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First principle investigation on structural and electronic properties of silicon oxycarbide ceramics

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Polymer-derived silicon oxycarbide (SiCO) ceramics are potential anode materials in Li battery due to large lithium capacity and little volume change during lithium insertion. In this study, first principle study is performed to investigate the structural and electronic properties of $Si_8C_xO_{16-x}$. The population analysis of Si–O and Si–C bonds demonstrate covalent character, which plays a key role in the mechanical properties of SiCO. The stronger mixing between the Si and C states indicates a stronger covalent bonding character of Si–C than Si–O bonding. The calculated electronic densities show a mixture of covalent and ionic behavior of Si–C and Si–O bonds.

1. Introduction

Li-ion batteries (LIBs) are promising chemical power sources for modern electronic devices. Graphite is used as the standard anode material for LIB, with a specific capacity of 372 $mAhg^{-1}$ [1–3], it is still necessary to seek novel anode material which has higher capacity. Polymer-derived silicon oxycarbide (SiCO) ceramics show perfect thermodynamic stability and zero creep behavior at around 1500 °C. Moreover, the volume change of SiCO ceramics is little during lithium insertion/extraction, which makes them as potential anode materials for LIBs [4]. Recent experiments show that SiCO ceramics present two or even three times larger lithium capacity than graphite. Measurements of SiCO anode give a total capacity of 1164 $mAhg^{-1}$, and a reversible capacity of 794 $mAhg^{-1}$ [4]. In order to better understand these superior properties of SiCO, further study needs to be conducted in terms of energy and electronic structure.

First principle stimulation is a widely used tool for investigating structural and electronic properties of materials, and was successfully used in the modeling and analysis of nano-crystalline silicon [5], SiCN [6], $Li_{15}Si_4$ [2], alloy and metal compound anodes such as Mg_2Si [7], CuF_2 [8], $Li_4Ti_5O_{12}$ [9] and FeF_3 [10]. The atomistic structure and formation enthalpy of amorphous SiCO were investigated by ab initio molecular dynamic simulations [11]. However, to the best of our knowledge, first principle simulation has yet to be used for investigating the properties of SiCO created by crystalline configuration. In this work, $Si_8C_xO_{16-x}$ was obtained by substituting O atoms with C atoms in β-cristobalite SiO_2, and a systematical and comparative first principles study was performed to investigate the structural and electronic properties of $Si_8C_xO_{16-x}$.

2. Model construction

The calculations were performed by CASTEP code [12,13] in Material Studio 5.5, which used the first principle calculation according to the density functional theory (DFT) ultra-soft pseudopotential method. The state of the electronic structure is described by density functional and the generalized gradient approximation (GGA) [14]. Kinetic cut-off energies for plane-wave expansion of the wave function were set at 300 eV, the number of plane waves would change to maintain the fixed cutoff energy. And 5 × 5 × 5 κ-points set with 63 irreducible k-points were used to ensure the convergence in the calculation. All the crystalline structures were fully relaxed by geometry optimization of both lattice parameters and atomic position. The geometry optimization was conducted by using the conjugate gradient method and under following conditions: residual force <0.01 eV/Å, convergence of energy change per atom <2 × 10−6 eV, stress <0.02 GPa.

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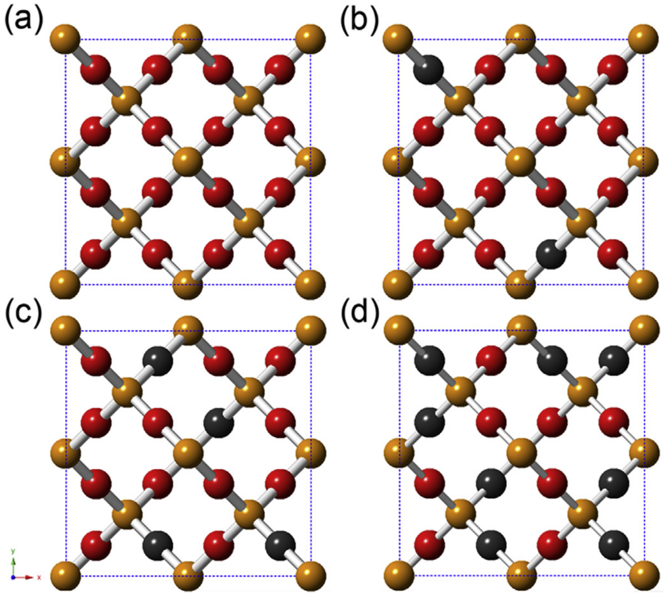

Fig. 1. Generation of crystalline SiCO structures by replacing oxygen atoms in β-cristobalite SiO_2 with carbon atoms. (a) β-cristobalite SiO_2; (b) Si_4CO_7; (c) Si_2CO_3; (d) SiCO. The yellow, red and black spheres represent silicon, oxygen and carbon atoms respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Comparison of crystal structure information of SiO_2, Si_4CO_7, Si_2CO_3 and SiCO.

	SiO_2	Si_4CO_7	Si_2CO_3	SiCO
Unit cell(Å)				
a	14.93	15.04	16.57	17.17
c	14.93	15.21	14.47	14.68
γ	90°	90°	89.8°	89.3°
Cell volume ($Å^3$)	1664	1738	1722	1680
Space group	$Fd\overline{3}m(O_h^7)$	P1(C1-1)	P1(C1-1)	P1(C1-1)
Bond distance(Å)				
Si—C (average)	–	1.75	1.75	1.85
S—O (average)	1.55	1.65	1.65	1.65
Q^* in electron				
Si	2.42	2.32	2.21	1.98
C	–	−0.99	−0.93	−0.83
O	−1.21	−1.19	−1.16	−1.15
Bulk modulus				
B (GPa)	199.1	129.1	116.5	115.8

The $Si_8C_xO_{16-x}$ structures are based on a starting structure of β-cristobalite SiO_2 which can be represented by a cubic structure with the space group of $Fd\overline{3}m(O_h^7)$, as shown in Fig. 1a. The structures of $Si_8C_xO_{16-x}$ are obtained by substituting O with C atoms in β-cristobalite-SiO_2, similar approach was also used to generate the structure of SiCN [15]. As the composition and bonding analysis experiments [16] clearly suggest the presence of mixture of Si—C and Si—O in SiCO, there exist several possible structures with low symmetry when different proportion of oxygen atoms are substituted by carbon atoms. In this work, three configurations are considered: Si_4CO_7, Si_2CO_3 and SiCO, which represent structures with different C/O ratios. For Si_4CO_7, two O atoms are substituted by C atoms in different stacking layers and generate Si—CO_3 tetrahedrons (Fig. 1b). In the models of Si_2CO_3, four O atoms in different stacking layers are replaced by C atoms, thus results in a structure with high concentration of Si—CO_3 tetrahedrons (Fig. 1c). For SiCO, eight O atoms are substituted, and create rich Si—C_2O_2 tetrahedrons (Fig. 1d). In order to improve the accuracy of calculation results, a 2 × 2 × 1 super cell that corresponds to 95 atoms was built for each case, as shown in Fig. 2. Then geometric optimization was performed to relax the atomic positions and lattice parameters.

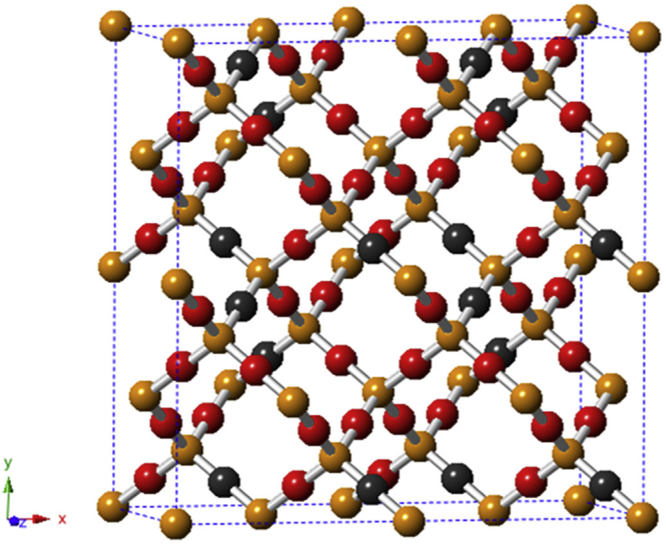

Fig. 2. A 2 × 2 × 1 super-cell of crystalline Si_2CO_3.

3. Results and discussions

3.1. Bonding mechanism

The detailed structure parameters of the four models are listed in Table 1. The primitive unit cell structure of SiO_2 before relaxation is cubic with lattice parameter of a = b = 14.32 Å and γ = 90°. The relaxed structure of Si_2CO_3 and SiCO exhibit a configuration with the angle between the unit cell vectors **a** and **b** slightly deviated from the ideal value of 90°, which is 89.8°for Si_2CO_3 and 89.3°for SiCO respectively. In order to study the bonding configuration of the structures, the effective charge for each atom is also calculated and listed in Table 1. The Si—C bond length is found to be close in ranging from 1.55 to 1.85 Å and the Si—O bond length ranges from 1.55 to 1.65 Å. The difference of the charge transfer from C or Si to O in SiCO leads to different bonding characteristic compared to SiO_2. The bulk moduli of SiCO range from 115.8 to 129.1 GPa, which is comparable to range of 97.9—110 GPa for the polysiloxane-derived SiCO glass [17,18]. With increasing ratio of C content, the O atoms show less anion like properties with less effective charge transfer, the Si atoms become less charged with the increase number of C neighboring atoms. The character of decreased covalent bonding is consistent with the calculated bulk modulus.

The Mulliken scheme based population analysis was performed according to plane wave states that generated from the used pseudopotential. The population value reflects the physical characters of structure and information on bonding properties. As shown in Table 2, the population value of Si—O bond is about 0.5 for all the four structures, and the population value of Si—C bond

Table 2
Comparison on bond population of SiO_2, Si_4CO_7, Si_2CO_3 and SiCO.

	SiO_2	Si_4CO_7	Si_2CO_3	SiCO
Si—O bond	0.53	0.52	0.51	0.52
Si—C bond	–	0.77	0.65	0.53