DFT Study of the Effect of the Li_{20} Coating Pattern on the Volume and Band Gap of C_{20} Fullerene Cages

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Hydrogen is a promising green energy source because of its abundance in nature. Hydrogen storage materials (HSM) have thus received much attention from researchers. The most remarkable theoretical reports of the HSM involve metal atoms coated on carbon fullerenes and nanotubes.[1-5] Alkali-metal-doped C_{60} has received much attention as an HSM. Recently, the structure and electronic properties of Na_nC_{60} and Li_nC_{60} ($n \le 12$) nanoclusters in the framework of density-functional theory were reported.[2] Carbon-based nanomaterials are promising novel materials for hydrogen storage because of their surface-to-volume ratio and porosity along with other unique properties. $Li_{12}C_{60}$ and Na_8C_{60} remarkably enhance hydrogen adsorption with a gravimetric density of approximately 9 wt %.[2,6,7] Previous studies on alkali-metal-doped C_{60} nanoclusters suggested that, depending on their concentration, alkali metal atoms either homogeneously cover the surface of C_{60} or form one or more metal islets in contact with the fullerene. A characteristic example of homogeneous contact is provided by $Li_{12}C_{60}$. Li-decorated C_{60} is a candidate for hydrogen storage and has an icosahedral symmetry with each Li atom capping the 12 pentagonal sites of C_{60}.[6,7] In $Na_{12}C_{60}$, the isomer with the lowest energy was reported to be made of 3 islands of 4 atoms, which implies that for each tetramer, 3 atoms are in contact with C_{60}, 2 *via* a pentagonal ring and 1 *via* a hexagonal ring, whereas the fourth atom is capped over the other metal atoms.

Thus, we have investigated $C_{20}Li_{20}$ cage regioisomers to determine the effect of the coating pattern of alkali metals on the volume and energy band gap of the C_{20} cage. In this study, we obtained 2 cage regioisomers, $C_{20}Li_{20}$ and $Li_{12}Li_8C_{20}$, which could be interesting candidates for HSM. To our knowledge, previous studies have not analyzed the effect of the coating pattern of alkali metals on the cage volume and HOMO-LUMO energy gap of the fullerene cage. Here, we study these effects for $Li_{20}C_{20}$ and $Li_{12}Li_8C_{20}$ fullerene cages. We used the hybrid density-functional theory (DFT) with Becke's 3-parameter hybrid method and the Lee-Yang-Parr exchange-correlation functional theory (B3LYP)[8-10] to optimize the geometries of the $Li_{20}C_{20}$ regioisomers. The electron basis set 6-31G(d,p) was used in this study.[11] We fully optimized the geometries of $C_{20}Li_{20}$ without constraints, using the Gaussian 03 B.04 package suite.[12] To obtain highly accurate geometries, we used the convergence criterion with tight optimization and an ultrafine pruned (99,590) grid (using the keywords Opt = Tight, Grid = ultrafine). We analyzed the relative energies, charge transfer and the HOMO and LUMO orbitals of the regioisomers.[13]

Here, we obtained 2 optimized cluster geometries and relative energies, which are shown in Figure 1. One geometry is a homogeneous coating of Li atoms on C_{20}, which is represented by $Li_{20}C_{20}$, and the other geometry is the formation of Li tetrahedral droplets on the surface of the cage, which is represented $Li_{12}Li_8C_{20}$. Both the clusters are in the T_h point group. The total energy of the $Li_{12}Li_8C_{20}$ cage isomer is 3.61eV lower than that of $Li_{20}C_{20}$. As shown in Table 1(a), the volume of the C_{20} cage fragment in $C_{20}H_{20}$, $Li_{12}Li_8C_{20}$, and $Li_{20}C_{20}$ cages is 23.9, 9.8, and 3.9%, respectively, which is higher than the corresponding volume of C_{20}. As shown in Figure 1, the bond lengths of C-Li and
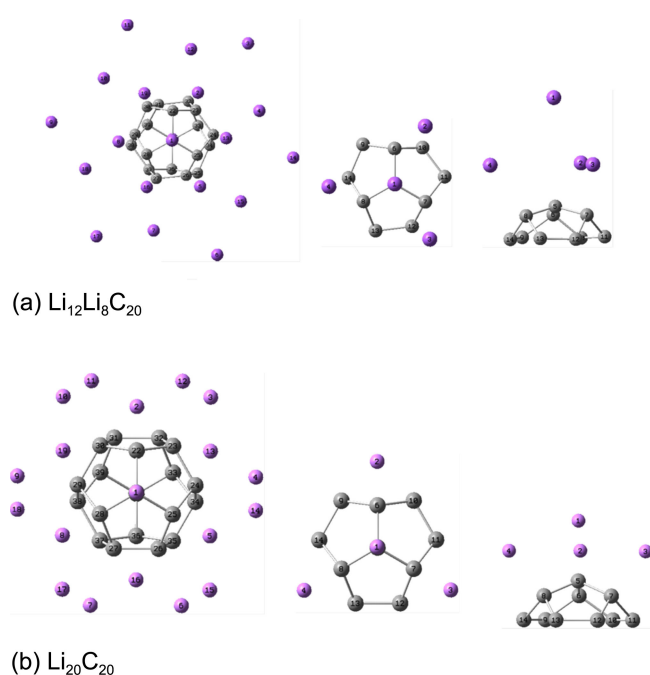

(a) $Li_{12}Li_8C_{20}$

(b) $Li_{20}C_{20}$

Figure 1. Local minimum energy structures of $C_{20}Li_{12}Li_8$ and $C_{20}Li_{20}$.

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Table 1. Properties of 2 optimized $C_{20}Li_{12}Li_8$ and $C_{20}Li_{20}$, compared with C_{20} and $C_{20}H_{20}$. (a) Volume of the C_{20} cage fragment and (b) the gap between HOMO and LUMO levels

(a) Volume of the C_{20} fragment cage

	Cage volume	Volume of C_{20} fragment over volume of C_{20} cage	% volume change compared to C_{20} cage
C_{20}	23.30	1.00	0.00
$C_{20}H_{20}$	28.85	1.24	23.85
$Li_{20}C_{20}$	25.59	1.10	9.84
$Li_{12}Li_8C_{20}$	24.20	1.04	3.88

(b) Energy gap between HOMO and LUMO energy levels (eV)

	HOMO	LUMO	E_{gap}
C_{20}	-0.18	-0.12	1.67
$C_{20}H_{20}$	-0.26	0.03	7.99
$Li_{20}C_{20}$	-0.10	-0.09	0.47
$Li_{12}Li_8C_{20}$	-0.13	-0.07	1.53

C-C in the $C_{20}Li_{20}$ cage are 1.49 and 2.16 Å, respectively, whereas those in $Li_{12}Li_8C_{20}$ are 2.11 Å for C-Li of Li_8, 1.46 Å for 2 C-C, and 1.54 Å for 1 C-C among the 3 C-C bonds around C-Li of Li_8.

As shown in Table 1(b), the HOMO-LUMO energy gap in C_{20}, $C_{20}H_{20}$, $Li_{12}Li_8C_{20}$, and $Li_{20}C_{20}$ cages was 1.67, 7.99, 0.47, and 1.53 eV, respectively. Hydrogen adducts on C_{20} increase the HOMO-LUMO gap, whereas Li adducts on C_{20} decrease the gap, which implies that the coating of both Li atoms on the C_{20} cage induces kinetic instability. Although the homogeneously coated $Li_{20}C_{20}$ is seriously and kinetically unstable, C_{20} coated with tetrahedral Li droplets is slightly unstable when compared with C_{20}. In $C_{20}H_{20}$ and $Li_{20}C_{20}$ cages, the Mulliken charges of all the H and Li atoms are the same, *i.e.*, 0.08 per atom, and those of all C atoms are -0.08 per atom, which implies that all H and Li atoms are electron donors and that the C_{20} cage is an electron acceptor. However, in $Li_{12}Li_8C_{20}$, the C_{20} cage fragment accepts -0.03 electrons per atom, whereas the Li atoms of Li_8 and Li_{12} accept −0.21 electrons per atom and donate 0.23 electrons per atom, respectively. Thus, the environment of the Li atoms in the $Li_{12}Li_8C_{20}$ cage cluster affects the electronic properties of the Li atoms, which show electron acceptor and donor properties depending on where they exist. This charge

pattern is topologically identical to that of C_{60} in contact with alkali metal clusters.[5] Therefore, owing to the particular electronic structure of Li_{20}-C_{20} cage isomers, it is expected that the investigation of hydrogen adsorption on these $Li_{12}Li_8C_{20}$ and $Li_{20}C_{20}$ cage isomers will be of particular interest.

In summary, we investigated the atomic structure and electronic properties of $C_{20}Li_{20}$ cage isomers. Two isomers were used: C_{20} homogeneously coated with Li and C_{20} coated with tetrahedral clusters of Li. Greater volume change was observed for C_{20} homogeneously coated with Li. The volume of both the isomers increased when they were compared with that of C_{20} but decreased when compared with that of $C_{20}H_{20}$. Although the HOMO-LUMO energy gap of C_{20} increased in $C_{20}H_{20}$, it decreased in both $Li_{20}C_{20}$ and $Li_{12}Li_8C_{20}$. The HOMO-LUMO gap of $Li_{12}Li_8C_{20}$ was slightly larger than that of $Li_{20}C_{20}$. The Mulliken charge of carbon atoms directly connected to Li atoms was positive in $Li_{12}Li_8C_{20}$ but negative in $C_{20}H_{20}$ and $Li_{20}C_{20}$.

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