

Ab initio Calculations of Polycyclic Aromatic Hydrocarbons Adsorbed on Graphite Edge for Molecular-Scale Surface Coatings of Lithium-Ion Battery Anodes

Takazumi Kawai^{1,2}

¹ Smart Energy Research Laboratories, NEC Corp.

34 Miyukigaoka, Tsukuba, Ibaraki, 305-8501, JAPAN

Phone: +81-29-850-1554 E-mail: t-kawai@da.jp.nec.com

² Graduate School of Pure and Applied Sciences, University of Tsukuba,

1-1-1 Tennodai, Tsukuba, Ibaraki, 305-8571, JAPAN

Abstract

We have investigated the atomic configurations and electronic structures of graphite edges adsorbed by polycyclic aromatic hydrocarbons for the application to lithium-ion-battery anodes, where thin and robust coating layers are required for fast charge-discharge process and long life time. In particular, we examined the adsorption of a perylene molecule on an edge of graphite. We considered that the edge of perylene connects two layers of graphite with σ -bondings. We found that the atomic structures are rather stable and there is no hybridization between the graphite edge and the perylene molecule near the Fermi level, even though they have chemical bondings between them. Thus, the electronic states of the chemisorbed perylene molecule are insensitive to the change in the electric potential of the graphite. These results are almost independent of the choice of edge structures, i.e., armchair or zigzag. Then, the surface coating by polycyclic aromatic hydrocarbons are one of the best candidate for the coating materials of graphite anode, which realize faster charge-discharge rate and longer lifetime.

1. Introduction

Recently, the rechargeable batteries are indispensable devices not only for ensuring stable supply of energy in areas with unreliable electricity but also for an efficient use of various energy resources including green energies in a network area of "smart grid". The lithium ion rechargeable batteries (LIBs) are one of the most fascinating devices for such applications due to the higher energy density and longer life time than that of conventional battery systems[1,2]. To meet the rising demands for battery systems, we need to develop a battery system with faster charge/discharge rate and longer lifetime at low cost.

The formation of solid electrolyte interphase (SEI) on graphite anodes is considered to play an important role for rapid charge-discharge operation and also lifetime[3-5]. Electrolyte molecules are decomposed and forming deposits on the anode graphite surface. A good SEI deposited on the anode surface would suppress further decomposition of electrolytes without disturbing the diffusion of lithium atoms. However, the usual SEI is usually getting thicker dur-

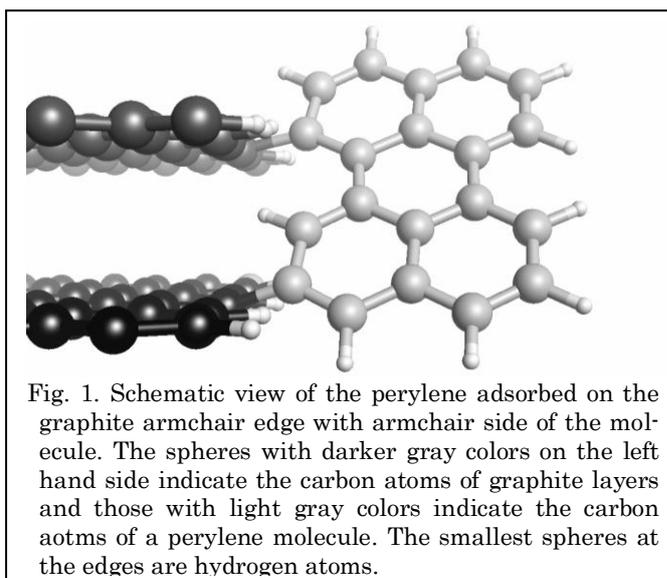


Fig. 1. Schematic view of the perylene adsorbed on the graphite armchair edge with armchair side of the molecule. The spheres with darker gray colors on the left hand side indicate the carbon atoms of graphite layers and those with light gray colors indicate the carbon atoms of a perylene molecule. The smallest spheres at the edges are hydrogen atoms.

ing the repeated use of batteries. Then, the thicker SEI disturbs the diffusion of lithium ions and it sometimes irreversibly-absorb the lithium ions, which reduce the number of charge carrier, that is, reduces the capacity of battery. Thus, we need thin coating which suppresses the electrochemical reactions on the anode surface and never disturbs the lithium diffusion.

Thin coating of amorphous carbons on the surface of anode graphite is also attempted in addition to the development of better SEI formation[6,7]. Such coating of amorphous carbons is effective for the cycle life of LIBs. The coating of amorphous carbons is considered to deactivate the dangling bonds at the defects and edges, which actively decompose the electrolytes and solvents. However, the coating does not disturb the formation of SEI completely. Then, it also requires additives for the better cycle life.

2. Calculation Models and Theoretical Tools

In this paper, we investigated the atomic configurations and electronic structures of the graphite edge adsorbed by polycyclic aromatic hydrocarbons (PAH) for the coating of lithium-ion-battery anodes using first principles electronic structure calculations within the density functional theory in the periodic boundary condition[8-10].

The schematic view of the perylene as a PAH adsorbed on the graphite armchair edge is shown in Fig. 1. In this model, a graphite is mimicked by the two layers of graphene nano-ribbons with ~ 1.0 nm width terminated by the hydrogen atoms. The perylene is chemisorbed on the graphite edge by σ -bonding. Although there are many possible chemisorbed structures, we consider the four typical configurations shown in Figs. 2(a) - (d). Here, we consider the connections between (a) graphite armchair edge with perylene armchair moiety, (b) graphite armchair edge with perylene zigzag moiety, (c) graphite zigzag edge with perylene armchair edge, and (d) graphite zigzag edge with perylene zigzag edge.

3. Results and Conclusions

The atomic structures of a perylene molecule adsorbed on a graphite edge after geometry optimization is shown in Fig. 2. The perylene molecule keeps its original planar structure. Even for graphite zigzag edges where the edges are not aligned along the surface normal direction, the perylene can form the σ -bonding successfully. For the adsorption of perylene zigzag edge and graphite armchair edge (Fig.2(b)), the interlayer distance of graphite becomes short only at the edge to fit the original perylene bonding angle.

For the electronic structures, we found that there is no hybridization between the chemisorbed perylene molecule and graphite edge near the Fermi level, although they make chemical bonding between them. This is because the electronic states of the σ -bonding that connects the perylene molecule and graphite edges are stable and far low in the energy diagram. Since the electronic states near the Fermi level consist of π -electrons, the network of π -electrons are disconnected at the boundary between graphite and perylene molecule.

Thus, the perylene molecule adsorbed on the graphite edges would block the change in the electric potential of the anode graphite, and suppresses the electrochemical decomposition of electrolytes and solvents on the anode surface. Here, only a few layers of perylene adsorption are considered to be effective for the suppression of electrochemical reaction. Furthermore, the planar surface of perylene is parallel to the insertion direction of lithium ion similar to the original graphite edges. Then, the coating would not disturb the diffusion of lithium ions during charge-discharge processes. We expect that such advantageous properties of perylene coating is common for other PAH molecules. Therefore, the coating of graphite anodes with PAH would reduce the deterioration rate of anodes during repeated use of the battery, and keep high charge-discharge rate with longer lifetime.

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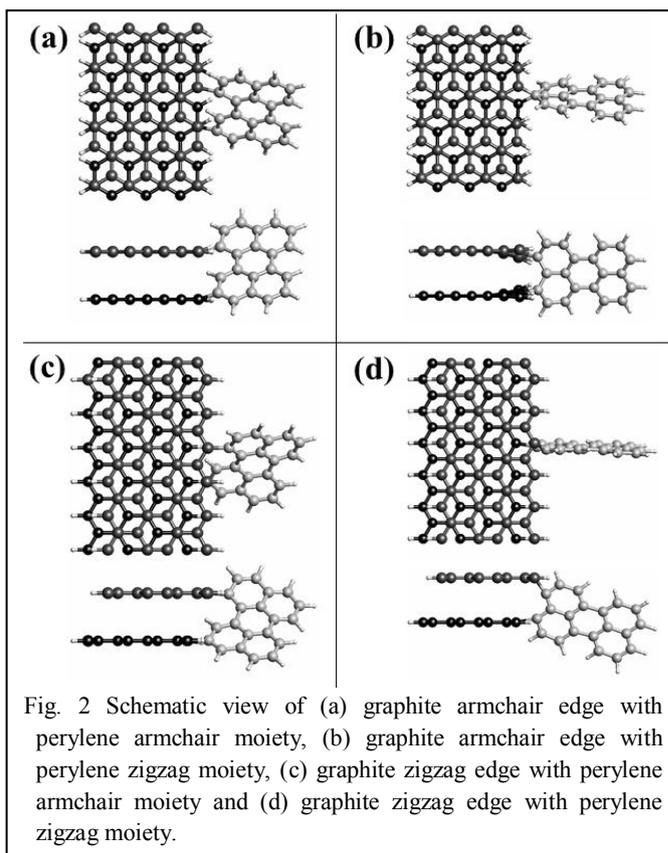


Fig. 2 Schematic view of (a) graphite armchair edge with perylene armchair moiety, (b) graphite armchair edge with perylene zigzag moiety, (c) graphite zigzag edge with perylene armchair moiety and (d) graphite zigzag edge with perylene zigzag moiety.

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