# Quantum-chemical modelling of the fullerene-type (SiC)12 nanocluster for high-performance lithium-ion batteries

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## Abstract

The lithiation processes in fullerene-like structure Si/C nanocomposites (with 30 % of carbon amount) were investigated via quantum-chemical study. The theoretical specific capacity value of such a system is 3051 mA*H*g-1, which is very attractive for use in lithium-ion batteries. Moreover, it was shown that the charge/discharge process in the nanocomposites almost does not affect the volume changes that lead to the improvement of the anode materials characteristics based on Si/C composites. Electrodes from associative agglomerates of n(SiC)12 nanocomposites also should not have the destructive effect of volume deformations. As a result, highly stable qualitative electrochemical characteristics of such electrode materials remain and a significant increase in the number charge/discharge cycles could be observed.

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## Introduction

In recent years, tremendous interest has been focused on the usage of silicon (Si) as anode material for lithium-ion batteries (LIB). Silicon has received increasing attention because it is abundantly available, cost-effective, eco-friendly, has the highest theoretical specific capacity (4200 mA*H*g$^{-1}$) and satisfactory working potential (~0.4 V vs Li$^+$/Li).[1-3] Simultaneously, electrode materials based on Si-Li alloys suffer from the main drawback – appearance of the strong anisotropic mechanical strain at lithium/delithium process, that leads to degradation of the electrochemical system and its huge volume change resulting the shunt contact loss, irreversible capacity fast loss, low initial coulombic efficiency, i.e. decreasing in quantitative and qualitative cycling characteristics. [4-7]

Covering Si particles with carbon is one of the most effective solutions to overcome the above disadvantages. Silicon-carbon (Si/C) electrodes have a higher reversible capacity and number of charge/discharge cycles compared to the uncovered Si. [8, 9]It was found that the best performance characteristics have electrode materials with carbon content approximately 30% per mass. Such experimental data were confirmed by our previous quantum-chemical study concerning lithium/delithium process modeling using $C_mSi_{13}$ (m = 0, 6, 10, 13, 18, 26, 39, 45) model clusters. [10]

Today various methods exist for the Si/C composites synthesis and any of them provide deposition or adsorption carbon atoms or their associates on the surface of Si producing more complex fragments of carbon nanostructure. [11-13] A wide variety of carbon nanostructures (graphene, CNT, fullerenes, etc.) have been used for the synthesis of Si/C composites. [2, 14, 15] Fullerene is a good alternative for Si coating because of its high electron affinity, high chemical, and mechanical stability, which is useful for electrochemical devices. [16] Moreover, fullerene could form a thin polymeric film on Si that acts as a buffer layer to reduce the volume

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expansion and to improve the LIB kinetic properties.[17-19] In addition, fullerene could be easily modified via attaching different functional groups (carboxyl, ester, piperazine) for decreasing the Si/C composite solubility or via doping of the other elements. [20-22] Simultaneously, it is well known, that after the metal intercalation to the fullerene cage the obtained material becomes soluble in the polar organic electrolyte solution that limited the use of pure $C_{60}$ anodes. Synthesis of the fullerene-type composite material with Si-C covalent bonds could be a great alternative to solve this problem.

The quantum-chemical calculation is a powerful tool for the study of various characteristics of Si/C anode materials. A lot of different clusters via various theoretical methods have been investigated earlier.[23-26] Continuing on our previous studies[10, 27, 28] and to expand our knowledge on the role of the electronic structure of Si/C nanocomposites to the lithium/delithium process, here we explore a series of $Si_nC_m$ clusters with various atomic ratios. In total, we report diffusion of Li in the Si/C systems and volume change under lithiation via first-principle calculations.

## Methods

The quantum-chemical investigation of the electronic structure of $Si_nC_m$ clusters where $Si_{12}C_{m=0,2,4,6,8,10,12}$ has been examined via semi-empirical method PM7 (MOPAC 2012 15.077W 64ITS programe).[29] The spatial structures of clusters Sin were borrowed from [30] and have a good correlation with the most stable isomers of the Sin nanoclusters, that have been obtained by *ab initio* methods. [24, 31, 32]

The starting coordinates of lithium atoms in the $(SiC)_{12}Li_p$ nanocomposites were determined by the method of molecular mechanics using HyperChem7-MM that adequately describes whole electrostatic and non-specific interactions between the host-guest clusters. For all the nanosystems studied, the electronic structure, optimized geometric structure, atomic net charge densities ($\rho$), the energy values for the frontier molecular orbitals (highest occupied $E_{HOMO}$ and lowest unoccupied $E_{LUMO}$), and the changes in the clusters volume at the lithium/delithium process were calculated.

## Results and discussion

$Si_nC_m$ nanoclusters

Our previous observation revealed that at the sequential introduction of carbon atoms into $Si_{13}$ nanoclusters the fullerene-like structures are formed (Fig. 1). [10] Such results are in good confirmation with other works where the possibility of the existence of fullerene-like structures $Si_nC_m$ composites was proved based on quantum-chemical calculations. [23]

**Figure 1**. Structures obtained at the intercalation of the carbon atoms in $Si_{13}$ nanocluster.

To gain more insight into the $Si_nC_m$ nanocomposite structures and their properties we modeled several isomers with m=0,2,4,6,8,10,12 via the sequential introduction of two carbon atoms into the $Si_{12}$ nanocluster. The result was the stable isomer $Si_{12}C_{12}$ with four- and six-membered cycles and electron-accepting properties (Fig. 2, Table 1).

Table 1 demonstrates that the introduction of the carbon atoms to the Si matrix leads to the obtaining of the clusters with almost constant changes of volume and binding energies – (22.0 ± 2.7) [3] and (-248 ± 3) eV, respectively. The final composite has $E_{HUMO}$ = -8.867 and $E_{LUMO}$ = -2.191 eV, which indicates to a definitely electron-acceptor property of such a structure. The carbon atoms concentration riches 29.96% of the total mass, and the volume of $(SiC)_{12}$ compared to $Si_{12}$ is increased by 25.29%.

**Figure 2.** Structure of the $Si_{12}C_{m=0,2,4,6,8,10,12}$ nanocomposites.

**Table 1**. Calculated binding energies ($E_{bind}$, eV), energy values for the frontier molecular orbitals ($E_{HOMO}$ and $E_{LUMO}$, eV

Cluster

**Si $_{12}$**

**$Si_{12}$ C$_2$**

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**Si$_{12}$C$_4$**
**Si$_{12}$C$_6$**
**Si$_{12}$C$_8$**
**Si$_{12}$C$_{10}$**
**Si$_{12}$C$_{12}$**

The specific electrostatic capacity Q$_{Si/C}$ of (SiC)$_{12}$ composites is determined by the formula Q$_{Si/C}$ = $\alpha_{Si}$Q$_{Si}$ + $\alpha_c$Q$_C$ = 3051 mAh/h (where $\alpha_C$=0.3, $\alpha_{Si}$=0.7 – mole fractions and Q$_C$ = 372 and Q$_{Si}$ = 4200 mAh/h – theoretical specific capacities of carbon and silicon respectively).

**Figure 3.** Structure of the (SiC)$_{12}$Li$_p$ nanoclusters and values of the Si/C matrices.

(SiC)$_{12}$Li$_p$ nanoclusters. Charge/discharge process

Investigation of the electron density distribution showed its transferring from carbon to silicon atoms that lead to the coordination of the Li atoms near the Carbon. Analysis of the (SiC)$_{12}$Li$_p$ structures (where p = 0,12,20,24,44) and calculated volumes of the matrix V$_{SiC}$= V$_{(SiC)12Lip}$ - V$_{Lip}$ (Fig. 3) demonstrate that lithiation process almost doesn't influence on geometry (lengths of the Si-C bonds and angles of the four- and six-membered cycles) and volume of the initial (SiC)$_{12}$ cluster.

In (SiC)$_{12}$Li$_p$ composites, the electron density is transferred from lithium atoms to the silicon-carbon matrix. Moreover, the average charge on lithium atoms is +(0.8 $\pm$ 0.1) e, and the negative charge is concentrated on the Si/C matrix. Therefore, the lithiation process leads to the formation of an ionic structure [(SiC)$_{12}$$^{-[?]q}$…Li$_m$$^{+[?]q}$] where the value of $\pm$ [?]q is determined by the degree of lithium p. The discharge process completely restores the initial structure of the nanocluster (SiC)$_{12}$.

Stabilization of the volume values (it is changing within only 1%) during the charge/discharge process leads to the disappearing of mechanical strain oscillation and improving the quantitative and qualitative electrochemical characteristics of the electrode materials based on (SiC)$_{12}$ nanocomposites. The electrostatic surface potential, that includes concentrated positive and negative charges on the Si and C atoms, has both nucleophilic (near Si atoms) and electrophilic (near C atoms) regions. Consequently, due to the electrostatic interaction between Si and C atoms of two different clusters (SiC)$_{12}$, different associative agglomerates of n(SiC)$_{12}$ could be formed (Fig. 4).

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**Figure 4.** Associated agglomerates of the n(SiC)$_{12}$ nanocomposites.

It was established that in n(SiC)$_{12}$ agglomerates separate nanoclusters have a distance from each other of 3.5-4.0 Å. The increasing of (SiC)$_{12}$ amounts in n(SiC)$_{12}$ leads to the raising of both electron-donor and electron-acceptor properties of the formed agglomerates; comparison of the E$_{HOMO}$ and E$_{LUMO}$ values indicates their clearly expressed electron-acceptor nature. It should be noted that with increasing degree of aggregation (n = 2, 3, 4), the energies of n(SiC)$_{12}$ formation ([?]Ie$_n$ = Ie(n(SiS)$_{12}$) – n*Ie((SiS)$_{12}$)) is also increasing and are -0.2209 eV, -0.56215 eV and -0.95091 eV for n = 2, 3, and 4 respectively. Such results are correlated with raising of a number of interaction contacts and are controlled by the entropy factor.

The changing of E$_{LUMO}$ with increasing of the aggregation degree leads to the raising of electron affinity in the n(SiC)$_{12}$ system. It was found that at lithiation process of the dimer 2(SiC)$_{12}$ composites the new 2(SiC)$_{12}$Li$_{p=0,12,24,36,44}$ are formed, in which the positive charges are concentrated on lithium atoms (Fig. 5). At further increasing of p negative charges appear on some lithium atoms, indicating the formation of a metallic phase in the Li$_p$ subsystem.

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**Figure 5.** Structure of the lithiated dimers $2(SiC)_{12}Li_{=0,12,24,36,44}$, sum of the Li charges (in brackets) and their dependenc

## Conclusions

Possibility of the Si/C composites forming with fullerene-like structure via quantum-chemical calculations has been shown. It has been established that nanoclusters $(SiC)_{12}$ form stable associative agglomerates $n(SiC)_{12}$ that has a higher electron affinity than monomer analogs. The charge/discharge processes do not affect the volume values of the silicon-carbon matrix. Therefore, electrodes based on composites $(SiC)_{12}$ and $n(SiC)_{12}$ will not have periodic oscillation of mechanical strain and the lithiation/dilithiation process will not affect their current tap settings. As a result, highly stable qualitative electrochemical characteristics of such electrode materials remain and a significant increase in the number charge/discharge cycles will be observed. In $(SiC)_{12}$ system the carbon concentration (~ 30%) is close to the optimal for the best Si/C based electrodes that lead to the 3051 mA*H*g$^{-1}$ specific capacity value. Based on the obtained theoretical result it could be concluded that Si/C composites are a very attractive electrode material for use in lithium-ion batteries.

**Keywords:** Si/C fullerene-like nanocomposites, lithiation/delithiation process, specific volume, quantum-chemical study

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## GRAPHICAL ABSTRACT

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The quantum-chemical study shows that Si/C fullerene-like nanocomposites have improved electrochemical properties and are a great alternative as electrode material for lithium-ion batteries. The introduction of the 30 mass% of Carbon atoms in the Si matrix leads to the disappearing of the electrode volume changing.

$Si_{12}$     +12C →     $(SiC)_{12}$