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Study of Defective Few-Layer Graphene Intercalated with Lithium

This paper presents results of computer modeling and quantum mechanical calculations of nanoscaled few-layer graphene (FLG) cells, containing lithium. The results obtained show the essential improvement of physical properties and mechanical dimension stability, in particular, the stiffness of these nanostructures by so called bridge-like defects. It can be supposed, that preliminary radiation modification of FLG nano-cells with formation of such structural defects might become a key technology by production Li-based energy sources and electrical batteries.

Key words: graphene, computer modeling, carbon nanostructures, defects.

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Литиймен интеркаляция жүргізілген ақаулы аз қабатты графенді зерттеу

Мақалада литий болшектерімен интеркаляция жүргізілген аз қабатты графен нанобөлшектерінің қасиеттерін компьютерлік моделдеуі және кванттық механикалық есептеулерінің нәтижелері ұсынылған. Жұмыс нәтижелері зерттелген наноқұрылымдардың физикалық сипаттамалары мен механикалық өлшемді тұрақтылығының, атап айтқанда, қатаңдығының көпіртәріздес атты дефектілер көмегімен айтарлықтай жақсарғандығын көрсетеді.Осындай құрылымдық дефектілерді тұғызатын FLGнаноқұрылымының алдын ала радиациялық модификациясы литий негізінде жасалған энергия көздері мен электр батареяларын өндіру кезіндегі кілттік технологияларының бірі болып табылу мүмкіндігі болжамдалады.

Түйін сөздер: графен, компьютерлік моделдеу, көміртекті наноқұрылымдар, дефектілер.

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Изучение дефектного малослойного графена, интеркалированого литием

В статье представлены результаты компьютерного моделирования и квантово механических расчетов свойств наночастиц малослойного графена, интеркалированного литием. Результаты работы показывают существенное улучшение физических характеристик и механической размерной стабильности, в частности, жесткости исследованных наноструктур с помощью, так называемых, мостиковых дефектов. Можно предположить, что предварительная радиационная модификация FLG наноячеек с образованием таких структурных дефектов может стать одной из ключевых технологий при производстве литиевых источников энергии и электрических батарей.

Ключевые слова: графен, компьютерное моделирование, углеродные наноструктуры, дефекты.

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STUDY OF DEFECTIVE FEW-LAYER GRAPHENE INTERCALATED WITH LITHIUM

Introduction

It is commonly known, that graphite microparticles are used as materials for electrodes in lithium based power devices, mainly due to their high reversibility, low weight and low operating potential [1,2]. But there are some obstacles with the progress in this field, in particular, using of relatively large graphite particles increases time of lithium diffusion motion by intercalation and de-intercalation processes that can significantly decrease the effectiveness of operating power devices [3]. Recently nanoscaled materials based on ultrathin graphite particles have found a use in the technological field relating to production of lithium-ion rechargeable batteries. Obviously, using of nanoscaled particles also allows to increase the ratio lithium / graphite in storing cells and make them more effective in technological and economy sense. Seemingly, the physical situation can become much better by using nanoscaled few-layer graphene (FLG). But it should be noticed, that the nanoscaled Li – FLG systems are not studied as extensive as graphite-based devices. Furthermore, one of the main problem relates to dimension instability of carbon cells caused by large possible deformation or even fracture of electrode materials due to charge – discharge processes [1, 4-7]. This paper presents results of computer simulation and density functional theory (DFT) calculations of possible configurations of nanoscaled FLG cells, containing lithium, with using local density approximation (LDA) [8,9] and one of the fastest method of energy optimization [10] within Dmol3. Furthermore, the effective way of modifying their mechanical properties with producing so called bridge-like radiation defects [11-14] is suggested. It can be supposed, that radiation modification of FLG nanocells with formation of bridge-like defects (BLD) might become a key technology for improving mechanical and physicochemical properties of FLG particles as Li- storing cells.

Simulations and calculations

In order to perform modeling more adequate to real nanocarbon structures, all DFT calculations in this work were performed by using the energy optimization procedure [8-10]. At the first stage of

simulations we considered possible stable configurations of Li on ideal graphene and calculated their energetic characteristics. Figure 1 illustrates modeling of Li atoms placed in three high symmetry positions on graphene surface.

Calculations performed for all of these configurations gave values of the binding energies of Li atoms on the graphene surface very low: – nearly 0.1 eV. These results show that it is unlikely, that Li can be accumulated on the external surface of graphene or an FLG ideal structure. Therefore, the next step of simulations was to study possible configurations with Li linked to structural defects in graphene (Figure 2).

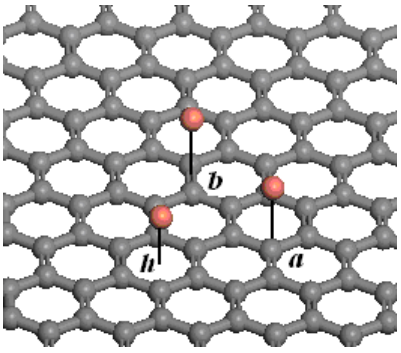

Figure 1 –The possible high-symmetrical positions of Li atoms on graphene surface: h – over the center of a hexagon; a- over a carbon atom; b – over the center of the C-C bond

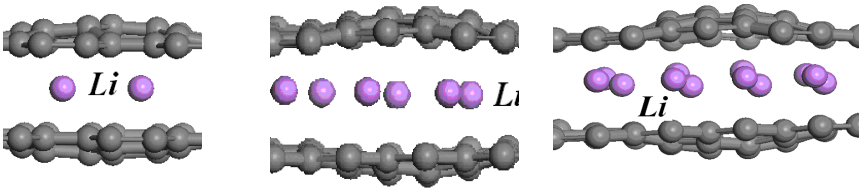

Figure 2 – The visual effect of Li atoms number on dimension of 2-layer graphene cell: N_{Li} = : (a)2 (Li-Li = 2.6 Å) ; (b) 6 (Li-Li = 2.5 Å); (c) 12 (Li-Li = 2.1 Å)

All computational experiments here and down were performed with two-layer graphene cell involving 112 carbon atoms in every plane. It should be noted, that by modeling the Li motion processes near the edge and defect zone we neglected of effects of possible passivation of dangling C- bonds due to formation H-C or OH-C bonds. It is known very well, that possible decorating of C atoms with H is quite important point in calculations of nanographene's electronic properties. In this case the assumption has been made, that in a real Li-battery environment there were not the high concentration of hydrogen in atomic state or OH radicals. Otherwise, it would be a much more complex system with quite different properties, too difficult for simulation. One can suppose that this way to avoid calculating obstacles could cause some limitations in final result, but it is difficult to perform any computer simulation without reasonable simplification.

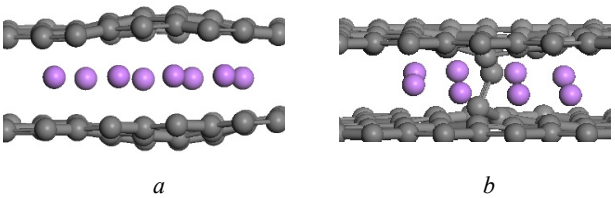

Figure 3 – The effect of BLD on perpendicular size of 2-layer graphene cell with 8 lithium atoms

One can see the obvious change of cells shape (blister – like deformation), increasing with the level of lithiation. This effect was revealed after using the energy optimization procedure. Figure 3 illustrates very essential effect of bridge-like defect on keeping the graphene –graphene distance of two-layer cells with 8 lithium atoms nearly as that in pristine state. One can see, that the cell, which has been modified by bridge-like defect shows very small signs of deformation. Calculations of energetic characteristics showed that Li atoms display no signs of a fast chemical bonding with BLD.

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