Advanced analysis of battery material and effect of doping on potential of molecules.

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Abstract

Compared to common batteries, lithium-ion batteries have higher energy and power density, longer life, and more environmentally friendly; thus, it is applied to wide electronical area. However, lithium-ion batteries for cars have high capacity and huge serial-parallel numbers, which, involved with such problems as protection, robustness, consistency and cost, levies boundaries on the varied request of lithium-ion batteries in the vehicle. (Ogihara, T., 2010) The fine area in which lithium-ion batteries activate with safety and reliability requires the efficient control and administration of battery supervision system. The paper will use softwares to compute potentials of molecules and change of potential as a result of doping. The paper will show how different location of doping will affect the potential of battery. This present paper gives a summarized introduction to the structure and potential of molecule that can be used in lithium ion battery in the hope of providing some stimuli to the design and research of the battery system through the inspection of literature with practical experience.

Introduction

Lithium ion battery has gained significance in recent years due to its great potential as power sources that can lead new era for electric vehicle (EV) revolution. In materials science electrochemistry field, the Li-ion battery has been the prominent focus of research for last two decades. In current society, the Li-ion battery activates most of portable devices, including cell phone or iPad, and seem to go beyond the psychological barriers from high energy density devices usage to more demanding applications, including EVs (Gaines, L. L., & Dunn, J. B., 2014). Due to the high potential, the Li-ion field has gained high attention from researchers, it has been important to provide current and timely record of development status of Li-ion batteries. There are several prominent aspects of Li-ion batteries. Basic science behind operation of Li-ion batteries include several components, including anodes, cathodes, electrolyte solutions (Gaines, L. L., & Dunn, J. B., 2014). Therefore, it is critical to understand the characteristics of each aspect to foresee future development of Li-ion batteries. Therefore, researches should be performed to come up with molecule with higher potential.

Compared with other batteries, lithium-ion batteries are expected to be applied in several fields, especially portable electronics and EV, due to high energy and power density, long service availability, and environmental friendly characteristics (Eder, D., & Schlögl, R.,2014). Currently, one of the biggest potential market for Li-ion batteries is EV. However, Li-ion batteries for EV cause safety, durability, uniformity, and cost problems at current technology.

Potential of lithium-ion battery is directly related to its efficiency and feasibility. To understand potential of battery, here I propose possible a method to compute potential of battery, and evaluation of doped molecules. A pristine molecule will be doped in different locations and difference in potential will be calculated through softwares.

Literature Review

Previous technological revolution during last few centuries was motivated by diverse combustion reaction, which marked dawn of humanity. However, the technique required payoff: global climate change from emission of carbon dioxide. (Armand, M. & Tarascon, J., 2008) For future generation, engineers needed alternative energy resources. To avoid combustion reaction, concept of batteries that involve electrodes and electrolyte was developed. However, mechanism of battery was too simple that its development was slower than other areas of electronics in the past. (Yoshino, A., 2012) As a result, technological barriers slowed new inventions, such as electric cars and wireless communication. To avoid further slow development of energy resources, efficient approaches had to be made.

The most prominent way to increase efficiency of researches for battery is to understand currently used materials and mechanisms, provide fields for future research and create infrastructure it. (Zhang, Z., & Ramadass, P., 2012) Powering diverse range of application, batteries are current used from cars to microchips. To increase efficiency of powering and energy storage mechanisms, engineers consistently anticipate demands of users. During first generation, for example, engineers focused on creating rechargeable ability battery. As a result, the engineers developed mechanisms to increase efficiency of lead-acid battery. (Nagai, H., & Sato, M., 2016) As portable electronic industry developed, second generation of battery required high voltage capacity. As a result, researches focused on using Lithium-ion battery, which was rechargeable and stored high energy. The shift of mechanisms fulfilled demand of industry and users. (Eder, D., & Schlögl, R.,2014) Researches have been performed

to point out the focus of lithium ion battery development since first appearance of Lithium ion battery, which can store high voltage and be recharged; furthermore, the paper will understand shift of required ability and provide future research field of Lithium ion battery.

Before invention of lithium-ion battery, researchers attempted to convert metallic lithium battery into rechargeable metallic lithium battery. However, precipitation of lithium on the negative electrode during charging process and high chemical reactivity of metallic lithium inhibited commercialization of it. Therefore, nonaqueous electrolyte was used to provide rechargeable characteristic of battery while meeting emerging need for smaller and lighter power source for portable electronics. (Gaines, L. L., & Dunn, J. B., 2014) As a result, energy density of battery increased by twice. However, the energy density cannot compensate the energy requirement for new technologies, such as electric vehicle. Therefore, deeper understanding of lithium ion battery is required.

The best way to understand efficiency of battery is use of DFT. B3LYP and PBE0 are approaches of hybrid functionals that is a class of approximation to exchange-correlation energy functional in DFT, density functional theory. The hybrid functionals advance total energy approximation with electronic density and individual electronic wavefunctions to compute total energy. It has advantage of accurately computing true total energy by including nearly exact expression for exchange component.

Internal energy represents energy that is contained within the system, excluding kinetic energy. Enthalpy represents sum of internal energy of system and product of pressure and volume. Gibb's free energy represents thermodynamic potential which is used to compute maximum reversible work at a constant temperature and pressure.

Throughout this paper, method to compute B3LYP, PBE0, internal energy, enthalphy, Gibb's free energy, and solvation energy will be presented, and with the method, molecule will be evaluated to show doping effect on the values. Therefore, the topics involved in the paper are (1) comparison of pristine and doped molecule (2) and molecules doped on different locations.

Approved Work Plan

Low Target:
Experiment #1: Data analysis completed and model completion by Oct 2017.

Experiment #2: Experiment on model's charge capacity by Jan 2018.
Experiment #3: Development of efficient model and modification by Feb 2018

Ideal Target:
Experiment #1: Data analysis completed and model completion by Sep 2017.
Experiment #2: Experiment on model's charge capacity by Dec 2017.
Experiment #3: Development of efficient model and modification by Jan 2018

High Target:
Experiment #1: Data analysis completed and model completion by Sep 2017.
Experiment #2: Experiment on model's charge capacity by Dec 2017.
Experiment #3: Development of efficient model and modification by Jan 2018
Experiment #4: Development of molecule based on combined models by Mar 2018

Material/Method

Softwares that were used throughout the researches include Terminal, Cerius2, Maestro, and Jaguar. Terminal can be used for diverse purposes, such as logging into different server, make directory, move into or out of the directory, see files in the directory, and move, rename, copy, or remove file. Cerius2 draws molecule and save drawings in .bgf and .msi files. Maestro receives .bgf files from that was drawn from Cerius2 and converts it into input file for simulation. Jaguar receives file from Maestro and runs simulation with .in file.

To draw molecules with Cerius2, 3D sketcher is required. During the sketch, hydrogens should be attached at the end. After drawing molecules, "Clean" button gives better view. After drawing molecules, "off methods" and minimizer were clicked. After clicking "off methods" and minimizer, energy minimization was clicked. After completing procedure, the sketch file was saved in both .bgf and .msi files.

The molecule sketch was imported into Maestro. Maestro can be turned on by typing maestro in terminal. By clicking "project" tab and pressing "import structure", .bgf file from Cerius2 could be imported. After importing the sketch file, proper values for spin multiplicity and charge were inserted. The file should be saved into .in file by clicking write. After saving file into .in file, maestro should be turned off, and using Terminal, the saved file should be found. By typing 'nedit (filename)', file can be opened. After opening the file, input commands should be edited with specific commands (Table 1,2). As well as the input commands, multiplicity and molecular charge should be properly determined. After file from Maestro is edited, Jaguar can run the simulation for it with command 'jaguar run (InputFileName).in'.

Result will be shown in .out file.

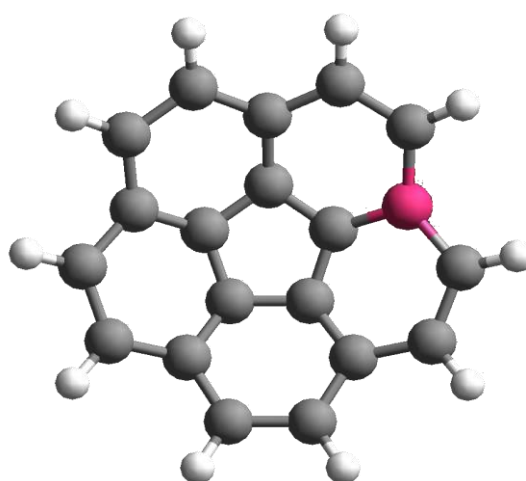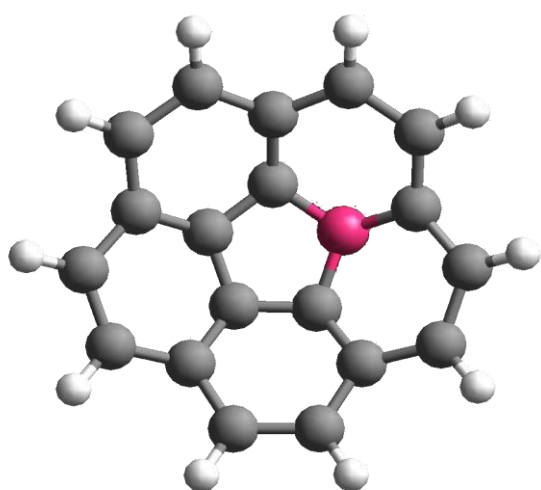Table 1. Input commands for Neutral molecule.

B3LYP – GO	PBE0 – GO	PBE0 – Solvation	PBE0 -Thermo
maxitg=250	maxitg=250	maxitg=250	maxitg=250
basis=6-31G**	basis=6-31g**+	basis=6-31g**+	basis=6-31g**+
gdftgrad=-14	gdftgrad=-14	gdftgrad=-14	gdftgrad=-14
maxit=250	maxit=250	maxit=250	maxit=250
gdftmed=-14	gdftmed=-14	gdftmed=-14	gdftmed=-14
igeopt=1	igeopt=1	**igeopt=0**	**igeopt=0**
mulken=1	mulken=1	mulken=1	mulken=1
gdftfine=-14	gdftfine=-14	iuhf=0	gdftfine=-14
dftname=B3LYP	dftname=pbe0	gdftfine=-14	dftname=pbe0
nops=1	nops=1	dftname=pbe0	nops=1
molchg=0	molchg=0	nops=1	iuhf=0
iuhf=0	iuhf=0	molchg=0	molchg=0
multip=Varies	**multip=Varies**	**multip=Varies**	**multip=Varies**
		epsout=16.14	**ifreq=-1**
		radprb=2.5124034	**tmpini=258.15**
		isolv=2	**ntemp=10**

Table 2. Input commands for Anion molecule.

B3LYP – GO	PBE0 – GO	PBE0 – Solvation	PBE0 – Thermo
maxitg=250	maxitg=250	maxitg=250	maxitg=250
basis=6-31G**	basis=6-31g**+	basis=6-31g**+	basis=6-31g**+
gdftgrad=-14	gdftgrad=-14	gdftgrad=-14	gdftgrad=-14
maxit=250	maxit=250	maxit=250	maxit=250
gdftmed=-14	gdftmed=-14	gdftmed=-14	gdftmed=-14
igeopt=1	igeopt=1	**igeopt=0**	**igeopt=0**
multip=Varies	**multip=Varies**	**multip=Varies**	**multip=Varies**
molchg=-1	molchg=-1	molchg=-1	molchg=-1
mulken=1	mulken=1	mulken=1	mulken=1

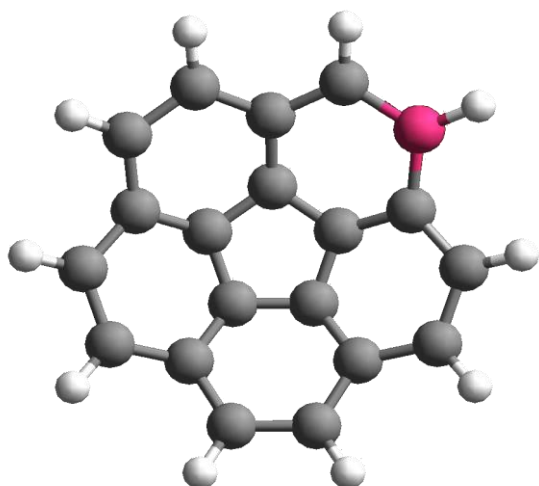|			
gdftfine=-14	gdftfine=-14	gdftfine=-14	gdftfine=-14
dftname=B3LYP	dftname=pbe0	dftname=pbe0	dftname=pbe0
nops=1	nops=1	nops=1	nops=1
iuhf=0	iuhf=0	iuhf=0	ifreq=-1
		epsout=16.14	nops=1
		radprb=2.5124034	**tmpini=258.15**
		isolv=2	**ntemp=10**
			iuhf=0

Result

Figure 1. Three types of corannulene doped with boron. Boron could be doped in one of the three positions (a,b,c). Gray molecules represent carbon, white molecules represent hydrogens, and red molecules represent boron.

Using Cerius2, corannulene doped with boron in 3 positions were sketched. Once sketched, the file went through method described in Material and Method section. The results were shown in Table 4, 5, and 7.

In Table 3, B3LYP, PBEO, thermo energy, solvation energy for both neutral and anion pristine corannulene are demonstrated. While multiplicity of neutral pristine corannulene is 1, B3LYP and PBEO values resulted in -768.163 and -767.297 hartrees respectively. Internal thermo energy, enthalpy and Gibb's free energy resulted in -767.036, -767.035, and -767.083 hartrees respectively. For pristine corannulene anion, B3LYP, PBEO, internal thermos energy, enthalphy, and Gibb's free energy resulted in -768.169, -767.318, -767.059, -767.058, and -767.107 hartrees, respectively.

For neutral corannulene doped with boron near center (Table 4), B3LYP, PBEO, internal thermos energy, enthalphy, and Gibb's free energy resulted in -754.886, -754.022, -753.765, -753.764, and -753.822 hartrees, respectively. For anion corannulene doped with boron near center, B3LYP, PBEO, internal thermos energy, enthalphy, and Gibb's free energy resulted in -754.969, -754.123, -753.867, -753.862, and -753.911 hartrees, respectively.

For neutral corannulene doped with boron between center and edge (Table 5), B3LYP, PBEO, internal thermos energy, enthalphy, and Gibb's free energy resulted in -754.872, -754.008, -753.750, -753.749, and -753.798 hartrees, respectively. For anion corannulene doped

with boron between center and edge, B3LYP, PBEO, internal thermos energy, enthalphy, and Gibb's free energy resulted in -754.967, -754.119, -753.862, -753.861, and -753.909 hartrees, respectively.

For neutral corannulene doped with boron near edge (Table 6), B3LYP, PBEO, internal thermos energy, enthalphy, and Gibb's free energy resulted in -754.858, -753.993, -753.736, -753.735, and -753.783 hartrees, respectively. For anion corannulene doped with boron near edge, B3LYP, PBEO, internal thermos energy, enthalphy, and Gibb's free energy resulted in -754.938, -754.091, -753.834, -753.833, and -753.881 hartrees, respectively.

Table 3. B3LYP, PBEO, Solvation Energy, and Thermo Energy of neutral and anion pristine corannulene.

corannulene	pristine	NEUTRAL	B3LYP	-768.16326462159	1
			PBEO	-767.29676030472	1
			Thermo	-767.03607500000	Internal(hartrees)
				-767.03513100000	Enthalpy(hartrees)
				-767.08298500000	Gibb's(hartrees)
			Solvation	-0.00970280000	Hartress
				-6.08860000000	kcal/kmol
		ANION	B3LYP	-768.16920792482	2
			PBEO	-767.31826308683	2
			Thermo	-767.05904700000	Internal(hartrees)
				-767.05810300000	Enthalpy(hartrees)
				-767.10687100000	Gibb's(hartrees)
			Solvation	-0.06987550000	Hartress
				-43.84750000000	kcal/kmol

Table 4. B3LYP, PBEO, Solvation Energy, and Thermo Energy of neutral and anion corannulene doped with boron near center.

corannulene	1boron_1	NEUTRAL	B3LYP	-754.88632612070	2
			PBEO	-754.02191864953	2
			Thermo	-753.76518300000	Internal(hartrees)
				-753.76375900000	Enthalpy(hartrees)
				-753.81299300000	Gibb's(hartrees)
			Solvation	-0.00871130000	Hartress
				-5.46920000000	kcal/kmol
		ANION	B3LYP	-754.96880794915	1
			PBEO	-754.12331055880	1
			Thermo	-753.86710900000	Internal(hartrees)
				-753.86276200000	Enthalpy(hartrees)
				-753.91127600000	Gibb's(hartrees)
			Solvation	-0.07292210000	Hartress
				-45.75460000000	kcal/kmol

Table 5. B3LYP, PBEO, Solvation Energy, and Thermo Energy of neutral and anion corannulene doped with boron at carbon between edge and center.

corannulene	1boron_2	NEUTRAL	B3LYP	-754.87197009726	2
			PBEO	-754.00790360015	2
			Thermo	-753.74981700000	Internal(hartrees)
				-753.74887300000	Enthalpy(hartrees)
				-753.79805600000	Gibb's(hartrees)
			Solvation	-0.00917120000	Hartress
				-5.75500000000	kcal/kmol
		ANION	B3LYP	-754.96694796283	1
			PBEO	-754.11907292498	1
			Thermo	-753.86180700000	Internal(hartrees)
				-753.86086300000	Enthalpy(hartrees)
				-753.90944700000	Gibb's(hartrees)
			Solvation	-0.07077900000	Hartress
				-44.41450000000	kcal/kmol

Table 6. B3LYP, PBEO, Solvation Energy, and Thermo Energy of neutral and anion corannulene doped with boron at the edge of molecules.

corannulene	1boron_3	NEUTRAL	B3LYP	-754.85755354196	2
			PBEO	-753.99308520075	2
			Thermo	-753.73585000000	Internal(hartrees)
				-753.73490600000	Enthalpy(hartrees)
				-753.78369700000	Gibb's(hartrees)
			Solvation	-0.00934800000	Hartress
				-5.86590000000	kcal/kmol
		ANION	B3LYP	-754.93825919179	1
			PBEO	-754.09051211415	1
			Thermo	-753.83403900000	Internal(hartrees)
				-753.83309500000	Enthalpy(hartrees)
				-753.88128200000	Gibb's(hartrees)
			Solvation	-0.06955200000	Hartress
				-43.64450000000	kcal/kmol

Discussion

The result from Table 3 to 6, showed that there are variances in potential of molecules due to existence and different location of doped boron and different location of doped boron. Pristine neutral and anion corannulene showed lower value of B3LYP, PBEO and thermo energy compared 3 different corannulene doped with a boron. However except for anion corannulene doped with boron at edge of molecule, pristine anion corannulene showed higher value of solvation energy compared to two other anion corannulene doped with boron in different locations. The result shows the effect of doped boron on pristine molecule. It shows how the energy status can change due to intervention of different molecules. Interesting fact is that location of doped boron could bring different results. Doped molecule doesn't always show lower value of energy status. Interesting fact is that the anion corannulene doped with boron at edge of molecule still showed higher value of solvation energy compared to pristine anion corannulene while anion corannule doped in either near center or between center and edge showed lower value. Therefore, there must be effect of different doping location of boron. The future study should aim to observe the difference that can be brought by intervention of

molecule on different location to understand mechanism of dopping.

Despite the computation was made based on software, to convince the efficiency of the software, comparison with actual potential was made. When compared to real potential that was measured through actual experiment, the computational approach showed similar results with previous studies. Therefore, it can be concluded that the approach can also be made to perform experiments on different molecules as well.

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