Density Functional Theory

First Principles Based Atomistic Modeling of Lithium Ion Battery

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ABSTRACT

The present article reports a review on the key materials used for making lithium ion battery. Five decades of research findings confirm that first principle based density functional theory (DFT) and classical molecular (CMD) dynamics simulations can play a decisive role for screening and design of cathodes, anodes and electrolyes. DFT and CMD simulations in conjunction with machine learning will further boost in the identification and design of next generation battery which will not be confined to only lithium but to sodium, calcium, zinc and others ions and thus offers ample scope for future research.

Specific energy density and volumetric energy density illustrates that Li-ion batteries are ahead of most other battery types

KEYWORDS: Energy density, Power density, Battery, Sulfur, Cycling, Electrode

Introduction

Lithium, the lightest metal, has many technological applications but one of the most commendables is as a constituent of high energy-density rechargeable Li-ion battery which was understandably awarded with Noble prize in 2019[1]. The need of rechargeable lithium-ion battery is further increased to reduce the global warming due to CO₂ generated from the burning of fossil fuels as well as to the large-scale implementation of intermittent renewable energy conversion devices like wind turbines and photovoltaics. Li metal may become even more important in large batteries for powering all-electric and hybrid vehicles which will generate huge requirement for this metal. The concept of intercalation electrodes was first discovered by Whittingham in the 1970s, who invented the first rechargeable Li-ion battery (LIB) using a Li-Al anode and titanium disulfide cathode[2] and further extended using lithium cobalt oxide as a cathode by Goodenough in 1980[3]. Subsequently, a prototype LIB was developed by Yoshino in 1985 based on the findings of Whittingham, Goodenough and Yazami[4] followed by a commercial LIB by a team led by Nishi in 1991. LIBs are commonly used for portable electronics and electric vehicles and are increasing in popularity for military and aerospace applications.

The chemistry, performance, safety and cost vary across different types of LIBs. Handheld electronics mostly use Li ion polymer batteries, LiCoO₂ cathode, and a graphite anode, which together offer a high energy density[5]. LiFePO₄, LiMn₂O₄ spinel, or Li₂MnO₃ based Li rich layered materials, LMR-NMC, and LiNiMnCoO₂ or NMC may offer longer lives and may have improved rate capability and are widely used for electric tools, medical equipment, and many others.

Working Principle of LIB

A LIB works on an advanced principle where Li ions are used as a key charge carriers (Fig.1). Li atoms in the anode are

ionized and separated from their electrons during discharge of the battery. The Li ions move from anode and pass through the electrolyte to reach the cathode, where they recombine with electrons and become electrically neutral.

Li ions are small enough to be able to move through a micro-permeable separator between cathode and anode and thus LIBs are capable of displaying a very high voltage and charge storage per unit mass and unit volume. LIBs can use a number of different materials as electrodes and typically ether as an electrolyte. LIBs have many advantages over nickel-cadmium (Ni-Cd) or nickel-metal-hydride (NiMH) rechargable battery (Fig.2) and most prominent is the highest energy density (100-265 Wh/kg or 250-670 Wh/L) than any other battery. Also, LIB can deliver up to 3.6 V, 3 times higher than that of Ni-Cd or Ni-MH and can generate high current for high-power applications with relatively low maintenance. LIBs are not affected by memory effect, a detrimental process where repeated discharge/charge normally cause a battery to



Fig.1: Schematic of Li-ion battery.

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Fig.2: Specific energy density and volumetric energy density illustrates that Li-ion batteries are ahead of most other battery types.

'remember' a lower capacity and thus offers an advantage over both Ni-Cd and Ni-MH. LIBs also have low self-discharge rate of ~ 1.5-2% per month and easier to dispose than Ni-Cd batteries due to non-presence of toxic Cd. Owing to these advantages, LIBs not only have become the market leader in portable electronic over Ni-Cd batteries but are also used for some aerospace applications, notable in the new and more environmental friendly Boeing 787, where weight is a significant cost factor. From a clean energy perspective, much of the promise of Li-ion technology comes from their potential applications in battery-powered cars. Now, the best selling electric cars, Nissan Leaf and Tesla Model S, both use LIBs as primary fuel source.

The major research topics for LIBs include extending lifetime, increasing energy density and charging speed, improving safety, and reducing cost[6]. Extensive research are being carried out in the area of non-flammable electrolytes to avoid the flammability and volatility of the organic solvents used in the typical electrolyte that comprise aqueous LIBs, solid electrolytes, polymer electrolytes, ionic liquids, and heavily fluorinated systems.

Extensive experiments were performed and are being performed to have a superior battery than the existing one. First-principles simulations were also performed to understand the structural, dynamical and thermodynamical behaviour of various constituents of the LIB.

Key Battery Properties from Simulations

Atomistic simulations can be used to simulate the structures and properties of less understood battery materials, offering deep insight into fundamental processes that are otherwise difficult to access, such as ion diffusion and electronic structure effects. Simulations can also predict the state of charge, state of health, and cycle life of batteries, coupled with experimental measurements for real-time evaluation of battery performance. This provides a precise quantitative assessment about absolute limits for performance, such as the remaining useful life, optimal fast charging rate, and risk of short circuits/premature failures, etc. The voltage[7], band gap[8], diffusivity[9] and ionic conductivity[10] are the major properties that are likely to decide the best battery materials and hence are used to screen the components of LIB.

Computational Protocols

Theoretical and computational modeling enables us to fundamentally understand the chemistry and physics of the components of the lithium ion battery. Primarily, atomistic models based on DFT[11], molecular dynamics (MD)[12] and continuum models[13] are being applied. These models can be used to study a wide variety of battery processes occurring at different length and time scales, including Li ion diffusion, dendrite growth, solid electrolyte interphase (SEI) formation/ growth and phase separation. In this article, we discuss atomistic view of Li ion battery using DFT and MD simulations.

First-principles calculations have proven to be quite successful in predicting and elucidating qualitative trends and behavior of materials and in some cases have been able to predict chemical and physical properties to a high degree of accuracy. The multi-electron Schrodinger equation and the associated electronic wave functions of a collection of atoms provide the basic properties such as the equilibrium structure and total energy. DFT is the most widely studied approach for solving the multi-electron Schrodinger equation[14].

The electron density, for any molecular system, is a function of only three spatial coordinates (for a given set of nuclear positions). The first Hohenberg and Kohn (H-K) theorem states that the ground state energy of an N-electron system in an external potential v(r) is a unique functional of its ground state electron density $\rho(r)$.

 $\rho(r_1) = N$

$$\int |\Psi(\vec{x}_{1},\vec{x}_{2},...,\vec{x}_{N};\vec{R}_{1},...,\vec{R}_{Nn})|^{2} d\sigma_{1} d\vec{x}_{2}...d\vec{x}_{N}$$
(1)

The integral of the density over all space equals N. The total energy can be written as

$$\mathsf{E}[\rho] = \mathsf{T}[\rho] + \mathsf{V}_{ee}[\rho] + \int \rho(\vec{r}) V(\vec{r}) d\vec{r}$$
(2)

In 1965, Kohn and Sham formulated an indirect way of evaluating the kinetic energy functional thus making the DFT an efficient method for carrying out rigorous calculations. The KS method relies on the introduction of a fictitious reference system of non-interacting electrons that is constructed to have the same electron density as the system of interest. These electrons must move in a complex potential that takes into account the actual forms of electron correlation and the difference between kinetic energy functional of the reference system and the real system. The reference system of fictitious non-interacting particles has a rigorous solution in terms of single electron wave functions, or molecular orbitals (K-S orbitals). One can express the kinetic energy exactly for the reference system as the sum of the expectation value of the Laplacian for each "electron".

$$T_{\rm s}[\rho_{\rm s}] = -\frac{1}{2} \sum_{i=1}^{N} < x_{i} |\nabla_{j}^{2}| x_{j} >$$
(3)

Provided that the density of the real system,

$$\rho = \rho_{\rm s} \Sigma \Sigma | x_j (\vec{r}, \sigma) |^2$$

Then, the energy functional of the real system is written as:

$$E[\rho] = T_{s}[\rho] + J[\rho] + V_{nn}[\rho] + Exc[\rho]$$
⁽⁴⁾

with exchange corelation energy,

$$\mathsf{E}_{xc}[\rho] = \mathsf{T}[\rho] + \mathsf{T}_{s}[\rho] + \mathsf{E}_{ee}[\rho] - \mathsf{J}[\rho]$$
(5)

The exchange-correlation energy includes the error in the kinetic energy, the correlation effects, and also the correction for the self-interaction of the electron that has been included

research and development

in the classical Coulomb integral (J). The main challenge in implementing DFT is to find a good approximation to $E_{m}[\rho]$. There are various approximations to calculate E_{vc}[p], such as Local Density Approximation (LDA), Generalized Gradient Approximation (GGA) and hybrid functionals[15]. The wellknown limitation of LDA and GGA functionals is that they significantly underestimate redox potentials due to the incomplete cancellation of electron self-interaction errors[16]. Hence, accurate calculations of the voltages of transition metal oxide electrodes are usually performed using the Hubbard U extension to DFT, where the U parameter is determined either self-consistently or by fitting to experimental oxidation energies[17]. Heyd-Scuseria-Erzern (HSE) functional was reported to generate acceptable redox potentials without variable parameters, although at higher computational cost[18].

Components of Battery: Present Status

Cathode Materials

Extensive atomistic simulations were carried out by Ceder group on electrode materials[19], specially on cathode. They reported intercalation voltage for LiCoO₂, LiNiO₂, LiTiO₂, LiVO₂, LiMnO₂ and LiZnO₂ compounds and concluded that metal cation, anion, and structure affect the intercalation voltage which in turn influence the ultimate voltage considerably. Later, the calculations were extended to various lithium-metal oxides, sulfides, and selenides. Further, few compounds were identified by replacing non-transition metals with transition metals based on the understanding that oxygen, rather than transition-metal ions, functions as the electron acceptor upon incorporation of Li ion as observed in Li(Co,Al)O₂, where the cell voltage was reported to be increased while decreasing both the density of the material and its cost due to replacement of Al. They have shown by ab-initio calculations that Li ion diffusion in layered Li,CoO₂ occurs via a divacancy mechanism. Ceder et al further demonstrated that LDA/GGA methods were not suitable for the determination of density of states and band gap in LiFePO₄ and LiMnPO₄ and recommended for use of GGA+U instead. Similarly, the Li ion intercalation potential of LiNiPO₄, LiMnSiO₄, LiFeSiO₄, LiCoSiO₄ and LiNiSiO₄ in the olivine structure, layered Li_xMO_2 (M = Co, Ni) and spinel-like $Li_{x}M_{2}O_{4}$ (M = Mn, Co) materials with GGA+U method was predicted to be more accurate than LDA/GGA methods when compared with experimental results. A highthroughput ab initio analysis of phosphates as cathode materials was screened by calculating capacity, voltage, energy density, and thermal stability using Perdew-Burke and Ernzerhof (PBE) functional with GGA. Using DFT under GGA+U approach they further showed that $Li_9M_3(P_2O_7)_3(PO_4)_2$ (M=V, Mo)



Fig.3: (a) One dimensional diffusion of Li ion in LiFePO₄ (Li:green, Fe:brown, P:silver, O:red) and (b) migration barrier for Li ion using NEB method.

could potentially generate a specific energy which is higher by 10% over LiFePO4. The performance of $\rm Li_{1.211}Mo_{0.467}Cr_{0.3}O_2$ was evaluated by studying Li ion diffusion in order to design disordered-electrode with high energy density and capacity[20]. DFT calculations were performed to explore the thermodynamics of fluorination in transition metal oxide cathodes[21] that provide higher capacity than conventional layered oxides. Starting from fundamental thermodynamics and phenomenological equations, rigorously derived theoretical relationships for key battery properties, such as voltage, capacity, ion diffusivity, and other relevant parameters were reported. The Li ion diffusion in LiFePO₄ was found to be one dimensiaonal[22] (Fig.3). The delithiation performance of disordered-rocksalt Li-Mn-V-O-F was investigated with PBE and Hubbard U correction[23] using a combination of lowvalence transition metal redox and a high-valence redox active charge compensator along with fluorine replacement for oxygen to attain high energy density, capacity and good reversibility.

The vacancy order-disorder, intercalation voltage profiles, and voltage-temperature phase diagrams of electrode materials were conducted employing linearized augmented plane wave (LAPW) method with the exchange correlation of Ceperley and Alder[24]. The Li ion migration in Li_xTiS₂ using a mixed-basis cluster expansion approach was predicted to occur between adjoining octahedral voids bypassing a nearby tetrahedral void. The diffusion barriers for Li ion were seen to be very sensitive to the local structure with lower diffusion barriers into a divacancy over an isolated Li ion vacancy[25]. The structural changes and voltages of LiMn₂O₄ spinel as a function of Li content were investigated with DFT-GGA+U[26].

DFT was used to determine the electronic, structural and electrochemical properties of $LiM_{1/2}Mn_{3/2}O_4$ (M =Ti, V, Cr, Fe, Co, Ni, and Cu)[27]. The inductive effect of different polyoxianions $(XO_4)_{e}(X = Ge, Si, Sb, As, P)$ on the Li ion deintercalation voltage of olivine-LiCo +2XO, LivV +40XO, and LivM +2XO, (M= Mn, Fe, Co, Ni within structure of Li₂FeSiO₄) was reported. Additionally, a correlation between the Li ion deintercalation voltage and the Mulliken electronegativity X at the GGA+U level was drawn which displayed a linear dependence for each structural type/redox couple[28]. Li-ion and ion-vacancy migration barriers were evaluated to elucidate the Li/Fe site-mixing during electrochemical cycling of Li₂FeSiO₄ and its effect in cell performance[29]. DFT findings on the polymorphs of Li₂FeSiO₄ and its delithiated products indicate a structural transformation from the pristine structure to cycled polymorph and confirmed that ${\sim}1.5$ Li ions could be extracted from Li₂FeSiO₄, representing two redox reactions resulting to high experimental capacity of over 200 mAh/g, recorded in experiments[30].

The doping performance, defect chemistry and Li ion migration in $\text{Li}_2\text{MnSiO}_4$ were explored by advanced modeling and has shown that the most favorable intrinsic defect type was cation anti-site defect, in which Li and Mn ions swap positions which affects the intrinsic Li ion mobility and thus the rate of recharging ability[31]. A DFT study for predictions of voltages of the Li ion intercalated LiMSO₄F and deintercalated MSO₄F systems (M = Fe, Co and Ni) and Bader's topological analysis of the electron density was also earlier reported[32].

Anode Materials

Generally, various forms of carbon or alloys were used as anode materials. For understanding anode chemistry, first principles computations were also used extensively. Typically graphite materials with a layered crystal structure made of graphene sheets were reported to be the best due to easy



Fig.4: Diffusion of Li ion within graphite anode.

intercalation with Li ion and therefore used in the batteries[4]. The thermodynamics and kinetics of Li_cC_e were investigated by dispersion corrected DFT[33] and shown that the interlayer interactions are dominated by van der Waals forces. The structural parameters for graphite intercalated Li compounds predicted with LDA were found to be well matched with the experimental results[34]. Energetic evaluation of stacking structures of Li-graphite intercalation compounds (Li-GICs) using LDA/GGA was shown to well reproduce the stability of the structures[35]. Li diffusion in a stage-1 structure of LiC₆ was investigated from first principles and transition state theory[36]. Mulliken population analysis were done to explain that the interlayer state of $\text{LiC}_{\mbox{\tiny 6}}$ contains significant amount of 2s character of Li[37]. Ab initio computations were conducted to evaluate the electronic structure of graphite and LiC_e and quantify the mechanism of Li ion diffusion (Fig.4) in highly oriented pyrolytic graphite[38].

The most common commercially used anode material for LIBs is graphite, which only has an ideal capacity of 372mAh/g limiting the energy density of the battery. To increase the capacity, Li alloys including Si, Sn, Al, Sb, Pb, In, Zn, and Ge have been considered as possible anodes owing to their low operating voltage, high volume energy density, and high theoretical capacity. Among which, the Ge-Li system has a high theoretical capacity of 1600 mAh/g by forming $Li_{22}Ge_5$ and relatively high Li ion diffusivity at room temperature[19].

Electrolytes

The electrolyte is normally an organic solvent (e.g., carbonates or ethers) comprising Li salt[39] which only allows the migration of Li^{\dagger} ions but prevents the passage of electrons. Li salts in the electrolyte is added so that individual Li ions don't have to make the complete journey from the anode to the cathode to complete the circuit. As ions are kicked out from the anode, other Li ions in the electrolyte, near the electrode surface, can easily be intercalated into the cathode. The reverse happens during recharging. The electrolyte solution must have a high ionic conductivity (at least 0.1 mS/cm with >1 mS/cm) coupled with low electronic conductivity. The electrolyte is subject to both low and high extrema in alkali chemical potential, being in contact with both cathode and anode at the same time. The nature of electrified electrode/electrolyte interfaces, i.e., the existence of any reactions, the products formed, and ionic transport across interface has been the focus of major studies.

The most common electrolytes are solutions of Li salts (LiPF_ $_{e^{1}}$, LiClO $_{_{4}}$ and Lithium bis (trifluoromethanesulfonyl) imide,

LiTFSI) in a mixture of solvents such as 1:1 ethylene carbonate (EC): dimethyl carbonate (DMC) which usually exhibit high Li⁺ ion conductivities (~1–10 mS/cm) with good electrochemical stability up to 4.5 V. The types of electrolytes can be liquid, polymers, amorphous or crystals and can be divided into two broad classes: "liquid electrolytes", which encompasses liquid and polymer, and "solid electrolytes", which encompasses amorphous and crystalline phases. First-principles computational techniques have been used heavily to the study of electrolytes.

Liquid Electrolytes

Computational studies of liquid electrolytes have focused on electrochemical stability and the reactions that occur at the electrode/electrolyte interface. The existence of strong ion-solvent interactions means that the electrochemical window of the electrolyte is not simply determined by the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for isolated components[40] although it was a frequently used approximation for high-throughput screening[41]. Explicit modeling of the Li salt and solvent mixture demands simulation boxes containing thousands of atoms. Hence, MD simulations using atomistic force fields are often used to obtain realistic liquid structures mostly for the commonly used EC/DMC solvent with or without LiPF₆ salt[42].

Recently, super-concentrated aqueous electrolyte solutions, known as the "water-in-salt" (WIS) electrolytes[43] are emerged to mitigate the solvent decomposition by controlling the free water molecules. It was shown that a LiTFSI- $(H_2O)_2$ WIS electrolyte was stable up to 3.0 V, well beyond the oxidation potential of water. DFT calculations reported that the Li₂(TFSI)(H₂O), aggregates become unstable at a much higher potential (2.9V versus Li ion) compared to an isolated TFSI anion (1.4V)[43]. Ong et al[44] investigated the electrochemical stability window for room temperature ionic liquids (RTILs) using a combination of classical MD and DFT simulations. Besides finding that explicit modeling of the RTIL structure yields much better agreement with experimentally measured electrochemical windows compared to simplified gas phase or polarizable continuum model calculations. The computed equilibrium structure of Li-TF2N system and diffusion of Li ion using molecular dynamics simulations are displayed in Fig.5.

Many computational studies have focused on poly(ethylene oxide) (PEO) and related polymers blended with Li salts, but the performance of such electrolytes are generally limited by poor low-temperature conductivity due to the unfulfilled requirement of segmental chain motion for ion transport[45].



Fig.5: (a) Snapshot of Li ion- TF_2N system that acts as electrolyte in Li ion battery and (b) Mean square displacement of Li ion using CMD.



Fig.6: Relaxed structure of a) LiGe₂(PO₄)₃ and b) LiAlGe₂(PO₄)₃.

Solid Electrolytes

Although solid electrolytes have been known for decades, they have enjoyed a resurgence of interest during the past decade with an increased emphasis on thermal safety as alkali-ion batteries move beyond consumer electronics to automotive and grid energy storage applications.

There are different types which include Li super ionic conductor (LISICON) type $Li_{14}Zn-(GeO_4)_4$ [46], perovskite-type $Li_{x}La_{2/3-x}TiO_{3}$ (LLTO)[47] and Li garnets, $Li_{x}Ln_{3}M_{2}O_{12}$ (x = 5-7, M = Te, W, Zr; Ln = lanthanides)[48]. Among sulfides, thio-LISICON LGPS family $Li_{4-x}M_{1-x}P_xS_4$ (0<x<1; M = Si, Ge, Sn)[49], and Na₃PS₄[50] and its analogues were reported. Extensive computational studies have been reported on the sulfide solid electrolyte because ionic conductivity of the sulfides tends to be higher than the oxides indicates adequate diffusion statistics can be accessed within reasonable AIMD simulation time[51]. Further, the recent explosion in the number of newly discovered crystalline sulfide superionic conductors in both Liion and Na-ion chemistries have given rise to many computationally driven discovery and optimization efforts. Among the most promising SEs to emerge in recent years is the $Li_{10}GeP_2S_{12}$ (LGPS) family of superionic conductors with ionic conductivities exceeding 10 mS/cm. Shortly after its reported discovery by Kamaya et al [49] computational works by Mo, Ong, and Ceder provided much needed insights into the diffusion mechanisms and electrochemical stability of the LGPS superionic conductor as well as potential avenues for further optimization. The high conductivity of the LGPS family, as well as $\text{Li}_7\text{P}_3\text{S}_{11}$ glass-ceramic has been attributed to their body-centered cubic-like anion framework, which allows direct hoping of Li ion between adjacent tetrahedral sites with low activation barrier. Using this design principle, Richards et al. identified a new lithium superionic conductor $Li_2Zn_{1-x}PS_4$ (x = 0-0.75) with room temperature Li^{*}-conductivity predicted to be >10 mS cm⁻¹[52]. However, the LGPS was observed to produce toxic H_2S gas when in contact with water which prompted the use of NASICON-type materials $(LiM_2(PO_4)_3)$. $LiGe_2(PO_4)_3$ and $LiAlGe_2(PO_4)_3$ are such materials and thus optimized using DFT (Fig.6).

Summary and Future Directions

First principles atomistic simulations along with simple and at the same time powerful, phenomenological models could be useful to complement experimentally measurable thermodynamic and kinetic parameters. The electrochemical processes of Li ion batteries are in general thermally activated and thus inclusion of temperature and entropy is very crucial. Therefore, any first principle-based approach that links to phenomenological models have to integrate statistical mechanics. These computational protocols have proven to be an important complement to experimental studies in gaining fundamental insights of battery materials. The properties of battery materials that can be computed from first-principles, is still incomplete. There are many phenomena where the connection between electronic structure and the macroscopic parameters is not well understood. Possibly, least understood are the atomic and electronic processes that take place at the electrode–electrolyte interfaces of Li ion batteries. Combined in situ experiments and multiscale modeling with electronic and atomic-level resolution are needed to decode the structure of the interface and associated kinetic processes.

It is known that charging and discharging of battery depends on the diffusional motion of Li ion. The Li ion with mass 6 is known to have higher diffusion than mass 7 and hence it will be of great academic and technological importance to explore the isotope effect on diffusion and ionic conductivity in Li ion battery. A critical gap remains in our ability to simulate materials with chemical accuracy at the meso-/micro-scales. This is particularly relevant to the understanding of chemical reactions and transport at the electrode-electrolyte interfaces as well as within the electrodes and electrolytes themselves. While recent developments in machine learning interatomic potentials show promise in relatively simple chemistries, methodological developments that enable universal application to complex chemistries and bonding types, especially electron transfer, are truly needed. In the development of anode side, silicon is being investigated as an anode material because it can form a 3D cage that has more capacity to absorb lithium ion.

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