Ab initio study of sodium cointercalation with diglyme molecule into graphite

Chol-Jun Yu*, Song-Bok Ri, Song-Hyok Choe, Gum-Chol Ri, Yun-Hyok Kye, Sung-Chol Kim

Department of Computational Materials Design, Faculty of Materials Science, Kim Il Sung University, Ryongnam-Dong, Taesong District, Pyongyang, Democratic People's Republic of Korea

A B S T R A C T

The cointercalation of sodium with the solvent organic molecule diglyme into graphite, forming a ternary graphite intercalation compound (*t*-GIC), can resolve the difficulty of making the stage 1 Na-GIC in order to use as a potential anode for Na-ion batteries (NIBs). To clarify the mechanism of such cointercalation, we investigate the atomistic structure, energetics, electrochemical properties, ion and electron conductance, and charge transferring upon the de/intercalation of the solvated Na-diglyme ion into graphite with *ab initio* calculations. It is found that the *t*-GICs $Na(digl)_2C_n$ have the lowest negative intercalation energy at $n \approx 21$, the $Na(digl)_2$ complex diffuses relatively fast in the interlayer space, and the electronic conductance can be enhanced upon the cointercalation compared with graphite. The calculations reveal that the diglyme molecule as well as Na atom donates electrons to the graphene layer, indicating an ionic bond between the graphene layer and the diglyme molecule. We belive that this work will contribute to the development of graphite-based anode materials for NIBs.

© 2017 Elsevier Ltd. All rights reserved.

Energy and environmental issues become increasingly global, actual and vital to all the nations on the Earth. This prompts people to break off the mass consumption of fossil fuels, which are being exhausted and moreover cause greenhouse gas emission, and to create new technologies for utilizing renewable and clean energy sources such as solar and wind power. However, these sources are changeable in time and widespread in space. For solar and wind power to become competitive with fossil fuels in the electricity market, therefore, it is necessary to develop an efficient energy storage system as well as an effective energy generating (or harvesting) device. Although Li-ion batteries (LIBs) have been widely used for portable electronics during the past two decades due to their high power density, growing concerns for the low abundance and high price of lithium resource [1–3] triggered an extensive recent research on Na-ion batteries (NIBs) due to a high abundance and low cost of sodium precursor [4–7]. When compared to Li$^+$ ion, however, Na$^+$ ion has lower ionization potential and larger ionic radius, which make it difficult to find suitable anode materials for NIBs [8,9].

Requirements for a good anode material of NIB can be summarized as follows; (i) high specific capacity and low redox potential for high energy density, (ii) high abundance, low cost and facile fabrication for economics, (iii) low chemical reactivity with electrolyte and small volume change during operation for safety and long cycling life, and (iv) non-toxicity for environmental friendliness. When surveying NIB anodes based on these requirements, metal sodium can be used surely but has a critical problem such as high reactivity with organic electrolyte solvents, while metal oxides and alloy based materials have in general high specific capacities but suffer from the large volume change [10–13]. In spite of relatively low capacity, carbon based materials might be the most widely used anode for NIBs because of their good electronic conductivity and excellent electrochemical performance [14,15]. The research has focused on mainly non-graphitic carbons like disordered hard carbon, which has a high specific capacity over $\sim$300 mAh g^{-1} but still shortcomings such as low coulombic efficiency in the first cycle due to a large surface area [16,17]. During the last few years, a significant progress in using graphitic carbons has been made [18–20]. From the studies of hard carbons, it was understood that desirable carbon materials should have a long-range order, high interlayer distance, low porosity and small surface area [19]. In this regard, Wen *et al.* [20] recommended expanded graphite, which has a large interlayer distance

* Corresponding author.
  E-mail address: ryongnam14@yahoo.com (C.-J. Yu).

of ~0.43 nm (0.334 nm in graphite) and a relatively small surface area of ~30 m^2 g^{-1}, being able to deliver a high specific capacity of ~300 mAh g^{-1} at the low current density of 20 mA g^{-1}. At the high current density, however, the modest performance was observed. Using the expanded synthetic graphite materials, Ramos et al. [19] increased the current density up to 100 mA g^{-1}, at which the capacity was of ~110 mAh g^{-1}.

Although alkali metals were known to reversibly intercalate into graphite, forming stage 1 binary graphite intercalation compounds (b-GICs), only sodium cannot form a stage 1 b-GIC but high stage b-GICs [21,22]. This leads to very low specific capacity for cells, e.g., ~35 mAh g^{-1} for NaC$_{64}$ versus ~372 mAh g^{-1} for LiC$_6$, hindering practical use of graphite as NIB anode. The reason might be the small interlayer spacing of graphite, i.e., big mismatch between graphite interlayer distance and Na ion size, and most likely, weak binding of Na ion (electron donor) to graphene sheet (acceptor) through π interaction [23–25]. A fortunate side for electrode performance is that the larger radius ions diffuse more smoothly in graphite [23].

To form stage 1 Na-GICs, cointercalation process, i.e., intercalation of sodium with a solvent organic molecule, has been suggested [26–33]. This process produces donor-type ternary GICs (t-GICs), denoting Na$_x^+$(solv)$_y$C$_n^-$ with C$_n$ the graphene sheet containing n carbon atoms and (solv)$_y$ the y solvent organic molecules [26]. The solvents are typically a series of alkylamines [31,34,30], and ether-based electrolytes [26–29]. Recently, Jache and Adelhelm [26] made use of t-GICs containing sodium atom and diglyme (diethylene glycol dimethyl ether: C$_6$H$_{14}$O$_3$) molecule with an estimated stoichiometry of Na(digl)$_2$C$_{20}$ as an effective NIB anode, which delivers moderately high reversible capacity close to 100 mAh g^{-1} for 1000 cycles and coulomb efficiency over 99.87%. Hasa et al. [35] demonstrated the NIB full cell consisted of a graphite anode, glyme-based electrolyte (tetraethylene glycol dimethyl ether (TEGDME)-NaClO$_4$), and a layered oxide cathode, i.e., Graphite/TEGDME-NaClO$_4$/Na$_{0.7}$CoO$_2$, which offers unique characteristics of long cycle life, high efficiency and high power density, though the lower energy density than LIBs.

In spite of such successful applications, there is still half in doubt about using t-GICs as NIB anodes [15]. This is in part due to a lack of sufficient understanding of the sodium cointercalation phenomena. Ab initio calculations within the framework of density functional theory (DFT) have proven to give valuable insights into

electrochemical performance of NIB anodes [36–39]. In this work, we perform systematic ab initio DFT calculations of t-GICs cointercalated with the sodium atom and the diglyme molecule, aiming to clarify the mechanism of the t-GIC formation and operation as NIB anodes.

1. Computational methods

Firstly we make models for the crystalline t-GICs cointercalated with the sodium atom and the diglyme molecule, Na$_x$(digl)$_y$C$_n$ with $x = 1$ and $y = 2$. Regarding the intercalant complexes, it was assumed in the previous works [26,40–42] that two diglyme molecules are bound to one alkali ion with six coordination number by ether oxygen atoms from the solvent molecules, and thus we make a model of solvated ion as one sodium atom surrounded by two crossing diglyme molecules, i.e., Na(digl)$_2$ (for reference, one Na and one diglyme Na(digl)$_1$, and one Li and two diglymes Li(digl)$_2$ are also considered). Note that different solvated ion models with two alkali atoms and two diglyme molecules Na$_2$(digl)$_2$ were also suggested and studied in the other previous works [27–29]. Regarding the graphite hosts with different carbon numbers n, we use (3×3), (4×3), (4×4), $(\sqrt{12} \times \sqrt{7})$, and $(\sqrt{12} \times \sqrt{13})$ cells, which correspond to $n = 18$, 24, 32, 20, and 28, respectively. The solvated ions are assumed to be intercalated into AA-stacked graphene layers, as shown in Fig. 1.

The ab initio DFT calculations are carried out using the pseudopotential-pseudo atomic orbital (PAO) method as implemented in the SIESTA package [43]. We test different exchange-correlation (XC) functionals, such as the Perdew-Zunger formalism within local density approximation (LDA) [44], and the Perdew-Burke-Ernzerhof (PBE) [45], the PBE for solid (PBEsol) [46] and the Lee-Yang-Parr (LYP) [47] functionals within the generalized gradient approximation (GGA). It can be thought that the dispersive van der Waals (vdW) interactions between graphene sheets may play an important role in Na(digl)-cointercalated graphite as well as pristine graphite [48–50]. To estimate such vdW interactions, we use the semi-empirical Grimme's approach [51], where the vdW energy is expressed as follows,

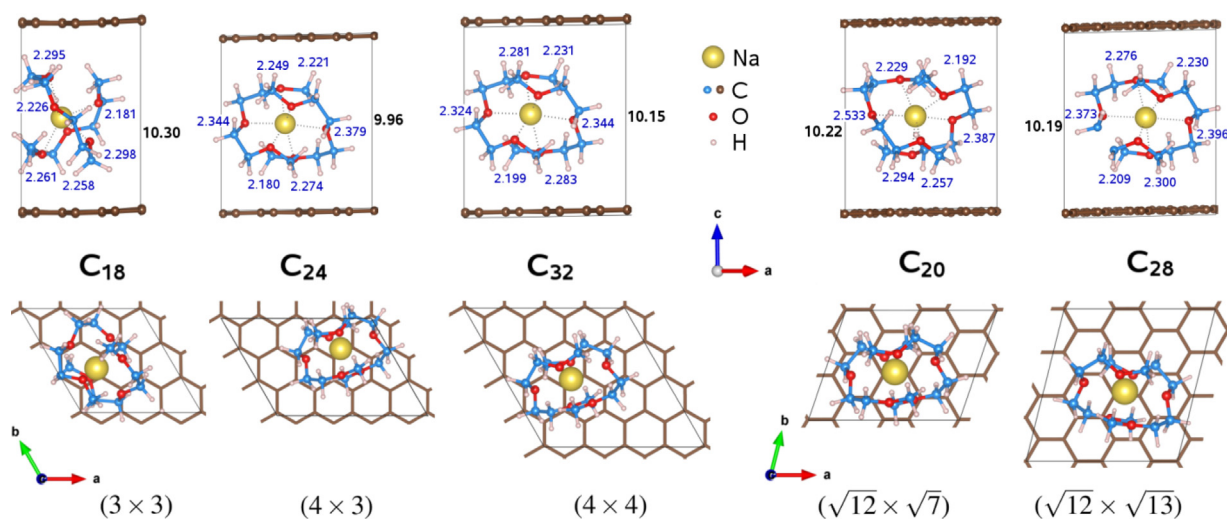$$E_{\text{vdW}} = -s_6 \sum_{j<i} \frac{C_6^{ij}}{r_{ij}^6} \frac{1}{1 + e^{-d(r_{ij}/R_{ij}^0 - 1)}} \tag{1}$$

Fig. 1. Side (top panel) and top view (bottom panel) of unit cells of Na(digl)$_2$C$_n$ GICs with n =18, 24, 32, 20, and 28, having (3×3), (4×3), (4×4), $(\sqrt{12} \times \sqrt{7})$, and $(\sqrt{12} \times \sqrt{13})$ cells with AA-stacked graphene layers. Carbon atoms of graphene sheet are represented by brown balls (hexagon), while carbon, oxygen and hydrogen atoms of diglyme molecule by small blue, red and white balls, and sodium atoms by big yellow balls. Interlayer distance and six Na−O bond lengths in Å unit optimized by PBEsol+vdW method are indicated in top panel.