of special significance to LIB anodes [39,40].

2.3 Electrochemical kinetics

As mentioned above, both the voltage profiles and the intrinsic capacities can be determined from the thermodynamic perspective, while the kinetic processes determine the rate properties, which influence the ion and electron mobilities and mechanisms of the phase transformations. Moreover, by the second law of thermodynamics, dissipation is present in all kinetic processes, requiring spontaneous processes to occur only in the presence of an overpotential. Therefore, in kinetic processes, the free energy dissipation can influence the battery performance significantly, including the rate capability, capacity, and polarization [41]. During charging/discharging, dominant kinetic processes mainly include ion transfer, elec-

Fig. 5. Dominant kinetic processes in LIB cathode materials during charging/discharging. (a) Transport kinetics producing a surface lithium concentration x_s that differs from the average concentration $\bar{x}$. (b) Interfacial ion-exchange kinetics, causing a decrease in the lithium-ion electrochemical potential η_{Li^+} across the electrode/electrolyte interface. (c) Phase-transformation kinetics, represented here by the hypothetical transformation of a phase β into phase α . Reprinted with permission from Ref. 41. Copyright © 2017 Wiley-VCH verlag GmbH&Co. KGaA.

tron transport, and phase transformations, as depicted in Fig. 5. Thus, to fabricate high-performance LIBs, it is extremely significant to improve the diffusion kinetics of lithium ions and the electrons.

With regard to the intrinsic electrode materials, ionic diffusivity is a critical parameter to characterize the lithium-ion diffusion ability, and electronic conductivity is an important parameter for describing the electron transport, which arises from their band structures. The ionic diffusivity (D) can be expressed as follows [36,42]:

$$D = \rho \lambda^2 \Gamma \quad (8)$$

where λ is the hop distance between adjacent interstitial sites, ρ denotes a geometric factor dependent on the sublattice symmetry of interstitial sites, and the hop frequency Γ can be described as [36]:

$$\Gamma = \nu \exp(\Delta E/kT) \quad (9)$$

where ν is a vibrational prefactor, and ΔE represents the variation in migration barrier. It can be inferred that even a very small ΔE shift caused by a variation of compositional, chemical, or crystallographic factors can significantly influence the diffusion coefficient.

In layered intercalation-type materials, lithium ions generally occupy octahedral sites, and they hop between neighboring octahedral sites through a curved path along an adjacent tetrahedral site, as depicted in Fig. 6 [41]. When lithium ions traverse

Fig. 6. Monovacancy and divacancy Li migration mechanisms. Each tetrahedral site shares faces with three octahedral Li sites. The two mechanisms differ in whether the third Li site is occupied or not. Reprinted with permission from Ref. 41. Copyright © 2017 Wiley-VCH verlag GmbH&Co. KGaA.

these tetrahedral sites, their hopping path is determined by the intermediate state energy. Along this hopping path, the distance between the lithium ions and the coordinated oxygen ions around them can be maximized. As a result, the migration barrier for hopping lithium ions becomes sensitive to the local ordering of lithium vacancy surrounding them. Based on the vacancy cluster diffusion mechanism, lithium ions can hop into not only isolated vacancies, but also divacancies, and triple vacancies as well. Among them, as the intermediate tetrahedral site is surrounded by an increasing number of vacancies, the migration barrier for the tetrahedral site decreases, as exhibited in Fig. 7 [36]. It can be inferred that the ion hopping paths have an important impact on the diffusion coefficient of the electrode materials.

Fig. 7. Crystal structures and Li hopping mechanisms in general intercalated compounds. (a) A layered crystal structure with an ABAB or ABCABC stacking of a close-packed anion sublattice; (b) A spinel crystal structure characterized by a three-dimensional interstitial network for Li ions. Diffusion in these crystal structures is often mediated by vacancy clusters (divacancies in the layered form and triple and divacancies in the spinel form) if Li occupies octahedral sites. Reprinted with permission from Ref. 36. Copyright © 2012 American Chemical Society.

3. Nanostructured electrode materials

On the basis of the discussions from both thermodynamic and kinetic perspectives in the above sections, a close relationship between the structure—particularly the crystal structure—and properties, such as the rate capability, voltage, and capacity, has been established. Meanwhile, a promising path has been laid for the rational design of optimized electrode materials so that LIBs with further improvements can be fabricated. LIB behaviors, including rate and cycling capacities, depend considerably on the properties of both the cathode and anode materials, including the theoretical capacity and reversibility [43]. Therefore, it is necessary for electrode materials to comply with the standards as follows: (1) showing rapid reaction kinetics for lithium ions and electrons; (2) having an excellent ionic diffusivity together with a high electronic conductivity; (3) possessing a short path for lithium-ion diffusion and electron transfer; (4) remaining as a tough structure facilitating fast lithium ion insertion/extraction.

Nanostructured materials, with a minimum of one dimension in the nano-size scale, can be classified into zero-dimensional (0D), such as nanodots and nanoparticles; 1D, such as nanorods, nanowires, and nanofibers; and 2D nanostructures, such as

nanosheets and nanoplates. In comparison with their bulk-sized counterparts, the dimensions of nanostructured materials are responsible for many unusual chemical, physical, mechanical, and electrical properties, thus, they find them potential for applications in various devices for energy storage [44,45]. Thus, nanostructured materials have many potential for LIBs, including (1) the short diffusion length of lithium ions (materials with lower lithium-ion diffusion coefficients can be used); (2) short electron transport pathways (poor electronic conductors can be used); (3) large electrode/electrolyte contact areas (advantage: higher rate capability); (4) capability of accommodating volume changes involved in charging/discharging processes (advantage: enhanced cyclability); (5) possibility of utilizing reactions not realizable with bulk materials (e.g. conversion electrode reactions); and (6) low complexity in processing and high flexibility in electrode geometries.

Unfortunately, nanostructured materials could also cause a number of problems:

(1) Poor particle packing, leading to lower volumetric energy density. Densification of the active mass can be a general solution to resolve the poor packing density of nanosized powder. As an alternative, the use of secondary nanoparticles can help increase volumetric energy densities.

Fig. 8. Potential versus capacity chart about cathode and anode materials for high-rate LIBs. Reprinted with permission from Ref. 48. Copyright © 2015 American Chemical Society.

(2) Unexpected side reactions at the electrode/electrolyte interface, resulting in high self-discharge, poor cyclability, and reduced lifespan. These major shortcomings may be overcome by selecting appropriate active materials with their operating potentials limited to the electrochemical energy window of the electrolyte. Additionally, an effective method of restricting the SEI formation is to utilize secondary nanomaterials, as their internal nanodomains are less subject to passivation.

(3) Complex synthetic strategies, leading to high costs for manufacturing. Progress in bottom-up and top-down synthesis of nanostructured materials is expected to pave the way toward cost-effective processes [46,47].

In the past decade, plenty of scientific investigations have been conducted on electrode materials, and some of them have already become practical options in the LIB industry. Fig. 8 summarizes some significant developments in electrode materials. In the following sections, we discuss these developments.

3.1 Nanostructured anode materials

Developing suitable anode materials having high capacity, enhanced lithium ion diffusion, long cycling life, high cycling stability, and no safety issues is highly advantageous for replacing conventional graphite anodes. Thus far, three main reaction mechanisms for anode materials during the charging/discharging process have been reported, such as intercalation, alloying, and conversion mechanisms, as illustrated in Fig. 9 [49,50].

Fig. 9. Schematic illustration of three typical reaction mechanisms for LIB anode materials during the charging/discharging process. Reprinted with permission from Ref. 48. Copyright © 2015 American Chemical Society.

3.1.1 Intercalation-type materials

From the conceptual perspective, as host materials, commercial anodes normally possess layered structure, and undergo reversible lithium ion intercalation/deintercalation in their lattices, which is defined as the “intercalation mechanism.” Lithium metal anodes used to be reviewed by some researchers [51]; however, the related topic is not covered in this section. Additionally, carbonaceous materials, titanium oxide-based materials, such as TiO_2 or $Li_4Ti_5O_{12}$, and other metal oxides (orthorhombic Nb_2O_5 ($T-Nb_2O_5$)) are alternative classes of anode materials based on the intercalation reaction mechanism [52-54].

Fig. 10. Crystal structures of (a) lithiated graphite. Reprinted with permission from Ref. 59. Copyright © 2014 American Chemical Society. (b) lithium titanate (LTO). Reprinted with permission from Ref. 80. Copyright © 2011 American Chemical Society.

3.1.1.1 Carbonaceous materials

In comparison with metal oxides, chalcogenides, and polymers, carbonaceous materials possess some advantages, such as more negative redox potentials and higher specific charges, and are therefore, considered the primary choice for anodes in LIBs [55]. In general, carbon is known for its low cost, abundance, low delithiation potential, high lithium ion diffusivity, good electrical conductivity, and somewhat small volume change during lithiation/delithiation [52,56-58]. They can be categorized into several different forms, such as graphite and graphitic materials, soft carbon and hard carbon materials.

It is known that graphite is an intercalation-type anode material which has been successfully used in commercialized LIBs. It possesses a layered structure composed of an ordered arrangement of carbon atoms in a hexagon network, leading to excellent mechanical stability, lithium diffusion, and electrical conductivity, as illustrated in Fig. 10(a) [59,60]. Because an ideal graphitic structure without defects is difficult to obtain, artificially fabricated polycrystalline carbon materials having a similar graphite structure—called highly ordered pyrolytic graphite (HOPG)—are often exploited. HOPG is produced with an expensive vapor transport approach, which increases the cost [61]. Lithium intercalation is predominantly determined by the crystallinity and morphology, together with the microstructure, of anode materials, which thus determines the lithiation/delithiation potential. Up to 1 lithium atom per 6 carbon atoms can be accommodated, leading to lithium-carbon alloys from the following reaction [60]:

Its theoretical capacity can reach 372 mA g⁻¹. However, the reversibility of the lithium intercalation reaction is affected by factors, such as the formation of SEI and the insertion of lithium solvation into the graphene layers, leading to an increased cell resistance and decreased power density with increasing cycling number [55,62]. Additionally, owing to its low melting point and rapid lithium diffusion, graphitic carbons cannot blend well with propylene carbonate (PC)-based electrolytes. PC-based electrolytes and lithium ions insert between the graphitic layers, causing the exfoliation of graphite, and thus a capacity loss [63]. During lithium intercalation, a uniaxial strain of ~10% along the plane edges is generated within single crystalline graphitic particles, which may damage the SEI layer and thus, decrease the cyclic life of the battery [58].

In addition to graphitic carbon materials, amorphous carbon has also been extensively studied for LIBs [64-66]. Amorphous carbon, categorized into hard carbon and soft carbon, has many excellent characteristics, including poor crystallinity, large lattice spacing, and high compatibility with the electrolyte. Soft carbon, being amorphous in nature, is normally produced by pyrolyzing petroleum pitch or polymers at high temperature of approximately 1500°C, leading to the formation of coke or carbon black. These carbonaceous products can also be referred to as “low-specific-charge non-graphitic carbon”, which has Li_xC₆ with x being 0.5-0.8, and graphite with x = 1. Under high-temperature treatment, graphitized carbon can be gradually evolved with weak crosslinking formed between the layers. Moreover, at much higher temperatures (>2800°C), sufficient crosslinking is developed, which makes the material mechanically much harder in comparison with normal graphite; this material is termed as a “high-specific-charge carbonaceous material”, also called “hard carbon”, with x ranging from 1.2 to 5 in Li_xC₆ [55]. Hard carbon is much less susceptible to exfoliation because it contains small graphitic grains that have a disordered orientation. Moreover, these graphitic grains contain nanovoids in between, leading to less volume expansion. With the nanovoids and defects, the gravimetric capacity can increase, causing the capacity to exceed the theoretical value of 372 mAh g⁻¹ [52,55,67-68]. Therefore, a combination of these properties results in hard carbon having an excellent capacity and a longer cycling life, mak-

ing it suitable candidate as an anode material. However, ease of the SEI formation is increased due to large amount of exposed edge planes, which reduces Coulombic efficiency (CE) during the first cycles. Moreover, the voids reduce the particle density, decreasing the volumetric capacity [69,70].

The above facts support the use of bulk carbonaceous materials to carbon nanomaterials of various dimensions. In comparison with graphite, carbon allotropes, including 1D carbon nanotubes (CNTs), 2D graphene nanosheets, and 3D porous carbon with nanosized pores, have some advantages, such as larger surface area, shorter diffusion length, greater electrical conductivity, and enhanced lithium storage. Despite these advantages, CNTs and graphene still face some intrinsic safety issues because of their low lithiation potential [71].

CNTs, formed by rolled graphene sheets containing one layer, i.e., single-walled CNTs (SWCNTs), or more layers, called multi-walled CNTs (MWCNTs), have been reported to have a large capacity due to their excellent electronic conductivity and chemical stability. Earlier researches demonstrated that lithium could be adsorbed onto both the interior and exterior layers of CNTs, with the former having a higher adsorption strength [72,73]. Additionally, in contrast to the radial direction, the axial direction is more beneficial for the lithium ion diffusion [74], and the length of CNTs is also critical to lithium ion diffusion [75]. Moreover, there are other aspects that influence the battery performance of electrodes fabricated from CNTs. For instance, it was reported that defects in CNTs help improve atomic and ionic diffusion, leading to improved battery capacity; the purity of the CNTs and the category of additives affect SEI formation, thus influencing the reversible capacity [76].

Graphene, 2D nanosheets exfoliated from bulk graphite, has been extensively researched in the last few decades. In comparison with graphite, graphene has many advantages as an LIB anode material. Similar to CNTs, graphene has a large surface area and electronic conductivity. Moreover, both the planes and edges of graphene nanosheets can accommodate lithium ions and electrons in the electrolyte, increasing the theoretical specific capacity up to 744 mAh g^{-1} , which is over twice that of graphite (372 mAh g^{-1}) [77]. By introducing defects into graphene sheets, the specific capacity can be improved to be higher than the theoretical value. Graphene is beneficial for

applications in flexible electronic devices because of its excellent mechanical flexibility. Despite all these advantages, graphene still suffers from some shortcomings that hinder its further development in the field of LIBs. For instance, due to its low density and structural design, graphene exhibits an irreversible capacity and poor CE as well. It is noticed that because of undesired side reactions between the lithium ions and oxygen-contained functional groups together with the SEI formed on the defects, the discharge capacity decreased from 1233 mAh g^{-1} in the first cycle to 672 mAh g^{-1} with a CE loss of 55%, following which a reversible capacity of $\sim 500 \text{ mAh g}^{-1}$ was still maintained after 30 cycles [77]. Additionally, because graphene nanosheet restacking may decrease the strength, fabrication of high-quality graphene with much fewer defects is challenging.

Porous carbon nanostructures, which have distinct pore sizes, are another class of anode materials that has been considered for LIBs. According to the pore size range, porous carbonaceous materials are generally classified into three main categories: microporous ($<2 \text{ nm}$), mesoporous ($2\text{-}50 \text{ nm}$), and macroporous ($>50 \text{ nm}$). Because of their large surface area and interlinked carbon networks, it is possible to enhance the electrical conductivity and accommodate the strain generated during charging/discharging, leading to excellent electrochemical performance [78]. Unlike 1D or 2D carbonaceous materials, the irreversible capacity loss can be inhibited by applying 3D porous carbon nanostructures. For instance, Li *et al.* reported that, via a so-called “soft-template” approach, hollow mesoporous carbon spheres with a novel double-shelled nanostructure were produced by the self-assembly of amphiphilic polymer PS-*b*-PAA, TEOS (tetraethyl orthosilicate) as the Si precursor, and dopamine as the carbon precursor. This unique structure resulted in a high specific capacity of 920.3 mAh g^{-1} at a current of 100 mA g^{-1} and maintaining a high retention rate over 100 cycles [78]. However, the large surface area can cause large irreversible capacity loss, which was demonstrated by Omichi *et al.* [79]. It was reported that, carbon nanostructures from designed synthesis possessed high surface area, leading to higher lithium storage battery anodes. However, high surface area inevitably resulted in obstacles, including the presence of high concentrations of defects and higher contribution of edge sites into the overall surface area. As a result, high lithium storage capacity for the

initial charge/discharge could be delivered due to the strong binding between lithium atoms and defects and edge sites, and owing to the trapping of lithium ions, large irreversible capacity loss could be caused, thereby reducing their availability in the electrochemical process.

Despite the foregoing discussions, carbonaceous materials alone cannot meet the increasing requirements for modern power because of their low theoretical capacity. Therefore, novel anode materials with other high-performance lithium storage materials hybridized with carbonaceous materials have attracted the interest for scientists aiming for further improvements.

3.1.1.2 Titanium oxide-based materials

Another class of anode materials is titanium oxide-based materials, including TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and so on. It is known that graphite exhibits a lithiation potential with the value of ~ 0.2 V vs. Li/Li^+ . This is so low that an electronically insulating SEI layer may form on its surface, as SEI formation is possible to occur below 1.0 V [60]. This may lead to a slower lithium insertion, lithium loss in the anode, and a safety issue especially at high rates. These disadvantages can be avoided by using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ having a spinel structure, as depicted in Fig. 10(b) [80], and as demonstrated by Zhao *et al.* in 2015 [81].

Due to its excellent thermal stability, high rate, large volumetric capacity, and long lifespan, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been successfully commercialized [82]. It possesses an equilibrium potential of ~ 1.5 V vs. Li/Li^+ , allowing it to operate at above 1.0 V, thus preventing the SEI formation. Additionally, due to its zero strain generated during charging/discharging, it exhibits a comparatively high specific capacity of ~ 170 mAh g^{-1} , maintaining excellent cyclic stability [83]. Moreover, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has a high potential, which restrains the lithium dendrite formation even at high rates. This makes it an extremely safe anode material. However, its poor electrical conductivity of $\sim 10^{-8}$ - 10^{-13} S cm^{-1} and low lithium diffusivity of 10^{-9} - 10^{-13} cm^2 s^{-1} limit its performance, which can be improved to a certain extent by decreasing the particle size and applying a conductive coating [84,85]. For instance, Wang *et al.* reported that porous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanofibers were produced with an average diameter of 230 nm, and they were composed of nanoparticles in an average diameter of ~ 47.5 nm, exhibiting values of 120 mAh g^{-1} in

the reversible capability at rate of 10C at 1.0-2.0 V [86]. Furthermore, other forms of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, such as nanosheets and mesoporous hollow spheres, also exhibit high performance with a retention rate of over 90% [87,88]. Additionally, processing with a conductive carbon coating and surface nitridation is also shown to improve their performances [89,90]. A study has reported a carbon-coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanostructured material through a facile solid-state strategy, showing a superior rate performance with discharge capacity of ~ 119 mAh g^{-1} at 30C [91].

Moreover, among many TiO_2 allotropes, TiO_2 -B with a layered structure, possesses favorable open channels that are beneficial for lithium-ion diffusion, which enables a remarkable theoretical specific capacity of 335 mAh g^{-1} to be obtained. Additionally, it has a distinguish pseudocapacitive mechanism for lithiation/delithiation, making it attractive and promising for ultrafast charging [92].

3.1.1.3 Other metal oxide materials

Based on the same intercalation pseudocapacitive mechanism, orthorhombic $\text{T-Nb}_2\text{O}_5$ materials are also considered a promising candidate for anode materials. They can deliver fast lithium insertion kinetics, and they also undergo considerably less structural change during charging [93]. With the redox reactions for the Nb +5/+4 couple, Nb_2O_5 gains a maximum capacity of 720 C g^{-1} by storing charges with 2 Li^+ per unit [94]. It can be inferred that nanostructured $\text{T-Nb}_2\text{O}_5$ can obtain high electrochemical performance in two ways. First, lithium ions insert the $\text{T-Nb}_2\text{O}_5$ electrode along preferential crystallographic pathways. Second, the open channels between the interconnected NbO_x sheets cause the energy barrier to decrease and enhance the transfer of local charge. Moreover, as the anode in LIBs, $\text{T-Nb}_2\text{O}_5$ is very appropriate because it can provide a relatively high power.

Lee *et al.* reported that core-shell nanostructured Nb_2O_5 @carbon crystals were fabricated into two distinct crystalline phases, orthorhombic (T) and pseudohexagonal (TT). They are both applicable for anode in LIBs [95]. Moreover, free-standing composite papers composed of composite between orthorhombic $\text{T-Nb}_2\text{O}_5$ and graphene nanosheets were fabricated by a polyol-mediated solvothermal method by Kong and co-workers, with the capacitive mechanism contributing to 83.2% of the current at a

scan rate of 5 mV s^{-1} [96]. However, due to the low electrical conductivity ($\sim 3 \times 10^{-6} \text{ S cm}^{-1}$) of Nb_2O_5 , applying a surface coating of carbon and introducing conductive scaffolds are both necessary to obtain an improvement.

3.1.2 Alloying-type materials

Another alloying reaction-based mechanism involving lithium and anode materials, including Si, Sb, Sn, Ge, Al, Bi, Cd, and their alloys, compensates for the poor capacity and safety risks associated with conventional graphite anodes [97, 98]. Huggins and Besenhard first proposed that binary metal alloys could be used as effective electrode materials for energy storage devices [99, 100]. Later, a large number of investigations were conducted on the design of different metals and metal oxide alloys and their performances evaluation. Among them, the preliminary metal alloys are mostly lithium-based alloys, namely, Li_xM , with M representing a different metal [97]. Here, M can support the strain within the electrode generated during charging/discharging by forming the matrix of the alloy, thus improving the electrical conductivity [101]. However, it is noticed that the very large volume expansion up to even several times of the initial volume causes crack formation on the alloy surface, leading to the loss of electrical contact and a short cycle life. To overcome this problem, employing electrochemically active binary metal alloy materials as the anode has been considered an effective strategy. In this context, electrochemically active metals include Si, Sb, Sn, Ge, Al, and so on [102-107]. Because they can accommodate multiple lithium ions per M, alloying materials Li_xM ($\text{M} = \text{Si, Sb, Sn, Ge, etc.}$) can deliver excellent volumetric and gravimetric energy densities, as depicted in Fig. 9.

3.1.2.1 Si-based alloys

Among the electrochemically active metals, Si has been the most studied, because it has some characteristic features, such as storage abundance, low cost, chemical stability, relatively low average delithiation potential ($\sim 370 \text{ mV vs. Li/Li}^+$), high gravimetric and volumetric capacities, and environmental friendliness. Its alloy formation with lithium comprises several steps involving the formation of different alloys, such as $\text{Li}_{12}\text{Si}_7$, Li_7Si_3 , $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{22}\text{Si}_5$, delivering a high theoretical capacity of $\sim 4200 \text{ mAh g}^{-1}$ for the

$\text{Li}_{22}\text{Si}_5$ form [108]. During charging/discharging, alloy formation is also accompanied by the transformation between the crystalline and amorphous phases, which is described as follows [109,110]:

Discharging process

Charging process:

Although the Si-based alloy electrodes exhibit an exceedingly high reversible capacity, they still unavoidably undergo a drastic volume expansion up to 400% during lithiation and SEI layer formation occurring at low potentials, which remain major challenges. Due to the large volume expansion, Si exhibits both poor reversibility and rapidly declined capacity.

3.1.2.2 Ge-based alloys

Similar to Si, Ge is another choice for an electrochemically active metal. Li-Ge alloys have also been considered an interesting candidate, with a theoretical capacity of $\sim 1568 \text{ mAh g}^{-1}$, which corresponds to the $\text{Li}_{17}\text{Ge}_4$ form [111]. Although this value is much lower in comparison with that of Li-Si alloys, Ge is still favored because it has a faster lithium diffusivity in comparison with Si.

Toward the development of effective electrodes for high-rate LIBs, Lim *et al.* combined X-ray absorption spectroscopy (XAS) and operando X-ray diffraction (XRD) studies to understand the influence of cyclic rate on the Ge phase transformation during charging/discharging process in Ge anodes [112]. It was demonstrated that under a sluggish cyclic rate (C/21), the time was sufficient for the lithium ions to diffuse into internal Ge particles, allowing the c-Ge to completely transform to an intermediate a- Li_xGe (a-amorphous) product. Next, further lithiation transformed the a- Li_xGe structure into a fully crystallized c- $\text{Li}_{15}\text{Ge}_4$ (c-crystalline) phase. This structural transformation, which occurred at much poor cyclic rates, resulted in improved structural reversibility of Ge

electrodes, which led to its cycling stability. However, as the cyclic rate was increased from C/21 to C/10, a mixture of both a-Li_xGe and c-Li₁₅Ge₄ phases was produced because of the partially reversible phase transformation under such conditions. Therefore, the effective access of lithium ions to redox sites is restricted, leading to decreased structural reversibility and shortened cyclic life. Such a phase mixture with different structures and phases would undergo severe stresses from nonuniform volume changes, leading to battery failure. When the cyclic rate was further increased, not only was a large amount of Ge found, but also the c-Li₁₅Ge₄ phase disappeared at the end of lithiation. The reason for this result may be that the time for lithium ion diffusion into the core of Ge was insufficient, enabling its core to remain unreacted and resulting in a highly heterogeneous feature. Therefore, incomplete lithiation at higher charging rates could result in a core-shell structure, with the c-Ge phase in the core and the a-Li_xGe phase as the shell layer. This phenomenon is essential for the design of novel electrode materials, particularly Ge-based alloy materials, that facilitate faster lithium-ion diffusion even at higher cyclic rates to acquire high-rate LIBs [113].

3.1.2.3 Other alloys

Similarly, there are other alternative electrochemically active metals. Sn metal can undergo a reaction with lithium that produces distinct Li-Sn phases, such as Li₂Sn₅, LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂, and Li₂₂Sn₅ [97]. Among them, Li₂₂Sn₅, which was identified as the Li₁₇Sn₄ phase, corresponding to 4.5 lithium atoms per Sn atom, is the most lithium-rich phase. It delivered a capacity of 959.5 mAh g⁻¹ under an operating voltage of 0.5 V vs. Li/Li⁺ [97]. Although the Li-Sn alloy anode exhibits a lower reversible capacity in comparison with the Li-Si alloy anode, Sn has several advantages, such as a lower melting point facilitating the formation of a Li-Sn alloy, and a higher mobility than that of other metals [114]. However, because of the nonuniform volume variation and the generation of distinct intermetallic Li-Sn alloy structures, poor capacity retention can be observed during charging/discharging [115]. To address this problem, the oxide of Sn was proposed as an effective solution. When Sn oxides reacted with lithium, Li₂O was formed, and Sn oxides were reduced to Sn as follows [116]:

After the first cycle, it is clearly observed that an irreversible capacity loss has resulted from the Li₂O formation, which is electrochemically inactive. During the following cycles, good stability remained, which could be explained by the reversible formation of the Li-Sn alloy, and the formed Li₂O acting as a matrix and thus preventing the aggregation of Sn nanoparticles.

Additionally, there are many other cost-effective metals capable of alloying with lithium. For instance, Zn, Cd, and Pb exhibit high volumetric capacity over their low gravimetric capacity, while Al undergoes serious cracking with dimensions down to the nanoscale. This has been verified by *in situ* transmission electron microscopy (TEM) [117]. P and Sb possess good capacity, and high-performance electrodes have been fabricated by them with carbon through the ball milling method [118]. However, both of them are toxic, and have relatively low lithiation potentials. Furthermore, P can cause safety issues due to the potential formation of dangerous phosphine, and Sb is not abundant in storage.

3.1.3 Conversion reaction-based materials

The third reaction mechanism, called the “conversion reaction mechanism”, theoretically stores lithium by reversible redox reactions between the lithium ions and TM compounds (M_aX_b, M = Mn, Fe, Co, Ni, X = O, S, Se, F, N, etc.), according to the reaction [119, 120]:

with the formation of Li_nX being thermodynamically feasible. Nevertheless, there is considerable difficulty in decomposing the electrochemically inactive Li_nX by the reduced elemental M powder [121]. Therefore, for the conversion mechanism, the critical solution to acquire its reversibility is to form electroactive elemental M nanoparticles that can help decompose the Li_nX matrix surrounded by the SEI layer [97,121].

Conversion-type anode materials (CTAMs) can generate high specific capacities. Because of the generation of reduced metal nanoparticles, conversion

reactions completely change the structures and compositions of electrode materials. Therefore, a critical requirement for excellent CTAMs is the capability of realizing the reversible process, leading to regeneration of their initial structure and composition, to achieve stable performance. In comparison with intercalation- and alloying-type materials, conversion-type materials have attracted a considerable amount of attention from researchers recently. To obtain more improvements, novel strategies should be developed.

It is known that a broad range of TM-based compounds, such as TM oxides, chalcogenides, fluorides, phosphides, and nitrides, have been investigated as CTAMs, considerably broadening the choices of materials for high-performance LIBs [122-130]. Moreover, in comparison with graphite anodes, CTAMs definitely demonstrate adjustable reaction potentials according to the strength of the ionic bonds formed between the TM cations and anions [131]. Therefore, the safety risks associated with the battery due to the lithium dendrite formation are avoided to a great extent [55]. In this section, we discuss several important types of CTAMs for LIBs and describe the advances made in some recent studies.

3.1.3.1 Metal oxides

Conversion-type metal oxides M_aO_b ($M = \text{Mn, Fe, Co, Ni, etc.}$) were discovered by Tarascon *et al.* There have been the subject of intensive research because they possess high specific capacities through multi-electron reaction per M and better capacity retention, as shown in Fig. 9 [121]. During the electrochemical reaction, metal oxides react with lithium ions and form metal nanoparticles, along with the Li_2O component as the matrix at the first lithiation, followed by reverse reactions to their initial state during delithiation [132]. Moreover, the working potentials of the conversion systems remain within the range of 0.5-1.0 V, and they increase with the M -O bond ionicity [133]. It is inferred that conversion-type materials must primarily possess two important characteristics, namely high specific capacity and secure lithiation potential, to obtain high-rate LIBs. Therefore, the voltage change due to reaction limitations causes voltage hysteresis, thereby leading to poor capacity and energy efficiency.

It is generally accepted that the particle size has a high impact on the physical properties that influence

the arrangement of bonds between surface atoms. Based on this, Piozot *et al.* reported that nanosized metal oxides were utilized for the first time, improving the performance owing to the large number of atoms. They are present on the surface having dangling bonds, which are available for transforming Li_2O to lithium ions and M -O [132]. Consequently, the division and aggregation of particles noticeably influence the cyclic performance of CTAMs [134]. To avoid this problem, Zhou *et al.* bonded SnO_2 particles to graphene nanosheets *via* nitrogen and oxygen pinning points in them [134]. They concluded that particles were chemically attached onto graphene nanosheets, inhibiting particle aggregation and thereby improving the capacity of $>1200 \text{ mAh g}^{-1}$ over 500 cycles. Furthermore, the composite material could bear high rate capability, maintaining a capacity of $>500 \text{ mAh g}^{-1}$ at 20 A g^{-1} (25°C), and $>1200 \text{ mAh g}^{-1}$ on retuning to 0.5 A g^{-1} (0.6°C).

Nevertheless, using graphene or other carbon materials to form composite materials with metal oxide nanostructures can considerably enhance the rate capability in that they can increase the rate of electronic flow to redox sites, thereby facilitating the redox process [135]. Wu *et al.* reported that the composite obtained by attaching Co_3O_4 onto graphene sheets improved the rate capability of Co_3O_4 particles to a significant extent [135]. Similarly, it is not sufficient to enhance the rate capability of metal oxides by just reducing the particle size to nanoscale to obtain a high surface area and a high proportion of surface atoms [137]. This can cause higher irreversible lithium loss and SEI layer formation on the particle surface after the initial cycles, which can result in an increased diffusion distance for lithium, leading to capacity loss and poor rate capability [133].

In addition, several aspects, such as composition, structure, and morphology, may play various roles in influencing the capacity and retention rate of the anode materials [137,138]. Yang *et al.* reported that another strategy was introduced to gain control over structural changes. At the same time, the hard inactive Fe_3C was combined with the electrochemically active Fe_2O_3 to gain improvement on its electrochemical performance [133]. The hard characteristic of the inactive material helps in maintaining the integrity of the anode's structure, and the electrochemically active material helps in maintaining the electronic transport, thereby improving capacity retention.

Moreover, according to the space layer charge phenomenon, this representative heterostructure at the interface of $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{C}$ provides additional energy storage.

Therefore, to obtain excellent electrode materials for high-rate LIBs, it is necessary to appropriately control the composition, structure, and morphology, as discussed in the various examples presented above.

3.1.3.2 Metal chalcogenides

Since the 1970s, metal sulfides have been mostly investigated as electrode materials for LIBs. One example is titanium disulfide, which exhibits high capacity as well as a long cycling life [139]. Owing to the ease of their morphology control, thermal stability, good conductivity, and high theoretical specific capacity, they have proved themselves as another class of significant conversion-type materials, compared with other anode materials in LIBs.

However, capacity fading is still one of the critical shortcomings that affects the performance of metal sulfides. As per our knowledge, there are two main causes for this problem. First, voltage hysteresis has been implicated, which can be avoided by methods similar to those discussed in the previous section. Second, the key obstacle to their real-world application is the generated polysulfide anions that shuttle against their gradient. According to reaction (16), during the continuous charging/discharging process, polysulfide anions of Li_2S_x ($6 < x \leq 8$) are generated, which tend to break down into Li_2S_x ($2 < x \leq 6$), which are relatively smaller. Because polysulfide anions easily dissolve in liquid organic electrolyte, creating a concentration gradient, these anions are driven to penetrate the separator and move against this concentration gradient, leading to their shuttle transport. This phenomenon significantly affects ion flow both in the electrolyte and through the separator, which negatively influences the cyclic performance of LIBs. Moreover, owing to the high resistivity of sulfur ($10^{-30} \text{ S cm}^{-1}$), polysulfide anions also deposit onto electrode surface, leading to a barrier layer that blocks the lithium diffusion and electron flow [140,141]. With this, the temperature of interior LIBs is further increased, and even more dangerously, a thermal explosion may occur [142]. To overcome the problems caused by the generated polysulfide anions, new nanostructures with compositions that prevent

the production of polysulfide anions, and new morphologies that minimize the dissolution of polysulfide anions, must be developed.

Another serious problem encountered is the volume changes of sulfur during charging/discharging. The volume change can reach ~80%, thereby increasing the total volume of the battery and decreasing the volumetric capacity [143]. Further, the expansion that the battery undergoes is also responsible for the voltage hysteresis, which renders the structure of metal sulfides unstable [143]. Various effective strategies, such as nanostructure engineering, composition tuning, morphologies control, and hybrid structures, have been developed to solve these problems. For instance, to enhance the ionic flow, Mahmood *et al.* reported that 2D graphene has been utilized to help 1D tubular Co_3S_4 product adsorb the polysulfide anions by forming a composite material between them [144]. The composite material exhibited an enhanced capacity of 720 mAh g^{-1} after 100 charging/discharging cycles, maintaining the CE value at 99.9%. However, because of the large irreversible loss after the first few cycles, the composite material exhibited poor rate capability. Additionally, Wang *et al.* demonstrated that a system with tiny nanoparticles encapsulated in a shell composed of nitrogen-doped carbon was produced [145]. With this special structure, cobalt sulfide acquired a highly improved rate capability as well as an improved capacity of 340 mAh g^{-1} at 2.5 A g^{-1} . In this study, the carbon shell not only provided better control over SEI layer but also inhibited the dissolution of polysulfide anions in the electrolyte. Similarly, nickel sulfide can also be considered an option for anode material [146].

Furthermore, molybdenum sulfide (MoS_2), an interesting material with 2D sheet-like structure and good electronic properties, has been extensively investigated by numerous researchers [147,148]. MoS_2 possesses an interlayer distance of $6.15 \text{ \AA}$, larger than that of graphene ($3.35 \text{ \AA}$), which increases the lithium intake [149]. Its theoretical capacity is $>670 \text{ mAh g}^{-1}$, holding 4 lithium ions per unit, based on the following reaction [150]:

Nevertheless, it is noticed that MoS_2 suffers from some severe shortcomings such as structural failure

Fig. 11. Crystalline configurations and electrochemical reactions of some types of typical cathodes: (A) layered LiMO_2 , (B) spinel LiM_2O_4 , (C) olivine LiMPO_4 , (D) Li_2MSiO_4 , (E) LiMBO_3 , (F) LiV_3O_8 , (G) V_2O_5 , (H) FeF_3 . Reprinted with permission from Ref. 158. Copyright © 2016 The Royal Society of Chemistry.

and undesirable ion mobility. Therefore, a more rapid capacity fading is caused, and Li_2S is very likely to react with the electrolyte and form the SEI layer over the electrode surface, thereby decreasing the cyclic stability and rate capability. Recently, it has been demonstrated that nanocomposites composed of MoS_2 and carbonaceous materials show promise with their improved reversible capacity of 900-1000 mAh g^{-1} and enhanced cyclic stability [151,152]. To maintain the ionic and electronic flow and structural stability, MoS_2 must not just form a simple mixture with carbonaceous materials but also chemically interact with them. Wang *et al.* have employed sulfur to bridge MoS_2 with sulfur-doped graphene sheets, aiming to stabilize its structure and improve its conductivity to obtain a longer cyclic life and higher capacity retention [146].

3.2 Nanostructured cathode materials

For LIBs, it is generally accepted that cathode materials are always considered the determining factor of the energy density of the fabricated devices. Therefore, developing high-performance cathode materials with high energy density, low cost, safety, and large-scale production efficiency is of high importance for use in LIBs.

Since the early application of LiCoO_2 [153], it has been proved that many cathode materials with a large

number of different crystalline structures, especially layered oxides (LiCoO_2 , LiMnO_2 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$), spinel oxides (LiMn_2O_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$), or olivine polyanions LiMPO_4 ($\text{M} = \text{Fe, Co, Ni, and Mn}$), enable lithium ions to undergo a reversible intercalation/deintercalation process that is accompanied by a valence change of the TM cations in a stabilized structural framework [154-157]. Beyond these materials, there are also other cathode materials, such as LiV_3O_8 , oxides (e.g. V_2O_5 , MnO_2) and fluorides that have also attracted considerable interests. The crystal structures of these cathode materials are summarized and depicted in Fig. 11 [158].

Similar to anode materials, the nanostructures of cathode materials could also play a pivotal role on their electrochemical performances in LIBs, which could include the morphologies, porosities, surface chemistries and so on [159]. For instance, the diffusion time for lithium ions within electrode materials can be estimated by the following equation [14]:

$$\tau = \lambda^2 / D_i \quad (18)$$

where λ and D_i refer to the diffusion length and diffusivity, respectively. Therefore, for a cathode material possessing a porous nanostructure, a high surface area provides superior contact between the electro-

lyte and the cathode surface in comparison with the bulk material. Meanwhile, the thin wall of the porous nanostructure could offer the greatly shortened diffusion path for lithium ions. As a result, an improvement could be obtained on the rate capability of LIBs.

3.2.1 Layered oxides

LiCoO₂, which was introduced by Goodenough, is the first LIB cathode material that was commercialized. As shown in Fig. 11(A), its layered structure is of a regular order, belonging to the space group of $R\bar{3}m$ [158]. It provides 2D channels through the CoO₂ interlayers composed of edge-shared CoO₆ octahedrons for rapid lithium-ion diffusion. However, there are some challenging problems associated with LiCoO₂, one of which is structural instability, which is a result of the weak van der Waals interaction between the CoO₂ layers. Therefore, a realistic capacity of only 140 mAh g⁻¹ can be delivered, which is nearly half its theoretical capacity (274 mAh g⁻¹) [160], and a potential plateau at 3.9 V is shown. Moreover, because Co is expensive and toxic, LiCoO₂ has a high cost, and environmental safety is a concern. For instance, flakelike LiCoO₂ with exposed {010} active facets were synthesized through a facile co-precipitation method and served as a cathode material for LIBs [161]. When operating at a high cutoff voltage of 4.5 V, the resultant LiCoO₂ delivered a reversible discharge capacity of 179, 176, 168, 116, and 96 mAh g⁻¹ at 25°C under the current rate of 0.1, 0.5, 1, 5, and 10C, respectively. Furthermore, a high specific capacity of 148 mAh g⁻¹ can be exhibited under charge/discharge cycling at 55°C, with a retention rate of 88% after 100 cycles under 1C. Besides, an excellent low-temperature specific capacities of 175 (0.1C) and 154 (1C) mAh g⁻¹ at -10°C, with the capacity retention rate of 52% after 80 cycles under 1C.

By substituting Co with Mn, a low-cost LiMnO₂ can form with a similar layered structure, exhibiting a high practical capacity of ~200 mAh g⁻¹. Owing to the Mn dissolution into the electrolyte resulting from the Mn³⁺ distortion due to the Jahn-Teller effect, and the generation of oxygen under a high charging voltage, it suffers from active material loss, and there are serious safety concerns.

LiNi_{0.5}Mn_{0.5}O₂, an effective cathode material based on the partial replacement of Mn³⁺ of LiMnO₂ with

Ni³⁺, has exhibited a high discharge capacity (~200 mAh g⁻¹) with a potential plateau at 3.8 V [162,163]. Additionally, the ion mobility is hindered by the combination of Li and Ni ions [164]. Ni can help in obtaining a higher lithium extraction capacity. However, cation mixing can result in low lithium diffusivity and thus, an unappealing rate capability [165]. Therefore, its practical application is limited by the capacity decay, cycling instability, and safety risk.

By combining the benefits of LiMnO₂, LiCoO₂, and LiNi_{0.5}Mn_{0.5}O₂, a series of LiNi_{1-x-y}Mn_xCo_yO₂ (NMC) cathode materials have been proposed. Their acquirable specific capacity and analogous working potential are comparable to, or even greater than, those of LiCoO₂, although the cost is much lower due to the reduced content of Co. Therefore, they are expected to provide optimized choices to replace LiCoO₂ and LiFePO₄ [164]. Among them, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ seems promising because of its more stable structure, lower cost, and moderate capacity [166,167]. It has been reported that lithium-ion intercalation/deintercalation was facilitated through nanostructure engineering, surface adjustment, and doping with other cations in LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ [168]. For instance, Zheng *et al.* reported that self-assembled LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ nanosheets were synthesized with combined methods of co-precipitation and hydrothermal reaction, with the width and thickness in the ranges of 0.7-1.5 μm and 10-100 nm, respectively [169]. As the cathode material, the synthesized nanosheets delivered excellent initial specific capacity of 193 mAh g⁻¹, maintained capacity of 189 mAh g⁻¹ at 0.2C after 100 cycles, and 155 mAh g⁻¹ at 1C after 1000 cycles. The high surface area of the LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ nanosheets provided efficient contact with the electrolyte, shortened lithium ion diffusion path, and sufficient void space to accommodate large volume variation.

Furthermore, some new cathode materials were also investigated. For instance, “Ni-rich” LiNi_{0.8}Co_{0.15}Mn_{0.05}O₂ showed a great potential for applications in electric vehicles due to its high capacity and low cost. However, it still suffered from the significant power fading and an increase in interfacial impedance resulting from the structural degradation [170]. Additionally, LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ combines the advantages of both LiCoO₂ and LiNiO₂, and maintains a layered structure by Co doping in LiN-

iO₂, leading to its lower cost compared to LiCoO₂ and a higher practical specific capacity of ~200 mAh g⁻¹. Moreover, using the electrochemically inactive Al³⁺ to partially substitute Ni³⁺ is beneficial for preventing overcharging and enhancing the thermal stability of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ at high potentials.

3.2.2 Spinel oxides

Spinel LiMn₂O₄ is another promising cathode material for high-rate LIBs owing to its abundance, environmental benignity, and low cost, of Mn, and exclusive 3D lithium-ion diffusion pathways, as shown in Fig. 11(B). In cubic spinel-structured LiMn₂O₄, oxygen anions are arranged uniformly into a face-centered cubic close-packed (CCP) framework, occupying 32e sites, where lithium and Mn occupy tetrahedral 8a sites and octahedral 16d sites, respectively, with the octahedral 16c sites remaining unoccupied. Lithium ions can be transported through the tetrahedral or octahedral interstitial sites that are vacant within the 3D spinel structure. Therefore, LiMn₂O₄ has great potential for high-performance LIBs [171]. Despite the high discharge plateau, excellent cyclic stability, and great rate capability of spinel cathodes, capacity fading (≤150 mAh g⁻¹) still occurred at 3 V during cycling. With further lithiation, the transition from spinel to new rock salt phase will occur at ~3 V [170]. Moreover, the dissolution of Mn²⁺ in the electrolyte *via* disproportionation reaction (2Mn³⁺ → Mn²⁺ + Mn⁴⁺) and the phase transformation from cubic to tetragonal caused by Jahn-Teller distortion are barriers to practical applications of spinel LiMn₂O₄ [172]. Lee *et al.* reported that through a combined methods of solvothermal reaction and followed solid-state lithiation, ultrathin LiMn₂O₄ nanowires with diameters less than 10 nm and lengths of several micrometers were fabricated [173]. These nanowires were capable of structural transformation between cubic and tetragonal phases with facile strain relaxation, exhibiting a discharge specific capacity of ~90 mAh g⁻¹ at 20C (3.1-4.3 V vs. Li) with high reversibility and good capacity retention rate.

With a structure similar to that of LiMn₂O₄, LiMn_{1.5}Ni_{0.5}O₄ also has significant potential as a high-performance cathode material for LIBs [174]. LiMn_{1.5}Ni_{0.5}O₄ has two crystallographic structures, that is, the stoichiometric ordered *P4₃32* phase and

non-stoichiometric disordered *Fd3m* phase [175,176]. In the disordered phase, Mn with Ni cations randomly occupy 16d octahedral sites, while lithium ions occupy tetrahedral 8a sites. For the ordered phase, Mn, Ni and Li cations occupy 12d, 4b, and 8c sites, respectively, whereas the unoccupied sites are split into 4a and 12d sites. By substituting Mn with Ni, the mean oxidation state of Mn ions is elevated to help in stabilizing the structure by eliminating the Jahn-Teller distortion. The potential for oxidizing Ni²⁺ to Ni⁴⁺ can reach 4.7 V, which makes LiMn_{1.5}Ni_{0.5}O₄ an encouraging high-voltage cathode material [177]. However, the ordered Ni and Mn cations retard the diffusion of lithium ion through the ordered LiMn_{1.5}Ni_{0.5}O₄, leading to the reduced rate capability [157]. Constructing hollow nanostructures may offer an effective strategy to address this problem. Li *et al.* reported the controllable synthesis of hollow LiMn_{1.5}Ni_{0.5}O₄ spheres with micro- and nanostructures by tuning the co-precipitation kinetics [178]. Their discharge capacity is 130 mAh g⁻¹ at the current rate of 0.1C, which is higher than 120 mAh g⁻¹ for their particulate counterparts. At various discharge rates, hollow LiMn_{1.5}Ni_{0.5}O₄ spheres all exhibit higher discharge capacities than those of LiMn_{1.5}Ni_{0.5}O₄ nanoparticles. Moreover, under several current rates (0.5, 1 and 2C), the discharge capacity showed slight decrease even after 100 cycles. The capacity retention rate remained as high as 95% after 100 cycles at 0.5C.

However, spinel materials still suffer from several intrinsic shortcomings because their lithium-ion mobility and electronic conductivity are over one order less compared with those of LiCoO₂, which strongly limits their practical application [179]. Therefore, some effective approaches, such as electrode nanostructuring, surface coating, and cation doping, have been employed to boost the charge transport kinetics and develop low resistance pathways, resulting in significant progress in LIBs. For instance, carbon coating was applied on mesoporous LiMn₂O₄ material to prevent Mn²⁺ dissolution and improve the rate performance. The resultant cathode material exhibited superior high-rate capability and long-life cycling stability, delivering the initial discharge capacity of 117.8 mAh g⁻¹ at 30C. Furthermore, it remained the retention rate of over 90% after 1500 cycles [180]. In addition, Mg doping into LiMn_{1.5}Ni_{0.5}O₄ was also reported to exhibit a high

capacity of 105.3 mAh g⁻¹ at 10 C rate, maintaining a retention rate of 96.9% after 100 cycles, in comparison with the capacity retention of 91.2% and capacity of 82.4 mAh g⁻¹ for the LiMn_{1.5}Ni_{0.5}O₄ [181].

3.2.3 Polyanion olivine oxides

In exploring novel cathode materials for LIBs, an emerging type of compounds, called polyanion-type oxides with polyanions, (XO₄)³⁻ (X = S, P, Si, Mo, W), occupying lattice positions, have been developed. These polyanions not only increase the redox potential but also help in maintaining the structural stability of cathode materials [182].

Olivine-type LiMPO₄ (M = Fe, Co, Mn, Ni), one of the representative polyanion-type cathode materials, has attracted significant attention owing to its high thermal stability, environmental benignity, safety, and low cost [183]. In comparison with cathode materials with layered and spinel structures, the stability of olivine-structured materials comes from their strong O-P bond of PO₄³⁻ anions and O-M, which ensures its long-term cycle stability. However, these compounds suffer from their sluggish electronic conductivity and low-rate lithium ion diffusion along the [010] direction.

Considering LiFePO₄ as an example, oxygen forms a hexagonal close-packed (HCP) matrix with a slight distortion, both Li⁺ and Fe²⁺ reside in octahedral sites, and P lies in tetrahedral sites, as shown in Fig. 11(C). Ma *et al.* reported that olivine LiFePO₄ materials with different morphologies such as nanoplate, rectangular prism nanorod and hexagonal prism nanorod were synthesized through a solvothermal method [184]. The rectangular prism nanorods exhibited superior electrochemical properties in comparison with other morphologies due to their moderate size and shortened lithium ion diffusion length along the [010] direction. In addition, LiMnPO₄ is another candidate having a theoretical specific capacity of 170 mAh g⁻¹ and a high operating voltage of 4.1 V. It is noticed that both the (010) plane and the [010] direction are beneficial for lithium ion diffusion, leading to its excellent electrochemical output [185]. However, because of its low intrinsic electronic conductivity and the large structural distortions caused by the Jahn-Teller distortion of the Mn³⁺ ions, it has a lower capacity and an inferior rate performance. To address this problem, several methods have been developed, such as size tailoring, surface modifica-

tion, and doping. For instance, Li *et al.* reported that the cathode material LiMnPO₄/C with honeycomb structure was synthesized with NaCl particles as the sacrificial template [186]. With the unique honeycomb-like architecture, the intimate interfacial bonding between adjacent LiMnPO₄/C networks provided more electroactive sites for both lithium ion diffusion and electron transport. As a result, a superior reversible capacity of 161.5 mAh g⁻¹ at 0.05C was delivered with a good retention rate of 96.4% after 200 cycles at a high discharge rate of 10C.

Other olivine structures, including Li₂MSiO₄ and LiMBO₃, have also been considered alternative cathode materials for LIBs, whose structures are shown in Figs. 11(D) and 11(E), respectively. For example, for Li₂MnSiO₄, during charging/discharging process, a possible reaction with two-electron exchange occurs based on Mn⁴⁺/Mn³⁺ and Mn³⁺/Mn²⁺ redox couples, delivering a theoretical capacity being 333 mAh g⁻¹ [187]. Similar to LiMnPO₄, Li₂MnSiO₄ also encounters several problems such as low intrinsic electronic conductivity and unsatisfactory structural stability arising from Jahn-Teller distortion of Mn³⁺ ions. In addition, considering LiFeBO₃ as another sample, a high capacity value of 200 mAh g⁻¹ was obtained through computational and experimental analyses [188]. Two main factors, kinetic polarization and sensitivity to moisture, limit its performance; therefore, optimized conditions for synthesis are established, and the operation becomes very crucial.

3.2.4 Other materials

In addition to traditional cathode materials discussed in the previous sections, TM halides, especially metal fluorides (MF) or chlorides (MCl), have been considered conversion-type cathode materials owing to their intermediate operating voltages and excellent theoretical specific and volumetric capacities.

Among various conversion-type materials, FeF₃ exhibits a high theoretical capacity of 712 mAh g⁻¹ with significant potential to double the energy density value delivered by present-day commercial cathodes [189]. Its structure and the redox reactions during the charging/discharging process are presented in Fig. 11(H). However, its poor electronic conductivity due to its large band gap degrades its electrochemical performance. Another cathode mate-

rial, FeF_2 , has the same disadvantage; however, its nanocomposites with carbon have been reported to enhance its electrochemical reversibility by confining FeF_2 into the conductive carbon [190].

It is known that numerous ionic compounds can dissolve into polar solvents, which is also true for many fluorides [191]. In comparison, metal chlorides are more soluble in many types of organic solvents, especially those employed as electrolytes in LIBs [192]. Meanwhile, MF and MCl both undergo relatively moderate volume expansions with a range of 2-25% for mostly studied MF and MCl materials.

Finally, for the rapid development of high-rate LIBs, excellent anode and cathode materials are necessary. They must offer advantages of low cost, environmental friendliness, high-rate capability, robust structural stability, and fast ionic and electronic conductivity. Because the intrinsic materials do not possess all the optimized properties that high-rate LIBs require, further processing is required. For instance, because most of the electrode materials exhibit semi-conducting properties, their conductivity may not meet the requirements. Therefore, it is crucial to pursue optimized materials engineering, together with electrode structure design, to achieve reduced diffusion length and improved ionic diffusion and electronic transfer, which are both essential for achieving excellent LIB performance.

4. Summary and outlook

In modern society, with the increasing demands for portable electronics and electrical vehicles, traditional fossil fuels are being rapidly depleted, accompanied by the damage due to the greenhouse effect and pollution caused by the emission of CO_2 and other toxic gases, respectively. Thus, the development of alternative energy storage systems for sustainable forms of energy that are environment friendly is a challenge faced by humans today. As a favorable candidate, rechargeable LIBs have attracted significant attention and have been the subject of intensive R & D efforts made by leading research groups and advanced industries across the world. Today, we see their applications in many fields, including smartphones, laptops, and power tools, demonstrating the high level of maturity of this technology and a strong confidence in more extensive applications.

It is known that the principal challenges facing the development of LIBs are cost, safety, rate capability, energy density, and lifespan. Ease of fabrication and abundance of choices are the key factors in the lowering of costs. To extend the lifespan, both elimination of unexpected chemical reactions during working and retention over many charging/discharging cycles are required. Development work on these requirements shall be based on a deep understanding of the operating mechanisms, the relationship between the structures and properties of each component in LIBs, and potentially harmful issues to be eliminated, which involve many branches of knowledge such as materials science, electrochemistry, chemical engineering, solid-state chemistry, computational chemistry.

In this review, we mainly focused on current progress made in both anode and cathode materials applied in LIBs. We began with a thorough introduction to the fundamental configuration and working principles of LIBs. As important devices for energy storage, LIBs operate predominantly via electrochemical redox reactions within electrode materials. In the following section, aided by an understanding of basic thermodynamics and kinetics, namely the electrochemical potential and conduction mechanism of lithium ions and electrons, respectively, we presented a detailed description of the correlation between the structure and properties of electrode materials. This provides a potential opportunity, with the aid of novel techniques and deep insights into materials science, to rationally design and fabricate appropriate nanostructured electrode materials for high-performance LIBs. Next, owing to the wide applications of nanotechnology in a variety of fields, with energy storage being no exception, nanostructured materials have almost completely replaced the traditional materials used for energy storage. Therefore, nanostructured materials have been widely applied in the electrodes of LIBs. Through detailed classifications of the types of both anode and cathode materials, we used some specific examples to discuss their advantages and disadvantages. This provides a fundamental understanding of the framework of LIBs, necessitating further rational design of electrode materials because the intrinsic materials for electrodes in LIBs are unable to meet the high-performance requirements for practical applications.

Today, despite all the extensive studies on improving the performance of LIBs, constant efforts are still

required to develop advanced materials or structures and achieve high performance and commercialization. Considering these objectives, some significant factors must be taken into account. First, combining theoretical and experimental investigations shall aid the development of novel promising electrode materials. Because the battery system is complex, with crystal structures and microstructures impacting the electrode potentials in important ways, some theoretical approaches to the electronic structure may have to be introduced, such as crystal field theory (CFT), molecular orbital theory (MOT), and even ligand field theory (LFT), which is more realistic and complex than the first two. Second, combining different characterization techniques is important for gaining a more comprehensive idea and collecting more complete information regarding changes in the structure of LIB electrode materials. For instance, synchrotron-based X-ray imaging techniques are capable of providing chemical and morphological information at a length scale from tens of nanometers to millimeters. Despite this, imaging at atomic-length scale still requires TEM techniques. Mass spectroscopy (MS) and nuclear magnetic resonance (NMR) can both help in collecting critical information complementary to the X-ray techniques. Third, the practical high-performance full cell battery shall remain a promising research focus in the near future. Currently, for high-rate LIBs, material design primarily focuses on individual electrode materials, i.e., the “half-cell system”. However, simultaneous high rate capability for both anode and cathode materials is critical for realistic LIBs. Therefore, the matching between anode and cathode materials must be the maximum, which makes the optimization of their electronic structures crucial. Last but not least, when LIBs operate under conditions such as uneven current density and short circuit, thermal runaway tends to occur. Therefore, the potential safety problems caused by rapid heat generation during the charging/discharging process at a high current density must be seriously considered. Additionally, for safer batteries, an effective system for battery management is essential. For this purpose, system engineering can play an important role in chemical engineering.

Significant advances have been made in LIBs in the last few decades. However, optimal designs, allowing them to perform well under all conditions, are still in short supply. More advanced characterization tools

and nanotechnologies, together with computer science, that can provide opportunities are required for further developments in LIBs. Therefore, continuous studies on the relevant science and technologies are essential for the development of next-generation LIBs. Through persistent endeavors, next-generation LIBs shall be developed as the foundation of our society and facilitate the sustainable evolution of the human civilization.

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Conflict of Interest

The authors declare no conflict of interest.

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