

Article

Density Functional Theory (DFT) Study on the Ternary Interaction System of the Fluorinated Ethylene Carbonate, Li^+ and Graphene Model

Mami Mutoh ¹, Shigeaki Abe ^{1,*}, Teruo Kusaka ¹, Mariko Nakamura ², Yasuhiro Yoshida ¹, Junichiro Iida ¹ and Hiroto Tachikawa ³

Received: 23 September 2015; Accepted: 21 December 2015; Published: 29 December 2015

Academic Editors: James Babb and Hyun-Kyung Chung

¹ Graduate School of Dental Medicine, Hokkaido University, Sapporo 060-8586, Japan; mutoh@den.hokudai.ac.jp (M.M.); kusaka.teruo@gmail.com (T.K.); yasuihiro@den.hokudai.ac.jp (Y.Y.); iidaj@den.hokudai.ac.jp (J.I.)

² School of Health Science, Kyushu University of Health and Welfare, 1714-1 Yoshino-cho, Nobeoka, Miyazaki 882-8508, Japan; marin@phoenix.ac.jp

³ Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan; hiroto@eng.hokudai.ac.jp

* Correspondence: sabe@den.hokudai.ac.jp

Abstract: The ternary interaction system composed of fluorinated ethylene carbonate, denoted by EC(F), lithium ion (Li^+) and a model of nano-structured graphene has been investigated by means of the density functional theory (DFT) method. For comparison, fluorinated vinylene carbonate, denoted by VC(F), was also used. The model of graphene consisting of 14 benzene rings was examined as a nano-structured graphene. The effects of fluorine substitution on the electronic state and binding energy were investigated from a theoretical point of view. It was found that both EC(F) and VC(F) bind to a hexagonal site corresponding to the central benzene ring of the model of the graphene surface. The binding energies of $\text{Li}^+\text{EC(F)}$ and $\text{Li}^+\text{VC(F)}$ to the model of graphene decreased with increasing number of fluorine atoms (n).

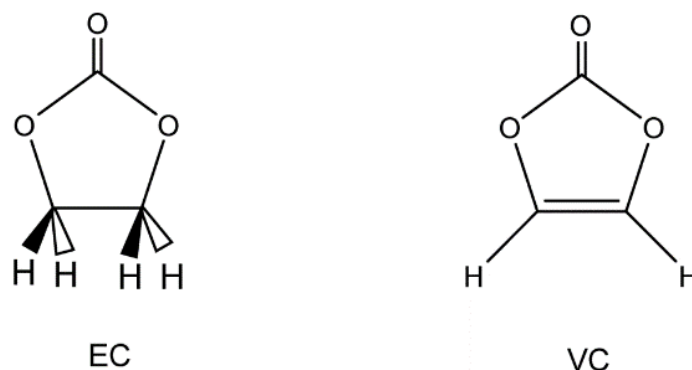
Keywords: density functional theory; fluorinated ethylene carbonate; nano-structured graphene model; lithium ion secondary battery; surface interaction

1. Introduction

There are several interactions in a lithium ion secondary battery.

Desolvation, $\text{Li}^+\text{-EC} \rightarrow \text{Li}^+ + \text{EC}$, is an important process in the movement of the Li^+ ion from the solvent to graphene. The weaker solvation of the Li^+ ion by ethylene carbonate (EC) is a positive factor as a solvent. Ethylene carbonate (EC) and its related compounds are widely used in the high dielectric solvent in the lithium secondary battery, because EC has many desirable properties as an electrolyte solvent for lithium batteries. For example, EC has a high dielectric constant and low viscosity [1–4]. The interaction of the electrode (graphite) with the solvent molecule (EC) plays an important role in the redox process in electrochemistry. Recently, Zhu *et al.* (2014) [5] have synthesized a new family of polyfluoroalkyl-substituted ethylene carbonates, and they have been tested as additives in lithium-ion cells. The four additives studied were 4-(trifluoromethyl)-1,3-dioxolan-2-one (TFM-EC), 4-(perfluorobutyl)-1,3-dioxolan-2-one (PFB-EC), 4-(perfluorohexyl)-1,3-dioxolan-2-one (PFH-EC) and 4-(perfluorooctyl)-1,3-dioxolan-2-one (PFO-EC). Differential capacity plots from graphite-Li cells suggest that PFO-EC is involved in solid electrolyte interphase (SEI) formation. Raman data from anodes after cycling suggest that structural disordering of graphite is reduced by the addition of

PFO-EC, which may explain the improved cell capacity retention. For comparison, fluorinated vinylene carbonate, denoted by VC(F), was also used. Figure 1 shows the typical interaction systems, such as solvent-graphene, solvent-lithium ion and lithium ion-graphene.



Scheme 1. Structures of ethylene carbonate (EC) and vinylene carbonate (VC).

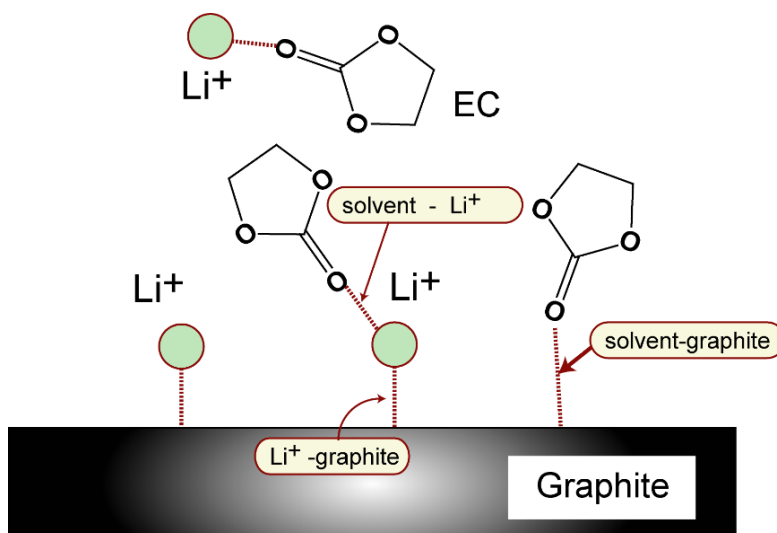


Figure 1. Schematic illustration of the types of interactions in the graphene-ethylene carbonate (EC)-lithium system.

Several theoretical works on the water in carbon nanotubes and on graphene have recently been performed to gain the dynamical feature of the interaction. Werber *et al.* (2003) [6] carried out a theoretical calculation of the carbon-water interaction system and showed the importance of the relation between the contact angle of a water droplet on graphite changes and the water-carbon interaction energy. Rana and Chandra (2007) [7] investigated the interaction of water containing a narrow carbon nanotube. The hydrogen bond distributions of water inside and also in the vicinity of the outer surfaces of the nanotube were obtained by a molecular dynamics (MD) simulation. The solvation mechanism of lithium ions in pure ethylene carbonate (EC) solutions was studied in a wide concentration range by different techniques and temperatures [8]. Thus, the interaction of solvent with carbon materials has been investigated by several groups. However, the interaction of EC- Li^+ with graphene is not clearly understood.

In our previous papers [9–11], we investigated the interaction systems of graphene- Li^+ , the graphene-Li atom and graphene-water and showed that the water molecule can bind an edge of graphene.

In the present study, the density functional theory (DFT) method [12–14] was applied to a ternary interaction system composed of fluorinated ethylene carbonate, denoted by EC(F), lithium ion (Li^+) and a nano-structured graphene. For comparison, fluorinated vinylene carbonate, denoted by VC(F), was also used.

2. Method of Calculations

As a graphene system, a carbon sheet composed of 14 benzene rings ($\text{C}_{42}\text{H}_{16}$) was used as the nano-structured graphene in the present study. The edge carbon atom of graphene was terminated by a hydrogen atom. First, each structure of graphene, EC and VC was individually optimized using the Handy and coworkers' long-range corrected version of B3LYP using the Coulomb-attenuating method (CAM-B3LYP) with a 6-31G(d) basis set [15]. Next, the graphene-EC- Li^+ ternary interaction system was fully optimized at the same level. All density functional theory (DFT) calculations were carried out using the Gaussian 09 program package [16].

3. Results

3.1. Structures of EC(F) and VC(F)

Figure 2 shows the optimized structures of EC(F) and VC(F) used in the present study. The notation of n in EC(F_n) and VC(F_n) means the number of fluorine atoms in EC and VC, respectively. The number n in EC(F_n) and VC(F_n) was varied as ($n = 0$ to 4) and ($n = 0$ to 2), respectively.

The bond lengths of C=O carbonyl and the C–O single bond of EC(F_0) were 1.190 and 1.355 Å, respectively. These bond lengths were slightly changed by the F-substitution: 1.078 and 1.367 Å in EC(F_4). A large, different point appeared as a distance of $r(\text{C}–\text{C})$: 1.628 Å in EC and 1.552 Å in EC(F_4). The F-substitution largely decreases the C–C single bond of EC.

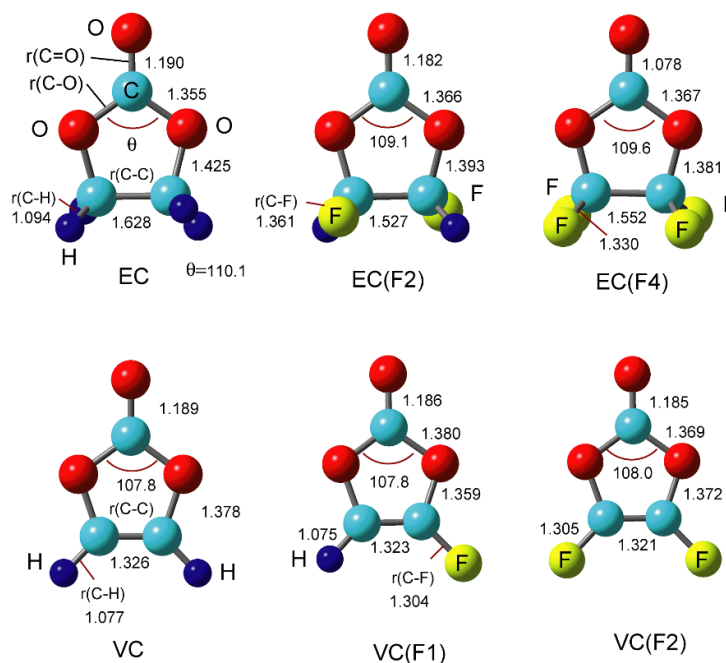


Figure 2. Optimized structures of EC, fluorinated ethylene carbonate (EC(F)), vinylene carbonate (VC) and fluorinated vinylene carbonate (VC(F)), calculated at the B3LYP/6-31G(d) level. The notation of n in EC(F_n) and VC(F_n) means the number of fluorine atoms. Bond lengths are in Å.

The dipole moments of EC(F) and VC(F) are given in Table 1. The dipole moment of EC in $n = 0$ was 5.42 Debye, which is in reasonable agreement with the experimental value (4.9 Debye). The

dipole moment decreased significantly with increasing n . In the case of EC(F), the value ($n = 4$) was 1.39 D, which is lower than that of $n = 0$ (5.42 D). This is due to the fact that the dipole moment of the C=O carbonyl vanishes in the presence of the C-F dipole. Thus, the effect of the halogen atom on the electronic state is very important in ethylene carbonate. In the case of the VC system, a similar diminishing was found after the F-substitution.

Table 1. Dipole moments of EC, EC(F), VC and VC(F) (in Debye). The number of fluorine atoms in EC is denoted by n . The experimental value of the dipole moment is given in parenthesis [17]. CAM, Coulomb-attenuating method.

n	Dipole Moment	
	CAM-B3LYP/6-31G(d)	CAM-B3LYP/6-311G(dp)
EC0	5.36 (4.9)	5.42
EC(F1)1	4.76	4.80
EC(F2)2	3.61	3.50
EC(F3)3	2.87	2.75
EC(F4)4	1.67	1.39
VC0	4.71	4.69
VC(F1)1	3.70	3.59
VC(F2)2	2.61	2.40

In EC, the C–C bond is composed of sp^3 - sp^3 carbons. On the other hand, the C–C bond in VC is the sp^2 - sp^2 carbons. Hence, the C=C bond length of VC is significantly shorter than that of EC. The C=C bond lengths of VC, VC(F1) and VC(F2) were 1.326, 1.323 and 1.321 Å, respectively.

3.2. Structures of Li^+ -EC and Li^+ -VC Complexes

The optimized structures of Li^+ -EC and -VC complexes are given in Figure 3. The procedure of optimization was carried out without symmetry restriction. The Li^+ ion binds to the oxygen atom of the C=O carbonyl of EC. The moiety of Li–O–C is almost linear in the Li^+ EC complexes. The bond distances of Li–O and C=O carbonyl were calculated to be 1.740 and 1.225 Å, respectively. The C–O bond in the C=O carbonyl is elongated by the interaction with the Li^+ ion. In the Li^+ -VC system, similar binding structures were obtained.

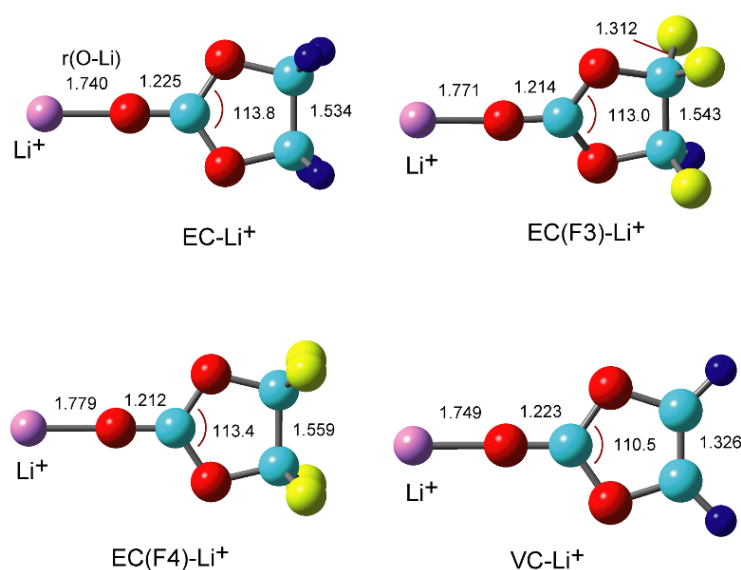


Figure 3. Optimized structures of lithium-EC and -VC complexes calculated at the B3LYP/6-31G(d) level. Bond lengths are in Å.

The distances of Li^+ from the oxygen atom of C=O carbonyl are plotted in Figure 4 as a function of the number of F atoms. The Li^+ -EC complex has a distance of 1.740 Å. The distance increases with increasing n . In $n = 4$, the distance is as large as 1.779 Å.

3.3. Binding Structures of Li^+ -EC Complexes on Graphene

The optimized structures of the complexes of EC(F) and EC(F4) with graphene are illustrated in Figure 5. In both complexes, the C=O carbonyl orients toward the center of the benzene ring of graphene. The bond lengths of the C=O carbonyl of EC and the height of the oxygen atom (h) of EC are 1.783 and 1.915 Å, respectively. In the case of EC(F4), the height becomes lower ($h = 1.882$ Å).

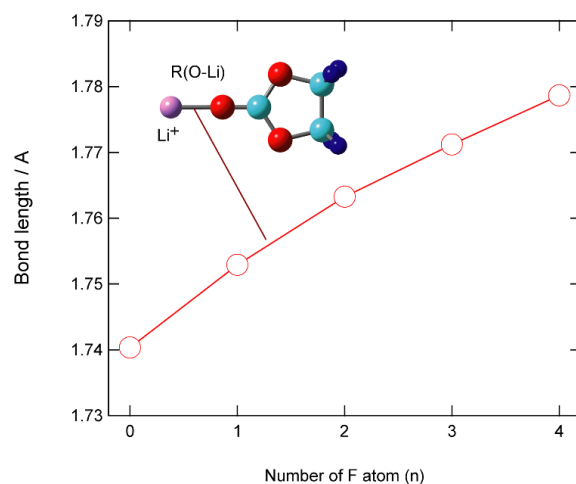


Figure 4. Bond lengths of the Li^+ -oxygen atom of Li-EC complexes plotted as a function of the number of F-atoms. The values were calculated at the B3LYP/6-31G(d) level.

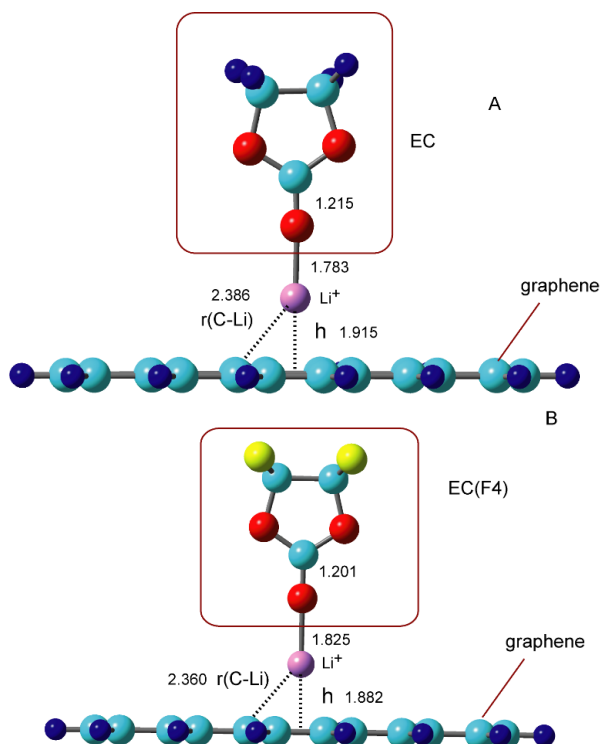


Figure 5. Optimized structures of EC- Li^+ -graphene ternary systems. Bond lengths are in Å. (A); Li^+ -EC Complexes on Graphene, (B); Li^+ -EC(F4) Complexes on Graphene.

Figure 6 shows the distance of the oxygen of EC from the graphene surface (h) plotted as a function of n . The distance decreases slightly from 1.915 to 1.883 Å. The values of Li^+ -VC are also plotted as a dashed line in Figure 6: 1.907 Å ($n = 0$), 1.899 Å ($n = 1$) and 1.893 Å ($n = 2$).

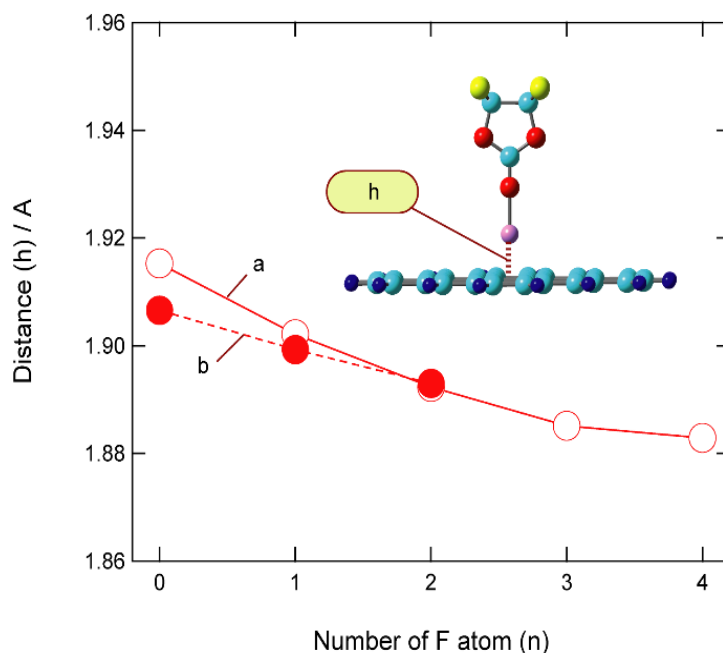
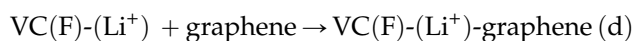
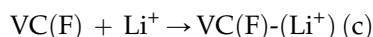
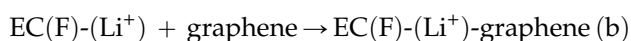
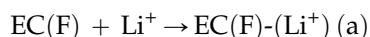


Figure 6. Distances of the lithium atom of Li^+ -EC (or Li^+ -VC) from the graphene surface (h) plotted as a function of n , the number of F-atoms. The values were calculated at the B3LYP/6-31G(d) level. (a) Li^+ -EC; (b) Li^+ -VC.

3.4. Binding Energies of Li^+ -EC Complexes on Graphene

The binding energies of EC and VC in several binding systems are calculated; these systems are expressed by:



Reaction (a) means the binding reaction of lithium ion to solvent EC(F). The solvated lithium ion is formed by Reaction (a). Reaction (b) is the binding reaction of the solvated lithium ion $\text{EC(F)}-(\text{Li}^+)$ to the graphene surface. Reactions (c) and (d) in VC(F) are the same as EC(F).

The reverse reaction of Reaction (a), *i.e.*, desolvation of Li^+ from solvent EC(F), $\text{Li}^+\text{-EC} \rightarrow \text{Li}^+ + \text{EC}$, is the most important process in the movement of the Li^+ ion from solvent to graphene. The weaker solvation of the Li^+ ion by EC is a positive factor as a solvent. Namely, the weak solvation of Li^+ is preferred as an effective solvent.

The calculated binding energies generated by Reactions (a) to (d) are plotted in Figure 7. The binding energies of Li^+ to EC(F) (Reaction (a)) decreases with increasing n : 56.1 kcal/mol ($n = 0$) and 39.6 kcal/mol ($n = 4$). The results suggest that EC(F4) is more preferred as the solvent than EC(H), because the weaker solvation of the Li^+ ion is the positive factor as the Li^+ solvent.

Furthermore, the binding energies for Reactions (b), (c) and (d) show the same tendency as Reaction (a).

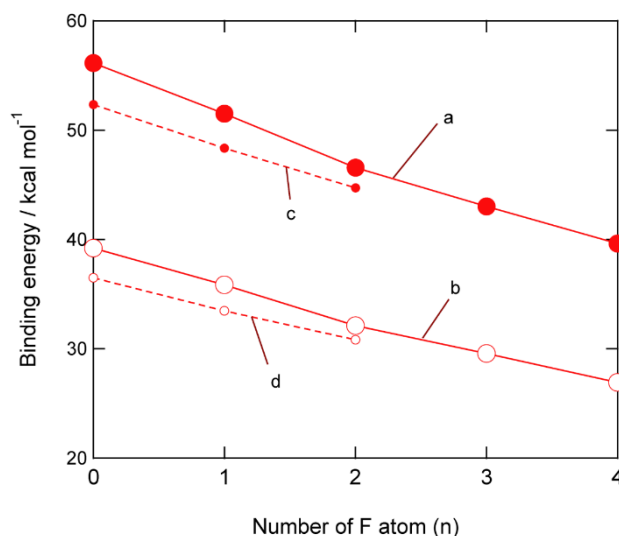


Figure 7. Binding energies in several systems plotted as a function of n , the number of F-atoms. (a) EC-Li⁺; (b) EC-Li⁺-graphene; (c) VC-Li⁺; and (d) VC-Li⁺-graphene.

4. Discussion

The weaker solvation of Li⁺ ion is a positive factor as the solvent. In the present study, the effects of F-substitution on the binding energies of EC to the Li⁺ ion and Li⁺(EC) to the graphene surface have been investigated by means of the DFT method. The calculations showed that the binding energy decreases with increasing n . F-substitution makes the interaction of graphene with EC(F) significantly weaker due to the small dipole moment of EC(F) (1.4 D *vs.* 5.4 D). This result implies that desolvation of the Li⁺ ion from the F-substituted system, EC(F)-Li⁺, occurs more easily than that of EC(H). Hence, the ability of EC(F) is greater than that of EC(H).

In the present study, a carbon sheet composed of 14 benzene rings (C₄₂H₁₆) was used as a model of the graphene surface. This is a small number of rings for modeling a finite graphene surface. However, recent theoretical calculations indicated that this size of graphene sheet can reasonably represent the electronic states of the graphene system [18–21]. Therefore, the present calculations would provide useful information on the ternary interaction system.

Acknowledgments: The author acknowledges partial support from JSPS KAKENHI Grant Number 15K05371 and MEXT KAKENHI Grant Number 25108004.

Author Contributions: Mami Mutoh, Teruo Kusaka and Mariko Nakamura carried out the DFT calculations of Li⁺-EC Complexes on Graphene. Yasuhiro Yoshida, Junichiro Iida, and Hiroto Tachikawa conceived of the study, and participated in its design and coordination and helped to draft the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bhatta, M.D.; Cho, M.; Cho, K. Interaction of Li⁺ ions with ethylene carbonate (EC): Density functional theory calculations. *Appl. Surf. Sci.* **2010**, *257*, 1463–1468. [[CrossRef](#)]
2. Nakagawa, H.; Fujino, Y.; Kozono, S.; Katayama, Y.; Nukuda, T.; Sakaebe, H.; Matsumoto, H.; Tatsumi, K. Application of nonflammable electrolyte with room temperature ionic liquids (RTILs) for lithium-ion cells. *J. Power Sources* **2007**, *174*, 1021–1026. [[CrossRef](#)]
3. Xing, L.; Li, W.; Wang, C.; Gu, F.; Xu, M.; Tan, C.; Yi, J. Theoretical Investigations on Oxidative Stability of Solvents and Oxidative Decomposition Mechanism of Ethylene Carbonate for Lithium Ion Battery Use. *J. Phys. Chem. B* **2009**, *113*, 16596–16602. [[CrossRef](#)] [[PubMed](#)]

4. Zhang, H.L.; Sun, C.H.; Li, F.; Liu, C.; Tan, J.H.; Cheng, M. New insight into the interaction between propylene carbonate-based electrolytes and graphite anode material for lithium ion batteries. *J. Phys. Chem. C* **2007**, *111*, 4740–4748. [[CrossRef](#)]
5. Zhu, Y.; Casselman, M.D.; Li, Y.; Wei, A.; Abrahama, D.P. Perfluoroalkyl-substituted ethylene carbonates: Novel electrolyte additives for high-voltage lithium-ion batteries. *J. Power Sources* **2014**, *246*, 184–191. [[CrossRef](#)]
6. Werber, T.; Walther, J.H.; Jaffe, R.L.; Halicioglu, T.; Koumoutsakos, P. On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes. *J. Phys. Chem. B* **2003**, *107*, 1345–1352.
7. Rana, M.; Chandra, A. Filled and empty states of carbon nanotubes in water: Dependence on nanotube diameter, wall thickness and dispersion interactions. *J. Chem. Sci.* **2007**, *119*, 367–376. [[CrossRef](#)]
8. Castriota, M.; Cazzanelli, E.; Nicotera, I.; Coppola, L.; Oliviero, C.; Ranieri, G.A. Temperature dependence of lithium ion solvation in ethylene carbonate-LiClO₄ solutions. *J. Chem. Phys.* **2003**, *118*, 5537–5541. [[CrossRef](#)]
9. Tachikawa, H. A direct molecular orbital-molecular dynamics study on the diffusion of the Li ion on a fluorinated graphene surface. *J. Phys. Chem. C* **2008**, *112*, 10193–10199. [[CrossRef](#)]
10. Abe, S.; Nagoya, Y.; Watari, F.; Tachikawa, H. Interaction of Water Molecules with Graphene: A Density Functional Theory and Molecular Dynamics Study. *Jpn. J. Appl. Phys.* **2010**, *49*, AH071–AH074. [[CrossRef](#)]
11. Abe, S.; Nagoya, Y.; Watari, F.; Tachikawa, H. Structures and Electronic States of Water Molecules on Graphene Surface: A Density Functional Theory Study. *Jpn. J. Appl. Phys.* **2010**, *49*, GJ131–GJ133. [[CrossRef](#)]
12. Amft, M.; Sanyal, B.; Eriksson, O.; Skorodumova, N.V. Small gold clusters on graphene, their mobility and clustering: A DFT study. *J. Phys. Condens. Matter* **2011**, *23*, 205301. [[CrossRef](#)] [[PubMed](#)]
13. Ding, N.; Lu, X.Q.; Wu, C.M.L. Nitrated tyrosine adsorption on metal-doped graphene: A DFT study. *Comput. Mater. Sci.* **2012**, *51*, 141–145. [[CrossRef](#)]
14. Lim, D.H.; Wilcox, J. DFT-Based Study on Oxygen Adsorption on Defective Graphene-Supported Pt Nanoparticles. *J. Phys. Chem.* **2011**, *115*, 22742–22747. [[CrossRef](#)]
15. Yanai, T.; Tew, D.; Handy, N. A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57. [[CrossRef](#)]
16. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A., Jr.; Vreven, T.; Kudin, K.N.; Burant, J.C.; et al. *Gaussian 03, Revision B.04*; Gaussian, Inc.: Pittsburgh, PA, USA, 2003.
17. Payne, R.; Theodorou, I.E. Dielectric properties and relaxation in ethylene carbonate and propylene carbonate. *J. Phys. Chem.* **1972**, *76*, 2892–2900. [[CrossRef](#)]
18. Mirzaei, M.; Ahangari, R.S. Formations of CNT modified 5-(halogen)uracil hybrids: DFT studies. *Superlattice Microstruct.* **2014**, *65*, 375–379. [[CrossRef](#)]
19. Peyghan, A.A.; Noei, M.; Yourdkhani, S. Al-doped graphene-like BN nanosheet as a sensor for para-nitrophenol: DFT study. *Superlattice Microstruct.* **2013**, *59*, 115–122. [[CrossRef](#)]
20. Jenness, G.R.; Karalti, O.; Jordan, K.D. Benchmark calculations of water-acene interaction energies: Extrapolation to the water-graphene limit and assessment of dispersion-corrected DFT methods. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6375–6381. [[CrossRef](#)] [[PubMed](#)]
21. Pisula, W.; Feng, X.; Mullen, K. Charge-Carrier Transporting Graphene-Type Molecules. *Chem. Mater.* **2011**, *23*, 554–567. [[CrossRef](#)]

