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Analysis of adsorption properties of typical partial discharge gases on Ni-SWCNTs using density functional theory

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ABSTRACT

To develop novel nanomaterial for online detection and diagnosis of insulated faults in SF_6 insulated equipment, the nickel-doped single wall carbon nanotubes (Ni-SWCNTs) are proposed and its sensing capabilities for the measurement of typical decomposition products (SO_2, SOF_2 and SO_2F_2) of SF_6 insulated gas are investigated in this work. The geometric configurations of decomposition products and (8, 0) zigzag Ni-SWCNTs, and adsorption properties are studied based on the first-principle density functional theory (DFT) methods implemented in the DMol^3 package of Materials Studio. Three interaction models, single molecule, double identical molecules and double foreign molecules adsorption, have been studied to fully characterize the gas sensing mechanism under different situations. Simulation results reveal that Ni-SWCNTs have different sensitivity and selectivity to SO_2 than SOF_2 and SO_2F_2. The conductivity of Ni-SWCNTs increases in the following order: $SO_2 > SOF_2$ after SO_2 and SOF_2 adsorption. Conversely, the adsorption of SO_2F_2 onto Ni-SWCNTs slightly decreases its conductivity.

1. Introduction

SF_6 is the most widely used insulating gas in gas-insulted equipment due to its excellent insulating property, arc extinguishing performance and chemical stability [1], which has been widely applied to gas insulated switchgear (GIS), gas circuit breaker (GCB) and gas insulated transmission lines (GIL) [2–4]. However a varying degree of inevitable insulation defects generated in the production and long run process can seriously damage the insulation property of SF_6, and cause it to decompose to typical products: SO_2, SOF_2 and SO_2F_2, etc. [5,6]. With the gradual deterioration of electric insulating strength, it may eventually lead to the breakdown of insulation equipment and even paralyze the whole power supply system. Therefore, detecting the insulation status becomes indispensable in an attempt to ensure the running stability of insulation equipment. Currently, plenty of studies have demonstrated that chemiresistor-based gas sensor detection method is an effective approach to detect various types of gases [7–9]. Based on this detection method, the insulation status of SF_6-gas-insulated equipment can be monitored on-line in real time through accurately detecting the typical decomposition products of SF_6 [10–12].

Since the carbon nanotube was first found by Iijima in 1991, it has been extensively used in energy storage material, electric device and gas sensors because of its prominent mechanical, electrical, and thermal properties [13]. A number of previous studies have enhanced the gas detection sensitivity of carbon nanotube via various approaches, including the adjustment of nanomaterial morphology, surface modification and composite doping [14,15]. Previous research has also shown that the sensitivity and selectivity of carbon nanotube for gas detection can be improved by decorating various metals on the sidewall of carbon nanotube [16]. Star et al. used the Pt, Pd, Au, Rh, Sn, Mg, Fe, Co, Ni, Zn, Mo, W, V and Cr-metal-decorated SWCNTs to detect CO, NO_2, CH_4, H_2S, NH_3 and H_2 [16–18]. Current research shows that the limit of detection has even reached 3 ppb [19], 50 ppb [20] and 5 ppm [21] for NH_3, benzene and H_2S, respectively.

Although these metal-decorated carbon nanotubes provide high sensitivity and selectivity for common gas detection, there have been few reports about using it to detect the decomposition products of SF_6 in gas insulation equipment. In this paper, the nickel-doped single wall nanotubes (Ni-SWCNTs) are proposed to detect the decomposition products of SF_6 as an attempt to monitor the insulation status of SF_6 gas insulated equipment. The adsorption mechanisms between Ni-SWCNTs and the typical decomposition

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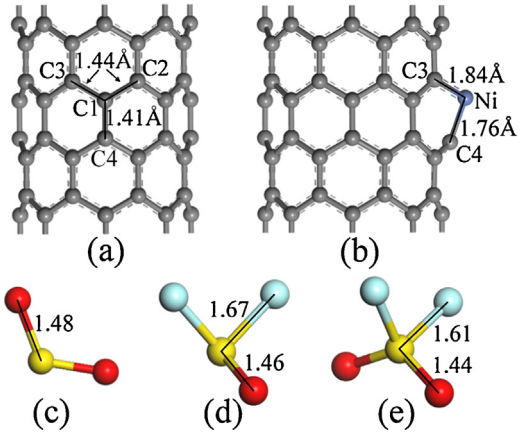

Fig. 1. Geometric structures after optimization, (a) intrinsic SWCNTs, (b) Ni-doped SWCNTs, (c) SO_2 molecule, (d) SOF_2 molecule, (e) SO_2F_2 molecule. The unit of the structural parameters is Å.

products: SO_2, SOF_2 and SO_2F_2 are analyzed by theoretical computation. The computation results show that the adsorption ability of SWCNTs is greatly enhanced by doping the nickel atoms.

2. Computation details

All calculations were performed using the DMol^3 package of Materials Studio, which is based on the density functional theory (DFT) methods [22,23] and predicts many chemical and physical properties of the atomic and molecular structure in the field of catalysts, polymers, metals and alloys. One carbon atom was substituted by a Ni atom at the side wall and then relaxed [24,25]. Simultaneously, the decomposition products SO_2, SOF_2 and SO_2F_2 were relaxed to the optimized structures, respectively. Then single and double gas molecules separately approached to various adsorption sites on the surface of Ni-SWCNTs to find the lowest energy structures. To prevent the interaction of adjacent periodic structures, the supercell established for pristine and Ni doped SWCNTs was restricted to 20 Å × 20 Å × 8.5 Å [26] in the whole calculation process. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof exchange-correlation function in DFT [27,28], and the basis set using double numerical plus polarization atomic orbitals were employed. The Brillouin-zone was performed by the Monkhorst-Pack scheme, sampled into 1 × 1 × 2 *k*-point [29]. The energy tolerance accuracy, maximum force, and displacement were set as 10^{-5} Ha, 2×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively. The established structures and test method have been validated by previous studies [30,31]. After the adsorption system was relaxed to the most stable structures, the binding distance *d* was defined as the nearest distance between the surface of Ni-SWCNTs and adsorbed gas molecules. The adsorption energy E_{ads} was used to describe the gas-surface interaction with Eq. (1), where the parameter $E_{surf/gas}$ represented the total energy of the adsorption structures, E_{surf} and E_{gas} were the energy for optimized Ni-SWCNTs and isolated gas molecules. Generally, $\triangle E_{ads} < 0$ signified that the adsorption process happens spontaneously due to the attractive interaction. Along with the interaction between Ni-SWCNTs and gas molecules, the atomic charge was redistributed. The Mulliken population analysis was implemented to evaluate the charge transfer (Q_t) displayed in Eq. (2).

$$\Delta E_{ads} = E_{surf/gas} - E_{surf} - E_{gas} \quad (1)$$

$$Q_T = Q_{absorbed\ molecule} - Q_{isolatemolecule} \quad (2)$$

Besides, the highest occupied molecular orbital (HOMO) energy level and lowest unoccupied molecular orbital (LUMO) energy level were studied to evaluate the energy needed for electrons to cross the energy barrier based on the frontier molecular orbital analysis [32]. After the adsorption, the energy gap of the adsorption structure can be calculated through the energy levels of E_{HOMO} and E_{LUMO} defined as Eq. (3).

$$Q_T = Q_{adsorbed\ molecule} - Q_{isolatemolecule} \quad (3)$$

3. Results and discussion

3.1. Geometric and electronic properties

We first studied the structure properties of pristine SWCNTs, Ni-SWCNTs, SO_2, SOF_2 and SO_2F_2 shown in Fig. 1. As an intrin-

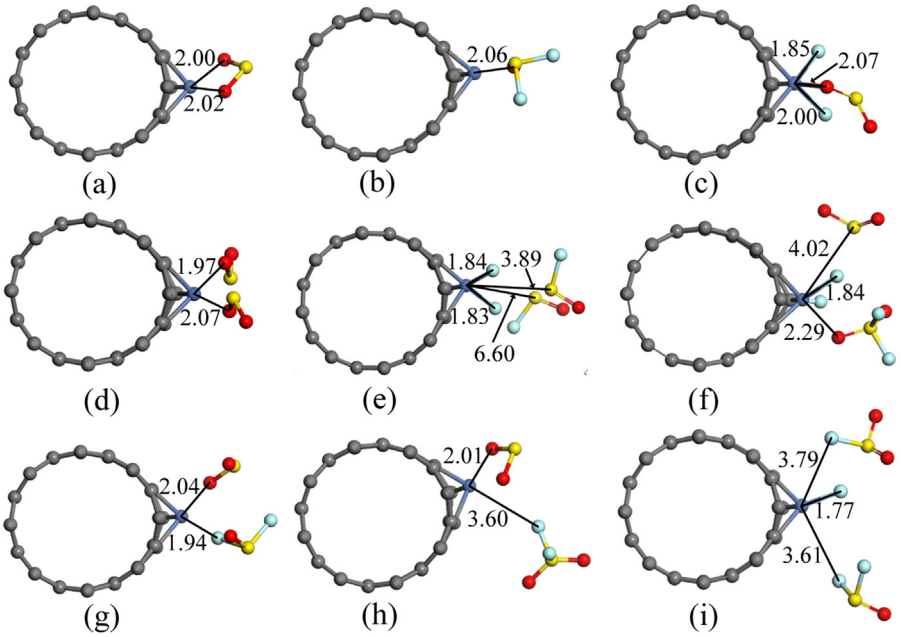

Fig. 2. Most stable geometries of gas molecules interacting with Ni-doped SWCNTs (distances in Å).