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Origin of excellent rate and cycle performance of Na+-solvent cointercalated graphite vs. poor performance of Li+-solvent case

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ABSTRACT

Despite its high reversibility for Li+ intercalation, graphite is known to be electrochemically inactive for Na+ intercalation. On the contrary, recent studies have demonstrated that graphite is active and shows excellent rate and cycle performance for Na+-solvent cointercalation but it exhibits poor performance for Li+-solvent cointercalation. Herein, we elucidate the mechanism of Li+- and Na+-solvent cointercalation into graphite and the origin of the strikingly different electrochemical performance of Li+- and Na+-solvent cointercalation cells. Na+ intercalation into graphite is thermodynamically unfavorable, but Na+-diglyme cointercalation is very favorable. The diglyme–graphene van der Waals interaction reinforces the interlayer coupling strength and thereby improves the resistance of graphite to exfoliation. The transport of solvated Na ions is so fast that the diffusivity of Na+-diglyme complexes is markedly faster (by five orders of magnitude) than that of Li+-diglyme complexes. The very fast Na+-diglyme conductivity is attributed to facile sliding of flat diglyme molecules, which completely solvate Na ions in the interlayer space of graphite. The slow Li+-diglyme conductivity is ascribed to steric hindrance to codiffusion caused by bent diglyme molecules that incompletely solvate Li ions. The bent and flat diglyme molecules surrounding Li and Na ions, respectively, are highly associated with the strong Li+–graphene and weak Na+–graphene interactions, respectively.

1. Introduction

Graphite intercalation compounds (GICs) are layered materials with periodically stacked intercalant and graphene layers, and they are formed by inserting guest species, such as atoms, molecules, and ions, into the interlayer space of the host graphite. The control of the type and amount of guest species can lead to the formation of GICs with peculiar features such as superconducting behavior [1] and high transparency [2]. The GICs have a variety of applications as chemical reagents, electrochemical electrodes, highly conductive materials, catalysts, and so on [3]. Since the discovery of monolayer graphene in 2004 [4], GICs have been widely used as starting materials to produce large-area graphene sheets via exfoliation [5]. Many hundreds of GICs have been examined by utilizing various intercalant species such as alkali metals, metal oxides, metal chlorides, bromides, fluorides, oxyhalides, acidic oxides, and strong acids [3]. Particularly, one of the most extensively studied GICs is Li_xC_6 ($0 < x \leq 1$), namely Li-GICs, used as the standard anode material in lithium-ion batteries (LIBs) [6–11].

LIBs are currently the most commonly used power sources for portable electronic devices, but are facing a potential challenge in price due to the low abundance of Li resources in the Earth's crust [12]. Sodium-ion batteries (SIBs) have attracted much attention as a promising alternative to LIBs. Unfortunately, however, Na+ intercalation into graphite is electrochemically difficult. The maximum sodiation capacity of graphite is < 35 mAh g^{-1} for NaC_{64}, which is much lower than that for lithiation (372 mAh g^{-1} for LiC_6). The poor Na+ storage capability of graphite has been thought to be due to the small interlayer spacing of graphite, which is not sufficient to accommodate Na ions [13–17]. However, this prevailing view has been contested in experiments showing that K ions, which are larger than Na ions, can electrochemically intercalate into graphite [18,19]. The low activity of graphite for sodiation can be ascribed to a weak Na+–graphene cation–π interaction rather than to any mismatch between the graphite interlayer spacing and ion size, considering that, among alkali metals, Na has the weakest binding to graphite [20]. Until recent years, graphite has been considered inappropriate for applications in SIBs unless it is modified by chemical methods such as oxidation, reduction [15,21], and heteroatom doping [22].

Intriguingly, Jache et al. [23] and Kim et al. [24,25] recently reported that pristine graphite can be successfully used as the anode

material for SIBs by utilizing the Na$^+$-solvent cointercalation mechanism. Na$^+$-solvent cointercalation into graphite occurred with the use of ether-based electrolytes, such as mono-, di-, tri-, and tetraglyme molecules [23–32]. These molecules are linear and have multiple O atoms that can simultaneously attract one Na$^+$ ion. This structural feature allows a much stronger solvation of Na$^+$ ions by these linear ether solvents than by other solvents (e.g., cyclic ether, linear carbonate, and cyclic carbonate) and leads to the frequent observations of cointercalation in linear ether electrolyte systems [29]. Especially when assisted by diglyme solvent molecules, Na ions are reversibly intercalated into graphite with reversible capacities of 100–150 mAh g^{-1} for several thousands of cycles at high currents, thereby forming ternary Na-diglyme-GICs [23,24,26]. Diglyme therefore shows the best electrochemical performance among the mono-, di-, tri-, and tetraglymes [24,28], and its performance is also better than that of diglyme derivatives having non-polar side groups attached to linear diglyme [28]. These findings motivated the present investigation of the Na$^+$-(linear diglyme) cointercalation into graphite. The most striking result is that Na-diglyme-GICs exhibit electrochemical performance much better than that of Li-diglyme-GICs [23,28,30]. The Na$^+$-diglyme cointercalation cell exhibits a robust cycle stability over one thousand of cycles and retains reversible capacities in the range of 0.1–1.0 C rate (1 C=372 mA g^{-1}), while the Li$^+$-diglyme cointercalation cell shows a rapid capacity decay within a few tens of cycles and gives much reduced capacities at current densities exceeding 0.1 C rate [23]. These poor and excellent performance of graphite in Li$^+$- and Na$^+$-solvent cointercalation cells, respectively, are directly opposite to the success and failure of graphite in Li$^+$ and Na$^+$ intercalation cells, respectively. However, a fundamental understanding of the cointercalation into graphite and the origin of the contrasting performance of Li$^+$- and Na$^+$-solvent cointercalation cells remain elusive.

In this study, using first-principles molecular dynamics simulations, we show how the thermodynamic, mechanical, and kinetic properties of Na$^+$-diglyme cointercalated graphite correlate with its electrochemical performance, which far surpasses that of its Li$^+$-diglyme counterpart. While Na$^+$ intercalated graphite is thermodynamically unfavorable, Na$^+$-diglyme cointercalated graphite is considerably favorable. The diglyme–graphene van der Waals (vdW) interaction leads to the formation of stable ternary Na-diglyme-GICs and reinforces the interlayer coupling strength, improving the mechanical integrity of the graphite. The diglyme molecules that surround the Na ions are nearly flat and move rapidly in the interlayer space of the graphite, without intermolecular interference. The diffusivity of the Na$^+$-diglyme complexes is strikingly faster (by five orders of magnitude) than that of the Li$^+$-diglyme complexes. The slow Li$^+$-diglyme conductivity is associated with steric hindrance arising from the bent diglyme molecules involved with partial Li$^+$ desolvation. The contrasting shapes of the molecules surrounding the Li and Na ions are ascribed to a difference in ion–graphene interaction, i.e., the strong Li$^+$–graphene and weak Na$^+$–graphene interactions, respectively.

2. Computational details

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) [33]. We used the projector augmented wave (PAW) method [34] and the van der Waals density functional (vdW-DF) [35], in which the revised Perdew–Burke–Ernzerhof (revPBE) exchange functional [36] is employed. The electronic wave functions were expanded on a plane wave basis set with a kinetic energy of 400 eV. We treated $1s^22s^1$ for Li, $2p^63s^1$ for Na, $2s^22p^2$ for C, $2s^22p^4$ for O, and $1s$ for H as the valence electron configurations. The [Li-diglyme]C$_{16}$ and [Na-diglyme]C$_{16}$ systems were simulated by a 4×4×1 hexagonal supercell including one graphene sheet consisting of 32 C atoms, two Li or Na atoms, and two diglyme molecules consisting of 12 C, 6 O, and 28 H atoms. The [Li-diglyme]C$_{50}$ and [Na-diglyme]C$_{50}$ systems were simulated by a 5×5×2 hexago-

nal supercell including two graphene sheets consisting of 100 C atoms, two Li or Na atoms, and two diglyme molecules. The [Li-2diglyme]C$_{32}$ and [Na-2diglyme]C$_{32}$ systems were simulated by a 4×4×1 hexagonal supercell including one graphene sheet consisting of 32 C atoms, one Li or Na atom, and two diglyme molecules. The LiC$_6$ and NaC$_6$ systems were simulated by a √3×√3×2 hexagonal supercell including two graphene sheets consisting of 12 C atoms and two Li or Na atoms. The AA stacking sequence of the graphite layers in LiC$_6$ and NaC$_6$ was considered because it is more stable than the AB stacking sequence in pristine graphite. The 3×3×3, 2×2×2, 3×3×3 and 6×6×3 *k*-point meshes in [A-diglyme]C$_{16}$, [A-diglyme]C$_{50}$, [A-2diglyme]C$_{32}$, and AC$_6$ (A = Li and Na), respectively, were used for Brillouin zone integrations. All the A-diglyme-GICs and A-GICs systems are uncharged. We optimized both the cell volume and the atomic positions until residual forces were less than 0.02 eV Å^{-1}. We carried out ab initio molecular dynamics (AIMD) simulations to determine the most stable structures of the A-diglyme-GICs. The equations of motion were integrated with the Verlet algorithm using a time step of 1 fs, and the temperature was controlled by velocity rescaling and a canonical ensemble using a Nosé–Hoover thermostat. Similar calculation schemes were successfully employed in our previous studies [37–40]. The DFT calculations of positively charged free A$^+$-solvent complexes were performed using the Gaussian 09 program package [41]. The B3LYP functional [42,43] and standard 6–31 G(d) basis sets were used.

3. Results and discussion

We first examined the solvation of carrier ions by solvent molecules. Ion-solvent cointercalation into an electrode can bypass the slow desolvation step at the electrolyte/electrode interface [44]. The strong binding of ions to solvent molecules is thus necessary for successful cointercalation at the interface without desolvation. Our optimized structure of a free Na$^+$-diglyme complex shows that the solvated Na ion is threefold coordinated with O atoms of diglyme (Fig. 1). We calculated the binding energy required to separate the Na ion from diglyme. The calculated binding energy for Na$^+$-diglyme is 2.88 eV, which is significantly larger than the values of 1.78 and 1.83 eV for Na$^+$-ethylene carbonate and Na$^+$-propylene carbonate, respectively. This result implies that the use of diglyme is more advantageous for preventing Na$^+$ desolvation at the electrolyte/graphite interface than is the use of ethylene carbonate or propylene carbonate, which are popular solvent molecules in LIBs. The binding energy for Li$^+$-diglyme is calculated to be 3.99 eV, larger by 39% than the value of 2.88 eV for Na$^+$-diglyme, reflecting an Li–O bond strength stronger than that of the Na–O counterpart [37].

By analyzing the weight change of Na-diglyme-GICs during sodiation, Kim et al. [25] quantified the ratio of Na$^+$ to diglyme in graphite at 1:1, indicating the formation of [Na-diglyme]$^+$[C$_n$]$^-$, where *n* is the number of C atoms per Na ion. The authors also suggested the formation of double layers of Na$^+$-diglyme complexes in the interlayer space of graphite because the *c* lattice parameters of Na-diglyme-GICs
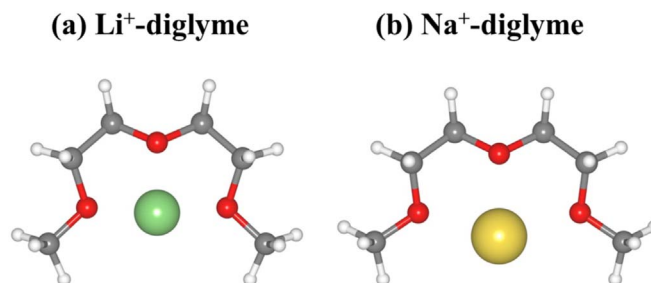
(a) Li$^+$-diglyme   (b) Na$^+$-diglyme

Fig. 1. Optimized structures of solvated Li and Na ions: (a) Li$^+$-diglyme and (b) Na$^+$-diglyme. Green, yellow, white, gray, and red balls represent Li, Na, H, C, and O atoms, respectively.