

Materials Design of Lithium Ion Rechargeable Battery by Quantum Chemical Calculation - Review and Search of Carbon Cluster Models -

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In order to develop higher performance lithium ion rechargeable battery, it is necessary to reveal structures and mechanism of lithium absorption or intercalation into carbon electrode. However, it's quite difficult to experimentally solve those structures and mechanisms, because carbon materials are amorphous clusters. We investigated structures and mechanisms of lithium absorption or intercalation into carbon clusters using *ab initio* molecular orbital calculation. As a result of calculations on the previous carbon model by Yamabe et al¹ and our modified models consisting of more than 100 carbon atoms, we found a suitable carbon cluster structure, and succeeded in the materials design of carbon electrode of lithium ion rechargeable battery.

Key words: Lithium ion rechargeable battery, carbon cluster, *ab initio*, materials design

Introduction

Recently high performance rechargeable battery for electric machinery, movable communicator and, electric automobiles is in great demand. This high performance rechargeable battery intensively requires high capacity, high output voltage, good reversibility and long cycle life. In order to develop higher performance lithium ion rechargeable battery, it is necessary to reveal an optimum structure of Li-doped carbon materials and Li absorption/intercalation mechanism into carbon electrode. However, it's quite difficult to experimentally make clear those structures and mechanisms, because carbon materials are amorphous clusters. Therefore, we have investigated suitable structures and Li absorption/intercalation mechanism into carbon clusters with MO calculations, aiming at the carbon material design of high performance lithium ion rechargeable battery. Using the *ab initio* calculations, we examined Yamabe's result on ovalene as a carbon cluster model with the modified neglect of diatomic overlap method¹. We also calculated orbital energy levels on some modified carbon cluster models consisting of more than 100 carbon atoms.

Computational Methods

The calculations using Q-Chem Ver.1.2² and Gaussian 94 Rev.D.4³ were carried out on IBM RS/6000 SP2 and SGI Origin 2000. In order to apply bigger carbon cluster molecules as possible, 3-21G⁴ as a basis

set was selected.

As a geometry of our modified carbon cluster models, all the C-C bonds were fixed as 1.415Å, and all the bond angle as 120°⁵. In order to make the circumstances like graphite, all terminal carbon atoms were free from hydrogen atoms. In addition, free terminated carbon models simplified and clarified the intercalation between lithium ion and carbon clusters. This modified model without terminal hydrogen caps kept closed shell structures because of even spins. This enabled all models to use the restricted Hartree-Fock levels. Total charges were controlled to a closed shell structure in a modified carbon cluster model with lithium atoms.

To review Yamabe's results, we used ovalene as the same model structure, too. The geometry of ovalene was fixed with D_{2h} symmetry, all the C-C and C-H bonds were fixed as 1.40Å and 1.08Å, respectively, and the entire bond angles as 120°. Besides, ovalene without terminal hydrogen caps was changed into same structural data of modified carbon clusters.

With regards to the basis set superposition error, Q-Chem can not handle the counterpoise correction method⁶ as same as Gaussian 94. Therefore, we adopted the asymptotic limitation method⁷, which made

it the reference point that the value of the first derivative got approximately zero except the minimum point in a potential curve. Though the total amount of calculation increases to obtain the reference point, this method made the basis set superposition error minimized.

To decide the value of asymptotic limitation, we compared Q-Chem and Gaussian 94 by using $C_6+Li(+)$ model, as shown in Figure 1(a). The optimized distance (2.25Å) and the depth (15.73 kcal \cdot mol $^{-1}$) in the potential curve with Q-Chem agreed with them by Gaussian 94. The value of asymptotic limitation was 8Å. Next the optimized distance and depth $C_{24}+Li^+$ model as shown in Figure 1(b) were 2.02Å and 23.67 kcal \cdot mol $^{-1}$, respectively. This value of asymptotic limitation was 8Å. The value of asymptotic limitation we used decided on 8Å.

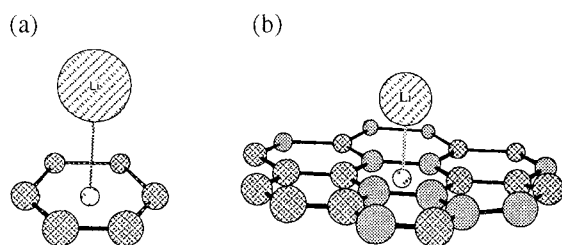


Figure 1 (a) C_6-Li^+ model and (b) $C_{24}-Li^+$ model

Results and Discussion

(1) Review of Yamabe's Model

Yamabe et al adopted ovalene as a model compound of the carbon materials in lithium ion rechargeable battery to obtain the properties and intercalation between lithium and carbon skeleton with MNDO calculations¹. They accomplished RHF calculations, since the model compounds including even Li atoms had even spins. As interesting results, they published energetically favorable configuration, different movement of Li-doped model, difference between intercalation and absorption models as a function of interlayer distance of two sheets, and their proposed absorption model doping even Li atoms. We had two questions to their results. The one was total charge or total spins in the calculated system. Another was the reason why the distance between ovalene and lithium atom was fixed at 2.00 Å. These were not mentioned minutely in their report. Moreover we needed more accurate value than MNDO calculation results in order to design high performance rechargeable battery using hard carbon as a cathode material. To treat correctly interaction between ovalene and naked Li atoms^{8,9,10} in this study, we selected RHF/3-21G of a double zeta

function.

First, six absorption configurations of two Li-doped ovalene systems were carried out, as shown in Figure 2. Because their treatment of Li state was not clear, we assumed two type of Li state: neutral state (a spin-up method is the treatment that total charge in this system is 0.) and ion state (a charge-up method is the treatment that total charge in this system is +2.). In any case, there was not a problem about RHF calculation because of even spins. Moreover, these calculations were performed by a single point calculation and the net charge of Li atoms was obtained from Mulliken's population analysis.

Table 1 indicated some difference between Yamabe's and our results, especially in the case of (b) acene-edge site, (c) bond-over site, (d) atom-over site, and (e) phenanthrene-edge site. The relative energy and optimized distance also were changed. The previous net charge of Li atoms were completely ionized. In our study, Li atoms were not always completely ionized. Though it was difficult to compare these results simply and easily, we thought these caused the difference of each calculation method and the correct treatment of the naked Li. Moreover, we supposed that total charge in Yamabe's calculation might be +2 from result of (f) coplanar site.

From calculated results of a neutral and an ion state for Li, lithium as a neutral state shifted an electron from itself to ovalene. On the other hand, lithium as an ion state received a little electron from ovalene. We thought these results indicated two Li ion states: Li^+ and $Li^{\delta+}$.

Secondly we calculated two states of six modified models without all terminal hydrogen caps as same as some cases of the above Li-doped ovalene, as shown in Figure 3. There were two reasons for removing all terminal hydrogen caps in models. The one was necessities for all cases and increment of calculated quantities for removing partially hydrogen caps in models. The another was that the hard carbon we targeted had no hydrogen from elementary analysis.

From calculated results as shown in Table 2, these results were different from the above-maintained results. Although the ring-over site became the relative minimum energy in case of the terminated hydrogen caps models, the reference point of the modified models was shifted accordingly to Li states. The minimum energy configurations were (b) acene-edge site as a neutral state and (f) coplanar site as an ion state, respectively. We thought that the change of minimum energy models directly affected aspects of orbitals in modified ovalene, especially edges positions in the model.

Furthermore there was not big difference between Li charges of models with and without terminal hydrogen caps. Our calculated results of Li charges

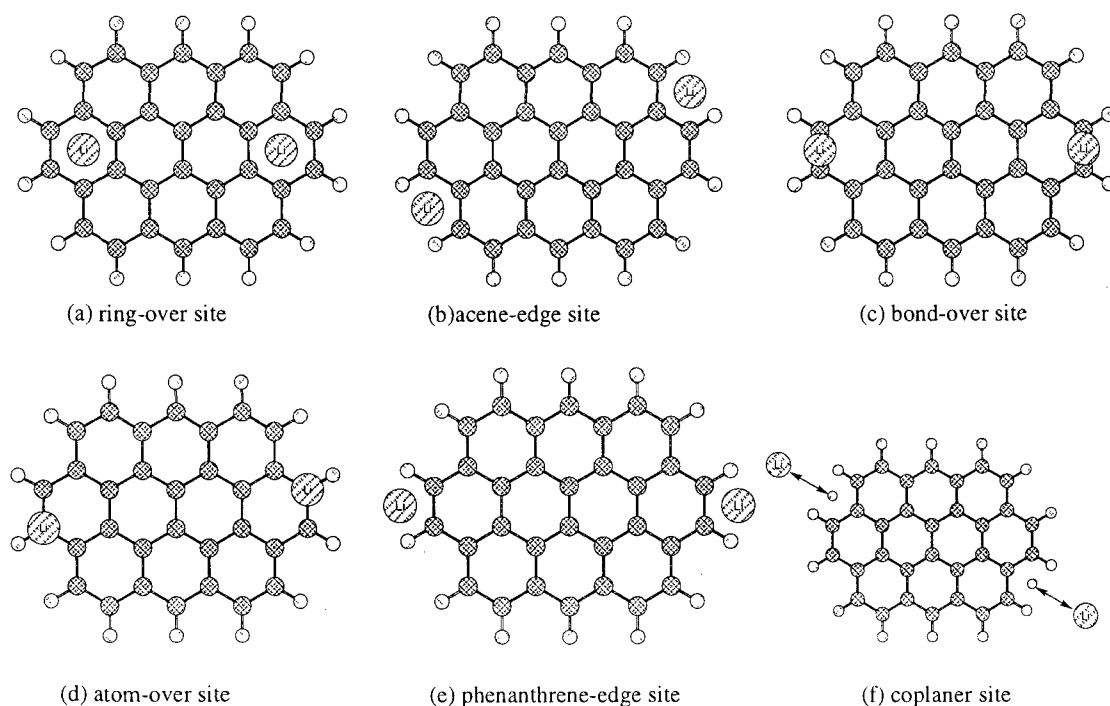


Figure 2 Configurations of two Li doped ovalene systems. Li atoms are located over (a) center of benzene (ring-over site), (b) acene-edge (acene-edge site), (c) C-C bond (bond over site), (d) C atoms (atom-over site), (e) phenanthrene-edge (phenanthrene-edge site). In configuration (f), the Li atoms are located on the same plane with ovalene (coplanar site).

Table 1 Calculated results for configurations of two Li doped ovalene systems

Location of Li atoms	Relative Energy (eV)	Relative Energy (kcal/mol)	Optimized Distance (Angstrom)	Li Charge
(a) Ring-over site	0.000	0.000	1.867	1.05
	0.000	0.000	1.80	0.79
	0.000	0.000	1.94	0.84
(b) Acene-edge site	0.701	16.165	1.713	1.00
	1.401	32.306	1.79	0.55
	0.845	19.490	1.94	0.84
(c) Bond-over site	1.005	23.176	2.023	0.98
	1.166	26.889	2.19	0.47
	0.464	10.706	2.20	0.84
(d) Atom-over site	1.046	24.121	2.017	0.98
	1.203	27.733	2.16	0.49
	0.561	12.930	2.20	0.85
(e) Phenanthrene-edge site	1.908	43.999	1.801	0.97
	1.882	43.393	2.38	0.08
	1.213	27.979	2.00	0.84
(f) Coplanar site	2.790	64.338	1.441*	1.03
	none	none	none*	none
	2.785	64.232	2.05*	0.90

Upper / Middle / Lower : Yamabe's results / Spin-up method / Charge-up method

The reference points of the relative energy were the lowest energy of each state.

*The starting position was shifted from the edge carbon to a dummy atom. The distance between the edge carbon and the dummy atoms is 1.40 Å

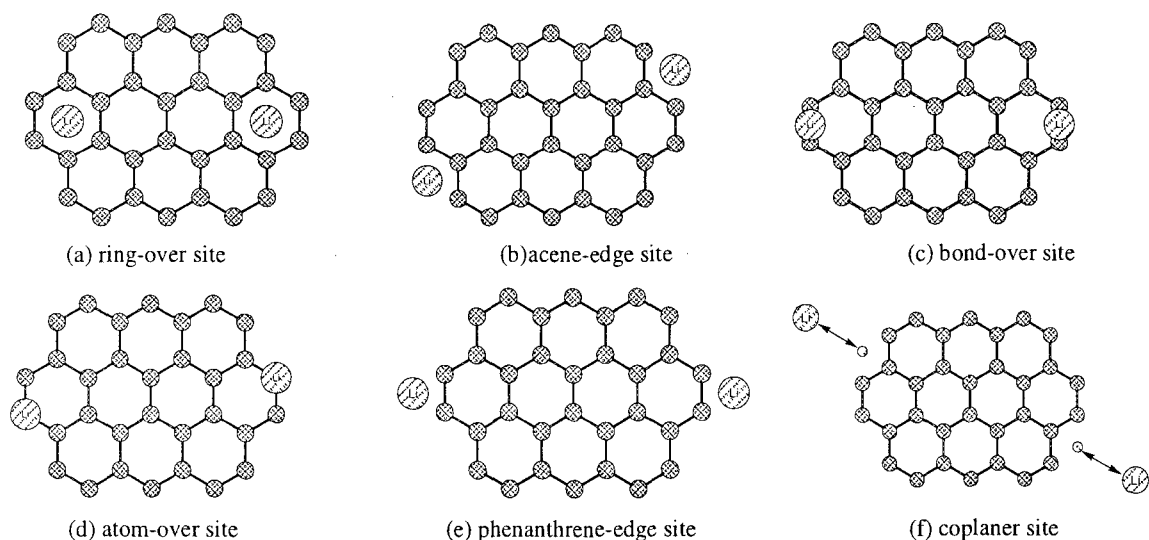


Figure 3 Configurations of two Li doped modified ovalene systems. Li atoms are located over (a) center of benzene (ring-over site), (b) acene-edge (acene-edge site), (c) C-C bond (bond over site), (d) C atoms (atom-over site), (e) phenanthrene-edge (phenanthrene-edge site). In configuration (f), the Li atoms are located on the same plane with ovalene (coplanar site).

Table 2 Calculated results for configurations of two Li doped modified ovalene systems without all terminal hydrogen caps

Location of Li atoms	Relative Energy (eV)	Relative Energy (k cal/mol)	Optimized Distance (Angstrom)	Li Charge
(a) Ring-over site	0.480	11.074	1.87	0.73
	1.784	41.142	2.08	0.82
(b) Acene-edge site	0.000	0.000	1.62	0.65
	0.836	19.271	1.84	0.79
(c) Bond-over site	0.972	22.412	2.08	0.68
	1.378	31.786	2.31	0.80
(d) Atom-over site	1.025	23.626	2.08	0.70
	1.300	29.979	2.26	0.80
(e) Phenanthrene-edge site	1.084	25.005	1.58	0.59
	1.078	24.861	2.03	0.78
(f) Coplanar site	1.640	37.808	1.03*	0.56
	0.000	0.000	1.16*	0.78

Upper / Lower : Spin-up method / Charge-up method

The reference points of the relative energy were the lowest energy of each state.

*The starting position was shifted from the edge carbon to a dummy atom. The distance between the edge carbon and the dummy atoms is 1.415Å

indicated not completely ionized states but completely ionized state. The two Li ion states in models without terminated hydrogen caps were as same as those models with terminated hydrogen caps. When the interaction between lithium and ovalene appeared strongly, lithium as an ion state received electron from ovalene, and lithium as a neutral state released electron to ovalene. So lithium looked like a carrier of electron shift. This fact is that the movement of lithium caused electron shift

to generate electromotive force as a battery.

(2) Survey of suitable carbon cluster material model

To miniaturize battery sizes and maintain high performance, carbon structures in carbon electrode also must be optimized. Within 252 carbon atoms which Q-Chem could perform on our computational resource, we searched the most suitable carbon material model for Li and Li⁺ to use orbital energy of

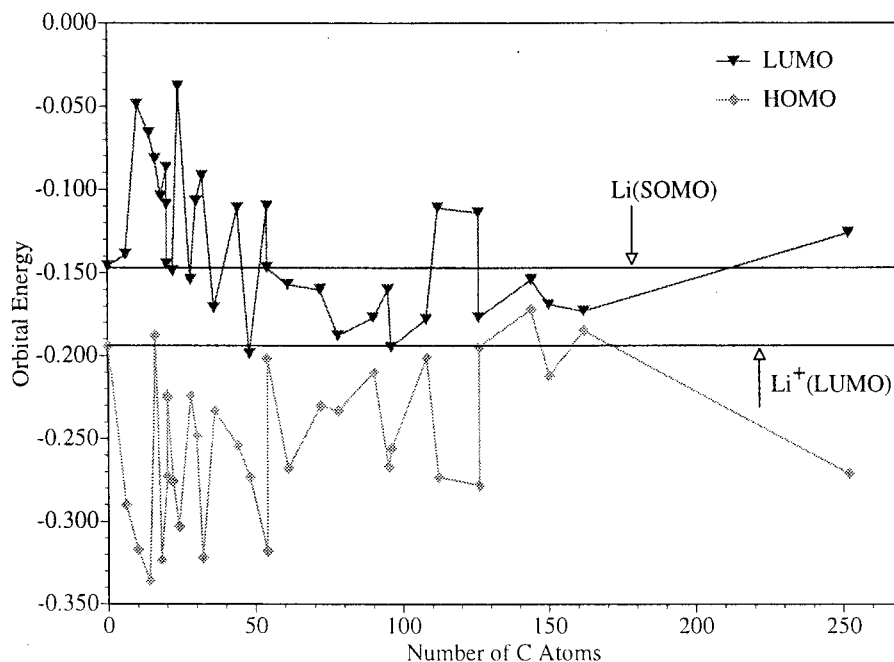


Figure 4 The relationship between number of carbon atoms and orbital energy of HOMO and LUMO

HOMO/LUMO as a maker. The most suitable carbon model got the minimum of energy loss, when electron transferred from Li to Li^+ via a carbon cluster in case of discharging or from Li^+ to Li in case of charging. So the suitable cluster model must have the values of orbital energies between -0.146 a.u. as SOMO of Li and -0.194 a.u. as LUMO of Li^+ . The relationship between number of carbon atoms and orbital energy of HOMO/LUMO that each proposed model has was shown in Figure 4.

This result showed that the smallest compound within the particular orbital energy was pyrene of 16 carbon atoms. The next compound was pentacene of 22 carbon atoms. However, these compounds belonged to no more than one of both orbital energies within the particular scope. That is to say, this calculation suggested that to bring in high efficiency should be combined with these small unit structures. It is impossible to use the combination of pyrene with pentacene because it is very difficult to manufacture hard carbon cathode in fact.

We wanted to look around a unit structure within the specific ranges for Li and Li^+ . As the result of searching bigger carbon clusters, the suitable carbon structure for the specific range was found beyond 120 carbon atoms. This supposed that there was a possibility that the most suitable minimum unit structure existed.

Conclusions

Our results were summarized up to the following four points.

(1) Our calculated results of ovalene as a model

compound of the carbon materials in lithium ion rechargeable battery showed that the Li ion state had two states; Li^+ and $\text{Li}^{\delta+}$.

(2) As the result of searching bigger carbon clusters, the suitable carbon structure for the specific range was found beyond 120 carbon atoms. This supposed that there was a possibility that the most suitable minimum unit structure existed.

Now we continue to study the most suitable minimum unit structure for the materials design of carbon electrode of high performance lithium ion rechargeable and detailed absorption/intercalation mechanisms.

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