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REVIEW ARTICLE

High-Performance Anode Materials for Rechargeable Lithium-Ion Batteries

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Abstract
Transformational changes in battery technologies are critically needed to enable the effective use of renewable energy sources, such as solar and wind, and to allow for the expansion of the electrification of vehicles. Developing high-performance batteries is critical to meet these requirements, which certainly relies on material breakthroughs. This review article presents the recent progresses and challenges in discovery of high-performance anode materials for Li-ion batteries related to their applications in future electrical vehicles and grid energy storage. The advantages and disadvantages of a series of anode materials are highlighted.

Keywords Li-ion battery · Anode materials · Graphite · Silicon · Lithium metal · Metal oxides · TiO_2

PACS 81 · 84

1 Introduction

Due to climate changes, especially exhaust of fossil fuels, a significant worldwide interest has been driven into the development of electrochemical power devices (batteries), which could significantly help to effectively use the renewable energy sources such as solar and wind, as well as to intensively expand the electrification of vehicles [1, 2]. To achieve such goals, innovative technology and advanced materials development of the battery are urgently required, where the batteries must have high volumetric (Wh/L) and gravimetric energy density (Wh/kg), and they must have long cycle life and calendar life with sufficient safety. When such a situation arises, it is essential to develop high-performance batteries in order to meet various requirements, which certainly relies on further breakthroughs in battery materials [3–7].

Non-aqueous rechargeable Li-ion batteries are definitely one of the most successful energy storage devices of the modern materials electrochemistry in the last century [1, 8–12]. Since Sony Corporation commercialized the first Li-ion battery in 1991 for small portable electronic devices, the relatively low-voltage, water-based batteries including Ni–Cd [13] and Ni–MH [14] systems have been gradually replaced by Li-ion technology. Nowadays, the usage of Li-ion batteries has been expanded largely into various devices, including robots, various power tools, stationary power storage units, uninterrupted power supply (UPS) units, as well as electrical vehicles (hybrid, plug-in or pure EVs) [15]. However, demand is still dramatically increasing for batteries with higher gravimetric and volumetric energy density to power EVs with long driving ranges (of approximately 300 miles per charge) and to store intermittent solar and wind energy for stationary power applications.

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Unfortunately, conventional Li-ion battery technologies fall short to meet the requirement for these applications [8, 16].

The existing concept of present lithium-ion batteries is based on the combination of a lithium-ion positive electrode "cathode" and a negative electrode "anode" with these being separated by a membrane soaked with a lithium-ion conducting electrolyte, for example a solution of $LiPF_6$ in alkyl organic carbonates, as schematically shown in Fig. 1. Lithium transition metal oxides or phosphates ($LiCoO_2$, $LiMn_2O_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiFePO_4$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), etc.) are generally adopted as the active cathode materials of the commercial lithium-ion batteries [17–20]. At the anode side, graphite is the common choice [21]. During charge of the cell, lithium ions move out of the cathode ($Li_{1-x}CoO_2$) and become trapped inside the anode (Li_xC_6) when external electrical current is applied, through which the electrical energy is converted to chemical energy. Upon the cell discharge, those lithium ions travel back to the cathode and release the chemical energy stored via producing an external electrical current. The electrochemical reactions occurring in a typical lithium-ion battery based on $LiCoO_2$ cathode and graphite anode can be described as follows:

$$(+)\ \mathrm{Li}_{1-x}\mathrm{CoO}_2 + x\mathrm{Li}^+ + xe \leftrightarrow \mathrm{LiCoO}_2 \tag{1}$$

$$(-)\ \mathrm{Li}_x\mathrm{C} \leftrightarrow \mathrm{C} + x\mathrm{Li}^+ + xe^- \tag{2}$$

Overall reaction:

$$\mathrm{Li}_x\mathrm{C} + \mathrm{Li}_{1-x}\mathrm{CoO}_2 \leftrightarrow \mathrm{C} + \mathrm{LiCoO}_2 \tag{3}$$

The reversible flow of lithium ions moving back and forth through the ionically conducting electrolyte between two electrodes allows the conversion of chemical energy and electrical energy repeatedly. During the initial battery cycling (charge/discharge), multicomponent (organic/inorganic) and multilayer passivation films form at each electrode known as solid electrolyte interphase (SEI) that is critical to protecting the electrodes from further reactions with electrolytes.

Although such lithium-ion batteries are commercially very successful, we must realize that we are reaching the limits in performance using the current electrode and electrolyte materials [22]. The performance limitation together with the cost concern of the commercially available Li-ion batteries seriously limits the fast expansion of the electrical vehicle market and efficient usage of renewable energy sources. In addition, some other technical bottlenecks of the current Li-ion technology including slow recharge cycles, relatively short calendar life as well as the safety issues need to be fully addressed.

Significant research has been conducted to exploring higher energy density electrode materials in order to meet the requirement for EV's application. Currently, $LiCoO_2$ [23], layered metal oxides such as $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) [24, 25] and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) [26, 27], electrode derived from spinel-type $LiMn_2O_4$ [28] and olivine-type $LiFePO_4$ [29] are the state of the art for cathode active materials. However, they deliver relatively low practical capacities in a lithium-ion cell, typically in the range of 100–180 mAh/g at moderate current rates. Clearly, it is important to develop new strategies to design alternative high-energy cathode materials that are superior to those achievable with standard $LiCoO_2$-, $LiMn_2O_4$- and

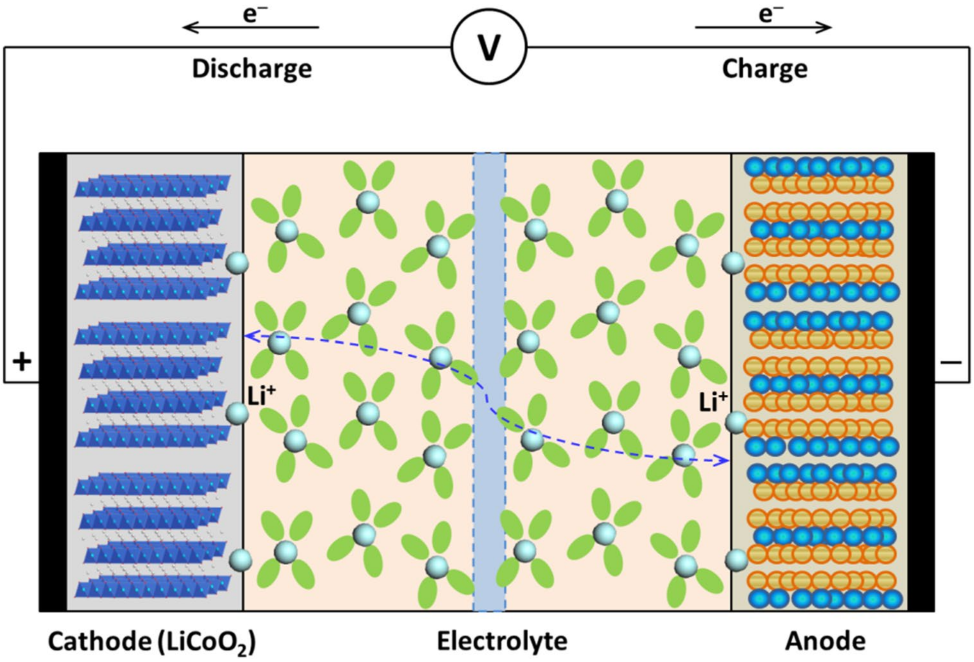


Fig. 1 Scheme of a common lithium-ion battery

$LiFePO_4$-type electrodes, yet they still have to maintain considerable structural stability, rate capability as well as long cycle life. For example, a family of high-energy manganese-based cathode materials have been developed recently by structurally integrating a Li_2MnO_3 stabilizing component into an electrochemically active $LiMO_2$ (M=Mn, Ni, Co) electrode, which boosts specific capacity up to 250 mAh/g due to the excess lithium in the system and, thereby, significantly improves the energy density of cell (based on the active materials) to 900 Wh/kg [30, 31]. However, the decay of capacity and voltage of these materials during the long time cycling led to the severe loss of the cell energy density that prevents its practical application in EVs [32, 33]. Going beyond the horizon of Li-ion batteries could offer another great opportunity to increase the energy density of the cell, although it requires the exploration of new electrochemistry and materials. For example, sulfur- and oxygen-based cathodes have recently been intensely investigated due to their potentially much higher theoretical capacity than the conventional lithium metal oxide [34–36]. These systems, however, are still in the early stage and facing a formidable challenge. The science and technology of the development of high-performance cathode materials have been extensively reviewed in the previous reported papers, to which the reader is referred for more details [22, 37–43].

Another effective approach of increasing the energy density of lithium-ion batteries is to search for high-capacity anode materials. As mentioned earlier, graphite is definitely the most widely used anode active material in the commercial Li-ion cells thanks to its excellent features including low working potential, low cost and good cycle life [44]. However, graphite only delivers a relatively low capacity of 372 mAh/g since it allows the intercalation of only one lithium for six carbon atoms forming a stoichiometric LiC_6, as shown in reaction 2. In addition, battery with graphite anode usually has moderate power density due to the relatively slow diffusion rate of lithium ion into carbon materials (between 10^{-12} and 10^{-6} cm^2/s) [45]. Therefore, there is an urgency to find alternative anode materials with high-capacity and high lithium-ion diffusion rate that could help to improve the energy and power densities of the cell. During the past decade, numerous efforts have been devoted to this blooming field with significant progress being achieved; yet there is still a sizable challenge facing those involved in the design and development of high-performance anode materials.

This review article will go through a brief description of the importance of high-performance anode materials for Li-ion batteries related to their applications in future electrical vehicles and grid energy storage. In the main part of this review, we will present the recent progresses and challenges of a new type of carbon materials, i.e., graphene. We will then discuss high-rate (power) anode material, since it is critical for the hybrid electrical vehicle (HEV) application. Moving toward the high-capacity anode, we will discuss the recent progresses on Si-based alloys and metal oxides as anode materials, although these materials are still facing significant challenges. Finally, the progresses and challenges faced by Li metal will be presented. Through this review, we intend to show that development of high-performance anode materials is one of the key factors toward high-energy and high-power battery research; and it also intends to familiarize the readers with the frontier research of different anodes for Li-ion battery and to evaluate and summarize the progress and challenges presently at hand.

2 Overview of Anode Materials

An ideal anode for Li-ion battery should fulfill the requirement of high reversible gravimetric and volumetric capacity; a low potential against cathode materials; high-rate capability; long cycle life; low cost; excellent abuse tolerance; and environmental compatibility. Pure lithium metal is clearly the best anode material since it does not carry any dead weight, if taking the specific capacity into account alone. However, the electroplating of dendritic lithium during charging can cause an internal short circuit, leading to severe safety concerns. Both carbon and non-carbon materials for high-performance anode have been intensively investigated [46], including but not limiting to carbon nanotubes [47, 48], carbon nanofibers [49], graphene [50–52], porous carbon [53], silicon [54] and silicon monoxide [55, 56], germanium [57, 58], tin [59, 60], and transition metal oxides [61, 62], sulfides [63], phosphides [55] and nitrides [63, 64]. The redox potentials versus Li/Li^+ and the corresponding specific capacity of these materials are shown in Fig. 2, which clearly shows that the selection of suitable anode materials has significant impact on improving energy density of the Li-ion cell.

Based on their electrochemical lithiation/delithiation mechanism, the innovative anode materials discussed in this review can be classified into three main groups as shown in Fig. 3, i.e., intercalation anodes, carbon-based materials and $Li_4Ti_5O_{12}$; alloy anodes such as Si, Ge, Sn; conversion anodes, mainly referring to transition metal oxides but also including metal sulfides, phosphides and nitrides. Compared to the conventional graphite anode, the above-mentioned materials show great promise in terms of energy density and/or power density (see Fig. 3). However, it requires significant research efforts in a variety of fields to unlock their full potentials. Fortunately, researchers and industry alike see a great chance in the development of high-performance anode materials with the recent progress in advanced technologies and fundamental understandings.

Currently, Si-based alloys are one of the most attractive anode materials and have been investigated intensively in

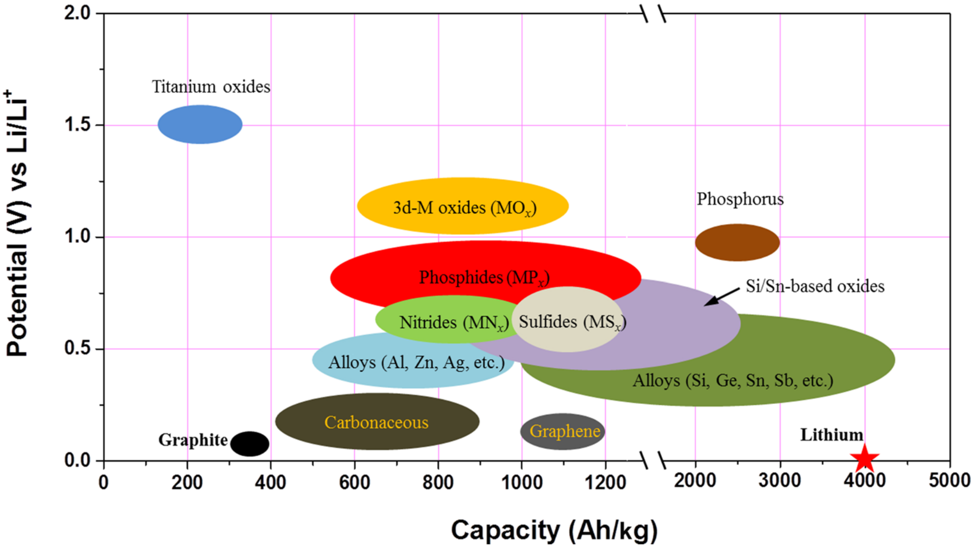
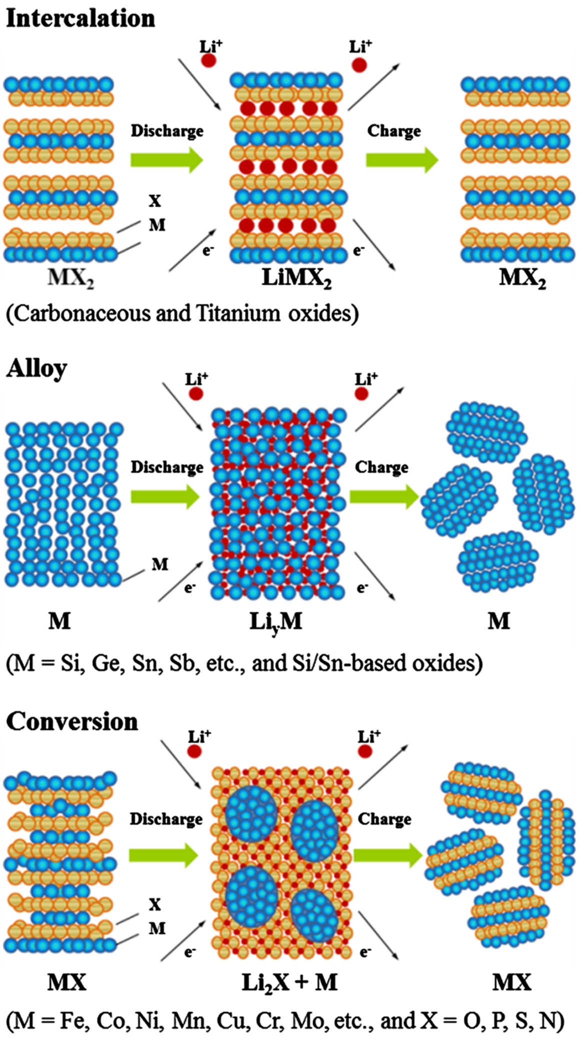


Fig. 2 Schematic illustration of active anode materials for the next-generation lithium batteries. Potential (vs. Li/Li$^+$) and the corresponding capacity density are shown



Advantages	Common Issues
Carbonaceous: good working potential, good safety, low cost.	high voltage hysteresis, high irreversible capacity.
Titanium oxides: extreme safety, low cost, long cycle life, high power capability.	very low capacity, low energy density.
Alloy materials: higher specific capacity, high energy density, good safety.	large irreversible capacity, huge capacity fading, poor cycling.
Metal oxides: high capacity, low cost, environmental benignity.	low coulombic efficiency, unstable SEI, poor cycling.
Metal phosphides/sulfides/nitrides: high capacity, low operation potential and low polarization.	poor capacity retention, short cycle life, high cost of production.

Fig. 3 Schematic illustration of three different types of anodes based on the lithium storage mechanism and their advantages and disadvantages

the past years due to their significantly high capacity. However, the large volume changes of these materials associated with the lithium alloying processes have been the main impediment, which needs to be addressed before their implementation. In terms of safety and rate capability of the anode, lithium titanate ($Li_4Ti_5O_{12}$, LTO) [65–68] and β-TiO_2 [69–71] are the best choice, since they offer a significant safety and power advantage over graphite anode. However, the potential of gassing issue of this type of material during the repeated charge–discharge cycles needs to be fully understood and addressed. Ultimately, Li metal is an ideal anode for rechargeable batteries, including Li-air, Li–S and other Li batteries using intercalation compounds or conversion compounds as cathode materials. However, Li dendrite growth and low coulombic efficiency during the charge/discharge process have largely prevented the use of Li metal for rechargeable batteries. To enable broad applications of Li anodes, more fundamental studies need to be conducted to simultaneously address these barriers. In the following sections, we will discuss the recent research to address the aforementioned issues and share our perspectives with readers on how to better understand the chemistries involved in these anode materials in order to improve their electrochemical performance.

3 Intercalation Anode: Graphene

Carbon-based materials with various morphologies have been long considered as potential anode materials due to their promising physical and chemical features. Indeed, graphite has very impressive electrical (~ 10^{-4} S/cm) and thermal (~ 3000 W/mK) conductivity, which makes it the most widely used anode material in the commercial Li-ion cells [72–74]. Equally impressive in terms of electrical conductivity and mechanical strength, graphene derived from exfoliated graphite provides a modular approach to study the lithium intercalation/deintercalation behavior in layered carbon as well as composite layered carbon materials [75]. Since the pioneering work on lithium insertion in carbonaceous materials by Dahn et al. [76], great progress has been made in understanding lithium intercalation mechanism for ordered and disordered carbon-based anodes in lithium-ion batteries which has been summarized in several reviews [63, 77, 78]; hence, this area will not be discussed here. We will only focus on the graphene-based materials as anode in the following discussion.

Graphene consists of sp^2 carbons bonded into two-dimensional sheets in a honey comb network with single-atom thickness. Due to its good electrical conductivity, mechanical strength, high charge mobility and surface area, graphene is considered as a suitable anode material for lithium-ion battery, which has been intensively investigated recently [75, 79–82]. In general, the detached graphene sheets (multiple layers) can significantly increase the lithium storage capacity by ameliorating the electrolyte infiltration and shortening the ion diffusion distance within active materials [78, 83], even though the amount of lithium stored by a single-layer graphene is low compared to graphite (372 mAh/g). In a defect-free graphene, three different sites are potentially available to absorb lithium ion, i.e., on hollow site (on the center of carbon hexagon ring), on top site and on bridge site (Fig. 4). Up to now, it is still not clear how the lithium ions store and arrange on the defect-free graphene, although the hollow site seems to be more energetically favorable based on the first principle calculations [84]. If the Li ions reside on the hollow sites of the graphene, the theoretical specific capacity could be as high as 1116 mAh/g by forming a stoichiometric Li_3C_6 compound [75, 76, 79, 85–87]. Theoretical calculation also predicted that both sides of graphene are available for Li-ion absorption, i.e, one Li ion on the top of a carbon atom and another under a different carbon atom in primitive unit cell to form a stoichiometric Li_2C_6, which corresponds to a specific capacity of about 780 mAh/g [88, 89]. Other theoretical studies suggest that lithium ions prefer to form clusters rather than being uniformly distributed on the graphene surface [90, 91]. Clearly, unlike graphite, the theoretical capacities of graphene are quite controversial and are strongly dependent of the lithium storage mechanisms on graphene surface. At this juncture, there is much to be learned on the mechanism of lithium-ion storage in graphene, and this should be a fruitful area for further research.

Experimentally, due to the presence of additional active sites for lithium-ion storage such as defects, graphene sheets normally deliver high gravimetric capacity in the range of 790–1050 mAh/g. A capacity as high as 1200 mAh/g was reported at the initial cycle with values around 850 mAh/g at 40th cycle for high-quality graphene sheets (~ 4 graphene layers) with a surface area over 490 m^2/g [92]. However, the disordered structure usually results in poor electrical

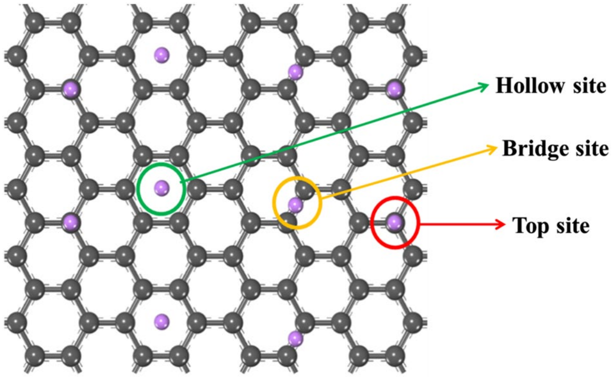


Fig. 4 Schematic illustration of a typical graphene structure and the potential sites for lithium storage

conductivity of graphene and therefore low power density. Results also demonstrated that the graphene characteristics including defect density and surface area associated with the electrical conductivity strongly impact the capacity for lithium storage, which highly depends on the processing methods of graphene.

One approach that potentially can increase the lithium storage capacity of graphene is using spacers to enlarge the interlayer distance of graphene sheets by reassembling a so-called pseudo-graphite-type material. Yoo et al. [75] were able to demonstrate that the specific capacity of graphene sheets can be improved from 540 to over 700 mAh/g by incorporating nanocarbon macromolecules [such as carbon nanotubes (CNT) and fullerenes (C_{60})]. Their study suggested that the *d-spacing* between the reassembled graphene sheets, which needs to be carefully tuned and controlled, plays the key role in determining the reversible capacity of graphene-based materials. If the *d-spacing* of the graphitic carbon layer in the graphene sheets can be expanded to 0.40 nm compared to 0.34 nm in graphite, large reversible lithium storage capacities up to 784 mAh/g could be expected. Other alternative approaches, including preparing graphene papers by filtration and reduction of prefabricated graphene oxide paper [93, 94] or using graphene sheets functionalized by oxalic acid molecules [95], have been also reported to expand the *d-spacing* of the graphene layers. Although the capacity increase in graphene beneficial from the expansion of the *d-spacing* of graphitic carbon layer is obvious, the first cycle irreversible capacity loss and poor cycle performance of this type of materials are very problematic in terms of their practical application, which requires further research to identify the underline reasons and to search for potential solution to address these issues.

Heterogeneous atom doping is another effective approach to improve the electrochemical performance of graphene for lithium-ion storage through tuning the electronic structure of the graphene base plane [96, 97]. Nitrogen doping appears to be more feasible one, which forms pyridinic, pyrrolic and graphitic structures [96–99]. Such structures are electronically deficient that could strengthen the binding energies of lithium to graphene layer and thus increase the lithium coverage. For example, doped hierarchically porous graphene (DHPG) electrodes exhibit high capacity with long cycling capability (~ 3000 cycles) at a current density of 5 A/g. Low- and high-magnification SEM and TEM images indicated that hollow graphene assemblies can contain small nanoscale pores [100]. These promising results are attributed to the synergetic effects of the hierarchically porous structure, good conductive network and heteroatom doping, which facilitate the mass transport and speed up the electrochemical reactions. In terms of the fabrication of the doped graphene, several approaches have been reported, including thermal treatment, arc discharge, high-energy irradiation, chemical vapor deposition, bottom-up chemical synthesis, electrochemical synthesis [101–103].

Although graphene-based materials show some promises as the anode for next-generation lithium-ion battery, they are facing formidable challenges. The restacking of graphene driven by the van der Waals forces between the adjacent layers leads to low specific surface area of the material and therefore low specific capacity. Introducing porosity in graphene-based materials appears to be an effective approach to address this issue, which can increase the accessible area and accelerate the transport of lithium ions in graphene [52, 100, 104]. In general, pores can be introduced either as in-planes holes within individual sheets [52, 105, 106], or as interstitial space between neighboring sheets [107]. In most cases, these types of pore can be integrated in graphene-based materials, which further enhance the electrochemical performance. Another issue of the graphene-based materials is the relatively high irreversible capacity loss during the initial discharge/charge cycle, which results in a low coulombic efficiency [108, 109]. Unfortunately, this problem is associated with the high surface area of graphene, since a solid electrolyte interphase (SEI) layer is required to form on the graphene anode (which consumes lithium from the cathode) during operation of the cell in order to protect the lithiated graphene from further reactions with electrolytes [110]. At the moment, limited attempt has been conducted to address this issue and, therefore, still remains an open question.

In line with the above concern, recent research effort has been focused on exploring graphene as a novel support for other anode materials such as silicon, tin or transition metal oxides by taking the advantage of graphene's high surface area, mechanical strength and good electrical conductivity [111]. In such graphene-based heterogeneous hybrid anode materials, a nanoporous 3-D structure with significant amount of void spaces is created by homogenously distributing the graphene nanosheets between the host particles such as SnO_2 or Si. This structure together with its mechanical strength can confine the host particles by the surrounding graphene sheets, which effectively limits the volume expansion during lithium intercalation, while the voids can act as buffering spaces to absorb the volume change during discharge and charge cycles. In addition, the good electrical conductivity of graphene can provide conducting network to improve the power density of the electrodes [112–117]. Although this compelling approach does help to improve the rate capability and capacity retention of the graphene-composited materials, long-term stability of these hybrids still needs further improvement to be applicable for commercial purpose.

4 Intercalation Anode: $Li_4Ti_5O_{12}$ (LTO) and TiO_2

In the above section, we mainly focused on the progresses and challenges for the potentially high-capacity anode based on the graphene materials that represent one of major research effort on development of next-generation lithium-ion batteries. It should be emphasized, however, similar to the graphite, a stable SEI layer is required to enable graphene-based materials as secondary Li-ion battery anode, despite other challenges facing these materials, as pointed out earlier. In general, because the SEI on the graphite surface will easily decompose at a temperature as low as 60 °C, the continuous heat flow from the exothermal reaction between the lithiated graphite and the electrolyte can quickly accumulate [118]. When a large amount of heat is generated on the anode side during a short period of time, it would eventually trigger the major reaction between the cathode and the electrolyte, leading to a thermal runaway associated with fire or explosion of the battery. Although it is widely accepted that the thermal runaway is associated with the thermal instability of the delithiated cathode ($Li_{1-x}MO_2$), more attention should also be paid to the anode side. Apparently, the thermal stability of the SEI plays a critical role in the safety of lithium-ion batteries using graphite as the anode, which is another major barrier that hinders the deployment of lithium-ion batteries in automobiles.

From the safety perspective, titanium-based oxides including $Li_4Ti_5O_{12}$ (LTO) and TiO_2 hold the great potential to be a class of attractive alternatives to graphite anode, since they operate at a potential above 0.8 V versus Li^+/Li where the formation of a SEI layer on the anode surface can be avoided by eliminating the reduction of electrolytes. In this sense, titanium-based anode materials showed great advantage over the graphitic carbon anode along with other features such as low cost, low toxicity, low volume change during discharge/charge process and outstanding power and excellent cycle life. Therefore, many research efforts have been devoted to develop large-scale Li-ion batteries for hybrid electrical vehicle (HEV) applications using Ti-based oxides anode materials, taking their advantages of the extremely safe lithium-ion chemistries, high power density and long cycle life. However, the main drawbacks of this type of materials are the low inherent theoretical capacities (in the range of 175–330 mAh/g) and low electronic conductivity in bulk materials with micrometer-sized particles. The structure, morphology and size of titanium-based oxides strongly determine their electrochemical performance in a cell. Nevertheless, spinel $Li_4Ti_5O_{12}$ (LTO) and TiO_2 with various allotropic forms have been extensively studied as one of the most promising anode materials.

$Li_4Ti_5O_{12}$ has a spinel structure which can be depicted as $Li[Li_{1/3}Ti_{5/3}]O_4$ with a cubic space group $Fd3m$. Crystallographically, lithium occupies all the tetrahedral 8*a* sites, lithium and titanium with an atomic ratio of 1:5 (i.e., $[Li_{1/3}Ti_{5/3}]$ unit) occupy the octahedral 16*d* sites, while oxygen atoms occupy the 32*e* sites, respectively. During lithiation at voltage of 1.55 V (vs. Li^+/Li), three Li atoms at the 8*a* sites together with external lithium ions move to the empty 16*c* sites accompanying with the conversion of the spinel structure to a rock salt structure $Li_7Ti_5O_{12}$ which is separated by an almost ideal heterointerface, i.e., two-phase reaction mechanism (see Fig. 5a). Such process exhibits excellent

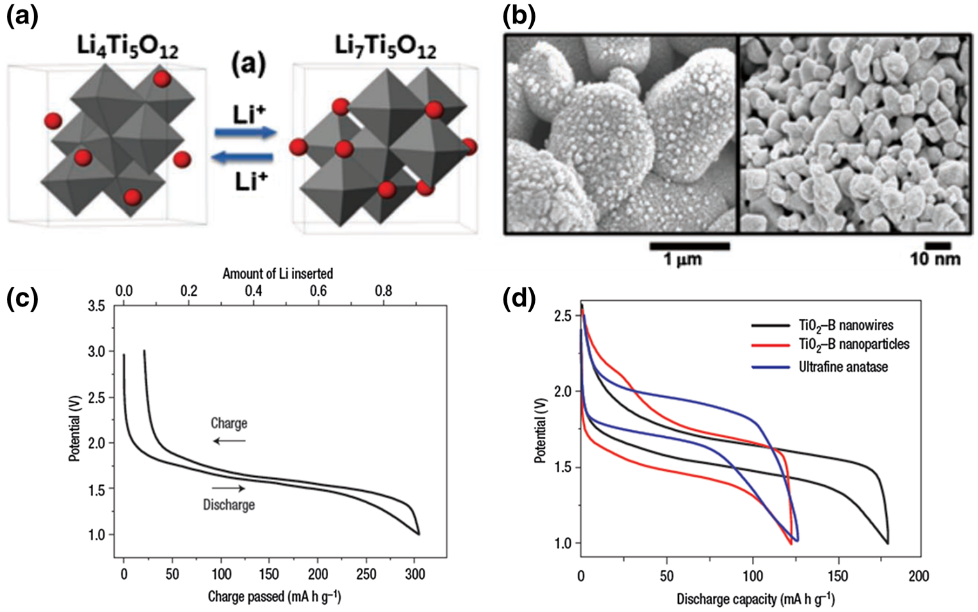


Fig. 5 Intercalation anodes for Li-ion batteries—LTO and TiO_2. **a** Structure of $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ showing no volume change after charge and discharge. **b** Scanning electron microscopy under low and high magnification of nanostructured $Li_4Ti_5O_{12}$ with micrometer-sized secondary particles and nanometer-sized primary particles. **c** Charge–discharge curve for nanostructured Li_xTiO_2-B nanowires (rate of 10 mA/g). **d** Comparison of cycling behavior for TiO_2-B nanowires, TiO_2-B nanoparticles and nanoparticulate anatase, all at 200 mA/g. **a**, **b** Adapted with permission from Ref. [134]. **c**, **d** Adapted with permission from Ref. [5]

reversibility of lithium insertion/extraction with a theoretical capacity of 175 mAh/g. The volume associated with this phase transformation is very small (~ 0.2%), and therefore, $Li_4Ti_5O_{12}$ is well known as a zero-strain material for lithium insertion that offers extremely long cycle life for lithium storage due to its structural stability. Lu et al. investigated the subtle structure evolution in the bulk/surface of LTO during lithium intercalation/deintercalation at atomic level, which showed significant Ti–O bond stretching/shrinking at different state of charge (SOC) [67]. Such structure torque plays a critical role in forming the capturing centers for the electron/hole pairs in a 3.80 eV insulating material as is LTO.

However, LTO is characterized by poor electronic conductivity (~ 10^{-13} S/cm) on the one hand and interfacial reactivity with the electrolyte on the other hand resulting in undesirable gas release that complicates the use of this important material in large-scale electrochemical energy storage applications [119]. The first issue can be addressed by either surface treatment of LTO [67, 120] or downsizing LTO to nanoscale [121] to enhance lithium-ion diffusion rate. During the past years, a variety of nanostructured LTO has been successfully explored as the anode materials which demonstrated much improved electrochemical performance in terms of the rate capability and cycling stability [122–126]. However, the drawback associated with the nanostructured material is the relatively low loading density of the electrode due to the high porosity created by the nanomaterials which, consequently, significantly reduces the volumetric energy density of the battery [127]. One potential approach to address this issue is to prepare micrometer-sized secondary particles with nanosized LTO primary particles (see Fig. 5b). In this type of particle design, the tap density and the loading at the electrode level can be effectively improved with all the benefits associated with nanostructure being maintained by the nanometer-sized primary particles. In particular, porous LTO with microspheres showed much improved electrochemical performance with high volumetric energy density because the spherical morphologies can efficiently minimize the Li-ion diffusion pathway [128, 129].

The intrinsic gassing issue of LTO is associated with the fact that the lithiated $Li_{4+x}Ti_5O_{12}$ has a tendency to react with the organic electrolytes such as ethylene carbonate when aged at high temperatures. Recent study by Lu et al. using electron energy loss spectroscopy (EELS) reveals that there is a reversible spontaneous charge transfer process of $Ti^{3+} \leftrightarrow e^- + Ti^{4+}$ occurring on the surface (ordered or disordered) of lithiated $Li_4Ti_5O_{12}$ that potentially could be an essential step of the gas-releasing phenomenon, although more work needs to be conducted to fully confirm the mechanism [67]. Nevertheless, it is urgently needed to address the gassing issue in order to enable the successful deployment of the LTO anode, especially in application that requires power such as HEVs. Surface modification on the LTO anode appears to show some promises in terms of avoiding the gas generation. For example, AlF_3 coating acted as the buffer layer to reduce the activity of the lithiated LTO surface has been explored to suppress the electrolyte decomposition [130, 131].

TiO_2 with various crystal structures, including anatase, rutile, brookites and especially TiO_2(B) (monoclinic *C*2/*m*), is also an ideal host for lithium insertion/extraction [132]. Similar to LTO, the electrochemical lithiation of TiO_2 operates at high potential (1.5 V vs. Li^+/Li) which provides excellent safety to the battery, but it delivers much higher capacity (330 mAh/g) than LTO since 1 mol of lithium can be inserted into TiO_2 theoretically (corresponding to the composition $LiTiO_2$). Experimentally, however, it has been proven that achieving the theoretical capacity is very challenging [133]. In general, the electrochemical performance of TiO_2 heavily relies on its crystal structure, morphology and particle size. Recent results demonstrated that controlling shape and size of TiO_2 nanoparticles can offer great advantages [134]. TiO_2-B nanotubes or nanowires with diameter in the range of 40–60 nm and length up to several microns synthesized from a simple aqueous route demonstrated significantly enhanced rate capability with much higher capacity (305 mAh/g corresponding to $Li_{0.91}TiO_2$-B), as shown in Fig. 5c, d [135].

5 Alloying Anode: High-Capacity Si, Sn, P

There are two types of mechanisms attractive to anodes beyond the intercalation process: alloying and conversion mechanisms. The alloying mechanism has the general reaction of $x\mathrm{Li}^+ + xe^- + \mathrm{M} \rightarrow \mathrm{Li}_x\mathrm{M}$, where typical examples of M are Si, Ge, Sn, P [55, 136–138]. In general, these materials can have multiple times of lithium-ion storage capacity of graphite, as shown in Fig. 2. For example, Si has 4200 mAh/g specific capacity which is about 11 times of graphite [139]. In addition to the gravimetric capacity, the volumetric capacity at the expanded (lithiated) state is also an important consideration for portable and electric vehicle applications. Another important parameter is their delithiation potential, which should be low in order to maximize the discharge voltage in the full cells. (Note that the delithiation potential is more important, not the lithiation potential.) The delithiation potentials of Si, Sn and P are 0.45, 0.6 and 0.9 V, respectively, which are all in the reasonable potential ranges.

The alloying mechanism shares some of the most challenge issues. The first one is volume expansion and fracture [140]. Large capacity of lithium storage in the materials unavoidably causes large volume expansion during lithiation, for example: by 4 times in Si, 3.7 times in Ge, 2.6 times in Sn, 3 times in P. The large volume expansion can cause mechanical fracture in individual particles, resulting in the loss of electrical contact and capacity fading. The second one is the instability of the solid-electrolyte interphase (SEI) [141, 142]. The volume expansion during lithiation and contraction during delithiation causes the movement of interface boundary between the particles and electrolyte and thus the challenge of forming stable SEI layer. The third one is the swelling at the electrode level. The volume expansion in the individual particle also results in the swelling at the whole electrode level and thus the challenges for the battery cell design.

In the past 10 years, nanomaterials design affords a new powerful route to overcome the issues outlined above. The most important and successful example is Si, which will be used to illustrate the materials design concepts here. The first critical milestone of nanostructured design is Si nanowires

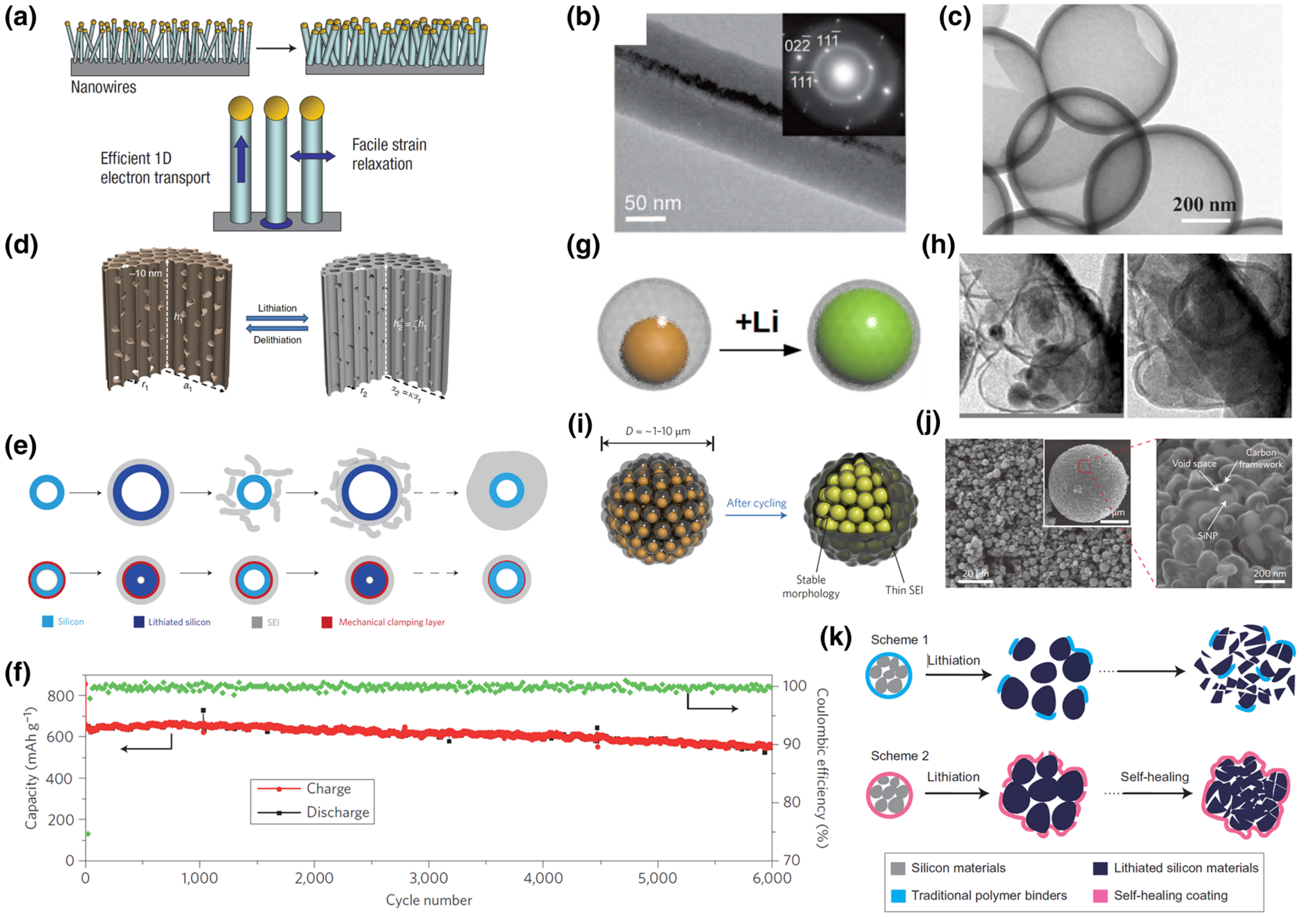


Fig. 6 Nanoengineering on silicon anodes for Li-ion batteries. **a** Si nanowires (NWs) grown directly on the current collector, allowing for efficient 1D electron transport. **b** TEM and SAED images of a core–shell Si nanowire with crystalline core and amorphous shell. **c** TEM image of interconnected hollow Si spheres (R_{in} ~ 175 nm, R_{out} ~ 200 nm). **d** Schematic images showing the nanostructure of the mesoporous Si sponge particle. **e** Schematic images showing the difference of SEI accumulation on the surface of Si nanotube with (bottom) and without (top) mechanical constraining layer. A thick SEI grows outside the Si nanotube without a mechanical constraining layer, which also has a varying and unstable interface with the electrolyte (top). Designing a mechanical constraining layer on the hollow Si nanotubes can prevent Si from expanding outside toward the electrolyte during lithiation. As a result, a thin and stable SEI can be built (bottom). **f** Lithiation/delithiation capacity and coulombic efficiency of double-walled Si nanotubes cycled at 12C for 6000 cycles. **g** Schematic images of a Si–C yolk–shell particle showing that the Si nanoparticle expands without breaking the carbon coating or disrupting the SEI layer on the outer surface. **h** TEM images of Si–C yolk–shell particle before (left) and after (right) lithiation. **i** Schematic images of one pomegranate microparticle before (left) and after (right) lithiation. **j** SEM images of silicon pomegranates showing the micrometer-sized and spherical morphology and the magnified SEM image showing the local structure of silicon nanoparticles and the conductive carbon framework with well-defined void space between. **k** Scheme 1: schematic illustration of the design and behavior of a conventional silicon electrode that shows failure of the electrode because of cracking in particles and polymer binder, which results in loss of electrical contact. Scheme 2: schematic illustration of the design and behavior of our stretchable self-healing electrode that shows the maintaining of electrical contact between the broken particles and no cracks in the polymer binder because of the stretchability and incorporation of self-healing chemistry. **a** Adapted with permission from Ref. [143]. **b** Adapted with permission from Ref. [154]. **c** Adapted with permission from Ref. [161]. **d** Adapted with permission from Ref. [160]. **e**, **f** Adapted with permission from Ref. [163]. **g**, **h** Adapted with permission from Ref. [164]. **i**, **j** Adapted with permission from Ref. [165]. **k** Adapted with permission from Ref. [167]

grown directly on stainless steel current collector (Fig. 6a), where Si nanowires do not fracture due to their small diameters and can maintain electrical connection during charge/discharge [143]. Fundamental studies with well-defined nanopillars patterned on Si wafers have revealed the anisotropic volume expansion of crystalline Si along (110) direction, while amorphous Si has isotropic volume expansion. The critical breaking diameter for crystalline Si is ~ 150 nm for particles and ~ 250 nm for nanowires, while the critical size for amorphous Si is much larger up to ~ 870 nm [144]. The differences between crystalline and amorphous Si are due to the bonding and structure of these two materials [145]. It is noted that during the first lithiation, crystalline Si is changed into amorphous LiSi phase and remains mostly as amorphous phase afterward although crystalline $Li_{15}Si_4$ phase was observed under certain conditions.

The design of nano-Si anodes can be categorized into four areas: The first one is solid Si nanostructures [146–153]. There has been a rich morphology of solid Si nanostructures including nanowires, nanoparticles and carbon-Si composite particles. The key of all these solid nanostructures is their small sizes, less than the critical breaking size of Si (Fig. 6a). An interesting further advancement in the solid nanostructure concept is the core-shell nanostructures (Fig. 6b), where the core materials provide stable mechanical support and efficient electron transport while the Si shell stores lithium ions [154]. Examples for the core materials include carbon [155, 156], NiSi [157], TiC [158]. The second design is hollow Si nanostructures since it provides facile strain relaxation which is important to enable Si anodes without fracture [159]. Compared to solid Si particles, hollow Si structures would provide the interior hollow space for strain relaxation (Fig. 6c, d) [160, 161]. Typical, hollow structures include Si nanotubes [162] and hollow Si nanospheres [161]. The third one is constraint hollow Si [163]. Nanostructured Si does not have a serious fracture problem; however, establishing stable SEI is much more challenging due to continuous volume expansion and contraction during charge/discharge. In order to solve this problem, a breakthrough materials design concept is to have a mechanically constraining layer on hollow Si structure. It was first realized by having a double-walled nanotube: Si as inner tube and SiO_2 as outer mechanical constraining layer (Fig. 6e) [54]. The SiO_2 layer allows the diffusion of lithium ions for reaction with Si but is mechanically strong to force volume expansion toward the interior space during lithiation. During delithiation, the interior Si interface moves back. Therefore, the outer SiO_2 surface remains static during charge/discharge. Such a concept enables the formation of stable and thin SEI, and a long life of 6000 was demonstrated (Fig. 6f). This powerful concept of constraint hollow structure was further confirmed with Si–C, S–TiO_2 and Al–TiO_2 yolk–shell structures (Fig. 6g, h) [164] and permanganate-like Si–C structures (Fig. 6i, j) [165]. The constrained hollow structures have additional benefit of avoiding the swelling at electrode level since there is empty space pre-reserved for interior volume expansion. For example, permanganate-like structures show negligible volume change at the electrode level. The final one is exploring polymer binder that represents another approach to bring the cohesions of Si particles and to maintain the electrical connection during the large volume change. One set of polymers (CMC, carboxymethylcellulose, alginate) have a strong binding with Si particle surface has been shown to have certain improvement over traditional polyvinylidene difluoride (PVDF) binder to maintain electrode integrity. Another set (conducting PANi hydrogel) is conducting polymers with engineered binding sites as well as electronic conducting function [166]. Recently, self-healing polymer has been shown as an exciting set of binder, which has dynamic hydrogen bonding to self-heal if the volume expansion causes the breaking of polymer (Fig. 6k) [167].

6 Conversion Anode: Transition Metal Oxide

The conversion mechanism has the general reaction: $M_xO_y + 2yLi^+ + 2ye^- \rightarrow yLi_2O + xM$ (Fig. 7a). Conversion materials with the potential being low enough have been shown in a broad range of compounds including oxides [168, 169], fluorides [170, 171] and sulfides [172]. Conversion oxides as anodes offer high specific capacities of 700–1200 mAh/g and volumetric capacities of 4000–5500 mAh/cm^3 [173]. Similar to alloy anodes, the conversion anodes also have the issues of material pulverization at the individual particle level, unstable SEI layer, and the morphology and volume change at the whole electrode level. However, additional challenging aspect of conversion mechanism is the large voltage hysteresis ~ 1 V (the difference between charge/discharge voltage), which reflects the sluggish pathways during charge/discharge (Fig. 7b) [12]. The delithiation potential spreads from 1 to 2 V [10], which reduces the full cell voltage and would need to be addressed in the future. The large voltage hysteresis results likely from interconversion of multiple solid phases (MO_x, Li_2O and M) with different structures that involves in breaking of strong chemical bonds. In addition, it requires not only lithium ions but also oxygen and M ions to diffuse to a long distance to form single particle domain size.

In order to be able to cycle the conversion oxides, nanoscale materials design is needed for interconversion of multiple solid phases [5, 11, 63, 174]. The small dimension of nanostructures reduces the strain of solid transformation and the distance for atomic diffusion. The pioneering work by Tarascon has shown that MO_x would be divided into very small particles of M and Li_2O after the first conversion reaction [62, 175]. The starting morphology and

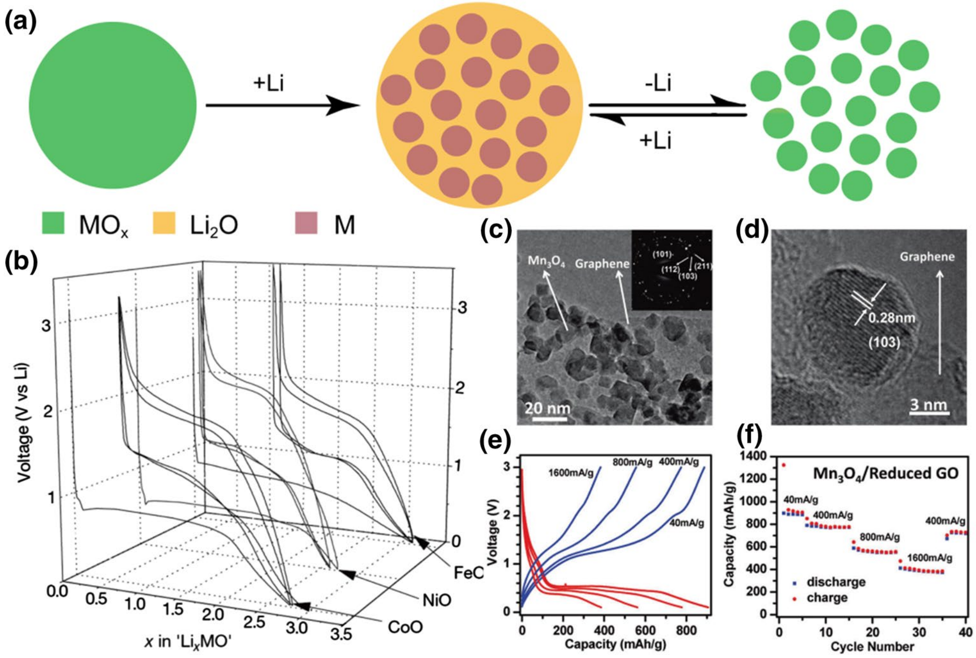


Fig. 7 Conversion metal oxide anodes for Li-ion batteries. **a** Schematic images showing the first lithiation of a metal oxide particle and the later lithiation/delithiation cycles. **b** The voltage composition profile for various MO/Li cells cycled between 0.01 and 3 V at a rate of C/5 (1 lithium in 5 h). **c** TEM image of Mn_3O_4/reduced graphene oxide (RGO); inset shows the SAED pattern of the Mn_3O_4 nanoparticles on RGO. **d** High-resolution TEM image of an individual Mn_3O_4 nanoparticle on RGO. **e**, **f** Representative charge and discharge curves (**e**) and capacity retention (**f**) of Mn_3O_4/RGO at various current densities. **b** Adapted with permission from Ref. [62]. **c**–**f** Adapted with permission from Ref. [111]

structure of MO$_x$ play an important role on the cyclability of electrodes. An attractive approach is to chemically attach small nanoparticles of MO$_x$ to the reduced graphene oxide (RGO) [111]. The RGO offers good electronic conductivity and strong chemically ankled point for MO$_x$ (Fig. 7c, d). Excellent cycling performance and rate capability have been demonstrated (Fig. 7e, f) in this case. Another set of materials design is to have void space design (similar as Si anodes) in MO$_x$ due to the large volume changes, which also show excellent performance [176].

7 Lithium Metal Anode

Li metal is a holy-grail anode with very high specific capacity of 3860 mAh/g for rechargeable batteries. Unfortunately, Li dendrite growth and low coulombic efficiency during the charge/discharge process have largely prevented the use of Li metal for rechargeable batteries [177, 178]. To enable broad applications of Li anodes, more fundamental studies need to be conducted to simultaneously address these barriers. In this part, techniques utilized to characterize the morphology of Li deposition and the results obtained by modeling of Li dendrite growth will be reviewed. Recent development on interfacial materials design, electrolyte additives and solid electrolyte approaches in limiting the dendrite formation will be also discussed.

These challenges of lithium metal anode are rooted to the following two fundamental reasons. The first reason is mechanical in nature. During battery charge and discharge, Li metal is plated and stripped without a host material. Compared with the finite volume expansion of lithium-ion battery anodes such as graphite and Si hosts, the “hostless” Li metal has virtually infinite relative volumetric change. The spatial control of Li deposition in Li metal anodes is absent, resulting in various possible morphologies including dendrites. Such an uncontrolled deposition creates significant mechanical instability and cracks in electrodes and the SEI. The second reason is chemical in nature. Li metal reacts with nearly all the chemical species in gas, liquid and solid phases. In liquid electrolyte, Li metal decomposes solvent and salts to form SEI. There is very little control over the SEI thickness, grain size, chemical composition or spatial distribution of the reaction products. Such an SEI layer is weak against the unavoidable mechanical deformation during Li plating/striping, and it continuously breaks and repairs by reacting with more electrolytes.

To enable broad applications of Li anodes, deep fundamental studies need to be conducted. For instance, Li metal anodes after cycling were examined using optical microscopy and scanning electron microscopy, showing valuable morphology information. In recent years, several new characterization techniques were applied to Li metal anodes that provide new knowledge and understanding. One powerful technique is in situ transmission electron microscopy (TEM), which was first developed in 2010 on the demonstration of SnO_2 nanowire battery inside TEM, revealing astonishing visual effect of electrochemical lithiation [179]. An ionic liquid electrolyte with low-vapor pressure or Li_2O on Li metal as solid-state cell is usually used in the in situ TEM cell configuration. For example, the dry solid-state cell configuration has been adopted to study the Li metal deposition onto Cu substrate with hollow carbon sphere coating (Fig. 8a, b), revealing that Li metal deposition took place underneath the carbon [161]. This helps guide the design of stable interphase layer on Li metal. The second technique is synchrotron hard X-ray microtomography. Balsara et al. applied it to symmetric lithium–polymer–lithium cells cycled at 90 °C and discovered surprising phenomena (Fig. 8c–e) [180]. At the early stage of dendrite formation, dendrites lie within the electrode and underneath the electrode/polymer interface. The portion of the dendrite protruding into the polymer increases on cycling. Eventually, it spans the polymer electrolyte thickness, causing a short circuit. The third technique is in situ nuclear magnetic resonance (NMR).

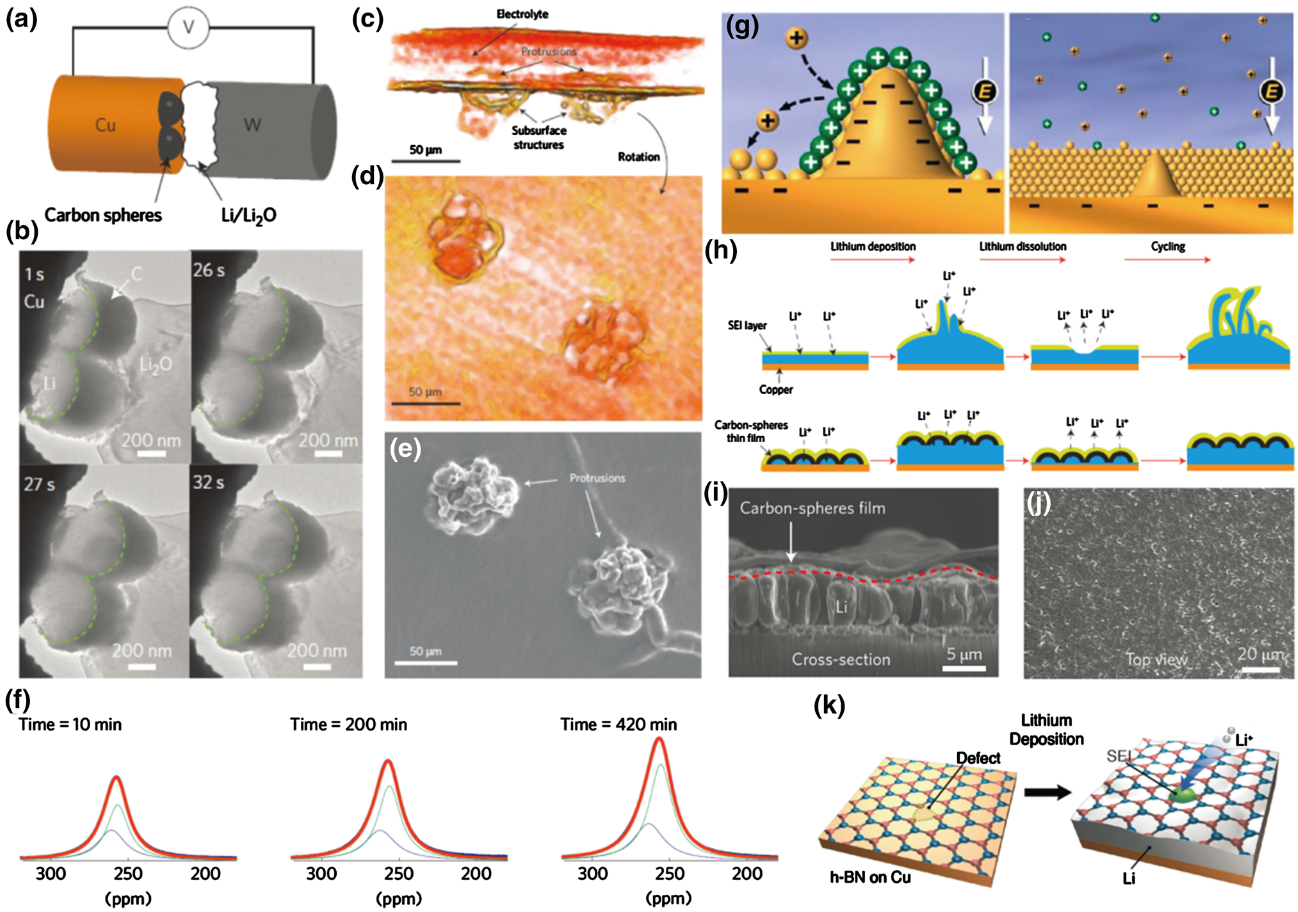


Fig. 8 Advanced characterization techniques and design principles for Li metal anodes. **a** A schematic image showing the configuration of a in situ TEM cell. **b** TEM images of the Li deposition process on Cu wires decorated with hollow carbon nanospheres taken at different times. Li metal approaches the carbon nanospheres from the right, and deposition is observed once a voltage bias is applied. **c** 3D reconstructed volume of a cell with $C = 84$ C/cm^2 containing two, closely spaced dendrites. **d** The reconstructed volume was rotated such that the viewer is within the electrolyte looking at the dendrites. **e** SEM micrograph of the bottom electrode of the same cell, after dissolving away the electrolyte, showing the dendritic structures. The SEM images contain no direct evidence for the presence of subsurface structures under the dendritic protrusions. **f** Deconvoluted ^{7}Li NMR spectra as a function of time. Time $t = 420$ min represents full charge. The deconvoluted peaks used to fit the NMR data are indicated with thin red, blue and green lines, in this and the next two figures. The thick red line and blue line (almost invisible under the red line) show the fit and the experimental spectra, respectively. **g** Schematic images showing the Li deposition process based on the self-healing electrostatic shield mechanism. **h** Schematic images of Li deposition on copper (Cu) current collector (top) where ramified Li can grow after continuous cycling. In contrast, Cu substrate modified with a hollow carbon nanosphere layer creates a scaffold for stabilizing the SEI layer, which results in uniform Li deposition. **i** Cross-section SEM image showing the lithium plating underneath and elevate the carbon nanosphere layer. **j** Top-view SEM image showing the smooth surface of the electrode with the carbon nanosphere modification. **k** Schematic images showing the design of h-BN film grown on copper for uniform Li deposition. The subnanometer defects in h-BN film can serve as channels for Li ions during lithium deposition. Lithium is deposited between h-BN and copper. The stiff B–N bond and chemical stability prevent dendrite formation and lithium corrosion, respectively. **a**, **b** Adapted with permission from Ref. [187]. **c–e** Adapted with permission from Ref. [180]. **f** Adapted with permission from Ref. [181]. **g** Adapted with permission from Ref. [183]. **h–j** Adapted with permission from Ref. [187]. **k** Adapted with permission from Ref. [188]

The Grey group has pioneered the development of NMR technique for in situ spectroscopy and imaging of lithium-ion batteries. The ^{7}Li NMR has high sensitivity and can be acquired on a timescale that is much faster than the typical charge discharge cycle. For lithium metal, the skin depth of radiofrequency field is ~ 10 μm. The diameter of Li metal dendrite is usually below 3 μm, and thus, they are fully penetrated by the NMR radiofrequency field. Therefore, the formation of Li metal dendrite can be monitored by the intensity of NMR peak signal, which provides quantitative information (Fig. 8f) [181].

The challenges of Li metal anodes calls for strategies to form a stable interfacial layer with the dual functions of suppressing the dendrite formation and stop the side chemical reaction. Liquid electrolyte and additives are an important area of research to stabilize Li metal anodes since the formed SEI can have significantly different morphology, composition and property. For example, Zhang et al. recently discovered that highly concentrated electrolytes composed of ether solvents and the lithium bis(fluorosulfonyl)imide salt enable the high-rate cycling of a lithium metal anode at high coulombic efficiency (up to 99.1%) without dendrite growth and demonstrated long cycling in symmetric Li/Li metal cells [182]. The authors attributed the excellent performance to the increased solvent coordination and increased availability of lithium-ion concentration in the electrolyte. Zhang et al. invented a self-healing electrostatic shielding mechanism to prevent dendrite growth (Fig. 8g). Certain cations (such as cesium) as additive at low concentrations have reduction potential below the standard reduction potential of lithium ions [183]. The additive cations form a positively charged electrostatic shield around the initial growth tip of Li metal protrusion and prevent further deposition of lithium onto it, effectively suppressing the dendrite growth. The cooperation effects of $LiNO_3$ and polysulfides in ether solvent are recently shown to work well on forming stable SEI layer on Li metal and suppressing the Li dendrite growth [184].

Solid electrolytes including polymers and ceramics have strong mechanical property for dendrite suppression, which is another interesting direction to go. The Young's modulus of Li metal is only 4.9 GPa. Indeed, Li metal is a soft metal and it would be easy to find materials with larger mechanical strength. However, most solid electrolytes have low ionic conductivity, resulting in low power output. Ceramic solid electrolytes with framework structure such as $Li_{10}GeP_2S_{12}$ [185] and garnet-type $Li_7La_3Zr_2O_{12}$ [186] are promising due to their high Li-ion conductivity (~ 10^{-2}–10^{-4} S/cm). Polymer–inorganic nanostructure composites recently show promising results in improving ionic conductivity. Another issue of solid electrolytes is the instability of interfacial layer and increased impedance with cycling, which result from the high chemical reactivity of Li metal with solid electrolyte as well.

In the past few years, nanoscale interfacial materials design emerges as a new approach to address the Li metal anode problems [187, 188]. The key design criteria of both mechanical and chemical stability need to be satisfied in order to have a stable interfacial layer. Such an interfacial layer might not be formed by electrolyte additive alone but needs to be pre-deposited before battery fabrication. Several exciting examples were recently demonstrated. One example is interconnected hollow carbon spheres as interfacial layer to promote Li metal deposition between carbon and Cu current collector (Fig. 8h–j) [187]. The morphology of deposited Li exhibits nice large column-like structures free of dendrites. The efficiency is higher than the bare Cu collector control. Another example is 2D layered materials such as h-BN and graphene, which are both chemically stable against Li metal and mechanically strong [188]. Li metal was found to be sandwiched between Cu metal collector and the 2D layers (Fig. 8k). Most recently, an interfacial layer of Al_2O_3 synthesized by atomic layer deposition is also shown to improve the Li metal cycling [189].

8 Concluding Remarks

The need for storage technologies with much greater energy density than the current Li-ion systems for applications such as electrical vehicles and grid storage calls for the search of higher-capacity electrode materials, both cathode and anode, which certainly relies on material breakthroughs. Although notable progress has been achieved in the development of high-performance anode materials for Li-ion batteries, further investigation of the underpinning mechanisms that limit their performance is required in order to aid the rational design and development of kinetically facile and chemically stable anode materials. As detailed in this review article, we mainly discussed the research activities and achievements of three different types of high-performance anode materials, i.e., *intercalation* anodes (graphene and $Li_4Ti_5O_{12}$); *alloy* anodes (Si, Sn, P); *conversion* oxide anodes; as well as the holy-grail lithium metal anode. Without a doubt, substantial challenges exist for each component, which requires significant research efforts in a variety of fields to unlock their full potentials as the next-generation anode material.

Graphene-based materials show some promises; their restacking issue and high irreversible capacity loss during the initial discharge/charge cycle seriously limit their application. Its high surface area leads to low CE and significant consumption of electrolyte, also making it not a practical anode material. However, graphene could be used as a novel support for other anode materials such as silicon, tin or transition metal oxides by taking the advantage of graphene's high surface area, mechanical strength and electrical conductivity. In this sense, further research is needed to find the best combination between the graphene and other materials that will give satisfactory capacity and capacity retention.

Alloy-type materials represented by Si and Sn are the most attractive anode due to their high capacity, but the large volume changes during cycling have been the main impediment to their implementation. To address this issue, one approach that demonstrates great success is using nanoscale design; however, future research is necessary in the following areas. First, quantitative understanding of the nanoscale design, such as size-dependent of the nanostructure properties, is still needed. Second, the nature of solid electrolyte interphase (SEI) layer that has the significant impact on the coulombic efficiency need to be fully investigated. Third, developing of advanced characterization techniques (both in situ and ex situ) together with multiscale modeling and simulation is vital to unravel the detail microscopic processes that occur during lithiation/delithiation, especially at both the atomic level and the electrode surface. Fourth, it is necessary to develop effective method to pack the nanostructured materials into the electrode and understand the deformation mechanism at the whole electrode level. Finally, in terms of the practical application, it is vital to develop large-scale and low-cost fabrication strategies for nanomaterials with desirable performance.

Similar to alloy anodes, the conversion anodes also have the issues of material pulverization at the individual particle level, unstable SEI layer, and the morphology and volume change at the whole electrode level. To enable good cycling performance for the conversion oxides, nanoscale materials design is needed for interconversion of multiple solid phases. Another challenging aspect of conversion anode is the large voltage hysteresis (~ 1 V) between charge/discharge, which needs to be addressed.

Titanium-based materials as the high-power anode showed much improved tolerance to thermal abuse compared with the conventional graphite anode. However, the main drawbacks of this type of materials are low inherent theoretical capacities and low electronic conductivity in bulk materials with micrometer-sized particles. Nanocrystallization, doping or surface doping could potentially solve the issue of low electronic conductivity. The intrinsic gassing issue of LTO is associated with that the lithiated $Li_{4+x}Ti_5O_{12}$ has a tendency to react with non-aqueous electrolyte when aged at elevated temperatures. Resolving the gassing issue would enable the successful deployment of the LTO as high-power anode for HEV applications.

Eventually, enabling the lithium metal electrode would be the ultimate goal for the high-performance anode of the next-generation Li-ion batteries. The challenges of Li metal anodes call for strategies to form a stable interfacial layer with the dual functions of suppressing the dendrite formation and stop the side chemical reaction. Liquid electrolyte and additives are an important area of research to stabilize Li metal anodes since the formed SEI can have significantly different morphology, composition and properties. Solid electrolytes including polymers and ceramics with strong mechanical property for dendrite suppression would be another interesting direction to go. Finally nanoscale interfacial materials design could be a promising approach to address the Li metal anode problems.

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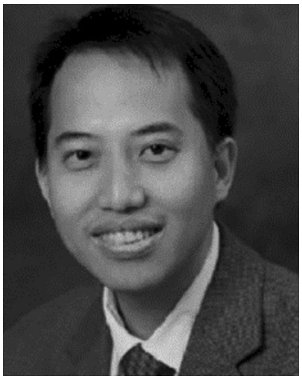

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