

## Review Article

# Advanced Electrode Materials in Lithium Batteries: Retrospect and Prospect

Xin Shen <sup>1</sup>, Xue-Qiang Zhang <sup>1</sup>, Fei Ding,<sup>2</sup> Jia-Qi Huang <sup>3</sup>, Rui Xu,<sup>3</sup> Xiang Chen <sup>1</sup>,  
Chong Yan <sup>1,3</sup>, Fang-Yuan Su,<sup>4</sup> Cheng-Meng Chen,<sup>4</sup> Xingjiang Liu,<sup>2</sup> and Qiang Zhang <sup>1</sup>

<sup>1</sup>Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

<sup>2</sup>Science and Technology on Power Sources Laboratory, Tianjin Institute of Power Sources, Tianjin 300384, China

<sup>3</sup>Advanced Research Institute of Multidisciplinary Science, Beijing Institute of Technology, Beijing 100081, China

<sup>4</sup>CAS Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001 Shanxi, China

Correspondence should be addressed to Jia-Qi Huang; [jqhuang@bit.edu.cn](mailto:jqhuang@bit.edu.cn), Xingjiang Liu; [xjliu@nklps.org](mailto:xjliu@nklps.org), and Qiang Zhang; [zhang-qiang@mails.tsinghua.edu.cn](mailto:zhang-qiang@mails.tsinghua.edu.cn)

Received 19 June 2020; Accepted 19 July 2020; Published 19 January 2021

Copyright © 2021 Xin Shen et al. Exclusive Licensee Beijing Institute of Technology Press. Distributed under a Creative Commons Attribution License (CC BY 4.0).

Lithium- (Li-) ion batteries have revolutionized our daily life towards wireless and clean style, and the demand for batteries with higher energy density and better safety is highly required. The next-generation batteries with innovatory chemistry, material, and engineering breakthroughs are in strong pursuit currently. Herein, the key historical developments of practical electrode materials in Li-ion batteries are summarized as the cornerstone for the innovation of next-generation batteries. In addition, the emerging electrode materials for next-generation batteries are discussed as the revolving challenges and potential strategies. Finally, the future scenario of high-energy-density rechargeable batteries is presented. The combination of theory and experiment under multiscale is highlighted to promote the development of emerging electrode materials.

## 1. Introduction

The development of lithium- (Li-) ion batteries (LIBs) brings us a wireless and nonfossil society, thus being the protagonist of 2019 Nobel Prize in Chemistry. Nowadays, the portable electronics, electric vehicles (EVs), and smart grids are more popular than ever before, which makes lifestyle more convenient and cleaner. Meanwhile, although the manufacturing technologies of LIBs improve rapidly and the market of LIBs increases booming due to the popularity of new energy vehicles and smart wearable devices [1], yet the energy density of LIBs is approaching to its theoretical value limited by the working principle and the growth rate of energy density has decreased from 7% to 2% per year [2]. In other words, the advancements of LIBs are gradually behind in meeting the demands for portable and clean lifestyle, especially in the fields of EVs and portable electronics [3, 4]. The contradiction of supply and demand is becoming conspicuous. Next-generation batteries with higher energy den-

sity are in strong pursuit around the world [5]. Recently, various battery technology roadmaps have been released from different countries, such as China (Made in China 2025), United States (DOE Battery 500), and Japan (NEDO RISING II), which reflects the global urgent demands and exploitation determinations for future high-energy-density rechargeable batteries [6–8].

Rechargeable Li battery based on the Li chemistry is a promising battery system. The light atomic weight and low reductive potential of Li endow the superiority of Li batteries in the high energy density. Obviously, electrode material is the key factor in dictating its performance, including capacity, lifespan, and safety [9]. Diverse electrode materials have been developed under considerable research efforts. According to the reaction mechanism with Li, electrode materials can be categorized into intercalation, conversion, and other types [10–13]. Intercalation electrode materials are widely employed in commercialized LIBs. Li ions reversibly intercalate/deintercalate in intercalation electrode without a large

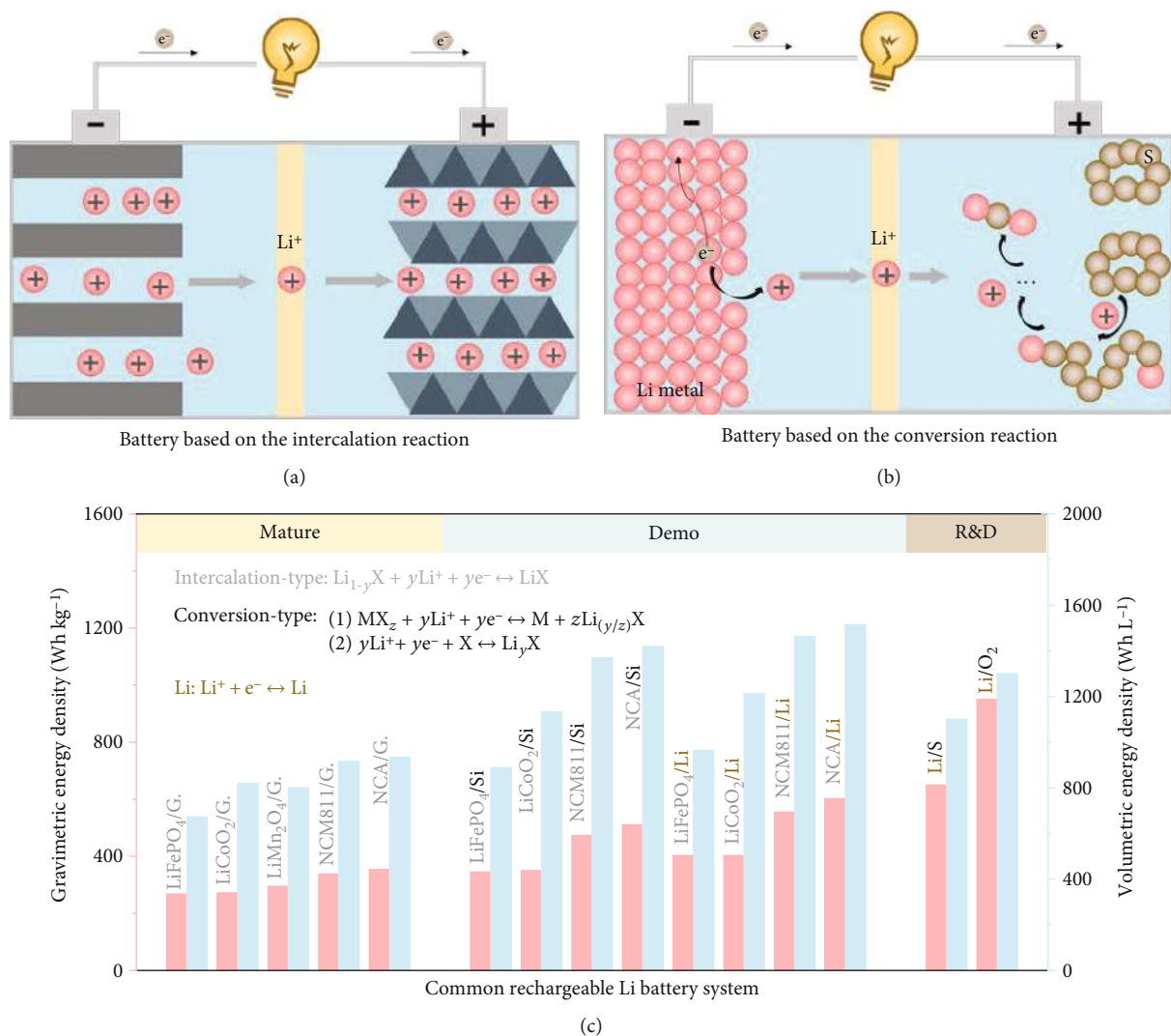


FIGURE 1: Common rechargeable Li battery systems. (a) Schematic diagrams of battery systems based on the intercalation reaction, taking LIB as an example. (b) Schematic diagrams of battery systems based on the conversion reaction, taking Li-S battery as an example. (c) Estimation of the gravimetric and volumetric energy densities of common rechargeable Li battery systems. Data from Reference [15, 16] are replotted. G.: graphite.

volume change, exhibiting a stable cycling but a limited specific capacity (Figure 1(a)). For instance, LiCoO<sub>2</sub>, LiFeO<sub>4</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811), LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA), and graphite, the state-of-the-art materials of the LIBs, all belong to this type. In conversion electrode materials, the charge/discharge process is a conversion reaction and always accompanied by phase transitions, not only effectively increasing the specific capacity but also introducing additional stability issues, such as structural collapse and poor reversibility (Figure 1(b)). According to the conversion route proposed by Armand and Tarascon [13], metal halides and metal sulfide/oxide can be classed as the conversion type (Equation (1) in Figure 1(c)). Thereafter, Nitta and coworkers extended the route (Equation (2) in Figure 1(c)) to enable alloy, sulfur, and oxygen materials included.

Compared with current intercalation electrode materials, conversion-type materials with high specific capacity are

promising for future battery technology [10, 14]. The rational matching of cathode and anode materials can potentially satisfy the present and future demands of high energy and power density (Figure 1(c)) [15, 16]. For instance, the battery systems with Li metal anode can reach a practical energy density of 400 Wh kg<sup>-1</sup> and 900 Wh L<sup>-1</sup>. However, there are new challenges with the introduction of emerging electrodes. With cycle life, rate capability, working temperature, safety, cost, and manufacture, any shortcoming can prevent its practicality for bulk applications. New fabrication methods, emerging characterization techniques, and the ever-deepening understanding of working principles are highly expected to overcome the shortcomings in emerging electrodes.

This review is aimed at providing a full scenario of advanced electrode materials in high-energy-density Li batteries. The key progress of practical electrode materials in the LIBs in the past 50 years is presented at first. Subsequently,

emerging materials for satisfying near-term and long-term requirements of high-energy-density Li batteries are discussed. Finally, a roadmap of future research towards high-energy-density Li batteries is provided. In particular, the combination of theory and experiment ranging from atomic scale to nanoscale and macroscale are highlighted, which bridges fundamental mechanisms and practical applications.

## 2. Practical Electrode Materials

The development of LIBs has gone through 50 years from the birth of the concept to the present commercialization, which is a journey full of twists and turns [17]. Just by looking at electrode materials, some materials have been eliminated while some have withstood the test of time and finally been commercialized. The methods of material design, electrode engineering, and evaluation system constructed in this process are premise and sills of future electrode material research. The research motivation and chasing target in this process will continue throughout the future electrode material research. Therefore, we present herein a concise retrospect on the birth and development of LIBs and the commercial electrode materials [18, 19].

**2.1. A Retrospect of LIBs.** In the early 1970s, the oil crisis directly enabled the research of LIBs. Exxon, an oil giant in America, estimated that oil resources will run out soon as a typical nonrenewable resource. Therefore, they decided to have a team to develop a next-generation energy storage technology for replacing fossil fuels. Whittingham who moved to Exxon in 1972 proposed an innovative cathode material (titanium disulfide,  $\text{TiS}_2$ ) [20]. This new intercalation compound, which can accumulate Li ions between transition-metal sulfide sheets, opened a novel world of electrode materials. When it is paired with Li metal anode, the voltage of battery is up to 2.0 V. However, Li metal is highly reactive, which induces big safety risks in battery due to the formation and growth of Li dendrites. Around 1980, Goodenough and co-workers proposed another intercalation cathode material, lithium cobalt oxide ( $\text{LiCoO}_2$ ) [21]. The constructed  $\text{LiCoO}_2 \mid \text{Li}$  battery can afford a double voltage of 4.0 V compared to  $\text{TiS}_2 \mid \text{Li}$ , achieving a significant breakthrough in energy density. Still, safety hazard caused by Li metal anodes remained a huge obstacle in commercialization. Then, Yoshino et al. found that a carbonaceous material (petroleum coke) can stably and safely intercalate/deintercalate Li ions in 1985 [22]. Replacing the Li metal anode with this carbonaceous material to pair with  $\text{LiCoO}_2$ , a novel rechargeable LIB was constructed where Li ions swing between both intercalating electrodes upon cycling. Subsequently, Sony corporation successfully commercialized the LIBs in 1991 which exhibited remarkable merits in safety, cycle life, energy density ( $80 \text{ Wh kg}^{-1}$ ), and operating voltage (4.1 V) [23]. The first generation of  $\text{LiCoO}_2 \mid \text{C}$  batteries is a great breakthrough in the history of LIBs and is still the mainstream of portable LIBs today.

The birth of LIBs led to a revolution in rechargeable batteries, gradually replacing lead-acid batteries (about  $40 \text{ Wh kg}^{-1}$ ) and touching every aspect of the society, laying

the foundation of a wireless, fossil fuel-free society. It is a fruit from who has contributed to the development of LIBs: proposing the fundamental working mechanism, creating the prototype in laboratory, and achieving the successful commercialization.

**2.2. Commercial Cathode Materials.** By far, LIBs have gone through around 30 years of development since its first commercialization in 1991 and have gradually become mature. Throughout the entire time frame of LIBs, its research goal never changes: high energy density or reduced size and weight for a given capacity, long cycle life, and high safety. To this end, a series of intercalation electrodes were proposed and some of them have been commercialized after heavy screening. Presently, commercialized cathode materials are mainly transition metal oxide, such as  $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ , and ternary metal oxides (including  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  and  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ , denoted as NCM and NCA, respectively) [17, 24]. Each material has its strength and weaknesses (Figure 2). Five-dimensional indicators, including cycle life, average working voltage, practical gravimetric capacity, safety, and cost, are used to evaluate electrode materials, helping to find their proper applications.

**2.2.1. Layered  $\text{LiCoO}_2$ .** Layered  $\text{LiCoO}_2$  created by Goodenough is the first generation of commercial cathode and still widely used for computer, communication, and consumer electronics (Figure 2(a)) [25, 26]. It displays a high theoretical specific capacity of  $274 \text{ mAh g}^{-1}$  and high theoretical volumetric capacity of  $1363 \text{ mAh cm}^{-3}$ . However, while the excessive Li ions ( $x > 0.5$ ) are extracted from the layered crystal lattice, a series of irreversible structural transformation happens in  $\text{Li}_{1-x}\text{CoO}_2$ , leading to irreversible capacity loss [27]. Amatucci reported that 95% of Li ions can be reinserted into the  $\text{CoO}_2$  structure, i.e., 5% irreversible capacity loss occurs in per charge/discharge cycle when Li is completely extracted [28]. Generally, element doping and surface modification can effectively improve the structure stability and reversibility and thereby reduce capacity loss [29, 30]. Nowadays, the practical specific capacity of commercial  $\text{LiCoO}_2$  can reach  $165 \text{ mAh g}^{-1}$ , corresponding to a charge cut-off voltage of 4.35 V. The major limitations of  $\text{LiCoO}_2$  applied in EVs are its high cost and poor thermal stability. The high-voltage  $\text{LiCoO}_2$  ( $>4.5 \text{ V}$ ) will be the research emphasis to further release the reversible capacity in future research [31].

**2.2.2. Spinel  $\text{LiMn}_2\text{O}_4$ .** Spinel  $\text{LiMn}_2\text{O}_4$  served as a cathode material is proposed by Goodenough's research groups in 1984 [32, 33]. The practical specific capacity of  $\text{LiMn}_2\text{O}_4$  is about  $120 \text{ mAh g}^{-1}$  (theoretical specific capacity,  $148 \text{ mAh g}^{-1}$ ), which is the relatively low in commercial cathode materials. However,  $\text{LiMn}_2\text{O}_4$  has a relatively high average operating voltage (4.0 V) and a good rate capability, making it promising for high-power batteries. The good rate capability is profited from the cubic spinel structure of  $\text{LiMn}_2\text{O}_4$ , where the three-dimension (3D)  $\text{MnO}_2$  host and Mn vacancies make a 3D diffusion tunnel for Li ions transportation (Figure 2(b)). The main issues of this spinel structure come from the Jahn-Teller effect and the dissolution of

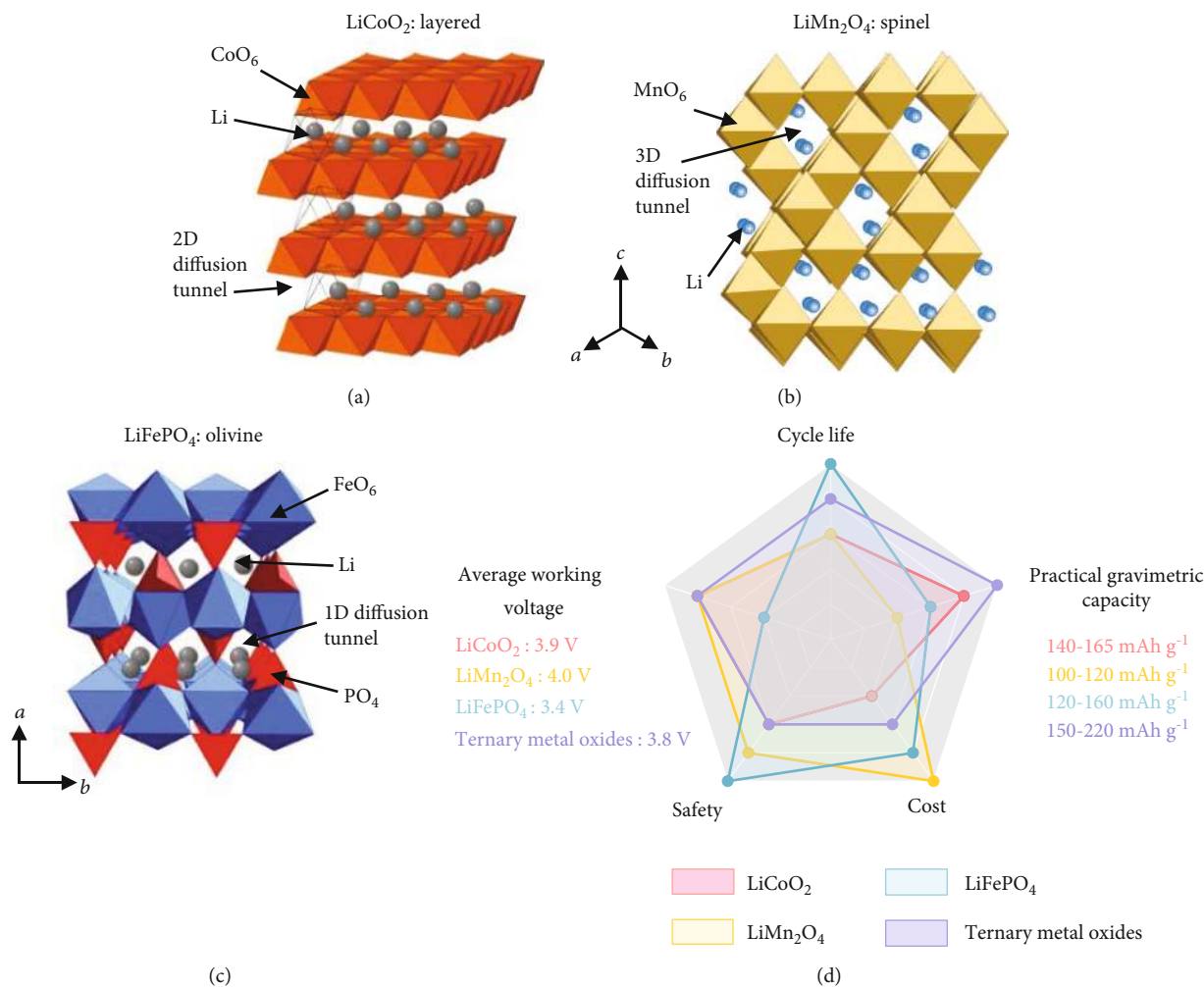


FIGURE 2: Commercial cathode materials. Crystal structure of (a)  $\text{LiCoO}_2$ , (b)  $\text{LiMn}_2\text{O}_4$ , (c)  $\text{LiFePO}_4$ , and (d) radar summary chart of the commercial cathode materials. (a) and (c) are reproduced under the terms of CC BY-NC-SA 3.0 license. Copyright 2011, the authors [26].

$\text{Mn}^{3+}$ , which lead to an irreversible structural transformation and capacity fading. Therefore, the study of  $\text{LiMn}_2\text{O}_4$  is focused on reducing the Jahn-Teller active  $\text{Mn}^{3+}$ . Nowadays, pure  $\text{LiMn}_2\text{O}_4$  cathode applied in batteries is losing market share of EVs, whereas it is more usually by mixing with NCM.

**2.2.3. Olivine  $\text{LiFePO}_4$ .** Olivine  $\text{LiFePO}_4$  is famous for its low cost and high stability. It was firstly proposed as a cathode material by Goodenough's research group in 1997 [34].  $\text{LiFePO}_4$  has a practical specific capacity of about 120–160  $\text{mAh g}^{-1}$  (theoretical specific capacity, 170  $\text{mAh g}^{-1}$ ) and a voltage platform of 3.4 V vs.  $\text{Li/Li}^+$ . As shown in Figure 2(c), the hexagonal close packed oxygen atoms and the separation function of  $\text{PO}_4$  polyanions lead to the slow 1D  $\text{Li}^+$  diffusion tunnel and low electronic conductivity ( $10^{-9} \text{ S cm}^{-1}$  at room temperature) in its crystal structure [26]. This issue can usually be solved by reduced particle sizes, carbon coatings, and cationic dopings [35, 36]. Although limited by low energy density,  $\text{LiFePO}_4$  are favored by the transport vehicles with relatively low mileage but high

safety requirements, such as electric buses, electric forklifts, and electric sight-seeing ships.

**2.2.4. Layered Ternary Metal Oxides.** Currently, the most popular cathode material in traction battery market belongs to the layered ternary metal oxides which display a similar voltage and a similar or higher practical specific capacity than  $\text{LiCoO}_2$  [37]. Both NCM and NCA systems are essentially designed to solve the thermal instability of the  $\text{LiCoO}_2$  or  $\text{LiNiO}_2$  [38, 39]. In the structure of ternary metal oxides, each metal element performs its own functions and delivers great synergy. The introduction of Mn and Al can maintain the structural stability and lower the cost. Ni allows for a high Li extraction and provides a high capacity, while Co prevents the Ni from occupying the Li sites and thus guarantees the reversible capacity. The common ratio of Ni:Co:Mn is 3:3:3, 5:2:3, 6:2:2, or 8:1:1 while the common ratio of Ni:Co:Al is 0.8:0.15:0.05. Increasing the Ni fraction in the cathodes can immensely increase the capacity and decrease the cost. However, capacity fading and thermal instability are aggravated [40]. There are multiple factors that

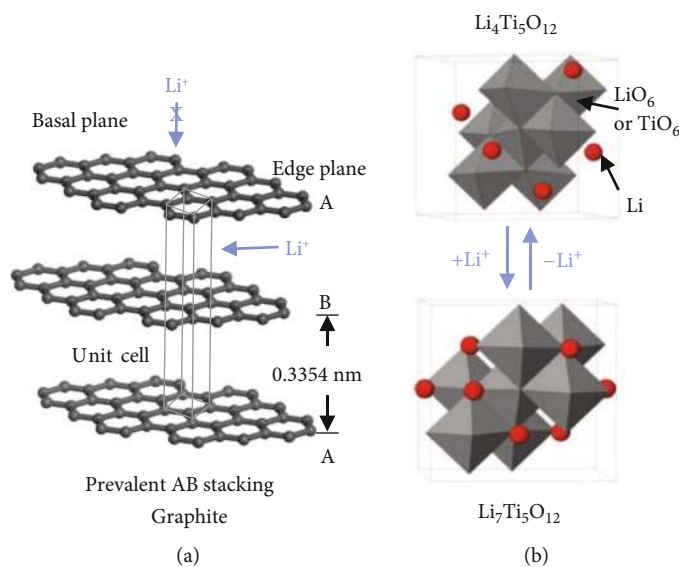


FIGURE 3: Commercial anode materials. Crystal structure of (a) graphite, prevalent AB stacking (hexagonal graphite). (b)  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (delithiation) and  $\text{Li}_7\text{Ti}_5\text{O}_{12}$  (lithiation). Reproduced with permission [53]. Copyright 2010, Wiley-VCH.

cause above issues, including the change or instability of chemical composition, structure, and morphology [41, 42]. To overcome the performance degradation, doping, coating, and size control have been proposed but need further understanding and development [43–45]. Overall, the layered ternary metal oxides are supposed to be a general trend as the electric vehicle market is experiencing a surge. Besides, safety should be the primary requirement when evaluating the materials.

**2.3. Commercial Anode Materials.** An ideal anode material for practical applications is expected to have low potential, high capacity, long cycle life, low cost, and high safety. As mentioned in the birth of LIBs, coke carbon is the first commercial anode material. The bottlenecks of coke carbon, however, are the high deintercalation overpotential (about 1.0 V vs.  $\text{Li}/\text{Li}^+$ ) and low capacity ( $<250 \text{ mAh g}^{-1}$ ) [46]. Therefore, a variety of carbonaceous (*e.g.*, graphite, soft carbon, and hard carbon) and noncarbonaceous materials were widely investigated and developed thereafter. Currently, commercial anode materials in markets are graphite and spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO).

**2.3.1. Graphite.** Graphite has merits of dimensional stability, moderate energy density (theoretical gravimetric capacity of  $372 \text{ mAh g}^{-1}$ , volumetric capacity of  $735 \text{ mAh cm}^{-3}$ ), and low cost, thus being the optimal choice for practical applications at present. Ideal graphite is a layer lattice structure where carbon atoms are arranged in a hexagonal ring and extend infinitely in two dimensions on each layer. Two stacking orders of graphite layers coexist, *i.e.*, the prevalent AB (hexagonal) (Figure 3(a)) and the less common ABC (rhombohedral) stacking order [47, 48]. The layer structure is easy for Li ions to be inserted (or extracted) from edge plane along with a layer spacing change (from 0.3354 nm to 0.3720 nm, about 10% volume expansion) [49]. Indeed, the actual structure of graphite is usually more complicated, including

defects and aggregates of graphite crystallites. In this respect, graphite materials can be subdivided into natural and artificial/synthetic graphite (*e.g.*, mesophase carbon microbeads, MCMB) in terms of origin. The main challenge that initially prevents graphite from practical applications is the cointercalation of solvents into layers, resulting in the exfoliation of graphite. Fortunately, it has been solved by the upgrading of electrolyte and the construction of stable solid electrolyte interphase (SEI). Nowadays, graphite can display a reversible capacity approaching to its theoretical capacity. Enhancing the fast charging capability of graphite with a safety guarantee is a focus of ongoing research [50].

**2.3.2. Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .** Spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) is ideal in terms of safety, cycle life, and rate capability, far superior to graphite anode (Figure 3(b)) [51–53]. The high delithiation potential (about 1.55 V vs.  $\text{Li}/\text{Li}^+$ ), which prevents the occurrence of Li plating and SEI formation, guarantees the high safety of LTO. The zero-strain characteristic, which avoids the volume change after the insertion of up to three  $\text{Li}^+$ , endows the superior cycle performance of LTO. The fast Li-ion diffusion coefficient (about  $2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ), which is one order magnitude higher than that of graphite, enables the potential rate capability of LTO. Therefore, despite the low capacity ( $175 \text{ mAh g}^{-1}$ ), LTO is an alternative material to graphite for battery system requiring fast charge, long life-span, and high safety.

Based on above discussions, it is not difficult to see that no one commercial intercalation material can completely replace another. All these materials display various strengths and weaknesses, which are derived from their specific chemical composition and structure. The market selection of materials is a compromise of all performance indicators under different scenarios. An ideal electrode with large capacity, high voltage, long cycle life, low cost, and high safety is bound to material breakthrough, which is a long way off.



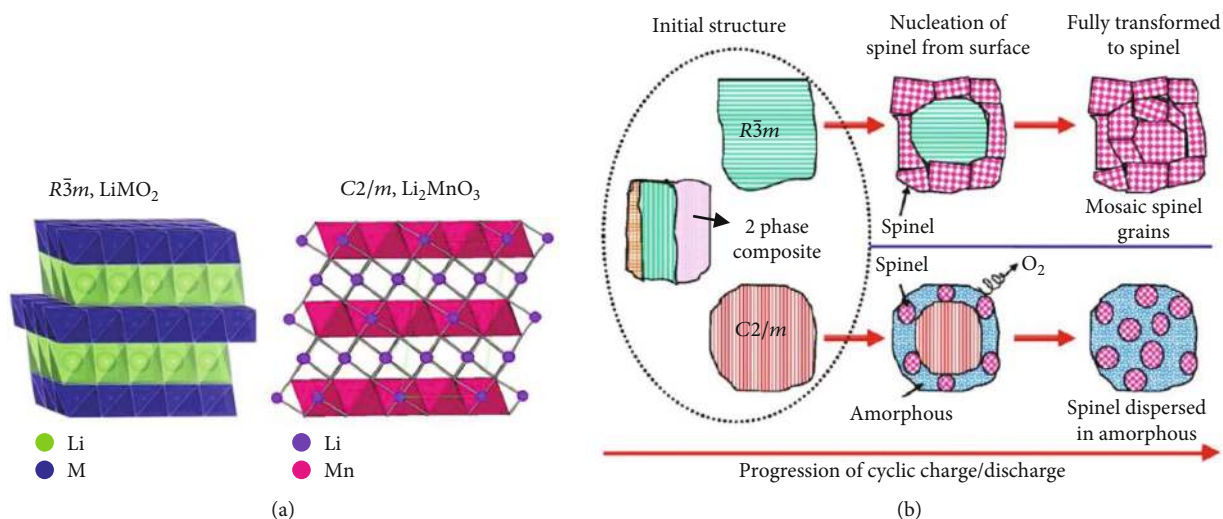


FIGURE 4: (a) Schematic of the crystal structure of LMR, where trigonal ( $R\bar{3}m$ )  $\text{LiMO}_2$  and monoclinic ( $C2/m$ )  $\text{Li}_2\text{MnO}_3$  coexist. Reproduced with permission [56]. Copyright 2015, American Chemical Society. (b) Structure transition of LMR during the progression of cyclic charge/discharge, resulting in a constant voltage and capacity decay. Reproduced with permission [58]. Copyright 2013, American Chemical Society.

### 3. Emerging Electrode Materials

In order to further promote the development of high-energy-density rechargeable batteries, novel materials with new working principles are highly required. Meanwhile, the fundamental understanding on the evolution of electrodes at the electronic, atomic, molecular, material, and battery level while working is also necessary toward practical applications.

#### 3.1. Promising Cathode Materials for High Energy Density

**3.1.1. High-Voltage Cathode.** High-voltage cathode materials ( $>4.0\text{ V vs. Li/Li}^+$ ), while maintaining the high capacity ( $>200\text{ mAh g}^{-1}$ ), are considered as the third-generation cathode of LIBs. Common classes that meet such requirements are Ni-rich materials (ternary metal oxides and Ni content  $>60\%$ ), Li- and Mn-rich materials ( $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ,  $M = \text{Ni, Co, Mn}$  or combinations, denoted as LMR), high-voltage spinel oxides, and high-voltage polyanionic compounds and high-voltage LCO [54]. Finally, it should be noted that high-voltage cathodes face not only material issues but also challenges from the electrolyte. Novel electrolytes with wide voltage window should be developed synchronously to resist the highly oxidizing condition. In particular, Ni-rich materials (NCM811 and NCA) have been commercialized preliminarily.

Another material that receives high attention and support from academics and industry is LMR [55]. LMR is a two-phase composite, where trigonal ( $R\bar{3}m$ )  $\text{LiMO}_2$  and monoclinic ( $C2/m$ )  $\text{Li}_2\text{MnO}_3$  coexist (Figure 4(a)) [56]. Its practical capacity can easily reach  $250\text{ mAh g}^{-1}$ . For instance, Zuo and his coworkers prepared a O2-type Li-rich material with a single layer  $\text{Li}_2\text{MnO}_3$  superstructure, exhibiting an extraordinary reversible capacity of  $400\text{ mAh g}^{-1}$  [57]. Furthermore, LMR possesses superiorities in cost and thermal stability. However, LMR suffers from severe voltage and capacity decay, which immensely hinder its practical applica-

tions. During the first charge, a high active voltage (around  $4.7\text{ V vs. Li/Li}^+$ ) required to form  $\text{Li}_2\text{MnO}_3$  component may destroy the material structure, resulting in a high irreversible capacity (*i.e.*, low initial Coulombic efficiency). On the other hand, there is a transition of LMR from layered to spinel structure during the following cycles, leading to a constant voltage and capacity decay (Figure 4(b)) [58]. A complete understanding on the relationship between composition and/or structure evolutions and battery performance variations is still lacked. Advanced characterization techniques and theory analysis are required for further research. For example, Qiu et al. described that the voltage decay is mainly originated from the metastable state of cycled Li-rich layered oxide through a combination of synchrotron X-ray diffraction, neutron diffraction, synchrotron transmission electron microscope, and first principle calculations [59]. Appropriate heat treatment can convert the metastable state to a stable state, acquiring a voltage recovery. Leifer and co-workers successfully used solid state  $^6,7\text{Li}$  NMR to link structure to the performance of LMR cathode materials [60].

**3.1.2. Sulfur.** Sulfur (S), with a theoretical specific capacity of  $1675\text{ mAh g}^{-1}$ , is able to realize a leap-forward improvement compared to conventional intercalation cathodes. Furthermore, low cost and high abundance also endow the S a significantly competitive advantage. It should be pointed out that S is a Li free cathode. Therefore, S cathodes should be paired with Li anodes to realize high energy density. As early as the 1960s, the prototype of Li-S battery has been demonstrated [61–63]. Ji and coworkers realized reversible capacities up to  $1320\text{ mAh g}^{-1}$  through introducing a carbon host into the sulfur cathode in 2009 and thus aroused an enthusiasm for Li-S battery [64]. The major limitation for sulfur cathodes stems from the soluble lithium polysulfides ( $\text{Li}_2\text{S}_n$ ,  $3 < n < 8$ , LiPSs), which are generated during charge/discharge (Figure 5(a)) [65–67]. During the charge process, long-chain LiPSs generated at the cathode side are able to

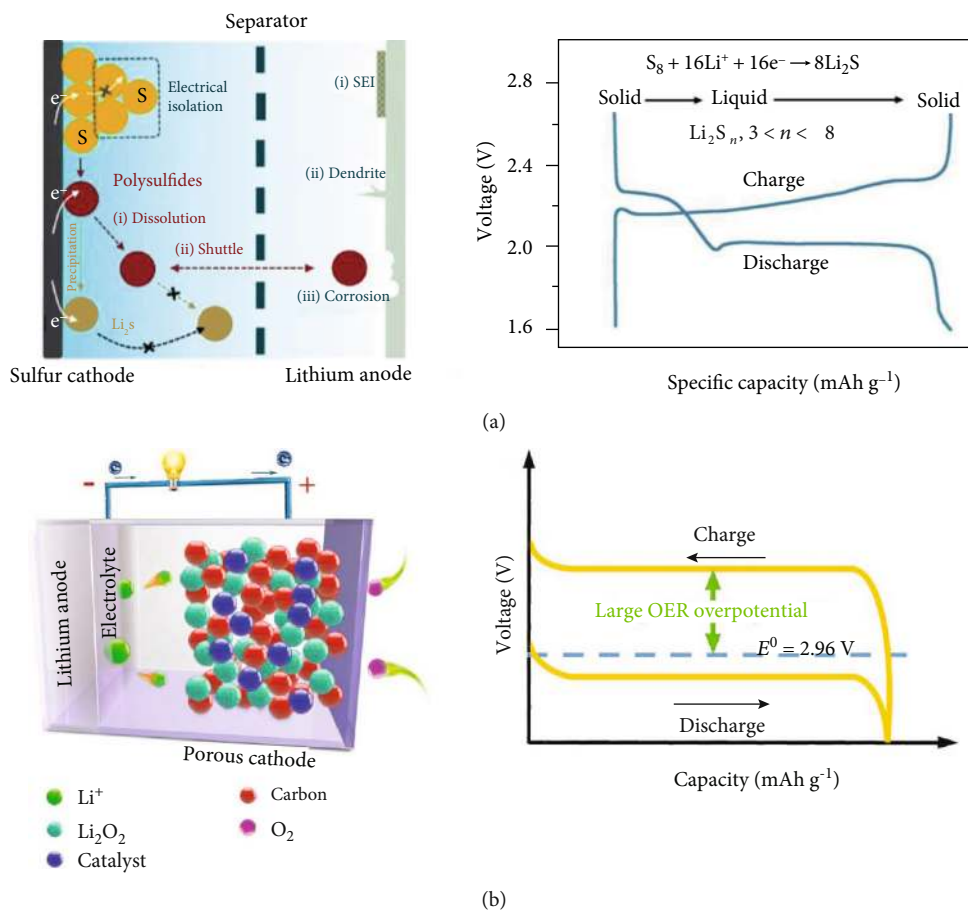


FIGURE 5: Schematic of the batteries with different cathodes and corresponding charge/discharge curves. (a) Sulfur cathodes. The main challenge derives from the formation of soluble LiPSs. The left figure is reproduced with permission [65]. Copyright 2017, Wiley-VCH. The right figure is reproduced with permission [67]. Copyright 2019, Wiley-VCH. (b) Oxygen cathodes. Reproduced with permission [85]. Copyright 2019, Wiley-VCH.

diffuse to the anode side and react with Li metal subsequently. In addition to the formation of solid sulfides on the Li surface, there will be a portion of short-chain LiPSs return back to the cathode side with the help of electric field. This notorious phenomenon is named as shuttle effect, leading to the cathode-active material loss and anode corrosion. In terms of battery performance, it displays as self-discharge, low Coulombic efficiency, and short cycle life.

Over the past decade, tremendous efforts have been devoted to partially solve this issue [68]. There are promising strategies including (1) sulfur hosts, interlayers, and modified separators with chemical/physical confinement function [69, 70], (2) molecularly designed active materials, such as long-chain solid organic polysulfide and small sulfur allotropes [71, 72], (3) advanced electrolytes with reduced polysulfide solubility [73], (4) catalysts/redox mediators with kinetic accelerating functions [74–76], and (5) protection of anode [77, 78]. The challenges in the Li metal anode will be discussed later. At present, the research focus of sulfur cathodes is stepping into a new stage—from lab-scale experiments to product-level applications [79, 80]. Lean electrolytes, limited Li anode, and high sulfur loading are appealed for battery fabrication, and the normalized processes are called for performance evaluation [67, 81, 82].

**3.1.3. Oxygen.** Oxygen ( $\text{O}_2$ ) is a gaseous active material that can be acquired from air, hence remarkably relieving the total weight of working batteries. Moreover, the conversion reaction between  $\text{O}_2$  and Li can deliver more capacity than intercalation-type cathode. Generally, it is quoted that aprotic Li– $\text{O}_2$  batteries can achieve the highest gravimetric energy density (theoretical energy density,  $3500 \text{ Wh kg}^{-1}$ ; practical energy density,  $950 \text{ Wh kg}^{-1}$ ) compared with other Li batteries [83, 84]. As shown in Figures 5(b), typical aprotic Li– $\text{O}_2$  battery comprises a porous catalytic cathode, a separator immersed with organic electrolyte, and a Li metal anode [85]. During discharge,  $2\text{e}^-$  oxygen reduction reaction (ORR) occurs at the cathode along with Li metal oxidation at the anode, exhibiting an output electrochemical force of 2.96 V. The charge process is reverse, i.e., oxygen evolution reaction (OER) occurs at the cathode accompanied with Li ions reduction at the anode.

Since the first report by Blurton and Sammells in 1979, aprotic Li– $\text{O}_2$  battery has obtained remarkable achievements in improving chemical instability, reaction kinetics (ORR and OER), and ion/electron transport kinetics through designing catalyst, protecting Li metal anode, and upgrading electrolyte [84, 86, 87]. However, it is far from practical applications. Continuous efforts in innovative solutions

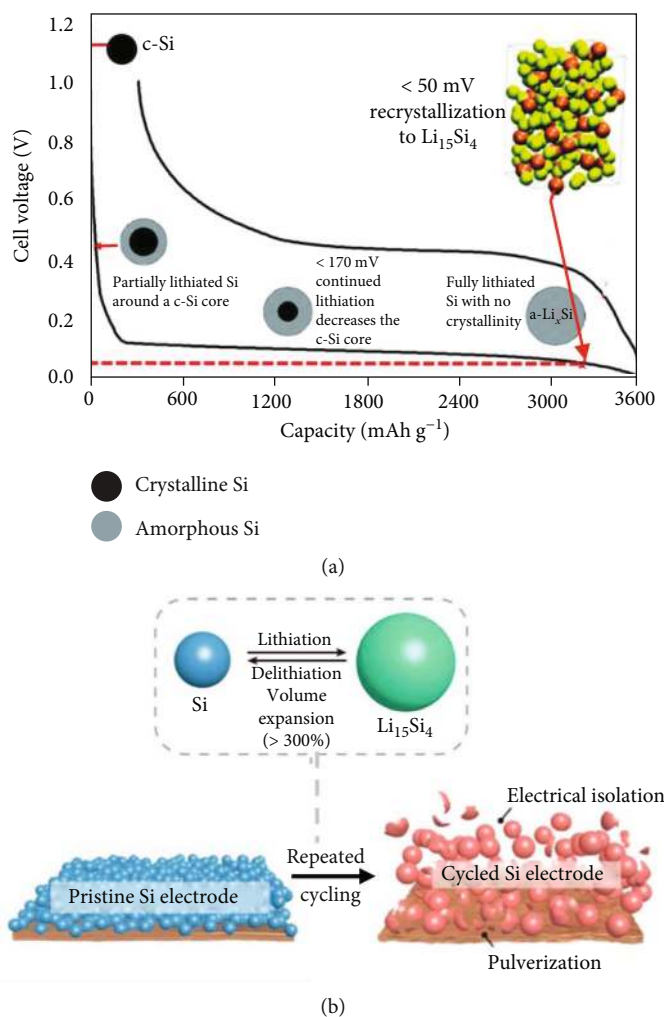


FIGURE 6: (a) Potential–capacity curves and corresponding lithiation status for silicon anode. Reproduced under the terms of CC BY 3.0 license [90]. Copyright 2018, the authors. (b) Schematic of the main challenges in silicon anodes. Reproduced with permission [93]. Copyright 2020, Wiley-VCH.

and deep understanding in reaction mechanism are necessary to ultimately and completely resolve the issues in Li–O<sub>2</sub> battery [88].

### 3.2. Promising Anode Materials for High Energy Density

**3.2.1. Silicon.** Silicon (Si) can alloy with Li, thereby delivering a high theoretical capacity of 3579 mAh g<sup>-1</sup> for forming Li<sub>15</sub>Si<sub>4</sub> in room temperature. Furthermore, Si is natural abundant and possesses a low electrochemical potential (Figure 6(a)) [89, 90]. Therefore, Si anode has been expected for the practical applications in third-generation LIBs. Unfortunately, Si anodes suffer huge volume change (>300%) because of the hostless conversion reaction, while the intercalation graphite anodes only change 10% [91, 92]. Such huge volume change leads to electrode pulverization during repeated charge/discharge processes, continuous rupture and regeneration of SEI, and electric disconnection between Si and current collectors (Figure 6(b)) [93], which are all responsible for the capacity fading and short cycle life of Si-based batteries.

Since the discovery of Li–Si alloy in the 1960s, excellent progress has been achieved in alleviating electrode degradation, such as nanosized Si, hierarchical structure Si, and composite Si [94–96]. In terms of industrial feasibility, including cost and scale-up fabrication, the cointegration of graphite and Si instead of pure Si receives strong attention [97]. Despite graphite-blended Si anodes and/or graphite/Si composites have been commercialized preliminarily, the mass fraction of Si is usually below 5%, immensely limiting the specific capacity. Further improving the weight fraction of Si is necessary for high energy density; however, maintaining an appropriate capacity retention and cycle life is precondition. In this respect, grasping the quantitative relationship of geometric structure, stress/strain evolution, and ion/electron transportation is the basis to determine the design, scale-up, and optimization of electrodes. For example, Jia and Li proposed a chemomechanical model to systematically study the intrinsic stress evolution during lithiation of amorphous Si [98]. The critical size of an amorphous Si anode without lithiation-induced fracture is predicted quantitatively and identified by experimental observations.



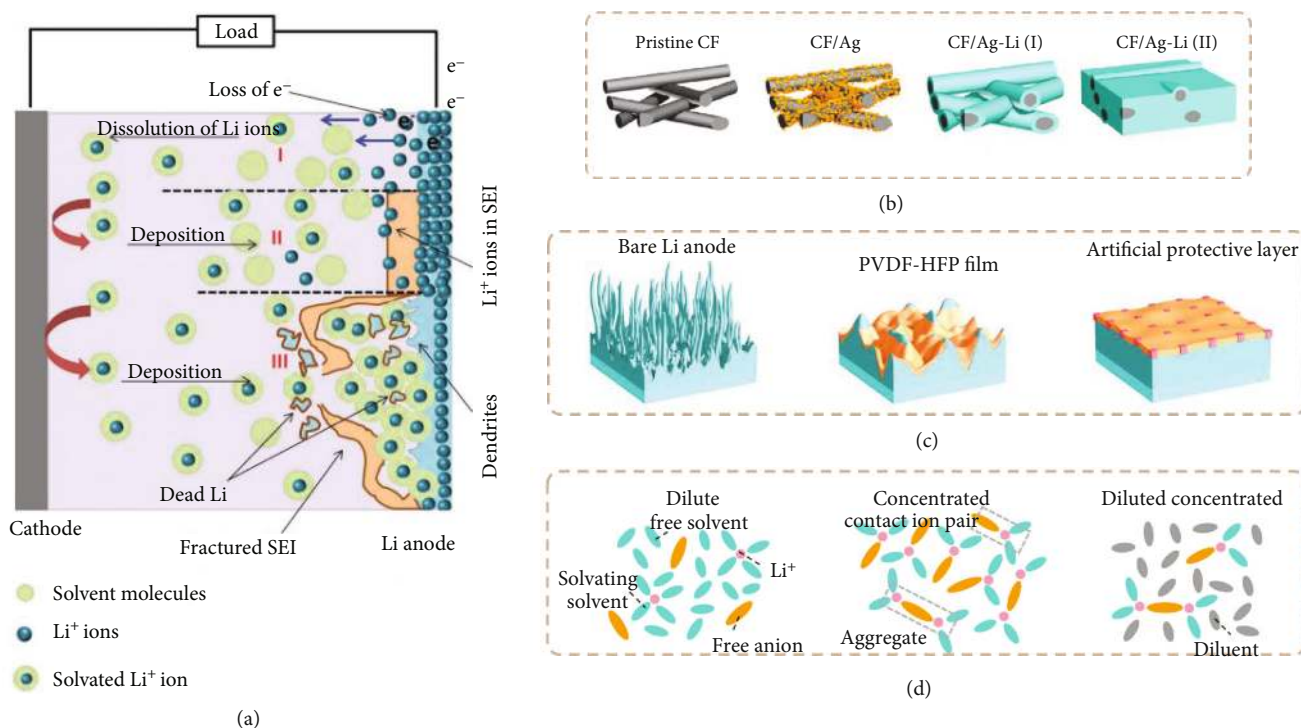


FIGURE 7: (a) Schematic of the main challenges in batteries with Li anodes. Reproduced with permission [101]. Copyright 2019, Wiley-VCH. (b) Strategies for nondendrite Li anodes and Li host. Reproduced with permission [103]. Copyright 2018, Elsevier. (c) Stable interface. Reproduced with permission [106]. Copyright 2018, Wiley-VCH. (d) Advanced electrolyte.

Numerical simulation based on phase field method and finite element method confers a large auxiliary function in mechanism analysis and electrode design [99, 100]. Future improvement on accuracy is expected in numerical simulation.

**3.2.2. Li Metal.** Li metal anode, benefiting from its ultrahigh theoretical capacity of  $3860 \text{ mAh g}^{-1}$  and extremely low potential ( $-3.04 \text{ V vs. standard hydrogen electrode}$ ), has long been regarded as the ultimate candidate for future high-energy-density Li batteries. Nevertheless, its implementation faces enormous challenges, which mainly stem from the nature of hostless, high reactivity, and dendritic deposition (Figure 7(a)) [101]. Due to the hostless nature, Li metal anode undergoes infinite volume change that is worse than Si anode. Furthermore, with the integrative effect of dendritic deposition and high reactivity, the rupture and regeneration of SEI repeatedly occur on the Li surface, thereby resulting in the depletion of active Li and electrolyte. In addition, dead Li generated during stripping process also leads to the loss of active Li. This uncontrollable process causes the poor electrochemical performance of Li metal anodes, such as high internal resistance, low Coulombic efficiency, and short lifespan. What is worse, dendritic Li may pierce the separator and induce safety concerns. For the Li metal anode in Li-S and Li-O<sub>2</sub> batteries, the corrosion from migratory cathode intermediates also leads to the loss of active Li, which must be taken into considerations.

To eliminate above issues, the main strategies developed over the past forty years can be summarized as follows. (1)

The introduction of a Li host (Figure 7(b)) [102–104]: Through providing prerreserved deposition space, Li host delivers unique superiority in decreasing volume change compared to other strategies. Besides, the position and behavior of Li plating can be regulated by modifying the electrical conductivity and lithiophilicity of hosts. (2) The construction of a stable Li/electrolyte interface (Figure 7(c)) [105–109]: It is a straight strategy in view of mechanically inhibiting dendrite growth and protecting Li from electrolyte and migratory cathode intermediates. (3) The development of advanced electrolytes (Figure 7(d)) [110]: It generally determines the composition/structure of SEI and the subsequent diffusion of Li ions. Localized high-concentration electrolytes and solid-state electrolytes have recently received intensive attention [111–114]. Detailed progress can refer to some insightful reviews [115–117]. Although the Li metal anode has made a huge leap forward in the last forty years, the challenges toward practical applications of the Li metal anode still remain. Future research directions may focus on the mechanism of Li dendrite growth, the fundamental understanding and regulation of Li/electrolyte interface, the design and scale-up fabrication of composite Li anodes, and the comprehensive evaluation of safety and performance under diverse practical conditions.

**3.3. The Roadmap toward Practical Applications.** From concept to commercial product with wide applications, an energy material often needs decades of continuous research and development. The success implementation of emerging electrode materials in batteries highly depends on the

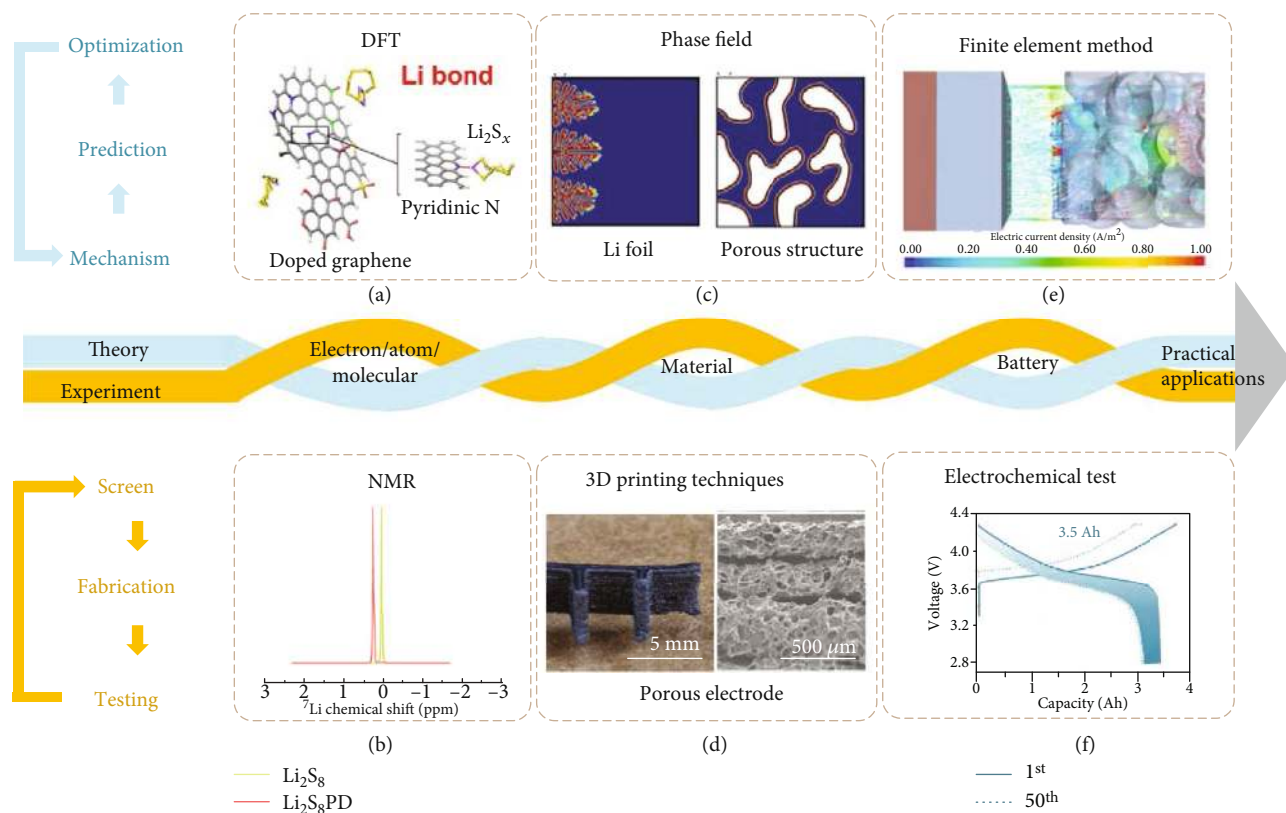


FIGURE 8: The roadmap of emerging materials toward practical applications with the combination of theory and experiment. Cases in point: combination of DFT and NMR for demonstrating the existence of Li bonds (a, b). Reproduced with permission [121]. Copyright 2017, Wiley-VCH. Combination of phase field method and 3D printing techniques for a Li host (c, d). Reproduced with permission [122]. Copyright 2019, Wiley-VCH. Combination of finite element method and electrochemical test for battery design (e, f). (e) Reproduced under the terms of CC BY-NC-ND 4.0 [123]. Copyright 2019, the authors. (f) Reproduced with permission [124]. Copyright 2019, Wiley-VCH.

cooperation from multidisciplinary, multifield, and multi-country. The research and development of emerging materials involves physics, chemistry, materials, energy, mechanics, automation, informatics, electronics, and other fields, in which the basic principle of energy storage relies on the internal electrochemical reactions. The popularization of emerging electrode materials requires not only the creation of original innovations from scientists but also the scale-up production from engineers to form a product, the establishment of standards in industry, the design of product according to the demand of end-users, the product marketing, and other aspects, which is a system engineering. A step-by-step development can be foreseen. The near-term development of high-energy-density rechargeable batteries is bound to still around the LIBs. It is believed that high-voltage and high-capacity cathodes combined with the silicon-containing anode are promising for commercialization in the near term. A shift of working principles from conventional intercalation reaction to conversion reaction is required for the further requirement in the energy demands. Sulfur, oxygen, and Li metal are highlighted.

In addition to route planning, it is crucial to develop new research methods. In order to bridge the fundamental understanding and practical applications, the combination of theory and experiment methods under multiscale becomes

highly desirable (Figure 8) [118–120]. The traditional development workflow for electrode materials based on experimental study is screen, fabrication, and performance testing. After repeated trial-and-error circuit, the desirable electrode material is finally acquired. The introduction of computer-aided theoretical study can help guide the development workflow in the right direction and speed up the research timeline. In recent years, multiscale theoretical methods, including but not limited to density functional theory (DFT), molecular dynamics (MD), phase field method, and finite element method, have achieved great progress in mechanism analysis, material prediction, and optimal design. However, due to the discrepancy between complicated experimental conditions and idealized physical model, the demonstration and complementation of experiment are highly requested for the innovation of advanced theoretical methods.

The combination of the experiment and theory methods can afford a multiscale bottom-up approach to practical applications of emerging materials. Herein, three cases that reasonably combine the experiment and theory methods are given. (1) Electronic, atomic, and molecular levels: Hou and co-workers employed quantum chemical calculations and  $^7\text{Li}$  nuclear magnetic resonance (NMR) spectroscopy to identify the Li bond between LiPSs and host materials (doped

graphene) and establish a fundamental guideline for mechanism analyses and host screen (Figures 8(a) and 8(b)) [121]. (2) Material level: Cao et al. reported a high-performance porous Li host through a novel fabrication technique of 3D printing and a theory demonstration of phase field model (Figures 8(c) and 8(d)) [122]. (3) Battery level: numerical model based on finite element method shows great vitality in geometry optimization, immensely reducing the workload of cell evaluation (Figures 8(e) and 8(f)) [123, 124]. The experimental exploration followed by theoretical interpretation or the theoretical prediction with experimental verification displays the great vitality in electrode material research. Future directions to further promote the combination of theory and experiments are expected: (1) developing emerging experimental method in atomic/molecular manipulation and characterization in order to realize and validate small-scale theoretical model, such as cryoelectron microscopy, *in situ* electron microscopy, and nondestructive imaging technique; (2) improving the accuracy of large-scale simulation method for engineering design; (3) enhancing the integration of theoretical methods under multiscale and multiphysics. The close academic collaborations are necessary because one researcher usually masters one modelling technique with high threshold; and (4) data flow management for developing machine learning and artificial intelligence. Machine learning and artificial intelligence can automate analytical model building, immensely freeing scientists from data analysis. The premise is massive and accurate data samples. Therefore, benchmarks, data sharing, and reasonable data management systems are appealed.

#### 4. Summary and Perspectives

As the energy densities, operating voltages, safety, and lifetime of Li batteries are mainly determined by electrode materials, much attention has been paid on the research of electrode materials. In this review, a general introduction of practical electrode materials is presented, providing a deep understanding and inspiration of battery designs. Furthermore, the emerging materials that may satisfy the future energy requirement are discussed, focusing on the remaining challenges and possible strategies. It is believed that the development of electrode materials will follow a shift of working principles from conventional intercalation reaction to conversion reaction for high energy density. The practical application of emerging electrode materials requires more advanced research techniques, especially the combination of experiment and theory, for material design and engineering implementation. Despite the property of high energy density, the future development of electrode materials also needs attention on the following aspects:

- (1) *Fast Charging*. It is a highly valued feature for EVs and portable electronics as the charge time is remarkably shortened. Unfortunately, performance decay and the structure destruction of electrode materials, meanwhile, readily occur under such high current density. The solution of above issues requires not only proper materials but also clear failure mechanisms.

- (2) *Safety*. The changes in chemical composition, crystal structure, and morphology of electrode materials may trigger side reactions and release heat or gas, thereby provoking safety issues. Internal failure mechanisms and triggering conditions need further investigation.
- (3) *Temperature Tolerance*. The environmental temperature difference brought by seasons and regions can reach 50°C, which remarkably affects the transport of Li ions and the stability of electrode materials. High discharge capacity at low temperature and high safety at high temperature are expected for electrode materials.
- (4) *Scale-Up Fabrication and Affordable Cost*. Most studies are based on lab-scale preparation without taking account of the scale up and cost issues. However, they can be the key constraints on the production chain. For instance, an environment gap exists between the glove box and plant. Manufacture art, process flexibility, and cost accounting will be more important as the practical process advances.
- (5) *Recycling*. Rapid growth in the utilization of electrode materials brings about the challenges of environment and resource. Therefore, it is an important part to recycle electrode materials at the end of life. On the one hand, separating harmful substances, especially heavy metal element, is favorable for minimizing environmental impacts. On the other hand, material or component recycling benefits to maximizing the economic value and promoting the development of sustainable society. Corresponding recycling methods are appealed.

Ultimately, the development of electrode materials is a system engineering, depending on not only material properties but also the operating conditions and the compatibility with other battery components, including electrolytes, binders, and conductive additives. The breakthroughs of electrode materials are on the way for next-generation batteries.

#### Conflicts of Interest

The authors declare no conflict of interest.

#### Authors' Contributions

X.S. conceived the figures, conducted the majority of the analysis, and wrote most of the paper. X.-Q.Z. and F.D. contributed to the analysis and editing of the paper. R.X., X.C., C.Y., F.-Y.S., and C.-M.C. helped with the editing of the paper. J.-Q.H., X.L., and Q.Z. supervised this work. All authors contributed to the discussion.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China (21776019, 21825501, and U1801257),

the National Key Research and Development Program (2016YFA0202500), the Beijing Natural Science Foundation (L182021), the Foundation of National Key Laboratory (6142808190201), the Scientific and Technological Key Project of Shanxi Province (20191102003), and the Tsinghua University Initiative Scientific Research Program.

## References

- [1] Y. Liang, C. Z. Zhao, H. Yuan et al., "A review of rechargeable batteries for portable electronic devices," *InfoMat*, vol. 1, no. 1, pp. 6–32, 2019.
- [2] H. Li, "Practical evaluation of Li-ion batteries," *Joule*, vol. 3, no. 4, pp. 911–914, 2019.
- [3] G. Crabtree, "The coming electric vehicle transformation," *Science*, vol. 366, no. 6464, pp. 422–424, 2019.
- [4] X. Zeng, M. Li, D. Abd El-Hady et al., "Commercialization of lithium battery technologies for electric vehicles," *Advanced Energy Materials*, vol. 9, no. 27, article 1900161, 2019.
- [5] X. Q. Zhang, C. Z. Zhao, J. Q. Huang, and Q. Zhang, "Recent advances in energy chemical engineering of next-generation lithium batteries," *Engineering*, vol. 4, no. 6, pp. 831–847, 2018.
- [6] Y. Lu, X. Rong, Y. S. Hu, L. Chen, and H. Li, "Research and development of advanced battery materials in China," *Energy Storage Materials*, vol. 23, pp. 144–153, 2019.
- [7] H. Hao, X. Cheng, Z. Liu, and F. Zhao, "China's traction battery technology roadmap: targets, impacts and concerns," *Energy Policy*, vol. 108, pp. 355–358, 2017.
- [8] D. Bresser, K. Hosoi, D. Howell et al., "Perspectives of automotive battery R&D in China, Germany, Japan, and the USA," *Journal of Power Sources*, vol. 382, pp. 176–178, 2018.
- [9] J. X. Zheng, Y. K. Ye, and F. Pan, "Structure units' as material genes in cathode materials for lithium-ion batteries'.,", *National Science Review*, vol. 7, pp. 242–245, 2019.
- [10] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, "Li-ion battery materials: present and future," *Materials Today*, vol. 18, no. 5, pp. 252–264, 2015.
- [11] J. Lu, Z. Chen, F. Pan, Y. Cui, and K. Amine, "High-performance anode materials for rechargeable lithium-ion batteries," *Electrochemical Energy Reviews*, vol. 1, no. 1, pp. 35–53, 2018.
- [12] S. Xin, Z. Chang, X. Zhang, and Y. G. Guo, "Progress of rechargeable lithium metal batteries based on conversion reactions," *National Science Review*, vol. 4, no. 1, pp. 54–70, 2017.
- [13] M. Armand and J. M. Tarascon, "Building better batteries," *Nature*, vol. 451, no. 7179, pp. 652–657, 2008.
- [14] W. Lee, S. Muhammad, C. Sergey et al., "Advances in the cathode materials for lithium rechargeable batteries," *Angewandte Chemie, International Edition*, vol. 59, no. 7, pp. 2578–2605, 2020.
- [15] D. Lin, Y. Liu, and Y. Cui, "Reviving the lithium metal anode for high-energy batteries," *Nature Nanotechnology*, vol. 12, no. 3, pp. 194–206, 2017.
- [16] F. Wu, J. Maier, and Y. Yu, "Guidelines and trends for next-generation rechargeable lithium and lithium-ion batteries," *Chemical Society Reviews*, vol. 49, no. 5, pp. 1569–1614, 2020.
- [17] M. Li, J. Lu, Z. Chen, and K. Amine, "30 years of lithium-ion batteries," *Advanced Materials*, vol. 30, no. 33, article 1800561, 2018.
- [18] The Nobel Prize in Chemistry, 2019, <https://www.nobelprize.org/prizes/chemistry/2019/summary/>.
- [19] M. Winter, B. Barnett, and K. Xu, "Before Li ion batteries," *Chemical Reviews*, vol. 118, no. 23, pp. 11433–11456, 2018.
- [20] M. S. Whittingham, "Electrical energy storage and intercalation chemistry," *Science*, vol. 192, no. 4244, pp. 1126–1127, 1976.
- [21] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, "Li<sub>x</sub>CoO<sub>2</sub> (0 < x < 1): a new cathode material for batteries of high energy density," *Materials Research Bulletin*, vol. 15, no. 6, pp. 783–789, 1980.
- [22] A. Yoshino, K. Sanechika, and T. Nakajima, "Secondary battery," US Patent 4668595A, US Patent, 1987.
- [23] Y. Nishi, "Lithium ion secondary batteries; past 10 years and the future," *Journal of Power Sources*, vol. 100, no. 1–2, pp. 101–106, 2001.
- [24] F. Schipper, E. M. Erickson, C. Erk, J. Y. Shin, F. F. Chesneau, and D. Aurbach, "Review—recent advances and remaining challenges for lithium ion battery cathodes," *Journal of the Electrochemical Society*, vol. 164, no. 1, pp. A6220–A6228, 2017.
- [25] Y. Shao-Horn, L. Croguennec, C. Delmas, E. C. Nelson, and M. A. O'Keefe, "Atomic resolution of lithium ions in LiCoO<sub>2</sub>," *Nature Materials*, vol. 2, no. 7, pp. 464–467, 2003.
- [26] J. Molenda and M. Molenda, "Composite Cathode Material for Li-Ion Batteries Based on LiFePO<sub>4</sub> System," in *Metal, ceramic and polymeric composites for various uses*, J. Cuppulletti, Ed., p. 621, InTechOpen, 2011.
- [27] X. Lu, Y. Sun, Z. Jian et al., "New insight into the atomic structure of electrochemically delithiated O3-Li<sub>(1-x)</sub>CoO<sub>2</sub> (0 ≤ x ≤ 0.5) nanoparticles," *Nano Letters*, vol. 12, no. 12, pp. 6192–6197, 2012.
- [28] G. G. Amatucci, J. M. Tarascon, and L. C. Klein, "CoO<sub>2</sub>, the end member of the Li<sub>x</sub>CoO<sub>2</sub> solid solution," *Journal of the Electrochemical Society*, vol. 143, no. 3, pp. 1114–1123, 1996.
- [29] H. Tukamoto and A. R. West, "Electronic conductivity of LiCoO<sub>2</sub> and its enhancement by magnesium doping," *Journal of the Electrochemical Society*, vol. 144, no. 9, pp. 3164–3168, 1997.
- [30] J. Cho, Y. J. Kim, T. J. Kim, and B. Park, "Zero-strain intercalation cathode for rechargeable Li-ion cell," *Angewandte Chemie, International Edition*, vol. 40, no. 18, pp. 3367–3369, 2001.
- [31] K. Wang, J. J. Wan, Y. X. Xiang et al., "Recent advances and historical developments of high voltage lithium cobalt oxide materials for rechargeable Li-ion batteries," *Journal of Power Sources*, vol. 460, article 228062, 2020.
- [32] M. M. Thackeray, P. J. Johnson, L. A. de Picciotto, P. G. Bruce, and J. B. Goodenough, "Electrochemical extraction of lithium from LiMn<sub>2</sub>O<sub>4</sub>," *Materials Research Bulletin*, vol. 19, no. 2, pp. 179–187, 1984.
- [33] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivines as positive-electrode materials for rechargeable lithium batteries," *Journal of the Electrochemical Society*, vol. 144, no. 4, pp. 1188–1194, 1997.
- [34] J. M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature*, vol. 414, no. 6861, pp. 359–367, 2001.
- [35] S. Y. Chung, J. T. Bloking, and Y. M. Chiang, "Electronically conductive phospho-olivines as lithium storage electrodes," *Nature Materials*, vol. 1, no. 2, pp. 123–128, 2002.



- [36] A. Yamada, S. C. Chung, and K. Hinokuma, "Optimized  $\text{LiFePO}_4$  for lithium battery cathodes," *Journal of the Electrochemical Society*, vol. 148, no. 3, article A224, 2001.
- [37] Y.-K. Sun, "High-capacity layered cathodes for next-generation electric vehicles," *ACS Energy Letters*, vol. 4, no. 5, pp. 1042–1044, 2019.
- [38] T. Ohzuku and Y. Makimura, "Layered lithium insertion material of  $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$  for lithium-ion batteries," *Chemistry Letters*, vol. 30, no. 7, pp. 642–643, 2001.
- [39] E. Rossen, C. D. W. Jones, and J. R. Dahn, "Structure and electrochemistry of  $\text{Li}_x\text{Mn}_y\text{Ni}_{1-y}\text{O}_2$ ," *Solid State Ionics*, vol. 57, no. 3-4, pp. 311–318, 1992.
- [40] J. Kasnatscheew, S. Röser, M. Börner, and M. Winter, "Do Increased Ni Contents in  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  (NMC) electrodes decrease structural and thermal stability of Li ion batteries? A thorough look by consideration of the  $\text{Li}^+$  extraction ratio," *ACS Applied Energy Materials*, vol. 2, no. 11, pp. 7733–7737, 2019.
- [41] W. Li, X. Liu, H. Celio et al., "Mn versus Al in layered oxide cathodes in lithium-ion batteries: a comprehensive evaluation on long-term cyclability," *Advanced Energy Materials*, vol. 8, no. 15, article 1703154, 2018.
- [42] L. Liu, M. Li, L. Chu et al., "Layered ternary metal oxides: performance degradation mechanisms as cathodes, and design strategies for high-performance batteries," *Progress in Materials Science*, vol. 111, article 100655, 2020.
- [43] J. Yang and Y. Xia, "Suppressing the phase transition of the layered ni-rich oxide cathode during high-voltage cycling by introducing low-content  $\text{Li}_2\text{MnO}_3$ ," *ACS Applied Materials & Interfaces*, vol. 8, no. 2, pp. 1297–1308, 2016.
- [44] F. Wu, N. Liu, L. Chen et al., "Improving the reversibility of the H2-H3 phase transitions for layered Ni-rich oxide cathode towards retarded structural transition and enhanced cycle stability," *Nano Energy*, vol. 59, pp. 50–57, 2019.
- [45] W. Liu, P. Oh, X. Liu et al., "Nickel-rich layered lithium transition-metal oxide for high-energy lithium-ion batteries," *Angewandte Chemie, International Edition*, vol. 54, no. 15, pp. 4440–4457, 2015.
- [46] J. R. Dahn, T. Zheng, Y. Liu, and J. S. Xue, "Mechanisms for lithium insertion in carbonaceous materials," *Science*, vol. 270, no. 5236, pp. 590–593, 1995.
- [47] J. Yan, J. Zhang, Y. C. Su, X. G. Zhang, and B. J. Xia, "A novel perspective on the formation of the solid electrolyte interphase on the graphite electrode for lithium-ion batteries," *Electrochimica Acta*, vol. 55, no. 5, pp. 1785–1794, 2010.
- [48] M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novak, "Insertion electrode materials for rechargeable lithium batteries," *Advanced Materials*, vol. 10, no. 10, pp. 725–763, 1998.
- [49] A. Satoh, "Electrochemical intercalation of lithium into graphitized carbons," *Solid State Ionics*, vol. 80, no. 3-4, pp. 291–298, 1995.
- [50] D. S. Kim, Y. E. Kim, and H. Kim, "Improved fast charging capability of graphite anodes via amorphous  $\text{Al}_2\text{O}_3$  coating for high power lithium ion batteries," *Journal of Power Sources*, vol. 422, pp. 18–24, 2019.
- [51] G. X. Wang, D. H. Bradhurst, S. X. Dou, and H. K. Liu, "Spinel  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$  as an anode material for lithium ion batteries," *Journal of Power Sources*, vol. 83, no. 1-2, pp. 156–161, 1999.
- [52] K. Zaghib, M. Simoneau, M. Armand, and M. Gauthier, "Electrochemical study of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as negative electrode for Li-ion polymer rechargeable batteries," *Journal of Power Sources*, vol. 81-82, pp. 300–305, 1999.
- [53] K. Amine, I. Belharouak, Z. H. Chen et al., "Nanostructured anode material for high-power battery system in electric vehicles," *Advanced Materials*, vol. 22, no. 28, pp. 3052–3057, 2010.
- [54] W. Li, B. Song, and A. Manthiram, "High-voltage positive electrode materials for lithium-ion batteries," *Chemical Society Reviews*, vol. 46, no. 10, pp. 3006–3059, 2017.
- [55] J. M. Zheng, S. J. Myeong, W. R. Cho et al., "Li- and Mn-rich cathode materials: challenges to commercialization," *Advanced Energy Materials*, vol. 7, article 1601284, 2016.
- [56] J. R. Croy, M. Balasubramanian, K. G. Gallagher, and A. K. Burrell, "Review of the U.S. Department of Energy's "Deep Dive" effort to understand voltage fade in Li- and Mn-rich cathodes," *Accounts of Chemical Research*, vol. 48, no. 11, pp. 2813–2821, 2015.
- [57] Y. Zuo, B. Li, N. Jiang et al., "A high-capacity O2-type Li-rich cathode material with a single-layer  $\text{Li}_2\text{MnO}_3$  superstructure," *Advanced Materials*, vol. 30, no. 16, article 1707255, 2018.
- [58] M. Gu, I. Belharouak, J. M. Zheng et al., "Formation of the spinel phase in the layered composite cathode used in li-ion batteries," *ACS Nano*, vol. 7, pp. 760–767, 2012.
- [59] B. Qiu, M. Zhang, S. Y. Lee et al., "Metastability and reversibility of anionic redox-based cathode for high-energy rechargeable batteries," *Cell Reports Physical Science*, vol. 1, no. 3, article 100028, 2020.
- [60] N. Leifer, T. Penki, R. Nanda et al., "Linking structure to performance of  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  (Li and Mn rich NMC) cathode materials synthesized by different methods," *Physical Chemistry Chemical Physics*, vol. 22, no. 16, pp. 9098–9109, 2020.
- [61] H. Danuta and U. Juliusz, "Electric dry cells and storage batteries," US Patent 3043896A, US Patent, 1962.
- [62] R. M. L. Bhaskara, "Organic electrolyte cells," US Patent 53681466A, 1968.
- [63] R. D. Rauh, K. M. Abraham, G. F. Pearson, J. K. Surprenant, and S. B. Brummer, "A lithium/dissolved sulfur battery with an organic electrolyte," *Journal of the Electrochemical Society*, vol. 126, no. 4, p. 523, 1979.
- [64] X. Ji, K. T. Lee, and L. F. Nazar, "A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries," *Nature Materials*, vol. 8, no. 6, pp. 500–506, 2009.
- [65] H. J. Peng, J. Q. Huang, X. B. Cheng, and Q. Zhang, "Review on high-loading and high-energy lithium-sulfur batteries," *Advanced Energy Materials*, vol. 7, no. 24, article 1700260, 2017.
- [66] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, and J. M. Tarascon, "Li-O2 and Li-S batteries with high energy storage," *Nature Materials*, vol. 11, no. 1, pp. 19–29, 2012.
- [67] M. Zhao, B. Q. Li, H. J. Peng, H. Yuan, J. Y. Wei, and J. Q. Huang, "Lithium-sulfur batteries under lean electrolyte conditions: challenges and opportunities," *Angewandte Chemie, International Edition*, vol. 59, pp. 12636–12652, 2020.
- [68] T. Liu, H. Hu, X. Ding et al., "12 years roadmap of the sulfur cathode for lithium sulfur batteries (2009–2020)," *Energy Storage Materials*, vol. 30, pp. 346–366, 2020.
- [69] A. Fu, C. Wang, F. Pei, J. Cui, X. Fang, and N. Zheng, "Recent advances in hollow porous carbon materials for lithium-sulfur batteries," *Small*, vol. 15, article 1804786, 2019.

- [70] B. Q. Li, S. Y. Zhang, L. Kong, H. J. Peng, and Q. Zhang, "Porphyrin organic framework hollow spheres and their applications in lithium-sulfur batteries," *Advanced Materials*, vol. 30, no. 23, article 1707483, 2018.
- [71] X. Y. Zhang, K. Chen, Z. H. Sun et al., "Structure-related electrochemical performance of organosulfur compounds for lithium-sulfur batteries," *Energy & Environmental Science*, vol. 13, no. 4, pp. 1076–1095, 2020.
- [72] S. Xin, L. Gu, N. H. Zhao et al., "Smaller sulfur molecules promise better lithium-sulfur batteries," *Journal of the American Chemical Society*, vol. 134, no. 45, pp. 18510–18513, 2012.
- [73] J. Zheng, G. B. Ji, X. L. Fan et al., "High-fluorinated electrolytes for Li-S batteries," *Advanced Energy Materials*, vol. 9, no. 16, article 1803774, 2019.
- [74] M. Zhao, H. J. Peng, Z. W. Zhang et al., "Activating inert metallic compounds for high-rate lithium-sulfur batteries through in situ etching of extrinsic metal," *Angewandte Chemie, International Edition*, vol. 58, no. 12, pp. 3779–3783, 2019.
- [75] M. Zhao, H. J. Peng, B. Q. Li et al., "Electrochemical phase evolution of metal-based pre-catalysts for high-rate polysulfide conversion," *Angewandte Chemie, International Edition*, vol. 59, no. 23, pp. 9011–9017, 2020.
- [76] B. Q. Li, H. J. Peng, X. Chen et al., "Polysulfide electrocatalysis on framework porphyrin in high-capacity and high-stable lithium-sulfur batteries," *CCS Chemistry*, vol. 1, pp. 128–137, 2019.
- [77] X. B. Cheng, J. Q. Huang, and Q. Zhang, "Review—Li metal anode in working lithium-sulfur batteries," *Journal of the Electrochemical Society*, vol. 165, pp. A6058–A6072, 2018.
- [78] C. Yan, X. Q. Zhang, J. Q. Huang, Q. Liu, and Q. Zhang, "Lithium-anode protection in lithium-sulfur batteries," *Trends in Chemistry*, vol. 1, pp. 693–704, 2019.
- [79] S. Dörfler, H. Althues, P. Härtel, T. Abendroth, B. Schumm, and S. Kaskel, "Challenges and key parameters of lithium-sulfur batteries on pouch cell level," *Joule*, vol. 4, no. 3, pp. 539–554, 2020.
- [80] A. Bhargav, J. He, A. Gupta, and A. Manthiram, "Lithium-sulfur batteries: attaining the critical metrics," *Joule*, vol. 4, no. 2, pp. 285–291, 2020.
- [81] X. Huang, J. Xue, M. Xiao et al., "Comprehensive evaluation of safety performance and failure mechanism analysis for lithium sulfur pouch cells," *Energy Storage Materials*, vol. 30, pp. 87–97, 2020.
- [82] L. Kong, Q. Jin, X. T. Zhang et al., "Towards full demonstration of high areal loading sulfur cathode in lithium-sulfur batteries," *Journal of Energy Chemistry*, vol. 39, pp. 17–22, 2019.
- [83] X. Guo, B. Sun, D. W. Su et al., "Recent developments of aprotic lithium-oxygen batteries: functional materials determine the electrochemical performance," *Scientific Bulletin*, vol. 62, pp. 442–452, 2017.
- [84] J. Lai, Y. Xing, N. Chen, L. Li, F. Wu, and R. Chen, "Electrolytes for rechargeable lithium-air batteries," *Angewandte Chemie, International Edition*, vol. 59, no. 8, pp. 2974–2997, 2020.
- [85] C. Z. Shu, J. Z. Wang, J. P. Long, H. K. Liu, and S. X. Dou, "Understanding the reaction chemistry during charging in aprotic lithium-oxygen batteries: existing problems and solutions," *Advanced Materials*, vol. 31, no. 15, article 1804587, 2019.
- [86] K. M. Abraham and Z. Jiang, "A polymer electrolyte-based rechargeable lithium/oxygen battery," *Journal of the Electrochemical Society*, vol. 143, no. 1, pp. 1–5, 1996.
- [87] K. F. Blurton and A. F. Sammells, "Metal/air batteries: their status and potential — a review," *Journal of Power Sources*, vol. 4, no. 4, pp. 263–279, 1979.
- [88] H. D. Lim, B. Lee, Y. Bae et al., "Reaction chemistry in rechargeable Li-O<sub>2</sub> batteries," *Chemical Society Reviews*, vol. 46, no. 10, pp. 2873–2888, 2017.
- [89] V. L. Chevrier and J. R. Dahn, "First principles model of amorphous silicon lithiation," *Journal of the Electrochemical Society*, vol. 156, no. 6, p. A454, 2009.
- [90] M. J. Loveridge, R. Malik, S. Paul et al., "Binder-free Sn-Si heterostructure films for high capacity Li-ion batteries," *RSC Advances*, vol. 8, no. 30, pp. 16726–16737, 2018.
- [91] Y. Jin, B. Zhu, Z. Lu, N. Liu, and J. Zhu, "Challenges and recent progress in the development of Si anodes for lithium-ion battery," *Advanced Energy Materials*, vol. 7, no. 23, article 1700715, 2017.
- [92] X. Zuo, J. Zhu, P. Müller-Buschbaum, and Y. J. Cheng, "Silicon based lithium-ion battery anodes: a chronicle perspective review," *Nano Energy*, vol. 31, pp. 113–143, 2017.
- [93] S. Chae, S. H. Choi, N. Kim, J. Sung, and J. Cho, "Integration of graphite and silicon anodes for the commercialization of high-energy lithium-ion batteries," *Angewandte Chemie, International Edition*, vol. 59, no. 1, pp. 110–135, 2020.
- [94] K. Feng, M. Li, W. W. Liu et al., "Silicon-based anodes for lithium-ion batteries: from fundamentals to practical applications," *Small*, vol. 14, no. 8, article 1702737, 2018.
- [95] H. Wu, G. Chan, J. W. Choi et al., "Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control," *Nature Nanotechnology*, vol. 7, no. 5, pp. 310–315, 2012.
- [96] H. Axel, H. Schäfer, and A. Weiss, "The crystal structure of lithium silicide Li<sub>2</sub>Si," *Angewandte Chemie, International Edition*, vol. 4, no. 4, p. 358, 1965.
- [97] F. Luo, B. N. Liu, J. Y. Zheng et al., "Review—nano-silicon/carbon composite anode materials towards practical application for next generation Li-ion batteries," *Journal of the Electrochemical Society*, vol. 162, no. 14, pp. A2509–A2528, 2015.
- [98] Z. Jia and T. Li, "Intrinsic stress mitigation via elastic softening during two-step electrochemical lithiation of amorphous silicon," *Journal of the Mechanics and Physics of Solids*, vol. 91, pp. 278–290, 2016.
- [99] Y. Kim, S. Sim, S. Kang, J. Yun, H. W. Lee, and S. W. Lee, "Highly robust silicon bimorph plate anode and its mechanical analysis upon electrochemical lithiation," *Energy Storage Materials*, vol. 23, pp. 292–298, 2019.
- [100] L. Chen, F. Fan, L. Hong et al., "A phase-field model coupled with large elasto-plastic deformation: application to lithiated silicon electrodes," *Journal of the Electrochemical Society*, vol. 161, no. 11, pp. F3164–F3172, 2014.
- [101] Z. A. Ghazi, Z. Sun, C. Sun et al., "Key aspects of lithium metal anodes for lithium metal batteries," *Small*, vol. 15, no. 32, article 1900687, 2019.
- [102] P. Shi, X. Q. Zhang, X. Shen, R. Zhang, H. Liu, and Q. Zhang, "A review of composite lithium metal anode for practical applications," *Advanced Materials Technologies*, vol. 5, article 1900806, 2019.

- [103] R. Zhang, X. Chen, X. Shen et al., “Coralloid carbon fiber-based composite lithium anode for robust lithium metal batteries,” *Joule*, vol. 2, no. 4, pp. 764–777, 2018.
- [104] X. Chen, X. R. Chen, T. Z. Hou et al., “Lithiophilicity chemistry of heteroatom-doped carbon to guide uniform lithium nucleation in lithium metal anodes,” *Science Advances*, vol. 5, article eaau7728, 2019.
- [105] T. Li, X. Q. Zhang, P. Shi, and Q. Zhang, “Fluorinated solid-electrolyte interphase in high-voltage lithium metal batteries,” *Joule*, vol. 3, no. 11, pp. 2647–2661, 2019.
- [106] R. Xu, X. Q. Zhang, X. B. Cheng et al., “Artificial soft-rigid protective layer for dendrite-free lithium metal anode,” *Advanced Functional Materials*, vol. 28, no. 8, article 1705838, 2018.
- [107] C. Z. Zhao, H. Duan, J. Q. Huang et al., “Designing solid-state interfaces on lithium-metal anodes: a review,” *Science China. Chemistry*, vol. 62, no. 10, pp. 1286–1299, 2019.
- [108] R. Xu, X. B. Cheng, C. Yan et al., “Artificial interphases for highly stable lithium metal anode,” *Matter*, vol. 1, no. 2, pp. 317–344, 2019.
- [109] C. Yan, H. R. Li, X. Chen et al., “Regulating the inner helmholtz plane for stable solid electrolyte interphase on lithium metal anodes,” *Journal of the American Chemical Society*, vol. 141, no. 23, pp. 9422–9429, 2019.
- [110] Y. Yamada, J. H. Wang, S. Ko, E. Watanabe, and A. Yamada, “Advances and issues in developing salt-concentrated battery electrolytes,” *Nature Energy*, vol. 4, no. 4, pp. 269–280, 2019.
- [111] K. Kerman, A. Luntz, V. Viswanathan, Y. M. Chiang, and Z. Chen, “Review—practical challenges hindering the development of solid state Li ion batteries,” *Journal of the Electrochemical Society*, vol. 164, no. 7, pp. A1731–A1744, 2017.
- [112] M. Zhu, J. Wu, Y. Wang et al., “Recent advances in gel polymer electrolyte for high-performance lithium batteries,” *Journal of Energy Chemistry*, vol. 37, pp. 126–142, 2019.
- [113] S. Xia, X. Wu, Z. Zhang, Y. Cui, and W. Liu, “Practical challenges and future perspectives of all-solid-state lithium-metal batteries,” *Chem*, vol. 5, no. 4, pp. 753–785, 2019.
- [114] X. B. Cheng, C. Z. Zhao, Y. X. Yao, H. Liu, and Q. Zhang, “Recent advances in energy chemistry between solid-state electrolyte and safe lithium-metal anodes,” *Chem*, vol. 5, no. 1, pp. 74–96, 2019.
- [115] X. B. Cheng, R. Zhang, C. Z. Zhao, and Q. Zhang, “Toward safe lithium metal anode in rechargeable batteries: a review,” *Chemical Reviews*, vol. 117, no. 15, pp. 10403–10473, 2017.
- [116] X. Zhang, Y. Yang, and Z. Zhou, “Towards practical lithium-metal anodes,” *Chemical Society Reviews*, vol. 49, no. 10, pp. 3040–3071, 2020.
- [117] X. Shen, H. Liu, X. B. Cheng, C. Yan, and J. Q. Huang, “Beyond lithium ion batteries: higher energy density battery systems based on lithium metal anodes,” *Energy Storage Materials*, vol. 12, pp. 161–175, 2018.
- [118] X. Chen, T. Hou, K. A. Persson, and Q. Zhang, “Combining theory and experiment in lithium-sulfur batteries: current progress and future perspectives,” *Materials Today*, vol. 22, pp. 142–158, 2019.
- [119] A. A. Franco, “Multiscale modelling and numerical simulation of rechargeable lithium ion batteries: concepts, methods and challenges,” *RSC Advances*, vol. 3, no. 32, article 13027, 2013.
- [120] Y. Fan, X. Chen, D. Legut, and Q. Zhang, “Modeling and theoretical design of next-generation lithium metal batteries,” *Energy Storage Materials*, vol. 16, pp. 169–193, 2019.
- [121] T. Z. Hou, W. T. Xu, X. Chen, H. J. Peng, J. Q. Huang, and Q. Zhang, “Lithium bond chemistry in lithium-sulfur batteries,” *Angewandte Chemie, International Edition*, vol. 56, no. 28, pp. 8178–8182, 2017.
- [122] D. Cao, Y. Xing, K. Tantratian et al., “3D printed high-performance lithium metal microbatteries enabled by nanocellulose,” *Advanced Materials*, vol. 31, no. 14, article 1807313, 2019.
- [123] A. W. Abboud, E. J. Dufek, and B. Liaw, “Communication—implications of local current density variations on lithium plating affected by cathode particle size,” *Journal of the Electrochemical Society*, vol. 166, no. 4, pp. A667–A669, 2019.
- [124] X. Q. Zhang, T. Li, B. Q. Li et al., “A sustainable solid electrolyte interphase for high-energy-density lithium metal batteries under practical conditions,” *Angewandte Chemie, International Edition*, vol. 59, no. 8, pp. 3252–3257, 2020.