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REVIEW ARTICLE

Recent progress of computational investigation on anode materials in Li ion batteries

Di-hua WU (吴迪华), **Zhen ZHOU** (周震)†

Institute of New Energy Material Chemistry, College of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

E-mail: †*zhouzhen@nankai.edu.cn*

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Computations have been widely used to explore new Li ion battery materials because of its remarkable advantages. In this review, we summarize the recent progress on computational investigation on anode materials in Li ion batteries. By introducing the computational studies on Li storage capability in carbon nanotubes, graphene, alloys and oxides, we reveal that computations have successfully addressed many fundamental problems and are powerful tools to understand and design new anode materials for Li ion batteries.

Keywords Li ion batteries, anode, carbon nanotubes, graphene, computation

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1 Introduction

Developing new and environment-benign electric vehicles is a hot topic nowadays; however, the bottleneck of this fascinating new technology is the battery. It is becoming increasingly urgent to develop new battery materials and energy storage systems. Owing to high specific capacities, Li ion batteries (LIBs) have been widely used as portable power sources in laptops, palmtops, cell phones, etc. Though Li ion batteries have so many marvelous performances, much improvement is still needed to meet the demand of electric vehicles. However, to develop batteries only through experimental methods is both money- and time-consuming; computations are helpful complements. Computational methodologies (such as first-principles computations based on density functional theory (DFT), molecular dynamics (MD) and Monte Carlo simulations) are powerful tools to predict the properties of materials. It is worthy to emphasize that first-principles computations do not need any experimental, semiempirical, and empirical data input (except the structure) because this theory is based on basic quantum mechanics; thus, properties such as crystal parameter, charge distribution, and magnetism can be investigated computationally immediately after the synthesis of materials, or new materials and phases can even be predicted before the synthesis. Also, by simple computations, many performances can be observed under critical conditions which can not be achieved in current experiments. Anode is the important component in Li ion batteries. Nowadays graphite-based materials are usually used as anodes for commercial LIBs. However, the theoretical specific capacity of graphite is only 372 $mA{\cdot}h{\cdot}g^{-1}$, and cannot meet the ever-growing need of the current society. Carbon nanotubes and graphene are expected to present more excellent lithium storage capability as new carbon forms. Alloys, especially Si-based materials, have received tremendous interest for the extremely high theoretical capacity (approximately 4200 $mA{\cdot}h{\cdot}g^{-1}$, with the formation of $Li_{4.4}Si$ alloy). Transition metal oxides (such as Fe_2O_3, Fe_3O_4, Co_3O_4, and NiO) also have high theoretical capacity ($\sim$928 $mA{\cdot}h{\cdot}g^{-1}$ for Fe_3O_4 as an example). However, low conductivity, dramatic volume expansion, and severe side reactions restrict the practical application of these new materials;

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therefore, further investigations including computational efforts are welcome to promote the development of this field. In this review, we mainly introduce recent progress in how first-principles computations have been applied to the studies on anode materials in Li ion batteries, exemplified by carbon nanotubes (CNTs), graphene, alloys and oxides. For computations on cathode materials in Li ion batteries, there have been many reports on oxides [1, 2] and phosphates [3–5], and there have also been some reviews [6–8].

2 Carbon nanotubes

Since the structural elucidation of CNTs in 1991 [9], massive relevant studies have been performed. Due to the vast space available to store lithium, CNTs were treated as promising anode materials for Li ion batteries. At first, the capacity of CNTs had only 25% improvement than traditional graphite anode materials (LiC_6) [10]. Later it was found that after fierce ball milling, the capacity could be increased to $Li_{2.7}C_6$ [11], corresponding to $\sim$1000 mA·h·g^{-1}, which was very impressive. Almost at the same time, first-principles computations were also used to study this new anode material. For example, Zhao *et al.* [12] investigated the maximum capacity and the structure of Li^+-intercalated CNTs. Their results indicated that the storage of Li could be increased to $Li_{0.5}C$, and the intercalation of Li^+ would not affect the CNT structure much. A very recent MD simulation performed by Song *et al.* [13] indicates that the increased capacity in CNTs results from Li storage between carbon nanotube bundles. Another recent report [14] shows the enhancement of Li adsorption in nanotube-fullerene systems. These studies revealed possible routes for improving Li storage in new carbon forms.

The reason why ball milling can enhance the Li storage capacity of CNTs [11] may lie in the fact that topological defects were introduced to CNT walls during this process, so that both interior and exterior can be employed to adsorb Li^+ ions. First-principles investigation demonstrated that, indeed, both sides of CNTs had the capability to adsorb Li^+ ions and the adsorption energies differed a little at either side [12–15, 16]. Therefore, it is necessary to analyze clearly how Li^+ ions diffuse into the inner side of CNTs. Several papers have focused on this topic. All the results revealed that it is impossible for Li to diffuse across the hexagons [17, 18], and the only path to the interior for Li is the open end of CNTs and enneagons (or larger ring) forming from topological defects. Also, a deep investigation displayed that the interaction between Li^+ and CNTs is somewhat covalent [18, 19].

Even though pristine CNTs have significant performances so far, Zhou *et al.* attested that boron- or nitrogen-doping could give a constructive change to CNTs [20, 21]. Compared with carbon, boron is an electron-deficient element in carbon-based materials, and on the contrary, nitrogen has one more electron than carbon. Doping these two elements may cause different charge distributions and accordingly cause different Li adsorption performances. B-doped CNTs display dramatical enlargement of adsorption energy when Li is taken in, while for N-doped CNTs, opposite results were achieved. Therefore, the Li storage capacity is highly related to the electronic structures of CNTs [22].

Another fact making B-doped CNTs more marvelous materials is that the diffusion barrier for Li to enter the inner side of B-doped CNTs was substantially reduced when both B substitution and topological defects (seven-, eight-, and especially nine-membered rings) are present. The activation energy for Li penetrating the tube wall is much lower in BC_3 nanotubes than in pristine CNTs; only an octagonal hole is available for Li to diffuse inside BC_3 nanotubes [Fig. 1(b)], and the corresponding case is enneagon in pristine CNTs [Fig. 1(a)] [23]. Also, the formation energies of topological defects are lower in composite BC_3 nanotubes than in pristine CNTs. Hence, boron–carbon composite nanotubes are promising anode materials to offer higher diffusion rate and greater Li storage capacity. Experimentally,

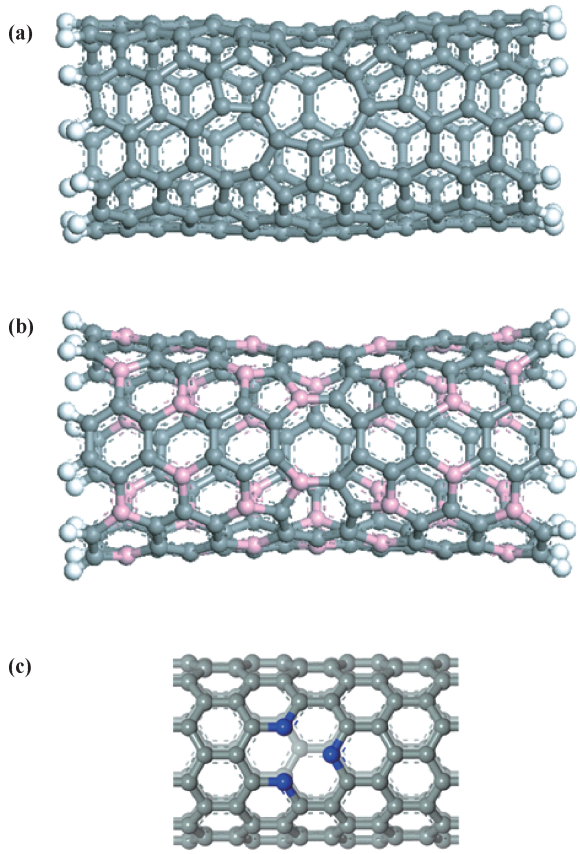


Fig. 1 Various single-walled nanotubes with defects: (6, 6) carbon nanotube with a enneagon hole **(a)**, (3, 3) BC_3 nanotube with a octagonal hole **(b)**, and (10, 0) carbon nanotube with a pyridine-like structure **(c)**. Grey, orange, blue, and white balls denote carbon, boron, nitrogen, and hydrogen atoms, respectively.

Mukhopadhyay *et al.* [24] found that, though the B-doping effects were not dramatic, B-doped multi-walled CNTs showed greater Li storage capacity because of higher specific surface area, larger defect concentration, and higher conductivity.

Since simple N-doping in carbon nanotubes results in electron-rich structure, and shows negative effect on Li adsorption, N-doped carbon nanotubes are not suitable for LIB anode materials [20–22]. CNTs with pyridine-like structure may bring some changes. The pyridine-like N doping is obtained by removing a C atom from the CNT sidewall and then substituting the three nearest neighbors of this C atom with N atoms [Fig. 1(c)]. Since N atoms have five valence electrons and C atoms have four, the nanotube with a set of pyridine-like doping is one electron deficient, compared with pristine CNTs. The electron deficiency brings CNTs with pyridine-like structures electron-accepting tendency. Li *et al.*'s studies indicate that the pyridine-like structure presents a diffusion barrier for Li penetrating the tube wall as low as 1.44 eV [25], comparable to the case of pristine CNTs with an enneagon hole [23]. However, due to the electron-deficient structure, Li is adsorbed at the site of the pyridine-like structure with large adsorption energies [25], and then Li or Li clusters may be trapped at this site and cause irreversible capacities in practical applications.

3 Graphene

Beside the well-known CNTs, a newly rising material called graphene attracts researchers' interest as LIB anode materials. Graphene is a two-dimensional semimetal material, which was first realized in experiments in Geim's group in 2004 [26]; since then, this new revolutionary material has become one of the hottest topics in the scientific field. Graphene is essentially single layered graphite, which is the current LIB anode material. Because of the unique geometric structure of graphene, it may adsorb Li^+ on both sides. Some initial investigations were conducted on this topic [27–29]. It was reported that the specific capacity of graphene was 460 $mA{\cdot}h{\cdot}g^{-1}$ after 100 cycles [27], which is better than graphite, but far from what people expected. Very recently it has been reported that oxidized graphene nanoribbons (GNRs), which was obtained by unzipping pristine multi-walled CNTs, presented an initial charge capacity of ~1400 $mA{\cdot}h{\cdot}g^{-1}$, and the reversible capacity was in the range of 800 $mA{\cdot}h{\cdot}g^{-1}$ [30]. The improved Li storage capacity may result from the abundant edges in GNRs.

Further investigation is still needed to deeply understand the lithium storage in graphene. Recent Raman studies have shown that, the interaction of lithium with few-layer graphene is similar to the case of graphite, but single-layer graphene behaves very differently. The repulsion forces among Li^+ ions at each side of single-layer graphene reduce the lithium adsorption amount greatly [31]. Computations have also been applied to this topic. The foremost first-principles study on Li-intercalated graphene appeared almost simultaneously at the time of the experimental realization of graphene [32]. Later extensive investigations provide more insight. As boron doping turns graphene into an electron-deficient system, more Li ions can be captured in boron-doped graphene; under limited conditions, boron-doped graphene (BC_5) can form Li_6BC_5 compound after Li adsorption, corresponding to a lithium storage capacity of 2271 mAh/g [33]. However, the Li desorption and diffusion in B-doped

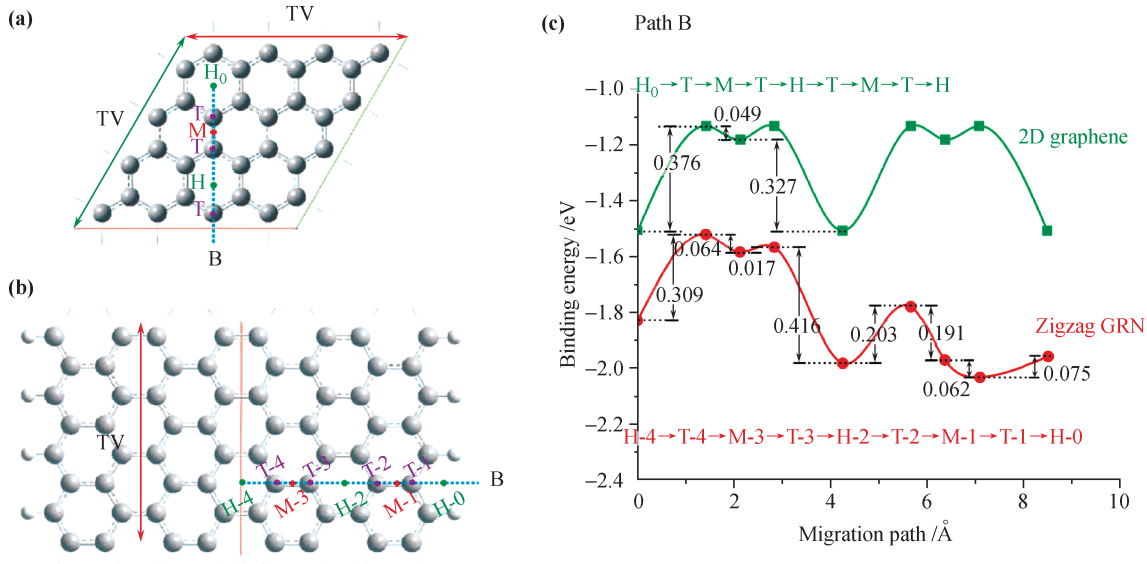


Fig. 2 Schematic representation of graphene **(a)** and zigzag GNR **(b)** cells and B migration paths. **(c)** Energy barriers for path B in graphene and the zigzag GNR. H, M, and T represent the Li adsorption positions on top of the hexagon, on the middle of the bond, and on top of a C atom, respectively. TV represents the translational vector. Reproduced with permission from Ref. [35], Copyright © 2010 American Chemical Society.

graphene are not mentioned. Another report implies that Li^+ intercalation may cause acute structure changes [34]. Recently, Uthaisar *et al.* have disclosed the Li diffusion in graphene and quasi-one-dimensional GNRs, and found that the presence of zigzag and armchair edges affects not only the Li adsorption but also the diffusion. Li tends to migrate to the edges of graphene for lower energy barriers there (Fig. 2) [35]. This result indicates that narrower graphene nanoribbons are promising LIB anode materials, in agreement with the experimental report [30].

Also, nitrogen-doped graphene was grown directly on Cu current collectors by liquid precursor based chemical vapor deposition (CVD) technique, and was explored as LIB anode materials. The reversible discharge capacity of N-doped graphene film was almost double that of pristine graphene [36]. Computations may also be applied to disclose the role of N-doping in this report.

4 Alloys

Alloys have a bright future as LIB anode materials. Si-based materials and other alloys attract much research interest [37, 38]. First-principles computations were successfully applied to study the thermodynamics of alloys in early time, and by using Nernst equation, voltage profile can also be obtained [39]. Recently, the phase diagram for the Li–Cu–Sb ternary alloys has been constructed by combining XRD measurements and first-principles computations [40].

In fact, the biggest problem of alloy anodes is the excessive volume change, e.g., 300% volume expansion occurs to Si anodes. A first-principles study on volume change in Li–Si phase was performed [41]. This paper not only provides detailed information about volume changes, but also implies the relationship between fracture energy and Li concentration, which may be of help for further improvement on this marvelous material. Accordingly, alloys with less volume change are needed. A computational investigation suggests that $Li_{2.5}Cu_{0.5}N$ bears less volume expansion when the extraction of lithium is less than 30% [42].

Another solution to the problem of volume expansion is to make materials into nanoscale, so that the space could hold the volume change. This scheme has been successfully applied to Si-based materials experimentally [43–45]. Chan and Chelikowsky discussed the Li diffusion in Si nanostructures by using *ab initio* computations [46], and found that the nanocrystal size has apparent influence on the Li diffusion barrier. Li^+ ions tend to stay in the inner of the Si nanocrystal, and the diffusion barrier of moving into the core is lower than that of moving towards the surface, which suggests that it is easier for Si nanostructures to be charged than to be discharged, which was also found in Si nanowires (SiNWs) [47]. The insertion sites, surface, intermediate, and core sites, are quite different, and surface sites are energetically the most favorable insertion positions. Compared with the other growth directions, [110] SiNWs are more favorable by Li doping. As for Li diffusion inside SiNWs, the Li surface diffusion has a much higher chance to occur than the surface-to-core diffusion (Fig. 3).

Sn is also a promising alloy-type LIB anode material. Li–Sn system was examined by combining experimental

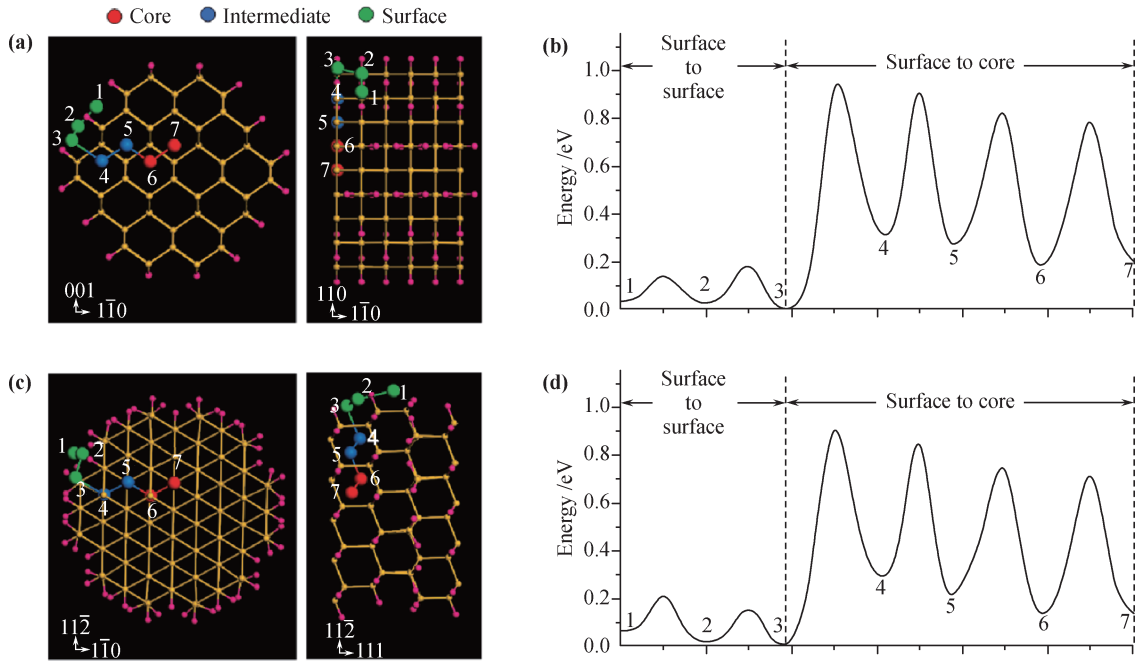


Fig. 3 Li diffusion in 1.5 nm [110] and [111] SiNWs. **(a)**, **(c)** The cross (*left*) and side (*right*) view of the pathways. The diffusion barriers along the pathways are shown in panels **(b)** and **(d)**, respectively. Reproduced with permission from Ref. [47], Copyright © 2010 American Chemical Society.

measurements and DFT computations [48]. Sn has the same problems as Si, and it was proposed that Sn can be filled into carbon nanotubes to solve the volume-expansion problem [49]. This proposal has been examined in detail by DFT computations [50, 51], which revealed some clues for future experimental explorations.

5 Oxides

Lithium transition metal oxides usually act as LIB cathode materials. Computational studies have contributed much to the progress of these materials [7, 52]. Here we will focus on oxides as LIB anode materials.

$Li_4Ti_5O_{12}$ is an anode material that exhibits good safety and cyclability in experiments [53, 54]. It has also been studied with computational method. The electrode potential curve was obtained with Monte Carlo method [55]. Later computations show that the volume expansion due to Li inclusion is not significant in this material. First-principles investigations also indicate that $Li_4Ti_5O_{12}$ is insulated and $Li_7Ti_5O_{12}$ is metallic [56]. A further computational study suggests that the concentration of Li^+ in this material can be increased to $Li_{8.5}Ti_5O_{12}$ [57]; thus, the energy density of this electrode can be significantly improved.

TiO_2 is a magical material with many applications [58], such as cosmetic and solar cell materials. It can also be employed as LIB anode materials and many experimental studies indicate that TiO_2 has great potential to improve the performances of LIB anodes [59–64]. Koudriachova *et al.* developed a model to predict the thermodynamics and kinetics of this material [65], and they explained why the Li^+ intercalation into rutile TiO_2 is unavailable. Also, some new phases were predicted using *ab initio* method and possible formation mechanics were given [66, 67]. Computations show that the volume change of TiO_2 is also not obvious during charging and discharging [68]. The Li diffusion is also an important factor in TiO_2; Li^+ migration pathway and energy barrier were calculated [69, 70], and the diffusion coefficients are in good agreement with experimental data. It was also revealed that, with the increase of Li^+ concentration, the energy barrier becomes lower for Li diffusion.

Most oxides used as LIB anode materials [71] do not adopt the intercalation or insertion mechanism as in cathode materials but a conversion procedure [72]. The mechanism for Li cycles can be interpreted as $M_xO_y+2yLi^+ \leftrightarrow yLi_2O+xM-2ye$, where M is a transition metal such as Ni, Co, Fe, Mn, and Cu [71–75]. Due to the complicated conversion mechanism, few computations touch this field. However, many problems remain unclear involving oxides as LIB anode materials, and computational efforts and new methodologies are highly needed.

6 Challenges and perspective

It is well known that DFT fails to describe long range interaction precisely; thus, graphite, which is a layered material stacked through van der Waals forces, is difficult to be computationally investigated properly. Early study shows that LDA have successfully computed the c parameter of graphite [76], while GGA, which is a more advanced approximation than LDA, fails to represent it. This unexpected result may benefit from the overbinding of LDA. Despite the failure of GGA in this particular situation, GGA gives a good description of lithium-intercalated graphite (LiC_6). Using nudged elastic band (NEB) method [77, 78] and Monte Carlo simulation [79], Li^+ diffusion in graphite can be discussed. Persson *et al.* presented a detailed Monte Carlo study in this topic [80], and predicted that there is still improvement potential in graphite materials.

Solid electrolyte interface (SEI) film is a very important factor which would affect the performances of anode materials. It is also related to the cell safety and the irreversible capacity of anode materials. However, for the reason of complexity of SEI film, it is hard to be simulated through computational method. Leung *et al.* tried to examine the formation of SEI film through *ab initio* molecular dynamics (AIMD) simulations [81]. Still, more efforts are needed to make the simulation better.

In this review, we have presented recent progress on LIB anode materials and discussed the important role of computations in this field. Several examples including CNTs, graphene, alloy and oxides were introduced. These studies surely accelerate the pace of exploring and developing new materials for high-performance Li ion batteries. With the rapid progress of computational capacity and new methodologies, computations and simulations will be more and more widely used to investigate and design new energy materials, and many current difficulties would be conquered.

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