X-doped Graphene Interaction with Anodic Material LIBs

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http://dx.doi.org/10.13005/ojc/330505

(Received: April 29, 2017; Accepted: June 05, 2017)

ABSTRACT

The structures of graphite carbonados and hexagonal boron nitride or h-BN, parent materials for carbonados and boron nitride nano-compounds are quite similar. The measured reversible Li+ capacities of X-G// (h-BN)// X-G (X=Be, B, N) in the anode materials are extremely improved compared to the graphite structures in the based anodes. In this study Boron nitride sheet has been localized inside twoX-graphene electrodes as an option to enhance electrochemical ratio. Additionally, we have found the structure of G-X/(h-BN)n/X-G can be forming the capacities and electrical transports in the C-BN sheets of LIBs. In addition, the BN sheet modified and designed of X-G/ (h-BN)/X-G structures provide a strategy to improve the yields of BN-G-sheet of anodes. X-G/h-BN/X-G could also be assembled into free standing electrode of any binder (current collector), which will causes for increasing specific energies and densities for the batteries design.

Keyword: Graphene, Doping, Anode lithium, Ion battery, LIBs.

INTRODUCTION

The carbon does such as graphite are layered materials composed of hexagonal lattices sheets; graphite1,2 is including of carbon atoms at all direction in the lattice points, while the h-BN is consist of alternating atoms from boron and nitrogen respectively. The lattice constants for graphite and h-BN are 2.46 Å and 2.50 Å respectively1,2. In other side, layered BN is transparent and is an insulator2,3 compare to graphite. The layers of h-BN are arranged as boron atoms in one layer which are located directly2 on the top of nitrogen2 atoms in a neighboring section and vice versa3. In graphite structures, stacking3 is slightly different2 whilehexagons are offset2 and cannot lie on the top of each other so interlayer distances can be consider similar: 3.35 Å for graphite1 and 3.33 Å for h-BN respectively Figure.1.

Recently, the theoretical approaches have been presented the band structures3 of alone layer of graphite and h-BN whilefor a layer of graphite which called graphene, 2 bands cross each other at the Fermi3 energies. For this matter, graphene is a semimetal4. In contrast graphene, for a alayer of the h-BN, equivalent5 bands cannot cross each other and amount 4.5 eV band gap forms. Via an
experiment, h-BN has been calculated to have a band gap around 5.8 eV. Crystallographic of BN is classified into four polymorphic forms: Hexagonal BN (h-BN) (Fig 1(a)); rhombohedral BN (r--BN); cubic B-N (c--BN); and wurtzite BN (w--BN).

![Fig.1. Crystal structures of (a) graphite; (b) hexagonal boron nitride](image)

In 1842, Balmain sensitized BN as reaction products via boric-oxide and potassium cyanide through atmosphere pressure. Then, various methods have been reported through h-BN and r-BN which formed under ambient pressure and c-BN has been synthesized from h-BN via high pressure and high temperatures. It is notable that w-BN is prepared from h-BN via high pressure at room temperature.

The discovery of amazing reversible, low-voltage Li-intercalation carbonaceous materials, Sony Company realized the commercialization of xC6/Li1-x CoO2 cells in 1991. Lithium ion batteries (LIBs) are widely used in small grid storage systems.

LIBs generally consist of positive and negative electrodes including a conducting electrolyte where store electrical energy in the two electrodes in the form of Li-intercalation compounds. Electrodes, separator, and electrolyte are the main components of the LIB where the anode plays an essential role in the performance of these devices.

In the charging mechanism of the LIBs, Li released from the negative electrode and move inside the electrolyte then inserted into the positive electrode. In the discharging mechanism, Li are extracted from the (+) electrode and move back to the (-) electrode. Although the electrolyte establishes high ionic conductivity between two electrodes, the electrolytes are not responsible for the conduction of free-electrons. So the electrons complete the 1/2 reaction will move in the way of an extra external wire.

Various experiments have accomplished for confirming the utilization of graphene in the forms of nano-sheets or nano-ribbons for enhancing lithium storage capacities and for improving recharge performance. Furthermore in this study, semi-empirical MM calculations have been done for investigating Li storage between two graphene sheets, as well as a few heteroatom-substituted carbon materials.

Dis-charging or charging of Li in carbonadoses is well established and arranged up to now. It has also been exhibited the mechanism of the repulsive forces in the mixed stages which can result in the pure stages during intercalation. In this study, charging and discharging of Li-ions has investigated in h-BN with the positive electrode reaction as: LiCoO2 ⇌ Li1-x CoO2 + x Li+ + x e- and the negative electrode reaction as: x B3N3 + x Li+ + x e- ⇌ LiB3N3, while the whole reaction is: LiCoO2 + xB3N3 ⇌ Li1-xCoO2+x LiB3N3. It has been suggested that lithium atoms are stored via two mechanisms: intercalation and alloying.

Recently many works has been established for describing the intercalation and diffusion of Li at different sites on carbonadoses graphite and many studies have been performed in order to explain the mechanism by which Li s are stored in electrodes, including theoretical works.

The electrical conductivities for the Li+-Graphene increases via increasing intercalation levels due to the donor nature of electrons for the lithium. This is in contrast of ionic conduction in which diffusivity decreases due to the insertion of Li ions. In the case of amorphous carbon as the disorder increases electrical conductivity significantly decreases. Recently, Fisher group fabricated a tube-in-tube structure with Li+ intercalation capacities times higher than that of the template-synthesized Carbon-NTs, as the inner tubes provided more electrochemical active sites for intercalation of Li ions.
Boron nitride tubes (BN-NT), which firstly predicted and synthesized by Rubio and Chopra respectively, has a structural similar to Carbon-NTs but, in contrast to the Carbon-NTs being metallic (semiconductor) depending on chirality. BNNTs are usually can be an insulator regardless of their helicity, tube diameters and number of tube walls.

Experimental results have exhibited that small SW-Carbon-NTs are usually found inside multi-walled Carbon-NTs. There is, therefore, also a strong motivation to study in detail the stability and interaction of small Boron-Nitride-NTs inside a larger one (viewpoint of diameters), which makes easier to understand the experimental results. Besides, the study on double-walled Boron-Nitride-NTs (DBN-NTs) has demonstrated an interesting variation in their electronic properties when compared with those of freestanding component of BNNTs. So it is also important to see the inter-wall coupling behavior and interaction energies associated with the small Boron-Nitride-NTs.

In summary, Graphene and h-BN compounds as one kind of classical materials with a mature studied history will play a significant role in the battery market of the near future, but how to combine hybrid materials together to obtain safe, stable, and high-capacity electrodes has always been the radical problem that many researchers are trying to solve.

**Theoretical background**

Diffusion properties of Li ion cell deter mines some of the keys performance metrics of Li ion batteries cells, consist fo the charges and discharges rate, practical capacities and cycling stabilities. The governing equation describing the diffusion process is known as Fick’ slaw as:

\[ j_i = -D_i \Delta C_i \quad (1) \]

and

\[ \sigma_{C_i} = \nabla \cdot (D_{C_i} \nabla C_i) \quad (2) \]

where “\(j_i\)” is ionic flux, mol cm\(^{-2}\) s\(^{-1}\), \(D_i\) is diffusivity of solute (i = 1, 2), cm\(^2\) s\(^{-1}\) and \(C_i\) is concentration of species i, (mol cm\(^3\)). The proportionality factor D is the diffusivity or diffusion coefficient as

\[ D_i = \frac{K_B T}{6 \pi \eta R} \quad (3) \]

Li\(^+\) ion cells consist of, all Keyes phenomena involves conducting charged particles as a primary cell from cathodes to anode or vice versa as a secondary cell from anode to cathodes. Typical commercially used lithium-ion battery consists of several interconnected electrochemical cells, where each cell is composed of a graphite anode (such as Meso-carbon microbeads), a cathode formed by lithium metal oxide (such as LiCoO\(_2\)) and electrolyte (such as LiPF\(_6\) dissolved in ethylene carbonate/dimethyl carbonate mixture) embedded in a separator felt.

**Anode materials**

In the case of anode, Li metal is found to be the most electropositive (-3.04 V versus standard hydrogen electrode) with large reversible capacity (= 4000 Ah kg\(^{-1}\)). However, due to safety considerations (explosion hazards as a result of dendrite growth during cycling), metallic Li has been substituted by various carbonaceous materials.

During discharge, Li\(^+\) ions are extracted from the layered graphite, they pass through the electrolytes and intercalate among the LiCoO\(_2\) layers. The electron densities have been defined as

\[ \rho(r) = \eta_i \phi_i(r) \quad (5) \]

\[ \nabla \rho(r) = \left( \frac{\partial \rho(r)}{\partial x} \right)^2 + \left( \frac{\partial \rho(r)}{\partial y} \right)^2 + \left( \frac{\partial \rho(r)}{\partial z} \right)^2 \quad (6) \]

\[ \nabla^2 \rho(r) = \frac{\partial^2 \rho(r)}{\partial x^2} + \frac{\partial^2 \rho(r)}{\partial y^2} + \frac{\partial^2 \rho(r)}{\partial z^2} \quad (7) \]

**Fig. 2** a typical commercial lithium-ion battery
The Hamiltonian kinetics energies densities $K(r)$

The kinetic energies densities are not defined, since it has been expected value for kinetic energies operators $<\varphi - (1)\varphi^2 \varphi >$ (8) has been recovered via integrating kinetic energies densities from an alternative definition. One of general used definition can be demonstrated as:

\[ k(r) = -\frac{1}{2}\sum_{\nu} \eta_{\nu} \varphi_{\nu}^* (r) \varphi^2 \varphi_{\nu}(r) \] (9) $G(r)$ is famous as positive definite kinetic energies densities.

Local Entropies
Local information entropies are quantification of information, which was proposed by Shannon to decompose di-atomic and tri-atomic molecules into space by a minimized information entropy.\(^{(52,57)}\) Parr has discussed the relationship between information entropies and atom partition as well as molecular similarity.\(^{(54)}\) Noorizadeh and Shakerzadeh suggested using information entropy to study aromaticity.

\[ S(r) = -\int P(\chi) d\chi \] (19) If $P(x)$ is replaced by $\frac{N}{N}P(r)$ then the integrand can be called LIE of electrons. $S(r) = -\frac{N}{\sum_{\nu} \eta_{\nu} \varphi_{\nu}^* (r) \varphi^2 \varphi_{\nu}(r)}$ (20)

Where, $N$ is the total number of electrons in current system.

At each inter-tube configuration, a single-point calculation is carried out and the total energy is recorded. The resulting sliding-rotation energy surfaces are used to fix our model in better position.

\[
(\varepsilon_{\text{total}} - \varepsilon_{\text{Li+}} - \varepsilon_{\text{h-BN sheets}}) + \varepsilon_{\text{BSSE}}
\]

Where the $\Delta \varepsilon$ is the stability energy of system. The contour line map has been drawn via Multiwfn software.\(^{(52-54)}\) The graph sareae habituated on interactive interfaces and the methods in this work has based on our previous work.\(^{(59-99)}\)

RESULT AND DISCUSSION

We have listed the data of density, energy, electron localization function (ELF), localized orbital locator (LOL) and local entropy, gap energy, charge from ESP, electrostatic potential, ionization energy, the charges of two doped graphene electrodes and the stability energy of X-G-(h-BN) - X-G and dielectric in 4 tables (tables 1-6) and these data have plotted in this figures (1-10).

We have calculated the gradient norm and the Laplacian of electron density via equals 7 and 8 for the lithium diffused in the X-G/(h-BN)/X-G system respectively and the data are listed in table1. For calculation the electron spin density from the difference between alpha and beta density, we have used $p(r) = \varphi_{\alpha}(r) - \varphi_{\beta}(r)$ then the spin polarization parameter function will be returned instead of spin density $\frac{N}{\sum_{\nu} \eta_{\nu} \varphi_{\nu}^* (r) \varphi^2 \varphi_{\nu}(r)}$ (20). The absolute value of going from zero to unity corresponds to the local region going from un-polarized case to completely polarized case Table1. In this work it has been calculated the local Information entropies for each of Li atoms via eqs. 19-20 and the integrating of those functions over whole spaces yield the information entropies. The data of local Information entropies are listed in Tables 1-5.

Weak interaction (equals 20 and 21) has significant influence on conformation of macro-molecules, however reproduction of electron densities by ab initio and grids data calculation of reduced density gradient (RDG) for such huge systems are always too time-consuming. In this work it has been exhibited the complex of X-G/(h-BN)/X-G which demonstrate a high electrical conductivity and a good mechanical strength, excellent flexibility, great chemical stabilities and high specific surfaces area. Those are especially noticeable when the graphene are chemically converted via greater proportion of functional groups, proving that they are suited for using as the basecomposite.
electrodes materials as well as enhancing the electrode’s mechanical stabilities. As a result, X-G/(h-BN)/X-G containing electrode materials have high capacity and good rate performance. X-G/(h-BN)/X-G flexibilities makes those as an ideal material for buffering metal electrode’s volume expansion and contraction during the charge or discharge phenomenon. Further, the excellent electrical properties of X-G/(h-BN)/X-G can enhance the conductivity of metal electrode material. Finally, the lithium storage capacity for most metal oxide composite materials with X-G/(h-BN)/X-G can be useful greatly.

![Image of h-BN sandwich inside two boron graphene doped as two electrodes of B-G/h-BN/B-G and Be-G/h-BN/Be-G capacitors.](image1)

![Image of Six diffused ion lithium between h-BN and B & Be doped graphene sheet layers.](image2)

### Table 1: Density, energy, Electron localization function (ELF), Localized orbital locator (LOL) and Local Entropy for each Li of 6 lithium diffused on X-G/(h-BN)/X-G (X=B, N and Be) mixed layers

<table>
<thead>
<tr>
<th>Lithium No</th>
<th>Density of all electron (x10^-4)</th>
<th>Density of α electron (x10^-4)</th>
<th>Density of β electron (x10^-4)</th>
<th>Spin density of electron</th>
<th>Potential Hamiltonian Energy (10^-3J)</th>
<th>Local Entropy (x10^-4)</th>
<th>Ellipticity ELF</th>
<th>Eta index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li+(2)</td>
<td>0.30</td>
<td>0.15</td>
<td>0.15</td>
<td>0.0</td>
<td>-0.23</td>
<td>0.16</td>
<td>0.50</td>
<td>-0.15</td>
</tr>
<tr>
<td>Li+(4)</td>
<td>0.26</td>
<td>0.13</td>
<td>0.13</td>
<td>0.0</td>
<td>-0.29</td>
<td>0.18</td>
<td>0.52</td>
<td>-0.30</td>
</tr>
<tr>
<td>Li+(6)</td>
<td>0.38</td>
<td>0.19</td>
<td>0.19</td>
<td>0.0</td>
<td>-0.27</td>
<td>0.17</td>
<td>0.53</td>
<td>-0.22</td>
</tr>
<tr>
<td>Li+(2)</td>
<td>0.22</td>
<td>0.11</td>
<td>0.11</td>
<td>0.0</td>
<td>-0.28</td>
<td>0.21</td>
<td>0.50</td>
<td>-0.19</td>
</tr>
<tr>
<td>Li+(4)</td>
<td>0.26</td>
<td>0.13</td>
<td>0.13</td>
<td>0.0</td>
<td>-0.27</td>
<td>0.18</td>
<td>0.54</td>
<td>-0.12</td>
</tr>
<tr>
<td>Li+(6)</td>
<td>0.34</td>
<td>0.17</td>
<td>0.17</td>
<td>0.0</td>
<td>-0.25</td>
<td>0.19</td>
<td>0.51</td>
<td>-0.41</td>
</tr>
</tbody>
</table>
Table 2: The Charges of two doped graphene electrodes and the stability energy of x-G/(h-BN)/x-G.

<table>
<thead>
<tr>
<th>X = 6 atoms of Be, B and N</th>
<th>Li_xG-(h-BN)-G</th>
<th>%Dielectric ( \Delta \varepsilon ) (eV)</th>
<th>( q_{x-G} )</th>
<th>( q_{m-G} )</th>
<th>( q_{h-BN/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_xG-(h-BN)-G</td>
<td>3.98</td>
<td>-14.55</td>
<td>+0.19</td>
<td>-0.15</td>
<td>-0.04</td>
</tr>
<tr>
<td>Li_xG-(h-BN)_2-G</td>
<td>4.02</td>
<td>-30.32</td>
<td>+0.007</td>
<td>-0.004</td>
<td>-0.003</td>
</tr>
<tr>
<td>Li_xG-(h-BN)_2-G</td>
<td>3.99</td>
<td>-49.29</td>
<td>+0.14</td>
<td>-0.10</td>
<td>-0.02</td>
</tr>
</tbody>
</table>

Table 3: The dielectric of X-G/(h-BN)/X-G modeled in various Lithium number.

<table>
<thead>
<tr>
<th>Li_nX-G/(h-BN)/X-G</th>
<th>%Dielectric ( \Delta \varepsilon ) (eV)</th>
<th>( \kappa )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li_2N-G/(h-BN)/N-G</td>
<td>3.97</td>
<td>3.6</td>
</tr>
<tr>
<td>Li_2G-(h-BN)_2-G</td>
<td>4.01</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Table 4: Nucleor list and HOMO/LUMO and Gap energy for the B-C/h-BN/B-G.

Note: Orbital 326 is HOMO of alpha spin, orbital 985 is HOMO of beta spin
LUMO/HOMO gap of alpha orbitals: 0.000289 a.u. 0.007873 eV
LUMO/HOMO gap of beta orbitals: 0.000011 a.u. 0.000387 eV
CONCLUSION

The structure of G-X/(h-BN)n/X-G can be for improving the capacities and electrical transports in the C-BN sheets of LiBs. In addition, the BN sheet modified and designed of X-G/(h-BN)/X-G structures provide a strategy to improve the yields of BN-G-sheet of anodes. X-G/h-BN/X-G could also be assembled into free standing electrode of any binder (current collector), which will causes for increasing specific energies and densities for the batteries design.

ACKNOWLEDGEMENT

Authors would like to thanks science and research branch of Islamic Azad University, Iran.

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