Rechargeable lithium batteries have achieved a rapid advancement and commercialization in the past decade owing to their high capacity and high power density. Different functional materials have been put forward progressively, and each possesses distinguishing structural features and electrochemical properties. In virtue of density functional theory (DFT) calculations, we can start from a specific structure to get a deep comprehension and accurate prediction of material properties and reaction mechanisms. In this paper, we review the main progresses obtained by DFT calculations in the electrode materials of rechargeable lithium batteries, aiming at a better understanding of the common electrode materials and gaining insights into the battery performance. The applications of DFT calculations involve in the following points of crystal structure modeling and stability investigations of delithiated and lithiated phases, average lithium intercalation voltage, prediction of charge distributions and band structures, and kinetic studies of lithium ion diffusion processes, which can provide atomic understanding of the capacity, reaction mechanism, rate capacity, and cycling ability. The results obtained from DFT are valuable to reveal the relationship between the structure and the properties, promoting the design of new electrode materials.

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1. Introduction

Rechargeable (secondary) lithium batteries are one of the most successful technologies that can reversibly transform electric energy into chemical energy for storage and repeatedly generate clean electricity for usage [1,2]. In the past decade, rechargeable lithium batteries have dominated the market of high power storage systems in portable electronic devices such as cellular phones and laptop computers [3]. However, the great demands in both electric vehicles (EVs) and back-up electricity storage units for renewable energy sources in smart grids raise big challenge for the next generation rechargeable lithium batteries [4]. Basically, rechargeable lithium batteries consist of a positive and a negative electrode separated by a separator with the infiltration of electrolyte solution containing dissociated salts, which enable ion transfer between the two electrodes [5]. The capacity and performance of a specific battery system are directly linked to the chemical reactions occurred in the active electrode materials. Therefore, to satisfy the new demand, developing new electrode materials is fairly important. Design of innovative electrode materials for practical applications must take full consideration of high gravimetric and volumetric density, superior power rates, long cycle life, low cost and good safety, and well balance of them [6]. Usually, material explorations are carried on following a thread of synthesis–structure–property, and interpretations are often made based on straight experimental observation and analysis. This process is usually time-consuming and not efficient. Thanks to the breakthroughs in computational technologies and advanced theoretical methods, a more efficient way has been paved for predicting material from atomic and electrical scales, which is the first-principles density functional theory (DFT) calculation [7].

DFT is a solution to the quantum many-body problem, where the ground-state energy is represented as a function of electron density [8,9]. The energy of a specific system is constituted by parts of non-interacting electrons, nuclei, Coulomb interactions and exchange–correlation term. The exchange–correlation energy, the exact form of which is hard to confirm, is often treated by the local density approximation (LDA) [10] or the generalized gradient approximation (GGA) [11]. With the inclusion of a fraction of Hartree–Fock exact exchange (HF), hybrid exchange functional such as PBE0 and HSE06, enjoy a remarkable development in accurate reproduction of atomic and electronic structures [12]. Besides, addition of the correlation term—Hubbard $U$ values, which can be determined using linear response method [13,14] is also widely used to solve electron localization and self-interacting of the transition metals and rare earth elements. An extensively used implementation of DFT combines plane-wave basis set with the ‘pseudopotential’ method [15] in which the pseudopotential replaces nuclear potential and chemical inert core electrons with an effective potential, so that only valence electrons are explicitly included in the calculation [16]. In support of Hellmann–Feynmann theorem [17], forces acting on atoms and stresses on unit cell could be derived straightforwardly, favoring the vibration studies and dynamic simulations [18,19]. With the combination of Monte Carlo technologies or molecular dynamics, the considered factors and scopes of theoretical investigations can be further expanded. Computer modeling works by DFT have strongly interacted with experimental studies, strengthening the reliability of this method.

Owing to the superior efficiency and accuracy, DFT has increasingly become a valuable tool in the exploration of energy related materials, especially the electrode materials of lithium rechargeable batteries in the past decades, from the positive electrode materials such as layered and spinel lithium transition metal oxides to the negative electrode materials like C, Si, Sn and titanium-oxide based compounds [20–22]. From this point of view, work carried on via DFT mainly involves the following aspects: crystal structure modeling and stability investigations of delithiated and lithiated phases, average lithium intercalation voltage calculations, prediction of charge distributions and band structures, and kinetic studies of lithium ion diffusion processes. In this review, we will present an introduction of the major studies on the typical electrode materials by means of the first-principles DFT approaches. We hope to provide a fresh view to gain insight into the design of electrode materials of rechargeable lithium batteries.

2. Positive electrode materials

The positive electrode materials can be divided into three main categories: layered lithium transition metal oxides, spinel lithium transition metal oxide and polyanion compounds. In this review, we discuss the applications of DFT calculation with the three kinds of positive electrodes and the main properties of representative materials are summarized in Table 1.

2.1. Layered lithium transition metal oxides LiMO$_2$

Layered lithium transition metal oxides LiMO$_2$ (M=Co, Ni, Mn, etc.) are now a category of most mature and extensively studied electrode materials [23]. Due to similar structural and electro-chemical properties, they have been systematically investigated and contrasted as a family by DFT methods [36].

The layered LiMO$_2$ compounds are originally of rhombohedral symmetry (R-3m) “ordered rocksalt” configuration, as shown in Fig. 1(a). Lithium ions can be reversibly removed from and inserted into this structure, creating or annihilating vacancies within the lithium layers [37]. First-principles calculation finds that the stacking sequences and stabilities of ordered layered compounds strongly depend on the interlayer Li-Li electronic interactions through M cations [38]. When exposed to electrochemical cycling or high temperature, the original layered host structures will go through undesirable phase transformations or decompositions, driven by spatial Li-vacancy interactions, electron count variations and oxygen packing changes [39–41]. These results demonstrate that DFT calculation can provide detailed atomic information, which is very difficult to gain in experiments. Another example is LiNiO$_2$, though isostructure to LiCoO$_2$, it acts differently in electrochemistry. Calculation explains that in these layered structures, Ni, with partially filled $e_g$ states, tends to reach a maximum of charge localization due to the $t_{2g}$\textsuperscript{tr}–(d$^5$) electronic nature of Ni$^{3+}$ and Jahn–Teller (J–T) distortion of NiO$_6$ octahedron, while in contrast Co prefers to achieve a maximum of charge delocalization [42,43].

Apart from the crystal and electronic structure evolutions, the average intercalation voltages of lithium transition metal oxides have also been successfully predicted by first-principles methods with fairly high accuracy [44,45]. The accurate results are mainly based on the phase diagram and surface property calculations. The phase diagrams of Li$_x$M$_2$O$_y$ have been investigated. For example, different phases of the layered Li$_x$CoO$_2$ have been searched by Van der Ven et al. [41,46]. The results show the richest phase diagrams with ordering and staging transitions and changes in host structure are at low lithium contents. At high lithium concentration, no two-phase region occurs. Besides, surface properties have
also been explored with DFT calculation, which is helpful in tailoring rate performance and inhibiting parasitic surface reactions in the electrolyte. Kramer and Cedar investigated the surface energies of several low-index surfaces of layered LiCoO₂ by means of DFT calculations embedded in a thermodynamic framework [47]. The surface energy and equilibrium shape are sensitive to the equilibration environment. The (0001) and (10–14) surface are present for all reasonable values of the Li and O chemical potentials. The undercoordinated oxygen atoms existing in (001) oriented surfaces significantly vary from the ones in the lattice, which as proposed by Dahéron et al. [48], is a peculiar oxygen signature of LiCoO₂.

Ionic diffusivity is a determinant aspect for electrode materials, which in DFT is expressed through activation barrier along the Li hopping paths. Kang et al. [49] systematically studied the issues related to Li mobility in layered lithium transition metal oxides. In close packed oxides, octahedrally coordinated Li ion migrates through intermediate tetrahedral site where it encounters strong repulsion from a nearby transition metal ion. Activation barrier for Li hopping (Fig. 1(b)) is strongly affected by local atom arrangement, size of the tetrahedral site and electrostatic interaction between Li⁺ and face-shared octahedron cations [50,51]. Little variation of the activation barrier by doping or substitution will influence the diffusion rate exponentially.

For the layered transition metal compounds, a major drawback is the poor cycling performance, especially for LiMnO₂. The electrochemical cycling of LiMnO₂ gives rise to not only the partial oxidation of manganese ions but also a thermodynamic driving force of irreversibly structural transformation from layered form to spinel, which exposes a potential failure mechanism of a layered positive electrode [52]. DFT calculation has shown that transformation is most susceptible around x = 1/2 and taken a two-stage procedure [53]. First, a significant fraction of Mn and Li ions successively migrate to adjacent planes to occupy tetrahedral sites and face each other across an octahedral vacancy in Mn layer, forming a metastable “Li–Mn dumbbell” intermediate. Then, the second stage involves an isolated tetrahedral Mn to migrate to a Li layer octahedron and formation of spinel nuclei. The activation barrier of the second stage is much higher and is attributed to large cationic repulsion, indicating a kinetic determining role. To minimize the transformation effects, three solutions are put forward: (1) inhibiting the insertion of Mn in the Li layer via fixed low-valence cations substitution; (2) hindering the collective cation rearrangements needed to form spinel; (3) preventing the reduction of the interlayer spacing by large cations pillaring the Li layer.

Doping of LiNiO₂ or LiMnO₂ with transition metals is a generally adopted strategy in suppressing the Jahn–Teller distortion of Ni³⁺ or Mn³⁺ as well as structure transformation upon delithiation. Previous energy calculations indicate that the dopant oxidation state together with the (100) and (010) subshell filling determines the effectiveness of a specific dopant. It has been verified that high contents of divalent dopant are especially effective [54]. In the system doped by divalent elements, the dopants will act as electrochemically active centers for valence change, leaving two trivalent ions to only take on +4 oxidation states stably, thus avoiding the Jahn–Teller effects.

Take LiNi₀.₅Mn₀.₅O₂ as an example, which is of particular preference as a safe and inexpensive Li-host material with a high capacity [55]. Electrochemical cycling mainly happens between the redox-active Ni²⁺ and Ni⁴⁺, leaving a stable Mn–O matrix and electrochemically inactive Mn⁴⁺ ions. Calculations have demonstrated the particular valence distribution leads to good cycling stability and the inherent safety of LiNi₀.₅Mn₀.₅O₂ [56]. The cycling process of LiNi₀.₅Mn₀.₅O₂ over a wide range of voltage is accompanied by structural changes attributed to 8–11% LiNi disorder, which reduces the distance of Li layers and thus limits its practical rate capacity [57–59]. The more vacancies lithium ion neighbors, the larger tendency it has to enter the adjacent transition metal layers. In the transition metal layers, lithium ions prefer to reside in the tetrahedral sites surrounded by Mn ions with few nearest Li–Ni bonds around [60]. These tetrahedral sites are energetically very stable, so Li ions will intercalate them at the early charging stage and can only be removed at high potential [61]. Detailed computing investigations further show that entering of Li into the Mn layers is accompanied by the migration of more than 75% of Ni ions into the sites vacated by Li. As the Li-excess case reported by Xu et al., transition metal migrations mainly happen on the surface layers thus leading to a surface phase transformation to defect-spinel and large irreversible capacity [59]. Since the migration energy strongly depends on the Ni environments in the transition metal.
layers, optimizing the Ni$^{2+}$ content of a material independently can be taken as an effective way to minimize or control the extent of Ni migration. Recently, researches have extended to multi-doped materials especially those with gradient core/shell/surface structures and variable transition metal concentrations, which have been proved to contribute well to thermal stability [62]. According these DFT calculations, one can conclude that to obtain the high energy density, it would be desirable to make Mn rich at the surface and Ni rich in the bulk for these materials.

2.2. Spinel lithium transition metal oxide

Spinel lithium metal oxide, in representative of LiMn$_2$O$_4$, is now paid more attention due to the intrinsic advantages of low cost, high abundance and environmental compatibility [27,63].

The space group of spinel materials is Fd-3m, in which lithium and transition metal atoms occupy the 8a tetrahedral and 16d octahedral sites of the cubic close-packed oxygen ions framework respectively, as shown in Fig. 2(a). Electronic structure, chemical bonding and Li mobility have been investigated extensively based on this structure by DFT calculations to give elementary information [64–68]. It is the easy recovery of Mn–O chemical bonding to its initial electronic state after Li occupation, as well as the host frame’s flexible accommodation of intercalated Li ion that gives explanation to the good reversibility of this material [65]. In this spinel structure, diffusion of Li ions occurs by hopping between 8a tetrahedral sites mediated by 16c octahedral sites, as illustrated in Fig. 2(b). The valence state of Mn ions and the arrangements surrounding the Li ions have profound effects on the activation barrier of Li diffusion [68]. In addition, to improve the accuracy of this system, Hubbard-like correction term (U) is often employed. Comparisons show that obvious Jahn–Teller induced $\varepsilon_g$ orbit split, mixed valence states of Mn$^{III}$ and Mn$^{IV}$, as well as z-axis elongated Mn$^{III}$O$_6$ octahedra can only be distinguished by GGA+U approximations [66,68].

However, the realistic application of LiMn$_2$O$_4$ is limited by its poor cycling performance, which is caused by the Mn dissolution induced by disproportionation reaction and structural transformation induced by Mn$^{III}$ Jahn–Teller distortion. Partial substitutions of Mn with other transition metals are taken as an effective approach to improve the cycling stability. LiM$_x$Mn$_{2-x}$O$_4$ (M = Ni, Co, Cr, Cu) system has been examined by DFT calculations and the results agree well with experiments [69–73]. The raises of intercalation voltages are the most obvious effects produced by doping which can be attributed to the high degree electronic reorganization around the dopant atoms and subsequently strong coupling between Li ion and M–O bonding [69,70,72]. According to the calculation results, Co and Cu doping will lower the Li diffusion barrier to better than Ni [74], as shown in Fig. 3. With the increasing amount of Cu, the co-doped spinel LiNi$_x$Cu$_{1-x}$Mn$_2$O$_4$ ($0 < x < 0.5, 0 < y < 0.5$) system exhibits decreased reversible discharge capacity but high capacities at high rates.

2.3. Polyanion compounds

Polyanion compounds Li$_y$M$_{1-x}$($XO_4$)$_3$ (M = Fe, Mn, Ni, Co; X = P, S, Si, Mo, W, etc.) are now regarded as the most competent positive electrode materials for future applications of large-scale rechargeable lithium batteries. Since the first report of LiFePO$_4$ by Goodenough’s group [75], the unique features such as cycle stability, safety, environmental friendliness and potential low cost have appealed much attention to this family [76]. Researches starting from olivine phosphates have extended to silicates, fluorophosphates, fluorosulphates, borates as well as anion and metal substitutions [28].

2.3.1. Phosphates

A typical ordered-olivine phosphate structure (space group of Pnma), taking LiFePO$_4$ as an example, is composed by each Fe$_{1+x}$O$_6$ octahedron linked with four Fe$_x$O$_6$ octahedra in a corner-sharing way in the bc plane, while Li$_x$O$_6$ octahedra forming edge-sharing chains stacking along the b-axis [77], as shown in Fig. 4(a). The insertion/extraction of Li ions would influence chiefly to the electron distribution but little to the LiFePO$_4$ host framework [78].

High stability is an outstanding thermodynamic feature of olivine phosphates, which as the phonon calculation shows, is mainly contributed by the extremely strong bond of oxygen–phosphorus [18]. All these phosphates are predicted to have high Li extraction potentials by GGA+U, the highest potential at above 5 V with LiNiPO$_4$ [14,30]. Recently, Hautier challenged the common statement that olivine-based compounds and phosphates in general are intrinsically safer than oxides. According to their results, most phosphate compounds evolve oxygen at lower temperature than oxides for the same oxidation state of the active redox metal. The reason that LiFePO$_4$ is so stable against reduction by the electrolyte is in part attributed to its low voltage. The one with higher voltage like LiCoPO$_4$, LiNiPO$_4$ is predicted not to share the excellent thermal stability of LiFePO$_4$ [80]. High-throughput ab initio calculations are especially useful and successful in constructing database and phase diagram. The systematic work of Ceder’s group gives a thorough understanding of the electrochemical and thermodynamic properties of olivine family including both LiMPO$_4$ and MPO$_4$ (M = Fe, Mn, Co, Ni, etc.),

![Fig. 1](image-url) (a) Crystalline structure of layered LiCoO$_2$ and (b) its corresponding lithium diffusion pathways.
providing directions for promising material design and experimental synthesis (see in Fig. 5) [80–83].

One obvious peculiarity of phosphates that held back its practical industry application concerns the low intrinsic electronic and ionic conductivity [84]. It is of significant meaning to examine its electronic and ionic transport mechanisms and propose reliably solutions by first-principles DFT investigations. According to the theoretical studies of Ceder's group [85] and then by Islam et al. [86], in the olivine crystal structures, motion of Li ion occurs along the one-dimensional [010] channel via a nonlinear, curved trajectory between Li sites, as displayed in Fig. 4(b). Later, this mechanism is confirmed by experiments [87]. The energy barrier of Li ion transport in bulk is calculated to be only 0.19 eV, indicating a rapid diffusion of Li ions (\( D \approx 10^{-6}\) cm² s⁻¹). However, the one-dimensional channel is easily blocked by impurities, disorder or defects, impeding the availability of active volume and long-range Li conduction, illustrating in Fig. 4(c). Besides, on the surface, the energy barrier of Li ions diffusion between channels is 0.52–0.77 eV, much higher than that of in subsurface (only 0.13 eV) [29]. The ability for Li ions to reach channel entrances is a possible rate-limiting step in charge/discharge kinetics. Therefore, short and unobstructed channels are important to enhance fluent surface and bulk ion diffusion [79]. Realization of LiFePO₄ with nanosize particles or specially created ion-conducting surface phase with composite, which predominates in few defect and available direct channels, is promising for the enhancement of ionic transport in avoid of energy density loss [88,89].

Effective electron transport is another important requirement for good kinetics, because insertion/extraction of Li ions must be accompanied by electrons transfer to keep the charge balance. Polaron model [90] has been successfully applied to LiFePO₄ and the electronic conductivity would be interpreted by the activation energy of small polaron hopping. LiFePO₄ is a half-metal with spin-sensitive band structure [91], and there is an obvious tendency for charge carriers (electrons or holes) to be strongly localized at individual sites with self-induced lattice distortion, thus forming polaron. The stronger the metal-to-ligand interaction through d–p orbital rehybridization, polarons with larger stability could form [92]. Unfortunately, the polaron would tightly bind to the defect that creates them (the lithium vacancies in LiFePO₄ or the Li ions in FePO₄) and their low mobility would prevent high electronic conductivity of this system. This hypothesis is confirmed by Ellis et al., who gave the first experimental evidence for a strong correlation between electron and lithium delocalization events. They also indicated that polaron hopping could be accelerated at higher temperature, which could explain the fact that the phase transition is driven by an increase in temperature [93].

According to the above discussions, defects are intrinsic and essential in determining the high-rate electrochemical behavior of LiFePO₄. The presence of immobile or low-mobility defects will sensitively affect the one-dimensional diffusion. Using DFT calculations, various defects have been detected. Systematic comparisons show that lithium vacancies, lithium anti-sites, iron anti-sites, and iron vacancies each has one stable charge state.
The anti-site pair (FeLi) couples a Li vacancy with large binding energy around the anti-site is facile for Li ions in FePO₄ but easier for vacancies in LiFePO₄ [29]. Dather et al. illustrated that relative to Li ions in LiFePO₄, energy [99]. Moreover, comparison of activation energies by long time binding to Li vacancy and therefore lower the system’s hole polaron and lithium vacancy for optimal conductivity [94].

In short, controlling the concentration, type and segregation of the native defects via tuning the synthesis conditions is an instructional way to enhance the electrical conductivity of LiFePO₄. It should be mentioned that anti-site defects sometimes suppress or enhancing the concentration and species of certain native defects in LiFePO₄ could increase the concentrations of hole polaron and lithium vacancy for optimal conductivity [94]. Particularly, the most common defect is the Li–Fe "anti-site" pair (FeLi) in which one Li²⁺ and one Fe²⁺ are interchanged [94–97]. The anti-site pair (FeLi) couples a Li vacancy with large binding energy. Recently, Chung et al. reported that iron anti-site defects (FeLi) would form preferentially in only a few channels along the b-axis instead of being homogeneously distributed in the lattice [98]. Lee et al. further gave explanation by first-principles calculations that the segregation of FeLi’s in just a few Li diffusion channels could bring about shorter FeLi-FeLi separations, create longer time binding to Li vacancy and therefore lower the system’s energy [99]. Moreover, comparison of activation energies by Dather et al. illustrated that relative to Li ions in LiFePO₄, diffusion around the anti-site is facile for Li ions in FePO₄ but easier for vacancies in LiFePO₄ [29].

In short, controlling the concentration, type and segregation of the native defects via tuning the synthesis conditions is an instructional way to enhance the electrical conductivity of LiFePO₄. It should be mentioned that anti-site defects sometimes offer an opportunity for Li ions to cross over between channels. Unfortunately, even the lowest energy path, which occurs by Li migrating to the nearest Li channel through a vacant intermediate Fe⁵⁺ site, has an activation barrier much higher than that within a certain channel [79]. Based on the understanding of anti-site defects, doping is viewed as another promising way to contribute to high electronic conductivity. Systematic contrasts of a range of dopants from the point of energy, valence and ion size demonstrate that substitutions of LiFePO₄ with divalent dopants like Mn, Mo or Mg on Fe sites are most favorable [86,100–102]. Aliovalent elements (such as Al, Ga, Cr, Zr, Ti, etc.) do not play roles because they are not accepted on both Li and Fe sites [97,103].

The electrochemical properties of LiFePO₄ can also be viewed from the relationship between two end member phases—the lithiated LiFePO₄ and delithiated FePO₄ [77]. The two phases differ in lattice volume, so strain is induced at the phase boundary, preventing effective fitness and transformation. Several models have been put forward to study the interface migration and syntactic, like the shrinking-core model [104], spinodal-type model [105], the domino-cascade model [106]. Recently, both theoretical and experimental studies revealed the importance of size confinement in decreasing the miscibility gap and improving the thermodynamics of two-phase equilibrium [107–109]. Issues such as coexistence form and solid solution behavior of LiFePO₄, FePO₄, as well as structural evolution during lithium insertion/extraction can be further simulated and comprehended precisely via first-principles DFT approaches aiming at thermodynamics, kinetic and reaction pathways.

Investigations of potential olivine positive electrode materials have extended to multi-component compounds such as binary, ternary, or even quaternary systems containing Mn, Fe, Co, Mg, and Ni [110–113]. DFT calculations have been employed to get an in-depth understanding of the new phenomena introduced by multi-component olivine systems, including the shift of transition metal redox potential, existence and conversion of a solid solution-like phase, and different rate behavior. For example, the distribution of Fe in LiCoPO₄ suppresses the anti-site mixing, promotes structural stabilization and enlarges Li ion transport channels [113]. Neighboring FeO₆ or CoO₆ constrains the asymmetric distortion of MnO₆ and thus remarkably reduces the Jahn–Teller distortion of LiMnP0₄, improving Li mobility and reducing polaron hopping [90,93,111]. In LiMn0.5Fe0.5Co0.1PO₄₅, as lithium ions deintercalate from the host stepwise, ion oxidations and corresponding volume shrinks occur on

Fig. 4 (a) Crystalline structure of LiFePO₄; (b) schematic of curved migration pathway calculated for lithium ion migration in olivine-structured phosphates LiMP0₄ (reproduced with permission from Ref. [20], Copyright 2009 The Royal Society of Chemistry); (c) schematic illustration of Li⁺ diffusion impeded by immobile point defects in one-dimensional channel (reproduced with permission from Ref. [79], Copyright 2011 American Chemical Society).

Fig. 5 Mean voltage in phosphates versus maximum gravimetric capacity achievable. Specific energy curves at 600 and 800 Wh/kg are drawn on the figure (blue dashed lines). The red dashed line indicates the upper voltage which we consider safe against decomposition of the electrolyte. Different colors and markers have been used for different elements (reproduced with permission from Ref. [80], Copyright 2011 American Chemical Society).
Li ion diffusion mainly concerning on Li$_2$FeSiO$_4$ and Li$_2$MnSiO$_4$. The formation of a solid solution between Li$_x$MnPO$_4$, Li$_x$FePO$_4$, and Li$_x$CoPO$_4$ at this composition has also been confirmed by the calculated energy, which is attributed to the driving force reduction of phase separation induced by dilution of unfavorable Li$^{+}$–M$^{4+}$ or vacancy-M$^{4+}$ pairs [112]. These works have verified that multi-component substitution is an effective strategy to counterweigh the limitations of single element counterparts and therefore improves kinetic and thermodynamic properties.

2.3.2. Silicates

Silicates such as Li$_3$FeSiO$_4$ and Li$_2$MnSiO$_4$ have been investigated recently after the initial successful preparation by Nyttén et al. [114], because iron and silicon are among the most abundant and safe elements, as well as at most two lithium ions per formula unit (F.U.) would be extracted. The orthosilicate compounds Li$_x$MSiO$_4$ (M=Fe, Mn, Co) belong to a family of tetrahedral structures that exhibit a rich polymorphism. Different structures have been identified by experimental approaches [114–118]. Studies are mainly focused on three phases with the space groups of orthorhombic Pnmb, Pmn2$_1$ (both are $\beta$-Li$_3$PO$_4$ derivatives) and monoclinic P$_2$$_1$/n ($\gamma$-Li$_3$PO$_4$ derivative), respectively [119,120]. The considered structures mainly differ in the local environments of transition metal ions as well as the interconnectivity and orientations of the corner shared one-dimensional MO$_4$–SiO$_4$ chains. Comparisons exhibit a more promising role of P$_2$$_1$/n configuration, in which all Li$_x$MSiO$_4$ systems are semiconductors with the decrease of band gap during the Li extraction and the corresponding fully delithiated MSiO$_4$ has better stability [121]. Different from the counterpart of Li$_x$MPO$_4$, the potentials of silicates are largely increased due to higher valence state of active redox couple (M$^{3+}$/M$^{4+}$) [30] and Li ion conduction exhibits a two-dimensional anisotropic character [122].

However, the main drawbacks of this family lie in a strong driving force for the transition metal ions to change their coordination together with randomized Li-site and M-site occupations upon lithium extraction [123,124]. As a result of this structure transformation, it is difficult to achieve the idealized two-step Li ions intercalation/deintercalation and the Li ion diffusion pathways are also significantly changed [32]. With the help of first-principles methods, detailed examinations have been carried out from the relationship of structure, energy, potential and Li ion diffusion mainly concerning on Li$_3$FeSiO$_4$ and Li$_2$MnSiO$_4$.

For Li$_3$FeSiO$_4$, small differences in the FeO$_4$ arrangements and bonding influence the equilibrium potential measured during the first oxidation of Fe$^{3+}$ to Fe$^{4+}$ in all polymorphs of Li$_x$FeSiO$_4$ [119]. The possibility of reversibly extracting the second lithium ion per FU is hindered by the high stability of the intermediate phase LiFeSiO$_4$ and destruction of stable electronic configuration by oxidation of Fe$^{3+}$ to Fe$^{4+}$ [123]. Calculations of Li-vacancy migration kinetics are studied based on the Pmn2$_1$ ($\beta$-Li$_3$PO$_4$) [31,32] and P$_2$$_1$/n ($\gamma$-Li$_3$PO$_4$) [125], respectively. The barriers for Li diffusion in Li$_3$FeSiO$_4$ are significantly higher than those found in other common positive electrode materials, implying a low rate capability. In the structure of P$_2$$_1$/n symmetry, favorite Li ion migration occurs along [101] direction and a zig-zag trajectory in the ac plane. Combining both experimental and computational methods, Armstrong et al. reported that when cycling the as-prepared P$_2$$_1$/n type of Li$_3$FeSiO$_4$ would undergo structural change to one [32]. In the Pmn2$_1$ structure, Li ion transport, with the lowest energy of 0.9 eV, involves zigzag paths between two corner-sharing Li sites and through intervening vacant octahedral sites that share faces with the LiO$_4$ tetrahedra, as shown in Fig. 6. The results demonstrate that future work should consider how to synthesize the terminal structure directly, thus avoiding the structural changes on cycling. In order to reduce the activation barrier of Li ion diffusion and increase rate capability, it is meaningful to do structure modification according to the identified pathway.

To promote the electrochemical performance of orthosilicate compounds, several attempts have been taken from different points. Li$_3$Mn$_{0.5}$Fe$_{0.5}$SiO$_4$ appears to be one of the most anticipated materials to achieve reversible exchange of up to two lithium ions per FU (with a capacity above 300 mAh g$^{-1}$). DFT calculations confirmed the feasibility of this idea through adopting appropriate Mn/Fe mixture proportion and stable configuration. For Li$_x$Mn$_{1-x}$Fe$_2$SiO$_4$, the voltage required to extract more than 1 Li ion/FU is predicted to be substantially lower, by 0.7 V, than that for the pure Fe counterpart, which is within the present experimental reach. If the potential is well controlled so that less than ~1.5 Li ion/FU is exchanged during the electrochemical cycling, the structure of MnFe mixture should not be collapsed [126]. However, Larsson’s results argued that when the ratio of Mn substitution lowered to 12.5%, the structural distortion and high voltage would destruct the feasibility of this design [127]. Substitution is another way for property improvement. Efforts involve of replacing O by N [128], substituting polyanion SiO$_4$ by AsO$_3$ [129], BO$_3$ [130], VO$_4$ [131], and doping trivalent Al and Ga on Si site [122].

2.3.3. Fluorophosphates and fluorosulfates

Stemming from the consideration of increasing operation voltage as well as the specific capacity, high electronegativity F$^-$ anion has been successfully introduced to the polyanion systems. Barker et al. first reported the lithium ion insertion/extraction behavior in the fluorophosphate phase LiVPO$_4$F [132]. The pioneered study of Li$_x$FePO$_4$F by Ellis et al. [133] aroused much attention to the lithium fluorophosphate by DFT calculation [34,35,134,135]. Systematic computations of structures and voltages proved little volume change, good mechanical stability and relatively high circuit potentials especially for the first delithiation step [34,135]. However, the undesirable decomposition products (LiF) would reduce the thermal stability and reversibility [135].

Recently, Recham et al. replaced phosphate groups with more electron-withdrawing sulfinate groups. The excellent electrode performance together with the cost advantage of LiFeSO$_4$F suggests it as a promising positive electrode material [33]. LiMn$_{1/2}$Fe$_{1/2}$SO$_4$F is studied systematically for M=Fe, Co, Ni and LiFePO$_4$ is often taken as a contrast for the understanding [35,135–141].

The most significant difference between LiFePO$_4$F and LiFeSO$_4$F lies in the lithium diffusion process. Transportation of Li ion is found to be effectively three-dimensional in LiFeSO$_4$F, with diffusion along tunnels in the [100], [010], and [111] directions, as shown in Fig. 7. The lowest energy path lies along the [111] direction, indicating high Li mobility [136,138]. Moreover, there would be no significant intrinsic concentration of Li–Fe anti-site defects at operating temperatures in these fluorosulfates. Phase separation of LiFeSO$_4$F and FeSO$_4$F expected during Li extraction can be easily tuned due to the very low formation energy [141]. Li ion extraction brings about general shrink of the M–O and M–F bonds, while the S–O bonds keep almost unchanged. The statements above ensure the confidence of maintaining good
In a word, for positive electrode materials, common applications of DFT calculations are summarized as follows: (1) predicting the cycling performance through calculating structure stability such as the changes before and after lithium intercalated; (2) forecasting the rate capacity by calculating lithium diffusion pathways and the corresponding activation energies; (3) interpreting the reaction mechanism with the calculation of phase diagrams and lithiated/delithiated voltage platforms. Besides, more importantly, DFT calculations could provide in-depth understanding for the major drawbacks of certain positive electrode materials and supply possible solutions to them, meaningful for designing new positive electrode materials. It is foreseeable that with the rapid development of modern computing technology, DFT calculations can play more important roles in lithium ion batteries.

3. Negative electrode

Negative electrode is also a key component of great necessity to be developed in order to satisfy the ever-increasing power requirement...
requirement for batteries. In terms of energy density, metallic lithium is of course the first choice. However, the generated lithium dendritic crystals arouse serious safety problems and limit its practical utilization. By now, graphite is still the most popular and mature negative electrode material for commercial rechargeable lithium batteries. Nevertheless, exploration of optional materials still continues intensely. Typical cases include new carbon based materials, alloys, titanium oxide based compounds, and metal oxides. DFT calculations provide efficient supports to better understanding of negative electrode properties [142]. Herein, we mainly focus on Si based and titanium oxide based negative electrodes due to their special properties.

3.1. Si based lithium alloys

Si has the highest theoretical specific capacity of 4200 mA h g⁻¹, and is the second most abundant element in the Earth's crust, so it has been taken as the most promising candidate to achieve high gravimetric and volumetric capacity [143].

Si will alloy with the inserted Li ion and transform into various Li silicide with medium-range ordering, and finally into a well-known crystalline phase, Li₁₅Si₄ [144–146], accompanying amorphization of crystalline Si [147]. At the onset of lithiation, the inserted Li atom energetically prefers a tetrahedral interstitial site and the charge transferred from Li ion leads to an isolated state of Li impurities and a significant weakening of nearby Si–Si bonds [148]. Chemical interactions of lithiation give rise to pronounced effects on the mechanical behavior of silicon structures. Calculations show the Li-rich Li–Si alloys no longer exhibit a continuous Si tetrahedral network and subsequently undergo breaking of Si–Si bonds and formation of weaker bonds between neighboring Si and Li atoms, which results in a decrease in Young's modulus, a reduction in strength, and a brittle-to-ductile transition [149,150]. The volume of the Li–Si alloy increases nearly linearly with Li content, while the fully lithiated amorphous-Li₄.₃₃Si and crystalline-Li₄.₄₄Si phase are predicted to yield a 334% and 296% volume expansion with respect to crystalline Si [151].

Nanostructures are feasible strategies to settle the cyclic degradation of Si-based materials, which could successively accommodate large volume changes and withstand mechanical bulk crack during repeated charging and discharging processes. DFT calculations also make contribution to understand the nano effects. In the Si nanostructures, Li favors to reside in the interstitial tetrahedral sites at the core and the migration is mediated by the hexagonal sites as saddle points, as illustrated in Fig. 8(a) [152]. When moving inwards from the surface as Fig. 8(b), the initial barrier of surface-to-intermediate intercalation is 0.38 eV higher than that of the deeper transport, indicating a unique role of surface intercalation [153]. Moreover, compared to the charging process, on discharging Li diffusion from the core to the surface occurs in a slower way [152,154]. Manipulating the nanostructure's size, such as reducing the diameter of nanowire and thickness of nanofilm, is suggested to be an effective way to accelerate Li ion diffusion.

Take Si nanowires (SiNWs) as an example, its excellent properties for Li insertion such as efficient electron transport along the axis and large Li ion flux are due to the high surface area to volume ratio [155]. Axis orientations and diameters of SiNWs as well as the insertion sites will introduce distinct influence to Li binding energies and diffusion barrier. Specifically, [110] SiNWs have the largest Li binding energy and are the most sensitive to external strain, while activation barrier decreases when the diffusion direction is inclined close to the SiNWs axis [156].

![Fig. 8](image-url) (a) Li diffusion pathway from the center tetrahedral site toward surface in Si (110) nanowire and corresponding energy change (reproduced with permission from Ref. [152], Copyright 2010 American Chemical Society); (b) Li transport pathway through Si (100) nanofilm and corresponding energy profile (reproduced with permission from Ref. [153], Copyright 2010 American Institute of Physics).
As the diameter of SiNWs grows, the Li binding energy gradually increases to the bulk value, while the surface sites are most favorable than the core and intermediate regions [154].

Besides, DFT study also suggests that surface doping can exert positive effects on the electrochemical performance of Si negative electrode. Si nanofilm, doped by group III/V elements, especially subsurface/surface Al doping or surface P doping, can effectively promote the Li intercalation kinetics [153]. Recently, Long et al. compared the impacts of p-type boron and n-type phosphorous dopants on the lithiation of crystalline Si [157]. The B-doped surfaces are found to insert Li at higher voltages than P- and undoped surfaces but result in less Li insertion.

Parallel to Si, Sn and Ge have also been investigated and face similar problems. Contrasts among these three materials inferred that the large effective interstitial space and softer matrix of Sn would profit Li insertion and alloying between Li and Sn is energetically most stable [158]. Compositions between Si, Sn, and C in modified morphologies such as core-shell structures, nanowires, and nanotubes have been designed to improve the mechanical and electrochemical properties as promising negative electrode materials [159–161].

3.2. Titanium oxide based compounds

The ability of titanium oxide polymorphs to accommodate and conduct lithium ions draws much interest to their performances as negative electrode materials for lithium rechargeable batteries. Many titania and lithium titanate polymorphs have been proposed, including the naturally occurring titania polymorphs namely, rutile, anatase, brookite, TiO$_2$-B, and lithium titanate phases LiTi$_2$O$_4$ and Li$_{4+x}$Ti$_x$O$_{12}$ with spinel structures [162]. The calculated structures are shown in Fig. 9.

Systematic phase stability analogy of various TiO$_2$ polymorphs investigated by Kerisit et al. [162] indicates that the main factors controlling the relative stability of the lithiated titania polymorphs are the lithium bonding environment, arrangement of LiO$_x$ and

![Fig. 9](https://example.com/fig9.png)

**Fig. 9** DFT-optimized structures of the eight LiTiO$_2$ (i.e., × 1.0) polymorphs: (a) rutile; (b) anatase; (c) brookite; (d) TiO$_2$-B; (e) ramsdellite; (f) hollandite; (g) spinel; (h) hexagonal (reproduced with permission from Ref. [162], Copyright 2010 American Chemical Society).
TiO$_2$ polyhedrons and extent of lattice deformation upon lithiation. In particular, anatase and rutile, the most common natural forms of TiO$_2$, have spurred extensively investigations via theoretical techniques. Upon lithium insertion, anatase is energetically favoured over rutile [163]. Nanostructure is believed to be a viable way to improve the rate capacity as well as the lithium insertion level over the bulk counterparts, which has been confirmed by experimental tests [164–166]. In TiO$_2$ nanoparticles, the conductivity strongly depends on the titania polymorph, the crystallographic direction for the conductivity, the nanoparticle size and Li concentration [167,168]. However, during lithium insertion into nanostructured TiO$_2$, the original rutile and anatase structure will evolve to lithium titanate, which has many polymorphs of hexagonal (R-3m), cubic spinel (Fd-3m), monoclinic (P2/m) and cubic rocksalt (Fm-3m) symmetries [163,169–171]. The phase transformation accompanied by volume change and structural rearrangement causes irreversible battery capacity degradation during electrochemical cycles.

Besides, TiO$_2$-B, the least dense polymorph of TiO$_2$, is newly viewed as a superior lithium intercalation host. Several works have established how the structure changes on Li intercalation, especially the occupancy of Li sites over a range of Li concentrations [172–174]. There are three distinct symmetry unique sites that emerge for Li (Fig. 10). The slightly off-center square planar C site and the A2 5-fold coordinated site are suitable in energy [172]. A low energy (∼0.3 eV) pathway for Li ion diffusion lies along the b-axis channel in the [010] direction, indicating a high Li ion mobility in this material. As the concentration of lithium increases, Li will stepwise populate all the sites, leading to a drop in the voltage for the material and a decline in the mobility of lithium [174].

Spinel-type titanium oxides, ranging from LiTi$_2$O$_4$ to Li$_4$Ti$_5$O$_12$, are both state-of-the-art subjects of negative electrode materials. The strong covalent bonds between O and Ti atoms are not only responsible for the excellent mechanical stabilities but also very crucial for the thermodynamic stability of LiTi$_2$O$_4$ compound [175]. For Li$_x$Ti$_2$O$_4$, when $x < 1/2$, solid solution behavior is found and as $x$ increases above 1, Li is thermodynamically inserted at octahedral sites 16c and can migrate between tetrahedral and octahedral sites with a low barrier. For Li$_4$Ti$_5$O$_12$, which is famous for excellent cyclability and high voltage, lithiation can be extended to the state of Li$_x$Ti$_5$O$_{12}$ and even Li$_{1/2}$Ti$_5$O$_{12}$, corresponding to the predicted intercalation potentials of 1.48 V and 0.05 V [176,177]. The zero strain property, which is induced by 1/6 replacement of Ti by Li, is of key technological importance to accommodate the lattice strain, insuring good ionic conductivity and avoiding the capacity decays [178].

As the above negative electrode materials shows, DFT calculations is meaningful for understanding the relationship between structure and properties and for searching limiting-step of rate capacities. Based on DFT calculations and experiments, the main properties of the negative electrodes are summarized in Table 2 [179].

Besides the traditional inorganic electrodes, organic materials such as organosulfur compounds [199–201], free radical compounds [202,203] and carbonyl compounds [204–206], have attracted increasing attentions in recent years due to their high theoretical capacities (usually > 400 mA h g$^{-1}$), low cost, recyclable and designable character [207,208]. DFT calculations also make contributions to this field mainly focusing on structure stability prediction, reaction mechanism explanation and electron structure calculation. For instance, through calculating the stability of radical intermediate obtained during the redox process of a certain organic materials, like 2, 5-dimethoxyl-1, 4-benzoquinone (DMBQ) [209], one can gain detailed structure information such as occupied molecular orbital (SOMO) and spin density (Fig. 11), which is helpful to understand the reaction process. Also, simply comparing the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) calculated from DFT, the quality of different organic materials can be obtained [210]. Besides, DFT calculations allow us to determine the character of the lithium binding site and predict crystal structure [211]. With fast development of organic materials, more important roles of DFT calculation will be acted in the future.

4. Conclusions

In this review, on the basis of the positive electrode and negative electrode components of rechargeable lithium batteries, we summarized the major progress obtained by DFT calculations and tried to provide an alternative view to better understand the material properties and electrochemical capability. Starting from fundamental quantum theories and input configuration, first-principles DFT computations can straightforwardly provide charge, energy and magnetism information without experimental or empirical data. Battery performance including energy density, rate capacity, cycle life and safety is directly linked with the crystal and electronic structures of the specific applied electrodes. Lithium intercalation voltage, phase stability and transformation, charge distribution, lithium diffusion kinetics can be accurately predicted, not only corresponding to the experimental results but also yielding deep insights to the mechanisms. The ever-growing challenge of energy storage and conversion increases the demand of new rechargeable battery electrode materials. With the help of advanced theory and computational techniques, effective design and deep exploration of battery materials can be accelerated. It has become an obvious tendency that future development of functional electrode materials is under a good combination of advanced experimental and computational approaches. However, one thing should be mentioned though the calculation method shows great

![Fig. 10](image-url) Possible lithium intercalation sites in TiO$_2$-B labeled C, A1, and A2. Large spheres are oxygen atoms (red) and small spheres are Ti atoms (blue) (reproduced with permission from Ref. [172]. Copyright 2009 American Chemical Society).
advantage, it is not possible to replace experiments as the model in
calculation is still simple and the method is not fully accurate.
Therefore, we can regard DFT calculation as a useful helper for
experiments when designing new materials.

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Table 2  Summary of the properties for negative electrode materials [179].

<table>
<thead>
<tr>
<th>Negative electrode materials</th>
<th>Theoretical capacity (mA h g⁻¹)</th>
<th>Maximum lithiated structure</th>
<th>Voltage/V (vs Li/Li⁺)</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWCNT</td>
<td>1117</td>
<td>LiC₂</td>
<td>~0.25</td>
<td>Good electronic conductivity, good stability, large irreversible capacity</td>
<td>[180,181]</td>
</tr>
<tr>
<td>MWCNT</td>
<td>~</td>
<td>~</td>
<td>~0.3</td>
<td>Smaller irreversible capacity, high Coulomb's efficiency, low capacity</td>
<td>[181]</td>
</tr>
<tr>
<td>Graphene</td>
<td>744</td>
<td>LiC₃</td>
<td>~0.5</td>
<td>Good stability, nice electronic conductivity</td>
<td>[182]</td>
</tr>
<tr>
<td>Metallic materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>4200</td>
<td>Li₂Si₅</td>
<td>~0.4</td>
<td>xM + yLi⁺ + ye⁻ ⇌ MₓLᵧ</td>
<td>[183–187]</td>
</tr>
<tr>
<td>Sn</td>
<td>994</td>
<td>Li₂Sn₃</td>
<td>~0.6</td>
<td>High capacity, poor cycling performance, poor rate performance</td>
<td>[187]</td>
</tr>
<tr>
<td>Ge</td>
<td>1600</td>
<td>Li₂Ge₅</td>
<td>~0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>993</td>
<td>LiAl</td>
<td>~0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiSi</td>
<td>1180</td>
<td>~</td>
<td>~&lt;1.0</td>
<td>MₓN + yLi⁺ → xM + LiₓN</td>
<td>[188]</td>
</tr>
<tr>
<td>Cu₂Sb</td>
<td>290</td>
<td>~</td>
<td>~0.8</td>
<td>Better cycling performance than metal, lower capacity</td>
<td>[189]</td>
</tr>
<tr>
<td>Titanium oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂-B</td>
<td>335</td>
<td>LiTiO₂-B</td>
<td>~1.6</td>
<td>High potential, low capacity, ordinary cycling performance</td>
<td>[190]</td>
</tr>
<tr>
<td>Li₄Ti₅O₁₂</td>
<td>175</td>
<td>Li₄Ti₅O₁₂</td>
<td>~1.6</td>
<td>High potential, low capacity, excellent cycling performance</td>
<td>[191]</td>
</tr>
<tr>
<td>Li₂Ti₂O₄</td>
<td>161</td>
<td>Li₂Ti₂O₄</td>
<td>~1.3</td>
<td>MX + Li⁺ + e⁻ ⇌ LiₓM + Liᵧ²⁺</td>
<td>[193,194]</td>
</tr>
<tr>
<td>Converted type materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoO</td>
<td>710</td>
<td>~</td>
<td>~1.8</td>
<td>High capacity, poor kinetics, low power density</td>
<td>[195,196]</td>
</tr>
<tr>
<td>FeO</td>
<td>700</td>
<td>~</td>
<td>~1.6</td>
<td></td>
<td>[197]</td>
</tr>
<tr>
<td>VₓFᵧ</td>
<td>745</td>
<td>~</td>
<td>~1.9</td>
<td></td>
<td>[198]</td>
</tr>
<tr>
<td>TiFₓ</td>
<td>767</td>
<td>~</td>
<td>~1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiPₓ</td>
<td>900</td>
<td>~</td>
<td>~0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FePₓ</td>
<td>720</td>
<td>~</td>
<td>~0.6</td>
<td></td>
<td></td>
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</tbody>
</table>

Fig. 11  Optimized structures of the anion radical state of DMBQ, its SOMO, and spin density distribution. Computation was performed at the unrestricted B3LYP/6-31+G(d) level with a polarizable continuum model to reflect polar solvent effects. Oxygen, carbon, and hydrogen atoms are shown in red, gray, and white, respectively (reproduced with permission from Ref. [209], Copyright 2010 Elsevier B.V. All rights reserved).
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