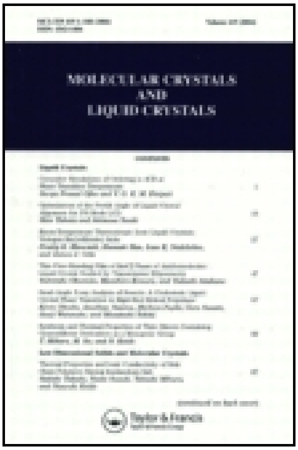

Molecular Crystals and Liquid Crystals

Molecular Orbital Calculations For The Effect Of Atom-Substitutions Into Disordered Carbons On Their Electronic And Li-Adsorption Properties

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MOLECULAR ORBITAL CALCULATIONS FOR THE EFFECT OF ATOM-SUBSTITUTIONS INTO DISORDERED CARBONS ON THEIR ELECTRONIC AND Li-ADSORPTION PROPERTIES

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We investigated the stable structures, electronic and Li-adsorption properties of $C_{54}H_{18}$ *and its substituted sheets* $X_2C_{52}H_{18}$ *(X = B, N, Si, P, S, Al and F) by a semiempirical molecular orbital method. The* $F_2C_{52}H_{18}$ *sheet was found to have a unique structure and adsorb more Li atoms than the other sheets. This result suggests that the F-substitution into disordered carbons may increase the Li-storage in disordered carbons.*

Keywords: molecular orbital calculations; substituted carbons; electronic properties; Li adsorptions; Li ion batteries; anode materials

INTRODUCTION

Recently, the application field of rechargeable lithium (Li) ion batteries has been extended rapidly, so that it becomes more important to develop anode materials, which can store a large amount of Li ions. New types of carbon materials have been developed for promising anode materials in rechargeable Li ion batteries. For example, the substitution of other atoms into carbon materials has been put in practice to modify the electronic properties and improve the capacity of the anode material in Li ion batteries. In particular, boron-substituted carbons produced by chemical vapor

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deposition method indicate large Li storage compared to a pristine carbon anode [1,2], although the maximum ratio of boron substitutions in carbons is a few atomic %. Sasaki and coworkers [3,4] obtained BCN ceramic alloys having a large amount of boron (B:C:N = 2:4:1) from borane-heterocyclic compounds. It is expected that these alloys can store more Li ions than the boron-substituted carbons.

In our previous studies [5,6], we investigated the change in Li-adsorption energy of disordered carbons induced by boron, nitrogen, silicon, phosphorus and sulfur substitutions, by using a semiempirical molecular orbital (MO) method. These investigations clarified that the boron-substitution into disordered carbons creates an electron acceptor level in a lower energy region than that calculated for pristine disordered carbons. This lower-lying acceptor-level can receive electrons from the adsorbed Li atoms more easily, so that the Li-adsorption energy for the boron-substituted disordered carbon is much larger than that for the pristine carbon. Our calculated result is consistent with the experimental result that boron-substituted carbons can store more Li ions than a pristine carbon anode [1,2]. In the present study, we investigated the stable structures, electronic and Li-adsorption properties of aluminium- and fluorine-substituted carbons, and attempted to clarify the effect of atom-substitutions on their electronic and Li-adsorption properties and to propose a substituted carbon material that would store more Li ions.

METHOD OF CALCULATION

We employed circum-coronene ($C_{54}H_{18}$) as a model cluster for disordered carbons and performed semiempirical MO calculations based on MNDO-*d* (modified neglect of differential overlap) [7] method, which includes *d*-orbitals for S, P, Si, Al atoms. The MO program MOPAC97 [8] was used.

RESULTS AND DISCUSSION

Structures and Electronic Properties of $X_2C_{52}H_{18}$ (X = Al and F) Sheets

We first optimized the structures for the five types of $AlC_{53}H_{18}$ with one Al-substitution, and the most stable structure was obtained from the comparison of heats of formation. Based on this stable structure, we replaced one more C atom by Al and optimized the structure. The same calculations were performed repeatedly for all possible substitutions, so that the most stable structure of $Al_2C_{52}H_{18}$ was obtained from the comparison of heats of formation. Figures 1(a) and 1(b) show the most stable structures of

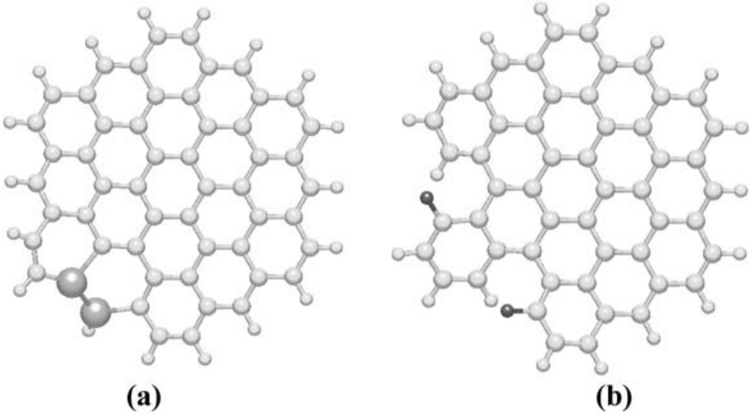

FIGURE 1 Most stable isomers of (a) $Al_2C_{52}H_{18}$ and (b) $F_2C_{52}H_{18}$.

$Al_2C_{52}H_{18}$ and $F_2C_{52}H_{18}$, respectively. The isomers with substitutions of carbons at the periphery of the sheet were found to be at least 10 kcal/mol more stable than the other isomers with substitutions of inner carbon atoms. The structure of $Al_2C_{52}H_{18}$ (Fig. 1(a)) is similar to those obtained for $X_2C_{52}H_{18}$ (X = B, N, Si, P, S)[5], whereas that of $F_2C_{52}H_{18}$ (Fig. 1(b)) is remarkably different. When the carbons of the periphery of $C_{52}H_{18}$ sheet are substituted by F atoms, the hexagonal rings at the periphery break to create the C-F and C-H bonds at the edge of sheet. It is noted that this unique structure is found only for $F_2C_{52}H_{18}$ and that this structure can produce unique electronic and Li-adsorption properties.

The atomic charges estimated by Mulliken's population analysis are 0.53, 0.37 (Al), −0.24, −0.26, −0.27 (neighboring C) and −0.26 (neighboring H) for $Al_2C_{52}H_{18}$; −0.18 (F), 0.16, 0.17 (C) and 0.06 (H) for $F_2C_{52}H_{18}$. Therefore, there is a large charge transfer from Al to the neighboring C and H atoms, whereas the charge transfer between F and C in $F_2C_{52}H_{18}$ is small and comparable to those in $N_2C_{52}H_{18}$: the atomic charge of N is −0.26 [5].

Energy levels of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital), and the adsorption energies for two Li addition on $C_{54}H_{18}$ and its substituted sheets $X_2C_{52}H_{18}$ (X = B, N, Si, P, S, Al and F) are listed in Table 1. The adsorption energy is defined as a decrease in heats of formation induced by adsorption of two Li atoms. Table 1 indicates that $B_2C_{52}H_{18}$ and $Al_2C_{52}H_{18}$ have large Li-adsorption energies, whereas $F_2C_{52}H_{18}$ has very small one. The LUMO of $Al_2C_{52}H_{18}$ is distributed around the substituted atoms, and its HOMO and the LUMO and HOMO of $F_2C_{52}H_{18}$ are not. Because LUMO accepts the 2s electrons of Li atom and stabilizes it, Li may be adsorbed around the Al atoms.

TABLE 1 Energy Levels of HOMO and LUMO, Adsorption Energies of Two Li Addition on $C_{54}H_{18}$ and $X_2C_{52}H_{18}$ (X = B, N, Si, P, S, Al and F)

	HOMO (eV)	LUMO (eV)	Adsorption energy (kcal/mol)
$C_{54}H_{18}$	−7.46	−1.74	29
$B_2C_{52}H_{18}$	−7.35	−2.51	77
$N_2C_{52}H_{18}$	−6.64	−1.83	39
$S_2C_{52}H_{18}$	−6.72	−1.78	44
$P_2C_{52}H_{18}$	−7.29	−2.02	49
$Si_2C_{52}H_{18}$	−7.00	−1.78	38
$Al_2C_{52}H_{18}$	−7.28	−1.88	70
$F_2C_{52}H_{18}$	−7.25	−2.09	10

Li Adsorption on $X_2C_{52}H_{18}$ (X = Al and F) Sheets

To clarify the effect of substitutions on the Li-adsorption properties of $C_{54}H_{18}$, we employed a model cluster composed of one $C_{54}H_{18}$ or its substituted sheet plus Li atoms and analyzed the stable structures and electronic properties. We considered only one sheet, because the lattice images of transmission electron microscopy on disordered carbons did not show the layered structure [9]. At first, we put two Li atoms above the center of hexagonal rings of the sheet at the 2.0 Å distance as an initial condition: there are 19 sites for putting Li atoms. For all possible sites, the structures of model clusters were fully optimized, and the most stable Li sites on the sheets were determined by the comparison of the heats of formation. For $Al_2C_{52}H_{18}$ (Fig. 2(a)), the two Li atoms are stabilized near the Al atoms, where the LUMO is distributed. This structure is similar to that for

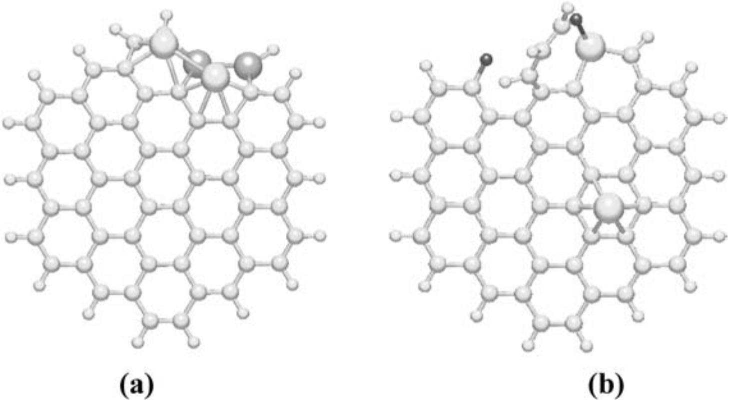
(a) (b)

FIGURE 2 Two Li adsorption sites on (a) $Al_2C_{52}H_{18}$ and (b) $F_2C_{52}H_{18}$.

$B_2C_{52}H_{18}$ [5]. The distances between Li atoms and their neighboring C and Al atoms are 1.98–2.37 (Li-C) and 2.52–3.04 Å (Li-Al), respectively. On the other hand, the Li-adsorption on $F_2C_{52}H_{18}$ is remarkably different from those on the other substituted sheets as shown in Figure 2(b). One Li atom is adsorbed in a normal way (the Li-C distance is 2.24–2.38 Å), whereas the other Li atom pushes out the F atom to be stabilized in the sheet: $F_2LiC_{52}H_{18}$. The action of the second Li atom may lead the small Li-adsorption energy of $F_2C_{52}H_{18}$.

In order to elucidate how many Li atoms can be adsorbed on these sheets and how this number is influenced by atom-substitutions, we finally investigated the change in stable structure and Li-adsorption energy by increasing the number of adsorbed Li atoms two by two, because an odd number of Li atoms makes open-shell electronic states that are difficult to analyze. Figure 3 shows the dependence of Li-adsorption energy on the number of adsorbed Li atoms for $C_{54}H_{18}$ and its substituted sheets $X_2C_{52}H_{18}$ (X = B, Si, Al and F). The results for N-, P- and S-substituted sheets are similar to that for $C_{54}H_{18}$. The most remarkable feature in Figure 3 is that the Li-adsorption energy on $F_2C_{52}H_{18}$ increases gradually to the 12-Li adsorption, whereas the adsorption energies of $C_{54}H_{18}$ and the other substituted sheets reach a maximum at the 8-Li or 10-Li adsorption. For $C_{54}H_{18}$, 8 Li atoms are stabilized above the hexagonal rings at the periphery of the sheet; further addition of two Li atoms destabilizes the adsorbed structure, resulting in a large decrease in Li-adsorption energy at the 10-Li adsorption [5]. $B_2C_{52}H_{18}$ has a larger Li-adsorption energy, however, the energy is at a maximum for the 8-Li adsorption. Compared with

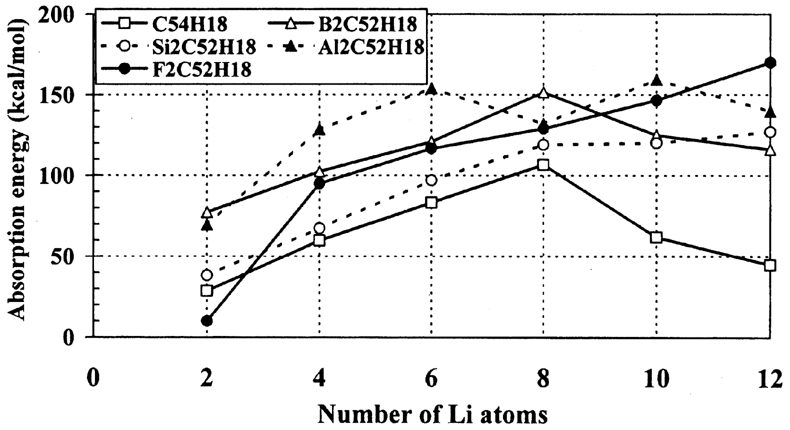

FIGURE 3 Dependence of Li-adsorption energy on the number of Li for $C_{54}H_{18}$ and $X_2C_{52}H_{18}$ (X = B, Si, Al and F).

these substituted sheets, $F_2C_{52}H_{18}$ has more desirable feature for anode materials, which can adsorb more Li ions. We thus conclude that $F_2C_{52}H_{18}$ is unique in Li-adsorption properties and can be a promising anode material of rechargeable Li-ion batteries.

To elucidate the difference in Li-adsorption process between $F_2C_{52}H_{18}$ and the other substituted sheets, we investigated the difference in the stable structures of adsorbed Li atoms on $B_2C_{52}H_{18}$ and $F_2C_{52}H_{18}$. For $B_2C_{52}H_{18}$, 8 Li atoms can adsorb on the periphery parts of the sheet, however, when 10 Li atoms are put on the sheet, one Li is 3.7 Å apart from the sheet, resulting in the decrease of Li-adsorption energy at the 10-Li adsorption. On the other hand, for $F_2C_{52}H_{18}$, 8 Li atoms make a cluster and can be adsorbed around the F-substituted part, so that all the 10 Li atoms can be stabilized within about 3 Å distance from the sheet. As a result, the adsorption energy is not reduced by the 10-Li adsorption. The situation is not changed at the 12-Li adsorption, whereas the Li cluster is broken at the 14-Li adsorption resulting the large decrease (70 kcal/mol) of Li-adsorption energy. We conclude from these results that the Li-adsorption properties on $B_2C_{52}H_{18}$ and $F_2C_{52}H_{18}$ are largely different from each other, and that $F_2C_{52}H_{18}$ can adsorb more Li atoms.

CONCLUSIONS

To elucidate the effect of atom-substitutions into disordered carbons on their electronic and Li-adsorption properties and to propose a substituted carbon material that would store a larger amount of Li ions, we investigated the stable structures, electronic and Li-adsorption properties of substituted sheets $X_2C_{52}H_{18}$ (X = B, N, Si, P, S, Al and F) by using a semiempirical molecular orbital method (MNDO-*d* [7]). The most striking finding of these investigations is that the fluorine-substituted $F_2C_{52}H_{18}$ sheet has a unique structure and can adsorb more Li atoms than $C_{54}H_{18}$ as well as the other substituted sheets $X_2C_{52}H_{18}$. Therefore, the fluorine-substitution into disordered carbons is expected to be effective for increasing Li-storage in disordered carbons and developing anode materials with a large Li-capacity.

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