

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/268131471>

Understanding Li^+ -Carbonate Interaction in Electrolytes With ^{17}O -NMR

CONFERENCE PAPER · OCTOBER 2013

READS

33

5 AUTHORS, INCLUDING:



[Xavier Bogle](#)

The New York Academy of Sciences

10 PUBLICATIONS 76 CITATIONS

[SEE PROFILE](#)



[Steve G. Greenbaum](#)

City University of New York - Hunter College

249 PUBLICATIONS 4,044 CITATIONS

[SEE PROFILE](#)



[Kang Xu](#)

Army Research Laboratory

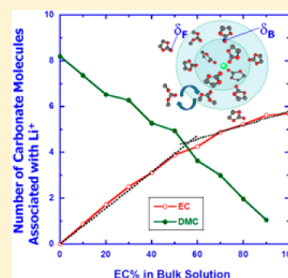
175 PUBLICATIONS 5,617 CITATIONS

[SEE PROFILE](#)

Understanding Li^+ –Solvent Interaction in Nonaqueous Carbonate Electrolytes with ^{17}O NMRXavier Bogle,[†] Rafael Vazquez,^{†,‡} Steven Greenbaum,^{*,†,‡} Arthur von Wald Cresce,[§] and Kang Xu^{*,§}[†]Department of Physics & Astronomy, Hunter College of the City University of New York, New York, New York 10065, United States[‡]Graduate Center of the City University of New York, New York, New York 10065 and 10016, United States[§]Electrochemistry Branch, U.S. Army Research Laboratory, Adelphi, Maryland 20783, United States

S Supporting Information

ABSTRACT: To understand how Li^+ interacts with individual carbonate molecules in nonaqueous electrolytes, we conducted natural abundance ^{17}O NMR measurements on electrolyte solutions of 1 M LiPF_6 in a series of binary solvent mixtures of ethylene carbonate (EC) and dimethyl carbonate (DMC). It was observed that the largest changes in ^{17}O chemical shift occurred at the carbonyl oxygens of EC, firmly establishing that Li^+ strongly prefers EC over DMC in typical nonaqueous electrolytes, while mainly coordinating with carbonyl rather than etheral oxygens. Further quantitative analysis of the displacements in ^{17}O chemical shifts renders a detailed Li^+ -solvation structure in these electrolyte solutions, revealing that maximum six EC molecules can coexist in the Li^+ -solvation sheath, while DMC association with Li^+ is more “noncommittal” but simultaneously prevalent. This discovery, while aligning well with previous fragmental knowledge about Li^+ -solvation, reveals for the first time a complete picture of Li^+ solvation structure in nonaqueous electrolytes.

SECTION: Kinetics and Dynamics

Lithium ion batteries (LIBs) power our digital daily life almost exclusively, while vehicle electrification and grid stabilization are offering even more significant markets for this relatively young battery chemistry. The state-of-the-art LIBs consist of a pair of intercalation compounds as hosts to accommodate Li^+ , and nonaqueous electrolytes to conduct it. The latter is based on nonaqueous solutions of lithium salts, usually LiPF_6 , dissolved in organic carbonate solvents.¹ Whereas there are numerous variations on this theme, the skeleton composition of the electrolytes used in majority of LIB has been mixtures of a cyclic carbonate, ethylene carbonate (EC), with one or more of its acyclic counterparts such as dimethyl carbonate (DMC).² Although the high melting point of EC (38 °C) makes it an unsuitable cosolvent for ambient or lower temperature applications, it has become an indispensable component of LIBs, mainly due to its unique electrochemical decomposition pathway leading to the formation of a stable solid electrolyte interphase (SEI) on the anode surface,³ which stabilizes the electrolyte/anode interface against further decomposition and supports the reversible intercalation chemistry of Li^+ .

The importance of SEI in defining the cycle life and power density of LIB has been well-recognized since the inception of LIB technology,⁴ while its elusive ad hoc nature has made it the least understood component in LIB, especially its formation mechanism.⁵ In recent years a “co-intercalation” model leading to a 3D SEI has been increasingly accepted by the community, in which the Li^+ -solvation sheath dictates the chemical composition of SEI in this mechanism.^{5–8} Thus a fundamental

question was raised about how Li^+ would be solvated in mixture solvents such as EC and DMC. Conflicting answers to this question have been provided by existing literature.^{9–13}

To resolve this important controversy, we have carried out an investigation of Li^+ -solvation preference using “soft” electrospray ionization mass spectrometry (ESI-MS), which identified EC as the solvent molecule that dominated the primary solvation sheath of Li^+ .^{14,15} Meanwhile a related work using ^{13}C NMR on ternary solvent mixtures has basically led to the same conclusion.¹⁶ However, neither study is ideal in that they do not describe the picture of Li^+ –carbonate interaction under conditions close enough to actual environments of applications in cells: in the former case, the solvated Li^+ was studied in gaseous state and probably already experienced partial desolvation before being detected, and in the latter, ^{13}C nuclei in the solvent molecules provide only an indirect probe of Li^+ solvation, and hence it is difficult to derive quantitative information from its chemical shifts.

The present letter represents a new approach that aims to visualize Li^+ solvation environment under more relevant conditions. We believe that it is preferable to look at the structural units that are directly responsible for Li^+ -solvation, that is, oxygen nuclei in the solvent molecules. Hence, the change in chemical shifts of ^{17}O nuclei in EC/DMC mixture

Received: March 26, 2013

Accepted: April 29, 2013

was monitored in the entire range of EC/DMC ratios as a function of both solvent mixing and Li salt induction. While the low natural abundance of ^{17}O (0.037%) and quadrupolar nature of its nuclei (leads to broader peaks in the spectrum) do present a technical challenge to facile data collection, its large chemical shift range and cation affinity make it a sensitive probe of ion solvation effects.

It is well known that, upon dissolution, the crystal lattice of Li salt is disrupted as solvent molecules interact with cations and anions, respectively, forming complexes known as “solvated ions”.¹⁷ Because of the formal charge localized on the small Li^+ (0.09 nm), it was generally accepted that Li^+ –solvent interaction far outweighs that between its anion counterpart and the solvents.^{17,18} For this reason, all nonaqueous solvents used in LIB are based on polar organic molecules containing oxygen atoms, whose lone pair electrons effectively coordinate to Li^+ and form a stabilized “solvated Li^+ ”. As illustrated by Figure 1, in such a solvated ionic complex, Li^+ is surrounded by

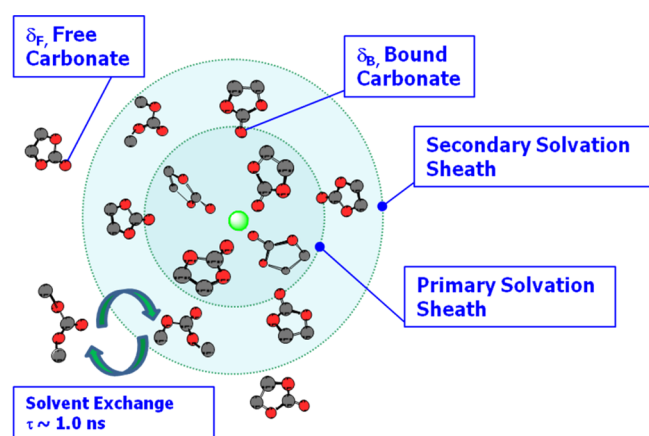


Figure 1. Schematic illustration of Li^+ –solvation sheath in nonaqueous electrolytes and the various ^{17}O nuclei in their coordination states with Li^+ .

a number of solvent molecules, which are aligned in such a manner that the ion–dipole interaction between Li^+ and the coordinating units (in this case, oxygens) be maximized. These molecules, now tightly bound by Li^+ through Coulombic attraction, form the so-called “solvation sheath”. It is this ion–dipole interaction that would be directly reflected by the change in electronic environment of the ^{17}O nuclei, as expressed in terms of chemical shifts (δ) in NMR spectroscopy.¹⁹ The latter would serve as a more direct parameter than ^{13}C chemical shifts in quantifying the binding strength between carbonate molecule and a Li^+ .

Figure 2 shows the ^{17}O NMR spectra for 1.0 M LiPF_6 solution in EC/DMC (50:50) mixture, along with those of the corresponding neat solvent mixture in the absence of Li salt and each individual solvent (neat EC and DMC). As the inset of Figure 1 indicates, there are two sets of inequivalent ^{17}O –nuclei in either EC or DMC, with the carbonyl ^{17}O (*a* and *c*) sitting between 200–250 ppm and ethereal ^{17}O (*b* and *d*) between 75–150 ppm, respectively.²⁰ With the addition of Li salt, chemical shifts of all carbonyl ^{17}O nuclei expectedly experience an upfield displacement due to the shielding effect of Li^+ on the lone pair electron density, while the ethereal ^{17}O nuclei show a downfield displacement attributable to an increased deshielding effect. Apparently, this displacement, when referenced against their corresponding spectra in the neat solvent mixture and

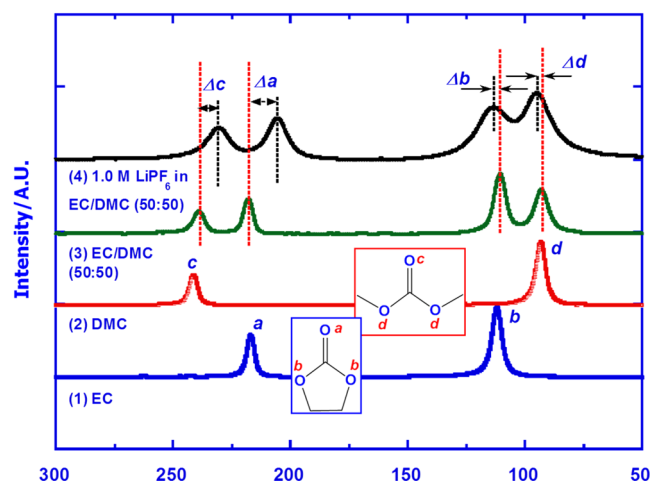


Figure 2. ^{17}O NMR spectra for neat EC, DMC, their 50:50 mixture and the 1.0 M LiPF_6 solution in the mixture, respectively. Attribution of individual ^{17}O signals and the displacements in ^{17}O chemical shifts as induced by Li^+ with respect to the mixture are labeled.

designated as Δa , Δb , Δc , and Δd hereafter, should be directly related to the ion–dipole interaction between Li^+ and solvent molecules (See the Supporting Information and Figure S1 for the reason why neat solvent mixtures rather than individual pure solvents were selected as references.)

It must be emphasized here that the presence of Li^+ in electrolytes does not induce the appearance of any new peaks, despite what Figure 1 might imply; that is, the ^{17}O resonance in carbonyl of “bound” EC should differ from that of “free” EC in terms of chemical shifts (δ_B and δ_F , respectively, in Figure 1). Instead, the fact that those peaks are displaced rather than being split indicates that all chemical shifts measured for LiPF_6 solutions are the result of an “averaging effect”; that is, the solvent exchange rate between the solvation sheath and solution bulk is much faster (<1.0 ns) than the reciprocal of the difference between those two imaginary peaks at δ_B and δ_F .²¹ Hence, all observed ^{17}O chemical shifts are the result of this averaging, hereafter designated as δ_A .

These displacements induced by Li^+ in ^{17}O chemical shifts were derived for all electrolyte solutions investigated, as shown in Table S1 in the Supporting Information, and their dependence on bulk electrolyte composition is plotted in Figure 3. It should be pointed out here that the absolute values of the displacements rather than the actual displacements were plotted to properly portray the relationship between the change in chemical shifts and increasing EC concentration. Immediately obvious from Figure 2 are two observations: (1) the displacements in carbonyl ^{17}O nuclei (Δa and Δc) are far greater than those in ethereal ^{17}O nuclei (Δb and Δd) for both EC and DMC and (2) between these two carbonyl ^{17}O nuclei, EC (Δa) is affected to a much larger degree than is DMC (Δc). The former strongly suggests that Li^+ does interact directly with carbonyl instead of ethereal O nuclei in the carbonate ester molecules, as illustrated in Figure 1, while the latter unequivocally identifies EC as the preferred solvent molecule in a Li^+ –solvation sheath because of its higher donicity (DN = 16.4) and dielectric permittivity ($\epsilon = 90$). Both observations are in excellent agreement with previous ^{13}C NMR and ESI-MS studies.^{14–16}

Beside these apparent agreements on solvation preference and location of Li^+ coordination, more detailed information can

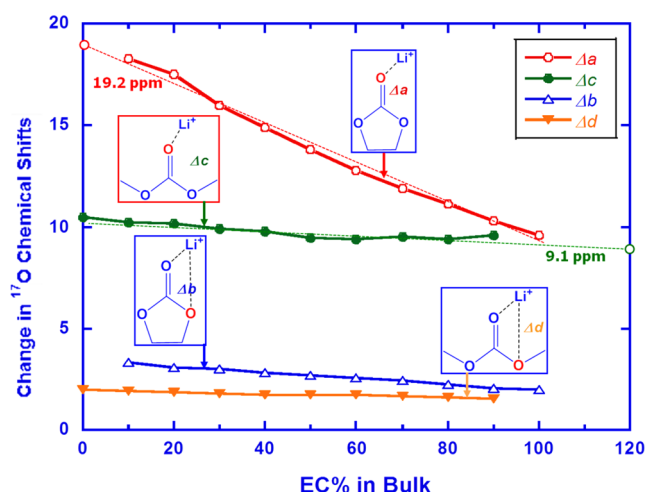


Figure 3. Displacements in ^{17}O NMR chemical shifts for both carbonyl and etheral oxygens of EC and DMC in 1.0 M LiPF_6 solutions with respect to corresponding solvents mixtures. Extrapolated values for Δa and Δc are derived for the ideal state of “bound” EC and DMC carbonyl ^{17}O signals, respectively.

be derived from Figure 3 about how the Li^+ -solvation environment changes with the bulk electrolyte composition. Particularly interesting is the steep dependence of EC carbonyl displacements (Δa) on electrolyte composition, which appears counterintuitive at first glance because the maximum displacement Δa occurs at the minimum EC concentration, while linearly decreasing as EC population increases in the bulk solution. Upon closer examination, it is revealed that the ratio between EC and Li^+ plays a key role in this peculiar relation. Because LiPF_6 was kept at constant concentration throughout all electrolyte compositions, at low EC population all EC molecules would be expected to be completely “recruited” by Li^+ into its solvation sheath and tightly bound. Because there is a minimum number of “free” EC molecules available in the bulk solution under this circumstance the chemical shift of ^{17}O nuclei would be more characterized by the “bound” EC, that is, with the largest displacement affected by Li^+ . With increasing EC population in bulk solution, “free” EC molecules start to appear outside of Li^+ -solvation sheath, and the observed ^{17}O nuclei chemical shift would be diluted according to an assumed simple linear relation:

$$\delta_A = \delta_B X_B^{\text{EC}} + \delta_F (1 - X_B^{\text{EC}})$$

where δ_A , δ_B , and δ_F have been defined above and X_B^{EC} represents the molar fraction of bound EC. The linear decrease behavior, as observed for Δa in Figure 3, can thus be reasonably accounted for. However, it must be cautioned that by classifying EC molecules into two distinct states of “free” and “bound” the above relation risks oversimplification, as EC molecules in transition states between these two extremes would certainly exist.

Both δ_A and δ_F are known quantities as the former is the measured ^{17}O chemical shifts in LiPF_6 solutions and the latter is that in the corresponding neat solvent mixtures (Table S1 in the Supporting Information). Because δ_B represents an ideal situation where all EC molecules are bound within the Li^+ -solvation sheath with no “free” EC existence, it cannot be experimentally measured. However, we can derive its value to a first order of approximation by extrapolating the Δa -dependence toward 0% EC, as shown in Figure 3. With $\Delta a = 19.2$ ppm

and $\delta_F = 217$ (taken from ^{17}O chemical shift in pure EC, Table S2 in the Supporting Information), δ_B is determined to be 197.8 for all electrolyte solutions, and X_B can thus be easily solved for 1.0 M LiPF_6 solution in EC/DMC (50:50) as 0.68 using $\delta_A = 204.1$. This fraction of bound EC corresponds to four EC molecules in each Li^+ -solvation sheath.

Repeating this operation for all electrolyte solution compositions, we can obtain the dependence of Li^+ -solvation number by EC molecules on electrolyte bulk composition, which is plotted in Figure 4 and tabulated in Table 1.

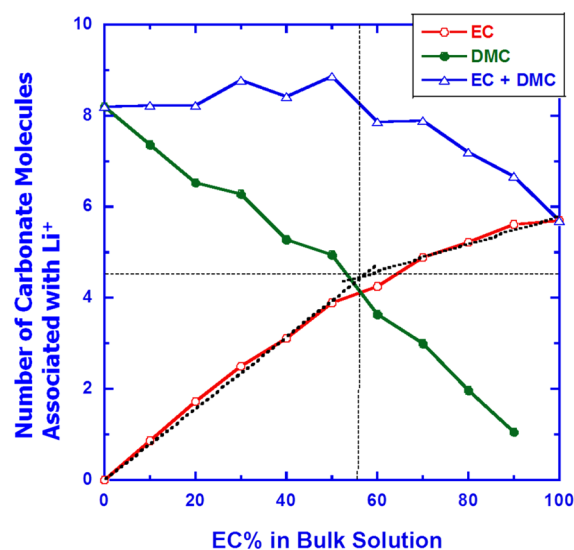


Figure 4. Numbers of carbonate molecules associated with each Li^+ as derived from ^{17}O NMR spectra data and its dependence on electrolyte composition.

Table 1. Population of EC or DMC Associated with Li^+ As Derived from Chemical Shifts of ^{17}O in Carbonyls

EC%	X_B^{EC}	EC associated with Li^+	X_B^{DMC}	DMC associated with Li^+	total no. of carbonates associated with Li^+
0		0	0.74	8.19	8.19
10	0.76	0.86	0.74	7.37	8.23
20	0.75	1.71	0.73	6.52	8.23
30	0.73	2.50	0.81	6.29	8.79
40	0.69	3.12	0.79	5.28	8.40
50	0.69	3.90	0.89	4.95	8.85
60	0.62	4.24	0.82	3.63	7.87
70	0.61	4.89	0.90	3.00	7.89
80	0.58	5.23	0.89	1.97	7.20
90	0.55	5.62	0.95	1.05	6.67
100	0.50	5.69		0	5.69

Obviously, when EC population increases in the bulk, the vicinity of Li^+ is gradually populated with EC molecules. The maximum number of EC molecules that a Li^+ can accommodate in its solvation sheath seems to be six. Because the oversimplified model used here (Figure 1) does not differentiate the possible structure of primary versus secondary solvation, this number should be inclusive of all solvent molecules associated with Li^+ in both manners.

Compared with the Li^+ –EC interaction, a rather different behavior is observed for the corresponding dependence of DMC carbonyl displacements (Δc), which is almost independent of the bulk electrolyte composition. While one

could be readily tempted to conclude that it reflects a weak interaction between DMC and Li^+ , it must be realized that the displacements (Δc) themselves have nonzero values, implying a weaker (as compared with EC) but nonetheless constant interaction. We believe that this peculiar dependence stems from a rather “loose” but prevalent association between DMC and Li^+ . Very likely the linear DMC molecules would enter and exit Li^+ -solvation sheath with a much higher degree of freedom than EC, thus almost all DMC molecules in the bulk electrolyte would be equally affected by Li^+ coordination. While the rationale of this phenomenon remains to be clarified, it is believed that the high donicity (DN = 15.1) but low permittivity ($\epsilon = 3.1$) of DMC might be responsible. The former factor suggests that the lone pair electron on DMC carbonyl is still highly available to Li^+ , while the latter dictates a weak binding strength.

The above hypothesis seems to be confirmed when the same quantitative analysis is performed on the carbonyl- ^{17}O chemical shifts in DMC (Table 1). Throughout the entire electrolyte composition range, the molar fraction of DMC bound by Li^+ ($X_{\text{B}}^{\text{DMC}}$) remains above 75% even when the bulk electrolyte is dominated by DMC (90%). In other words, although Li^+ –DMC is weaker in bonding strength, the DMC presence in the Li^+ -solvation sheath is prevalent. This apparent paradox, unexpected from previous ESI-MS and ^{13}C NMR studies, is able to resolve the controversy about whether Li^+ has preferential solvation in EC/DMC mixture.^{9–13} It also explains why, in the ESI-MS study, the DMC could be barely identified in the solvated ionic species and the solvation numbers were lower than three. As in any MS technique, partial desolvation may have occurred before the ionic species arrived at the detector, and during the flight the weakly bound DMC molecules will likely be stripped away, leaving the tightly bound EC behind as the dominant member in the sheath. Therefore, while ESI-MS does effectively identify the solvent molecules tightly bound to Li^+ , it would underestimate the Li^+ -solvation number by ignoring the weakly bound molecules. The Li^+ solvation number, when measured by ^{17}O NMR in the present work, should be closer to reality in bulk electrolyte solutions.

On the basis of X_{B}^{EC} derived, the DMC population associated to Li^+ can be calculated. The results along with the total numbers of carbonate molecules associated with Li^+ are summarized in Table 1 and Figure 4. As DMC is gradually replaced by EC in bulk, the Li^+ vicinity is more rapidly populated by the latter, until a near-saturation is reached between five and six, which should be the largest number of EC molecules that a single Li^+ can accommodate. The total number of carbonates (EC and DMC) ranges between 6 and 10, with a general decreasing trend when electrolytes become EC-concentrated. This was the case because the more rigid structure of cyclic EC molecule is more sterically demanding than the flexible linear DMC; hence, at higher EC concentrations the total number of molecules in the solvation sheath approaches its lower limit. It should be noted that the above numbers, as derived from ^{17}O chemical shifts on the basis of a simple model of Figure 1, should reflect all of the solvent molecules in both primary and secondary solvation sheaths, while in retrospect, the solvation numbers and composition as revealed by ESI-MS should be closer to that of the primary sheath. By using those two complementary techniques, for the first time, we are able to reveal a detailed picture of a structured Li^+ -solvation sheath.

In summary, for the first time ^{17}O NMR was employed as an accurate probe to understand how Li^+ interacts with carbonate molecules in typical nonaqueous electrolytes. The spectra unequivocally established that Li^+ is preferentially solvated by EC, and the primary location of coordination is carbonyl rather than ethereal oxygens. Further quantitative analysis on ^{17}O chemical shifts revealed that although DMC bonding with Li^+ is weaker than EC its presence in Li^+ -solvation sheath is not negligible; rather, almost all DMC molecules in the bulk electrolyte solution participated in interaction with Li^+ . Complementary to ESI-MS previously employed for the same purpose, a complete picture of primary and secondary structures of Li^+ -solvation sheath can be speculated: while the Li^+ primary solvation sheath can accommodate typically three to four carbonate molecules, more carbonate molecules (two to four in number) can still maintain a weaker interaction with Li^+ by being in its secondary solvation sheath. EC seems to be able to “shield” Li^+ more effectively than does DMC, as the total number of solvent molecules decreases as EC concentration becomes higher.

■ ASSOCIATED CONTENT

● Supporting Information

All displacements in ^{17}O -chemical shifts and the calculation of “bound” carbonyl ^{17}O -chemical shifts for both EC and DMC are tabulated in Tables S1 and S2. The overlay of all ^{17}O NMR spectra is shown in Figure S1, the effect of solvent-mixing on ^{17}O -chemical shift displacements is shown in Figures S2 and S3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: steve.greenbaum@hunter.cuny.edu (S.G.); conrad.kxu.civ@mail.mil (K.X.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Army Research Office under contract number W911NF-12-2-0059. The Hunter College NMR facility is supported by a National Institutes of Health RCMI infrastructure grant (RR 003037). We thank Dr. Matthew Devany of the NMR facility for technical assistance.

■ REFERENCES

- (1) Kim, Y.; Goodenough, J. B. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, *22*, 587–603.
- (2) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303–4417.
- (3) Peled, E.; Golodnitsky, D.; Penciner, J. In *Handbook of Battery Materials*, 2nd ed.; Daniel, C., Besenhard, J. O., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 2011; Ch.16.
- (4) Fong, R.; von Sacken, U.; Dahn, J. R. Studies of Lithium Intercalation into Carbons Using Nonaqueous Electrochemical Cells. *J. Electrochem. Soc.* **1990**, *137*, 2009–2013.
- (5) Besenhard, J. O.; Winter, M.; Yang, J.; Biberacher, W. Filming Mechanism of Lithium-Carbon Anodes in Organic and Inorganic Electrolytes. *J. Power Sources* **1995**, *54*, 228–231.
- (6) Abe, T.; Fukuda, H.; Iriyama, Y.; Ogumi, Z. Solvated Li-Ion Transfer at Interface Between Graphite and Electrolyte. *J. Electrochem. Soc.* **2004**, *151*, A1120–1123.

- (7) Xu, K. 'Charge-Transfer' Process at Graphitic Anode/Electrolyte Interface and Solvation Sheath Structure of Li^+ in Non-aqueous Electrolytes. *J. Electrochem. Soc.* **2007**, *154*, A162–167.
- (8) Xu, K.; Lam, Y.; Zhang, S.; Jow, T. R.; Curtis, T. Solvation Sheath of Li^+ in Non-Aqueous Electrolytes and Its Implication of Graphite/Electrolyte Interface Chemistry. *J. Phys. Chem. C* **2007**, *111*, 7411–7421.
- (9) Morita, M.; Asai, Y.; Yoshimoto, N.; Ishikawa, M. A Raman Spectroscopic Study of Organic Electrolyte Solutions Based on Binary Solvent Systems of Ethylene Carbonate with Low Viscosity Solvents Which Dissolve Different Lithium Salts. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3451–3456.
- (10) Jeong, S. K.; Inaba, M.; Abe, T.; Ogumi, Z. Surface Film Formation on Graphite Negative Electrode in Lithium-Ion Batteries: AFM Study in an Ethylene Carbonate-Based Solution. *J. Electrochem. Soc.* **2001**, *148*, A989–993.
- (11) Yanase, S.; Oi, T. Solvation of Lithium Ion in Organic Electrolyte Solutions and Its Isotopic Reduced Partition Function Ratios Studies by Ab Initio Molecular Orbital Method. *J. Nucl. Sci. Technol.* **2002**, *39*, 1060–1064.
- (12) Wang, Y.; Balbuena, P. In *Lithium Ion Batteries: Solid Electrolyte Interphase*; Wang, Y., Balbuena, P., Eds.; Imperial College: London, 2004; Chap. 9.
- (13) Borodin, O.; Smith, G. Quantum Chemistry and Molecular Dynamics Simulation Study of Dimethyl Carbonate: Ethylene Carbonate Electrolytes Doped with LiPF_6 . *J. Phys. Chem. B* **2009**, *113*, 1763–1776.
- (14) Cresce, A. v.; Xu, K. Preferential Solvation of Li^+ Directs Formation of Interphase on Graphitic Anode. *Electrochem. Solid State Lett.* **2011**, *14*, A154–156.
- (15) Xu, K.; Cresce, A. v. Li^+ -Solvation/Desolvation Dictates Interphasial Process at Graphitic Anode in Li Ion Cells. *J. Mater. Res.* **2012**, *27*, 2327–2341.
- (16) Yang, L.; Xiao, A.; Lucht, B. L. Investigation of Solvation in Lithium Ion Battery Electrolytes by NMR Spectroscopy. *J. Mol. Liq.* **2010**, *154*, 131–133.
- (17) Berger, K. *Solvation, Ionic, and Complex Formation Reactions in Non-Aqueous Solvents: Experimental Methods for Their Investigation*; Akademiai Kiad: Budapest, 1983.
- (18) Bockris, J. O'M.; Reddy, A. K. N. *Modern Electrochemistry*, 2nd ed.; Plenum Press: New York, 2000; Vol. 1.
- (19) Dahn, H. Understanding Chemical Shifts in pi-Systems: ^{13}C , ^{15}N , ^{17}O NMR. *J. Chem. Educ.* **2000**, *77*, 905–908.
- (20) Raos, G.; Castiglione, F.; Baggioli, A.; Citterio, A.; Mele, A. Organic Peracids: A Structural Puzzle for ^{17}O NMR and Ab Initio Chemical Shift Calculations. *J. Phys. Chem. A* **2012**, *116*, 1814–1819.
- (21) Izutsu, K. *Electrochemistry in Non-Aqueous Solutions*; Wiley-VCH; Weinheim, Germany, 2009.