THE JOURNAL OF
PHYSICAL CHEMISTRY C

Article

Cite This: *J. Phys. Chem. C* 2018, 122, 1990−1994

pubs.acs.org/JPCC

The Interplay between Salt Association and the Dielectric Properties of Low Permittivity Electrolytes: The Case of $LiPF_6$ and $LiAsF_6$ in Dimethyl Carbonate

Julian Self,[†,‡] Brandon M. Wood,[‡,§] Nav Nidhi Rajput,[‡] and Kristin A. Persson*[,†,‡,§]

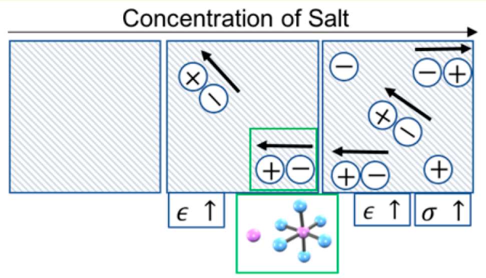
[†]Department of Materials Science and Engineering, University of California Berkeley, 210 Hearst Mining Building, Berkeley, California 94704, United States

[‡]Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[§]Department of Applied Science and Technology, University of California Berkeley, Berkeley, California 94704, United States

Supporting Information

ABSTRACT: In this article, we present evidence that the dielectric constant of an electrolyte solution can be effectively used to infer the association regime of the salt species from computational methods. As case studies, we consider the low dielectric constant solvent dimethyl carbonate with $LiAsF_6$ and $LiPF_6$ salts at low concentrations. Using both quantum "*ab initio*" methods as well classical molecular dynamics simulations, we elucidate the salt's contribution to the dielectric constant as well as the dipolar relaxation times, which act as quantitative signatures. By comparing to previously published measurements, we provide strong evidence for the presence of contact-ion pairs at these low concentrations. Interestingly, these ion pairs increase the dielectric constant of the solution, allowing for significantly improved ionic conductivity as a function of salt concentrations. We also discuss the role of multimeric equilibrium species as contributors to the functional properties of designer electrolytes, such as dielectric properties of the solution and ionic conductivity.



INTRODUCTION

The accurate identification and prediction of solvated species in solution as well as their impact on the properties of the solution, as a function of solvent, salt, and concentration are imperative to enable rational design of high stability, high conductivity electrolytes for Li-ion energy storage solutions. However, the definite identification of speciation equilibria in electrolyte solutions remains a challenge, from both a simulation and an experimental perspective. Solvate salt species present in solution are frequently categorized as free ions, solvent separated ion pairs (SSIPs), contact-ion pairs (CIPs), and aggregates (AGGs). Well-solvated ions are denoted as free ions and complexes comprising two and more than two counter-charged ionic species in the first solvation shell are deemed as CIP and AGG, respectively.[1,2]

One of the simplest models to understand the effect of the solution dielectric properties on salt association is obtained through the formalism of Bjerrum.[1,3,4] To promote association, the electrostatic contribution to the binding energy of the salt species (e.g., two oppositely charged point charges q_1 and q_2) should exceed the dissociative energy due to thermal fluctuations ($\sim 2k_BT$). For a permittivity of free space ϵ_0 and intercharge distance r, we can formulate the condition for association as

$$\left| \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon r} \right| > 2k_BT \tag{1}$$

Thus, a higher dielectric constant ϵ, just like higher temperature, acts as a driving force for dissociation. In reality, the precise requirements for association are more complicated due to the explicit and dynamic solvent−salt interactions. Recently, classical molecular dynamics (MD) was employed to study the dielectric properties of electrolytes. For example, You et al. focused on the dielectric properties of strictly neat solvents, such as propylene carbonate (PC),[5] Schroder et al. focused on the orientational polarizability of free ions in ionic liquids (with no significant bound ion pairs),[6,7] and Rinne et al. on the aqueous solvent's contribution when NaCl is present, while neglecting the polarity contribution from any bound pairs.[8] To the best of our knowledge, the impact of associated salt complexes on the dielectric behavior of liquid electrolytes has not been comprehensively addressed from a modeling perspective.

In this work, we use both *ab initio* and classical MD simulation methods to (i) identify the salt association regimes of the system based on the dielectric constant of the bulk electrolyte and (ii) analyze the effect of salt association on the dielectric properties of the electrolyte as a function of concentration. We apply our methodology (see Computational Details section for details) to two representative systems: 0.1 M

Received: November 8, 2017
Revised: December 18, 2017
Published: December 20, 2017

ACS Publications

DOI: 10.1021/acs.jpcc.7b11060
J. Phys. Chem. C 2018, 122, 1990−1994

$LiAsF_6$ and 0.1 M $LiPF_6$ in dimethyl carbonate (DMC), where DMC is chosen due to its low dielectric constant which makes possible the formation of various complex solvated species. In particular, $LiAsF_6$/DMC at low concentrations (~0.1 M) exhibits interesting behavior as compared to higher dielectric electrolytes (e.g., $LiAsF_6$/PC) such that the conductivity as a function of concentration is concave-up instead of concave-down.[9] In 1999, Doucey et al. found that the conductivity of $LiAsF_6$/DMC increases exponentially from 0.0 to 0.3 M (see Figure 1). For small concentrations ~ 0.1 M (see Figure 1), the lack of conductivity was suggested as due to an absence of free ions, resulting from the low dielectric constant of DMC (ϵ = 3.1).[12] A subsequent increase in conductivity with salt concentration was speculated to originate from the formation of dissolved, but associated, salt $LiAsF_6$ CIPs (bound and polar $Li^+\cdots AsF_6^-$), or other neutral associated salt species. These results were furthermore supported by Delsignore et al., who confirmed the nonlinear conductivity increase as well as measured an increase in the dielectric constant from 3.1 to 5.0 for 0−0.1 M $LiAsF_6$ using spectroscopy measurements.[10] Similar behavior was also observed for other low dielectric constant electrolytes.[1,13]

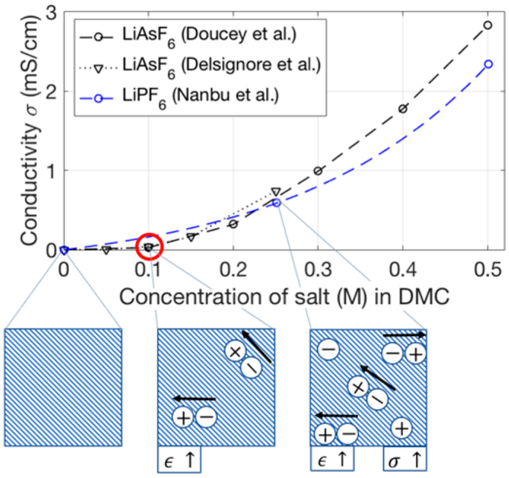


Figure 1. Experimentally measured conductivity as a function of salt concentration for $LiAsF_6$ and $LiPF_6$ in DMC.[9−11] The bottom rectangles (left to right) illustrate the neat solvent, an electrolyte with only associated salt (with dipole moments drawn as directed arrows), and finally an electrolyte with both associated (arrows) and dissociated salt (no arrows).

To compare to the relevant available experimental results, we focus on the low concentration regime of $LiAsF_6$/DMC. First, we assess the association regime by using quantum *ab initio* techniques while comparing to published conductivity results. Next, an existing MD force field[14,15] of DMC is modified to accurately reproduce the dielectric constant of the neat solvent. The reparametrized force field is then used to simulate the $LiAsF_6$/DMC and $LiPF_6$/DMC electrolytes as a function of concentration to estimate the contribution from the salt to the total ϵ of the solution. This contribution is then used *in tandem* with the *ab initio* results to obtain dissociation constants as a function of the dielectric constant (and concentration). Finally, from the MD calculations, we recover the dipolar relaxation times of the DMC solvent and CIP associated species, which correspond to measurable peaks in dielectric spectra.

■ COMPUTATIONAL DETAILS

Quantum chemistry calculations were undertaken with the Q-Chem software.[16] The B3LYP functional was used with the 6-311++(d,p) basis set[17] in conjunction with the PCM solvation model IEFPCM.[18−20] The justification for the methods used herein follows those of Hall et al.,[21] who obtained similar results for $LiPF_6$ dissociation, albeit with a different quantum chemistry software package.

MD calculations were carried out with the GROMACS software,[22] following the methodology of Rajput et al.[23] Initial configurations were prepared using the Packmol package.[24] We then used a steepest descent minimization procedure, an equilibration in an NPT ensemble (3 ns with the Berendsen thermostat), followed by simulated annealing (400 K for 2 ns) and cooling to 298 K (3 ns). Finally, NVT equilibration was undertaken at 298 K from which ϵ was calculated. Initial DMC charges were taken from Soetens et al.,[15] and subsequently scaled to reproduce the experimental dielectric constant. The other relevant force field parameters are standard in the OPLS library.[14] For the salt, the force field parameters were taken from Lopez and Padua and Ishida et al.[25,26]

The fluctuation dissipation theorem (FDT) allows the calculation of ϵ from the variance of the total dipole moment $\mathbf{P}$ of the system[27] (see the SI). We here extended the framework previously set up for molecules[5] by adding to the total dipole moment the contribution from CIPs. We implemented the FDT via Python code with help from the MDAnalysis package.[28] In order to investigate the dielectric increment from CIPs, we simulated a smaller box of 127 DMC molecules with one Li^+ species and one AsF_6^- species which associated into a CIP when the solvent charges were the ones that yielded a DMC of ϵ = 3.2. We here define the dielectric increment $\Delta\epsilon$ as the increase of the total dielectric constant of the electrolyte for a given addition of salt.

The relaxation times τ of the DMC, CIP, dimer, and trimer species were found by fitting an exponential (Debye)[27] fit to the autocorrelation function $\langle \mathbf{P}(0)\mathbf{P}(t)\rangle$. τ was inspected from a fit $ae(-t/\tau)$ and an average was taken in three possible Cartesian directions. Further details are provided in the SI.

■ RESULTS AND DISCUSSION

Figure 2 shows the first-principles calculated free energy of dissociation for $LiAsF_6$ incorporating mean-field solvation

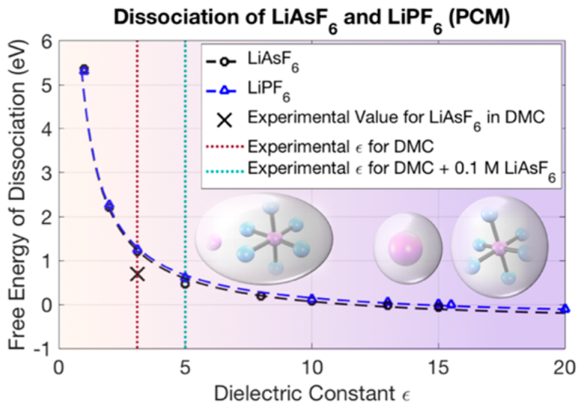


Figure 2. Free energy of dissociation for $LiAsF_6$ (black) and $LiPF_6$ (blue) into their respective free ions as computed from quantum mechanical methods with the PCM model. Fits (dashed) follow the inverse relationship proposed by Cavell and Knight.[13]

effects through a polarizable continuum solvation model (PCM). To represent a variety of (implicit) solvents, the dielectric constant ϵ of the solvent continuum was varied accordingly. As expected, for high dielectric constants, the dissociation of $LiAsF_6$ is favorable. For the case of neat DMC (ϵ = 3.1), dissociation is highly unfavorable, consistent with the observation of negligible conductivity at very low concentrations (e.g., < 0.1 M). We note that a calculated free energy of dissociation derived from the experimental equilibrium constant (shown in black ×)[10] shows fair agreement such that, at sufficiently low concentration, $LiAsF_6$/DMC exhibits majority species such as CIPs and/or AGGs in the electrolyte.

Using an existing force field for DMC,[14,15] however adjusted such that it reproduces the experimental dielectric constant of the neat solvent (see the SI), we calculate the contribution of the salt species to the total dielectric constant of the electrolyte. Figure 3 shows the calculated ϵ (with contributions from both salt and solvent) for both $LiAsF_6$ and $LiPF_6$. Between 0 and 0.1 M for $LiAsF_6$ in DMC, the dielectric increment due to the presence of the polar CIP is $\Delta\epsilon \sim 1.7$, which agrees with the measured increment $\Delta\epsilon \sim 1.9$. Repeated MD simulations resulted in a numerical error bar of $< \pm 0.2$, which we omit in Figure 3 for visual clarity. We note that the $\Delta\epsilon$ values for $LiPF_6$ (1.5) and $LiAsF_6$ (1.7) are similar to each other, as the difference is within the error estimate for our calculations. The substantial dielectric increment of the electrolyte can be rationalized as the CIP dipole is approximately 20 times that of the DMC solvent (see the SI). Intuitively, we expect $LiPF_6$ to behave analogously to $LiAsF_6$ such that both salts associate at low concentration in DMC and result in an electrolyte with increased polar behavior due to the formation of CIP or aggregate salt species. This expectation is supported by the simulated results presented in Figure 3, which shows comparable behavior for $LiAsF_6$ and $LiPF_6$ in DMC, in agreement with (albeit limited) conductivity data from Nanbu et al.[11] (see Figure 1).

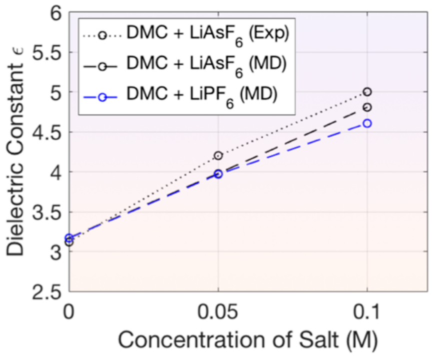


Figure 3. The calculated dielectric constant ϵ for 0.05 and 0.1 M of $LiAsF_6$ in DMC and $LiPF_6$ in DMC, including contribution from salt associated as CIPs. Dashed and dotted lines are drawn for visual ease. Experimental values taken from Delsignore et al.[10]

Utilizing the ϵ derived from the MD simulations, we employ *ab initio* methods to yield the dissociation constant K_d, as a function of ϵ and, effectively, concentration. We express K_d with the following relation[29]

$$K_d = \exp\left(-\frac{\Delta G_{diss}}{RT}\right) \tag{2}$$

from which the relative concentrations of the associated with dissociated salt species are recovered.[29] Table 1 shows K_d as a function of salt concentration for $LiAsF_6$ and $LiPF_6$ in DMC, using both the *ab initio* and MD results reported in Figures 2 and 3. We note that the low dissociation strength of the electrolyte yields a very low concentration of charge-carrying salt species, and hence prohibit a reliable MD calculation of the electrolyte conductivity in this regime. However, the orders of magnitude increase in K_d with increasing salt concentration is consistent with the originally stated hypothesis as well as the conductivity data presented in Figure 1. Furthermore, although the qualitative trend is in agreement with experiment, we observe a large relative discrepancy with absolute experimental values of K_{exp}. It is speculated that the relative error is due to systematic errors in the calculation of the solvation energies in the PCM model used here. Systematic errors in the solvation energy, which can be on the order of 0.5 eV,[30] are transferred into the exponential in eq 2, and could yield the relative differences observed in Table 1.

We note that, in addition to CIPs, there is a possibility of formation of larger aggregates (dimers, trimers, etc.) in these electrolytes at low salt concentrations. Formation of such species is in agreement with Delsignore et al.'s results, who reported salt dimers (quadrupoles)[10] and Doucey et al.'s suggestion of "polymeric salt species",[9] inferred from FTIR measurements. However, a quadrupole dimer would contribute significantly less to the dielectric properties of the electrolyte than CIPs and hence their presence over CIPs would in fact reduce the dielectric increment calculated in Figure 3. Thus, the experimental observations suggest the presence of larger polar aggregates, beyond dimers, as well as CIPs, which would contribute to the increment of the dielectric constant from 3.1 to 5.0.

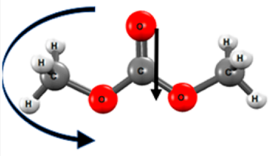
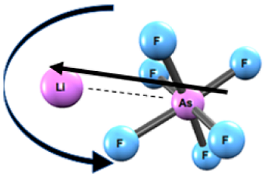
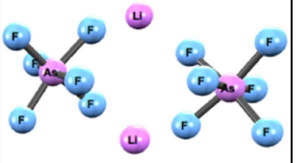
Finally, we report calculations of the relaxation times of $LiAsF_6$ CIP, dimers and trimers, and DMC which are compared to measured peaks in the frequency dependent dielectric spectra where a peak at frequency f is related to a relaxation time of $\tau = \frac{1}{2\pi f}$.[10] Table 2 shows τ for various chemical species. For neat DMC and $LiAsF_6$ CIP, we found τ = 4.7 ps and τ = 80 ps, respectively, in qualitative agreement with experimental values of τ = 7 ps and τ = 100 ps.[10] For dimers and trimers, the reconfiguration of the constituent ions during the simulation causes a change in the total dipole moment, yielding a characteristic relaxation time corresponding to τ = 18 ps and τ = 20 ps, respectively. As discussed above, the contribution to ϵ from larger neutral clusters is expected to be less as compared

Table 1. Calculated Dissociation Constant K_d and Dielectric Constant ϵ, Reported as a Function of Salt Concentration for $LiAsF_6$ and $LiPF_6$ in DMC and Compared to Experimental Results,[10] When Available

	$\gtrsim$ 0 M $LiAsF_6$	0.05 M $LiAsF_6$	0.1 M $LiAsF_6$	$\gtrsim$ 0 M $LiPF_6$	0.05 M $LiPF_6$	0.1 M $LiPF_6$
ϵ	3.2	4.0	4.8	3.2	4.0	4.6
K_d	2.4×10^{-21}	4.0×10^{-15}	2.0×10^{-11}	2.0×10^{-22}	2.4×10^{-16}	1.7×10^{-13}
K_{exp}	1.1×10^{-12}	1.7×10^{-9}	5.0×10^{-8}	N/A	N/A	N/A

DOI: 10.1021/acs.jpcc.7b11060
J. Phys. Chem. C 2018, 122, 1990−1994

Table 2. Relaxation Times τ of Different DMC and $LiAsF_6$ Species Calculated from MD and Compared to Experiment[a]

	DMC	CIP	salt dimer	salt trimer
				
τ (MD)	4.7±0.3 ps	80±20 ps	18±4 ps	20±6 ps
τ (exp)[10]	7 ps	100 ps	N/A	N/A

[a] Salt CIP value is reported for 0.1 M solutions, and the DMC τ value was calculated from a 0 M MD run. The experimental τ value is identical for both 0 and 0.1 M.[10] The straight arrows denote the dipole moment, and the curved arrows exemplify orientational fluctuations.

to the CIPs. We note that MD provides a dielectric signature for AGGs which can be used to compare with future spectroscopy results of characteristic relaxation times. For example, the presence of $LiAsF_6$ dimers and trimers in DMC is now verifiable through the results of Table 2.

CONCLUSIONS

In summary, we find that both our calculations and reported experiments infer abundant $LiAsF_6$ (or $LiPF_6$) CIP salt species at 0.1 M concentration in DMC, which result in an increase of the dielectric constant. This in turn causes an increase of K_d by orders of magnitude, which provides a highly plausible explanation for the drastic increase in observed conductivity. Our work highlights the importance of including the salt while considering electrolyte overall dielectric behavior, even at low concentrations. Furthermore, we suggest that similar behavior should be expected in other linear carbonates such as diethyl carbonate (DEC) and ethyl methyl carbonate (EMC),[31] which have similar dielectric constants to DMC.[21] This finding bears significant relevance for designer higher conductivity Li-ion electrolytes as linear carbonate solvents with low dissociative behavior have recently attracted considerable attention.[32−34]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b11060.

Supplemental details on computational methods (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: KAPersson@lbl.gov.

ORCID

Julian Self: 0000-0002-5486-9559
Nav Nidhi Rajput: 0000-0003-4740-8217

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was intellectually led by the Battery Materials Research (BMR) program, under the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, Contract No. DE-AC02-05CH11231. B.M.W. and N.N.R. were supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES), under Contract No. DEAC02-06CH11357. Finally, this research used resources of the National Energy Research Scientific Computing Center (NERSC).

REFERENCES

(1) Marcus, Y.; Hefter, G. Ion Pairing. *Chem. Rev.* **2006**, *106* (11), 4585−4621.

(2) Seo, D. M.; Borodin, O.; Han, S.-D.; Boyle, P. D.; Henderson, W. A. Electrolyte Solvation and Ionic Association II. Acetonitrile-Lithium Salt Mixtures: Highly Dissociated Salts. *J. Electrochem. Soc.* **2012**, *159* (9), A1489−A1500.

(3) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104* (10), 4303−4418.

(4) Wright, M. R. *An Introduction to Aqueous Electrolyte Solutions*; Wiley: Chichester, U.K., 2007.

(5) You, X.; Chaudhari, M. I.; Rempe, S. B.; Pratt, L. R. Dielectric Relaxation of Ethylene Carbonate and Propylene Carbonate from Molecular Dynamics Simulations. *J. Phys. Chem. B* **2016**, *120* (8), 1849−1853.

(6) Schröder, C.; Rudas, T.; Steinhauser, O. Simulation Studies of Ionic Liquids: Orientational Correlations and Static Dielectric Properties. *J. Chem. Phys.* **2006**, *125* (24), 244506.

(7) Schröder, C.; Rudas, T.; Boresch, S.; Steinhauser, O. Simulation Studies of the Protein-Water Interface. I. Properties at the Molecular Resolution. *J. Chem. Phys.* **2006**, *124* (23), 234907.

(8) Rinne, K. F.; Gekle, S.; Netz, R. R. Dissecting Ion-Specific Dielectric Spectra of Sodium-Halide Solutions into Solvation Water and Ionic Contributions. *J. Chem. Phys.* **2014**, *141* (21), 214502.

(9) Doucey, L.; Revault, M.; Lautié, A.; Chaussé, A.; Messina, R. A Study of the Li/Li+ Couple in DMC and PC Solvents: Part 1: Characterization of LiAsF6/DMC and LiAsF6/PC Solutions. *Electrochim. Acta* **1999**, *44* (14), 2371−2377.

(10) Delsignore, M.; Farber, H.; Petrucci, S. Ionic Conductivity and Microwave Dielectric Relaxation of Lithium Hexafluoroarsenate

(LiAsF6) and Lithium Perchlorate (LiClO4) in Dimethyl Carbonate. *J. Phys. Chem.* **1985**, *89* (23), 4968−4973.

(11) Nanbu, N.; Watanabe, S.; Takehara, M.; Ue, M.; Sasaki, Y. Electrolytic Characteristics of Fluoromethyl Methyl Carbonate for Lithium Rechargeable Batteries. *J. Electroanal. Chem.* **2009**, *625* (1), 7−15.

(12) Rumble, J. R., Ed. *CRC Handbook of Chemistry and Physics*; CRC Press/Taylor and Francis: Boca Raton, FL, 2018.

(13) Cavell, E. A. S.; Knight, P. C. Effect of Concentration Changes on Permittivity of Electrolyte Solutions. *Z. Phys. Chem.* **1968**, *57*, 331−334.

(14) Kaminski, G. A.; Friesner, R. A.; Tirado-Rives, J.; Jorgensen, W. L. Evaluation and Reparametrization of the OPLS-AA Force Field for Proteins via Comparison with Accurate Quantum Chemical Calculations on Peptides. *J. Phys. Chem. B* **2001**, *105* (28), 6474−6487.

(15) Soetens, J.-C.; Millot, C.; Maigret, B. Molecular Dynamics Simulation of LiBF4 in Ethylene Carbonate, Propylene Carbonate and Dimethyl Carbonate Solvents. *J. Phys. Chem. A* **1998**, *102* (7), 1055−1061.

(16) Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; et al. Advances in Molecular Quantum Chemistry Contained in the Q-Chem 4 Program Package. *Mol. Phys.* **2015**, *113* (2), 184−215.

(17) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98* (7), 5648−5652.

(18) Cancès, E.; Mennucci, B.; Tomasi, J. A New Integral Equation Formalism for the Polarizable Continuum Model: Theoretical Background and Applications to Isotropic and Anisotropic Dielectrics. *J. Chem. Phys.* **1997**, *107* (8), 3032−3041.

(19) Cancès, E.; Mennucci, B. Comment on "Reaction Field Treatment of Charge Penetration" [J. Chem. Phys. 112, 5558 (2000)]. *J. Chem. Phys.* **2001**, *114* (10), 4744.

(20) Tomasi, J.; Mennucci, B.; Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105* (8), 2999−3094.

(21) Hall, D. S.; Self, J.; Dahn, J. R. Dielectric Constants for Quantum Chemistry and Li-Ion Batteries: Solvent Blends of Ethylene Carbonate and Ethyl Methyl Carbonate. *J. Phys. Chem. C* **2015**, *119* (39), 22322−22330.

(22) Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. GROMACS: High Performance Molecular Simulations through Multi-Level Parallelism from Laptops to Supercomputers. *SoftwareX* **2015**, *1−2*, 19−25.

(23) Rajput, N. N.; Qu, X.; Sa, N.; Burrell, A. K.; Persson, K. A. The Coupling between Stability and Ion Pair Formation in Magnesium Electrolytes from First-Principles Quantum Mechanics and Classical Molecular Dynamics. *J. Am. Chem. Soc.* **2015**, *137* (9), 3411−3420.

(24) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A Package for Building Initial Configurations for Molecular Dynamics Simulations. *J. Comput. Chem.* **2009**, *30* (13), 2157−2164.

(25) Canongia Lopes, J. N.; Pádua, A. A. H. Molecular Force Field for Ionic Liquids Composed of Triflate or Bistriflylimide Anions. *J. Phys. Chem. B* **2004**, *108* (43), 16893−16898.

(26) Ishida, T.; Nishikawa, K.; Shirota, H. Atom Substitution Effects of $[XF_6]^-$ in Ionic Liquids. 2. Theoretical Study. *J. Phys. Chem. B* **2009**, *113* (29), 9840−9851.

(27) *Broadband Dielectric Spectroscopy*; Kremer, F., Schönhals, A., Eds.; Springer: Berlin, 2003.

(28) Michaud-Agrawal, N.; Denning, E. J.; Woolf, T. B.; Beckstein, O. MDAnalysis: A Toolkit for the Analysis of Molecular Dynamics Simulations. *J. Comput. Chem.* **2011**, *32* (10), 2319−2327.

(29) Qu, X.; Persson, K. A. Toward Accurate Modeling of the Effect of Ion-Pair Formation on Solute Redox Potential. *J. Chem. Theory Comput.* **2016**, *12* (9), 4501−4508.

(30) Pliego, J. R.; Riveros, J. M. The Cluster−Continuum Model for the Calculation of the Solvation Free Energy of Ionic Species. *J. Phys. Chem. A* **2001**, *105* (30), 7241−7247.

(31) Xiong, D. J.; Hynes, T.; Dahn, J. R. Dramatic Effects of Low Salt Concentrations on Li-Ion Cells Containing EC-Free Electrolytes. *J. Electrochem. Soc.* **2017**, *164* (9), A2089−A2100.

(32) Ma, L.; Glazier, S. L.; Petibon, R.; Xia, J.; Peters, J. M.; Liu, Q.; Allen, J.; Doig, R. N. C.; Dahn, J. R. A Guide to Ethylene Carbonate-Free Electrolyte Making for Li-Ion Cells. *J. Electrochem. Soc.* **2017**, *164* (1), A5008−A5018.

(33) Wang, J.; Yamada, Y.; Sodeyama, K.; Chiang, C. H.; Tateyama, Y.; Yamada, A. Superconcentrated Electrolytes for a High-Voltage Lithium-Ion Battery. *Nat. Commun.* **2016**, *7*, 12032.

(34) Gmitter, A. J.; Plitz, I.; Amatucci, G. G. High Concentration Dinitrile, 3-Alkoxypropionitrile, and Linear Carbonate Electrolytes Enabled by Vinylene and Monofluoroethylene Carbonate Additives. *J. Electrochem. Soc.* **2012**, *159* (4), A370−A379.

DOI: 10.1021/acs.jpcc.7b11060
J. Phys. Chem. C 2018, 122, 1990−1994