Applied Surface Science 292 (2014) 488–493

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Fluorine interaction with defects on graphite surface by a first-principles study

Song Wang[a,d], Xuezhi Ke[b,*], Wei Zhang[a,e], Wenbin Gong[a,d], Ping Huai[a,f], Wenqing Zhang[c], Zhiyuan Zhu[a,e]

[a] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China
[b] Department of Physics, East China Normal University, Shanghai 200062, China
[c] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
[d] Graduate University of Chinese Academy of Science, Beijing 100049, China
[e] Key Laboratory of Interfacial Physics and Technology, Chinese Academy of Sciences, Shanghai 201800, China
[f] Key Laboratory of Nuclear Radiation and Nuclear Energy Technology, Chinese Academy of Sciences, Shanghai 201800, China

ARTICLE INFO

Article history:
Received 19 July 2013
Received in revised form 1 December 2013
Accepted 1 December 2013
Available online 8 December 2013

Keywords:
Graphite
Diffusion
Reaction
First principles
Molten salt reactor
Fluorine

ABSTRACT

The interaction between fluorine atom and graphite surface has been investigated in the framework of density functional theory. Due to the consideration of molten salt reactor system, only carbon adatoms and vacancies are chemical reactive for fluorine atoms. Fluorine adsorption on carbon adatom will enhance the mobility of carbon adatom. Carbon adatom can also be removed easily from graphite surface in form of CF_2 molecule, explaining the formation mechanism of CF_2 molecule in previous experiment. For the interaction between fluorine and vacancy, we find that fluorine atoms which adsorb at vacancy can hardly escape. Both pristine surface and vacancy are impossible for fluorine to penetrate due to the high penetration barrier. We believe our result is helpful to understand the compatibility between graphite and fluorine molten salt in molten salt reactor system.

1. Introduction

As a result of the increasing consuming of energy, sustainable and renewable energy source becomes more necessary. Nuclear energy is the most important sustainable energy source in future utility. Molten salt reactor (MSR), one of the promising generation IV nuclear reactors, is liquid fuel reactor that used for producing electricity or hydrogen [1]. In this system, the flowing molten salt (LiF, BeF_2) is used as coolant, and graphite is used as neutron moderator. The compatibility of nuclear graphite with flowing molten salt is one of the technology gaps for MSR. Yang et al. [2] investigate the interaction between IG-110 nuclear graphite and molten salts (46.5 mol% LiF, 11.5 mol% NaF, and 42 mol% KF). In the experiment, a huge number of C–F bond are found in products. The behavior of graphite is not satisfactory after two days of immersion of graphite in molten salt at 500 °C [3]. Thus, the fluorine anions play a key role in this system, and it is worth studying the interaction between graphite and fluorine theoretically.

The interaction between fluorine and carbon based materials has been studied for several decades [4–10]. A large number of experiments indicate that graphite can react with fluorine and oxidizing fluorine compounds, resulting in the formation of graphite fluoride CF_x where x is from 0 to 1 depending on the reaction temperature and pressure [7,8,11]. It has been found that CF_x will decompose into gaseous product, including CF_2 molecule, in high temperature [12–14]. Fluorinated carbon nanotube can also decompose into CF_4 molecule at about 800–1200 K [15]. Lee et al. [16] and Tse et al. [17] demonstrate that the successive adsorption of fluorine atom on graphene and carbon nanotube weakens the C–C bond significantly, and eventually the bonds can be broken by pyrolysis. All these studies indicate that graphite fluoride is thermally unstable. However, based on the energetics studies, we find that graphite is stable in MSR system, which consists with the experiment of Oak Ridge National Laboratory [18,19].

This study focuses on the surface reaction in MSR system, which is quite different from previous studies [16,17]. In molten salt system, LiF is in form of Li+ and F−. While, some chemically reactive defects will interact with molten salts, resulting in the formation of F radicals on graphite. Thus, we actually study the interaction between the F radicals and graphite defects. We point out that defects, including carbon adatom and vacancy, are

---

[*] Corresponding author. Tel.: +86 21 5571113/+86 21 52711138.
E-mail address: xzke@phy.ecnu.edu.cn (K. Xuezhi).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.12.001

Table 1
Convergence tests for different graphite layers. E_{ads} and E_{adsv} are adsorption energy of fluorine atom on pristine surface and vacancy, respectively.

Layers	One layer	Two layers	Four layers
E_{ads} (eV)	−0.87	−0.88	−0.88
E_{adsv} (eV)	−3.98	−4.00	−4.00
CF group diffusion barrier (eV)	0.34	0.35	0.35

chemically reactive to fluorine in MSR. Fluorine atoms could adsorb on carbon adatom, forming CF or CF_2 group. The stable adsorption of fluorine on vacancy explains the formation of C–F bond which has been found in experiment. The high penetration barrier of fluorine atom through graphite surface consists with the experiment that fluorine ion can't penetrate graphite surface even with kinetic energy of 10 eV. Our result explains the compatibility between graphite and molten salt theoretically.

2. Methodology

In this work, all the first-principles calculations are carried out using Vienna *Ab initio* Simulation Package (VASP). Both the local density approximation (LDA) [20] and the generalized gradient approximation (GGA) [21] were used as the exchange-correlation functional in our calculations. The projector augmented wave potential method [22] is used with a plane wave basis set limited by the cutoff energy of 450 eV. The momentum space integration is performed using 2 × 2 × 1 Monkhorst–Pack [23] k-point mesh. The total energy convergence within 2.5 meV per atom was achieved compared with the more dense mesh 4 × 4 × 1 *k*-point. To see the influence of other layers on the adsorption, we have performed a convergence test by using different graphite layers as shown in Table 1. To check the convergence of the fluorine adsorption energy on pristine graphite surface (E_{ads}) and vacancy (E_{adsv}), and diffusion barrier, one-, two- and four-layer graphite surfaces were considered using LDA exchange-correlation functional. Table 1 shows that the two-layer graphite is good enough for our purpose. Thus, most graphite surfaces are modeled as a supercell composed of 5 × 5 × 1 graphite unit cell with periodic boundary condition as illustrated in Fig. 1, which is large enough to simulate the graphite and graphene supercell [24,25]. The 6 × 6 × 1 supercell is used in the study of divacancy. The vacuum slab is 13.0 Å and the second graphene layer is fixed along z direction in all the calculations. It is well-known that the LDA coincidentally yields nearly the correct interlayer spacing for the graphite, thus, the results of graphite system were calculated by using the LDA. The one-layer graphite (graphene) is also acceptable for our calculations with the convergence of 0.02 eV per fluorine, thus, all of the results computed in the GGA are obtained from the graphene. In the calculation of structural optimization, the ionic relaxation will be stopped if all the forces are smaller than 10^{-2} eV/Å. The climbing nudged elastic band (cNEB) method [26,27] is employed to calculate the reaction barrier with the force tolerance of 4×10^{-2} eV/Å. The preferential sticking of hydrogen and fluorine atoms on graphene has been studied by many groups, and the spin density is important for both fluorine and hydrogen sticking [28,29]. However, in our study, the preferential adsorption is related to the dangling bond of defects, which is much stronger than the spin effect. Thus, the spin polarization is not considered in our calculations.

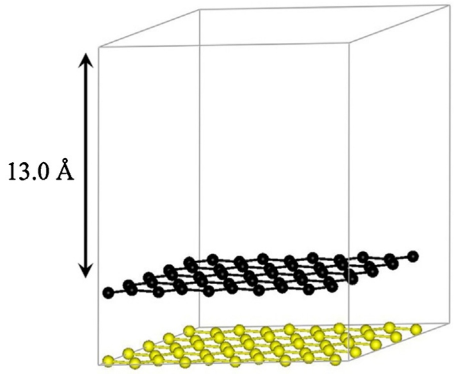

Fig. 1. Supercell model used in our simulations. Black balls are the carbon atoms that can relaxed in three directions, while, yellow balls are carbon atoms fixed in *Z*-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Interaction between fluorine atoms and carbon adatom

For the pristine graphite surface, the adsorption energy of fluorine atom on graphite surface is calculated to be −0.88 eV (−0.55 eV in the GGA) according to the following equation:

$$E_{ads} = E_{G+F} - E_G - \frac{1}{2}E_{F_2}$$

where E_{G+F}, E_G and E_{F_2} are the total energy of the graphite with fluorine adsorption, total energy of the graphite, and the total energy of an isolated F_2 molecule, respectively. Considering the existence of LiF molecule in the environment of MSR system, we also calculate the formation energy of LiF molecule with respect to Li crystal and F_2 molecule by using following equation:

$$E_{\mathrm{Formation}} = E_{\mathrm{LiF}} - E_{\mathrm{Li}} - \frac{1}{2}E_{\mathrm{F}_2}$$

The calculated formation energy for the LiF is −3.32 eV with LDA. This energy is much lower than the energy (−0.88 eV) for fluorine adsorption on the graphite, indicating that in the MSR system it is almost impossible for the fluorine to adsorb on the graphite surface.

The adsorption energy for fluorine atom on the carbon adatom is calculated according to the following equation:

$$E_{\mathrm{ads}} = E_{G+C+G} - E_{G+C} - \frac{1}{2}E_{\mathrm{F}_2}$$

where E_{G+C+F} and E_{G+C} are the total energy of graphite with the CF group adsorption and total energy of graphite with the adatom, respectively. The calculated adsorption energy is −4.00 eV (−3.61 eV in the GGA). This energy is lower than the formation energy −3.32 eV of the LiF molecule, indicating that the fluorine prefers to adsorb on the adatom forming CF group in the MSR system.

Actually, the CF group has been detected on the graphite surface [30,31] and also in the gaseous decomposition product of graphite fluoride [13]. It is interesting to see how the CF group diffuses on the surface. Due to the symmetry, the two different diffusion paths are identified for the CF group, i.e., path A and path B, denoted on the top panel of Fig. 2. In path A, the CF group diffuses to the neighboring bridge site within the same hexagon, and in path B, the CF group diffuses to the neighboring bridge site of another hexagon. The corresponding energy profile for path A and path B are shown on the bottom panel of Fig. 2. The diffusion barriers for path A and path B are 0.43 eV and 0.35 eV (0.23 and 0.18 eV in the GGA), respectively. Compared with the pure carbon adatom diffusion barrier of 0.52 eV [32] (in the GGA) these barriers are much lower. Therefore, the fluorine adsorption on the adatom can enhance the mobility of the carbon adatom.

It is also interesting to see how the CF group separates from the graphite surface. The energy profile for the separation is presented in Fig. 3. Fig. 3 shows that the energy profile for the process