Title

Solvation Effects on the Dielectric Constant of 1 M LiPF6 in Ethylene Carbonate: Ethyl Methyl Carbonate 3:7

Journal

Energy & Environmental Materials, 7(1)

ISSN

2575-0356

Authors

Self, Julian
Hahn, Nathan T
Persson, Kristin A

Publication Date

2024

DOI

10.1002/eem2.12494

RESEARCH ARTICLE

Energy & Environmental Materials WILEY

Batteries

Solvation Effects on the Dielectric Constant of 1 M LiPF6 in Ethylene Carbonate: Ethyl Methyl Carbonate 3:7

*Julian Self, Nathan T. Hahn, and Kristin A. Persson**

We report the dielectric constant of 1 M LiPF$_6$ in EC:EMC 3:7 w/w (ethylene carbonate/ethyl methyl carbonate) in addition to neat EC:EMC 3:7 w/w. Using three Debye relaxations, the static permittivity value, or dielectric constant, is extrapolated to 18.5, which is compared to 18.7 for the neat solvent mixture. The EC solvent is found to strongly coordinate with the Li$^+$ cations of the salt, which results in a loss of dielectric contribution to the electrolyte. However, the small amplitude and large uncertainty in relaxation frequency for EMC cloud definitive identification of the Li$^+$ solvation shell. Importantly, the loss of the free EC permittivity contribution due to Li$^+$ solvation is almost completely balanced by the positive contribution of the associated LiPF$_6$ salt, demonstrating that a significant quantity of dipolar ion pairs exists in 1 M LiPF$_6$ in EC:EMC 3:7.

Despite remarkable and thorough investigation of the baseline electrolyte for current Li-ion batteries, 1 M LiPF$_6$ EC:EMC 3:7 (ethyl carbonate: ethyl methyl carbonate, 3:7 w/w), the dielectric properties, specifically the constant ε_s, have never been measured. In this work, we report measurement of the value and quantification of the underlying dielectric contributions within the microwave frequency range.

In 1 M LiPF$_6$ in EC:EMC 3:7, the EC co-solvent is electrochemically reactive and can passivate Li-metal or graphite electrodes. EC also serves as a strongly polar solvent that facilitates dissociation of LiPF$_6$.[1] However, EC exhibits a high melting point, above that of room temperature, incurring sluggish kinetics. Hence, a linear carbonate (such as EMC) is added primarily to lower the viscosity. A concentration of 1 M LiPF$_6$ is used as it allows for high conductivity. This electrolyte has been the subject of considerable research as well as technological interest, for which we refer readers to previous reviews.[1,2] However, the dielectric constant has never been measured, despite being a fundamental thermodynamic property used in many of the theoretical models to understand solvation and transport properties of electrolytes. Properties that depend on the dielectric constant include concentration-dependent activity coefficients,[3–7] bulk conductivity,[8] and degree of salt dissociation.[9] Moreover, the dielectric constant is included in continuum solvation models employed in quantum chemistry (e.g. DFT-based) methods,[10,11] making it an important parameter for calculations of electrochemical stability and chemical reactivity.[12–15]

Previous work concerning the dielectric constant of EC:EMC 3:7 electrolytes has focused on measuring the dielectric constant of neat blends of EC and linear carbonates,[16] or using statistical mechanics-based modeling or classical molecular dynamics simulations to predict the value in the presence of added salt.[8,17,18] To the best knowledge of the authors, no experimentally measured value has so far been reported. Experimental work has been undertaken for various salts in propylene carbonate[19,20] or linear carbonates.[21,22] Due to the technological importance of 1 M LiPF$_6$ in EC:EMC, we here report the value of ε_s and demonstrate resolution of the three primary dipolar relaxation processes contributing to this value. We leave further detailed analysis, for example to quantify degree of salt association,[17,23,24] solvation number,[25–33] and preferential solvation,[28,34,35] to an upcoming publication.

Electrolyte synthesis was performed in an actively purified argon glove box with typical water and oxygen levels below 1 ppm and 0.1 ppm, respectively. Anhydrous EC (99%) was purchased from Sigma-Aldrich and used as received. EMC (99%) and LiPF$_6$ (99.99%) were purchased from Sigma-Aldrich. EMC was dried over molecular sieves, and LiPF$_6$ was dried under vacuum at 60 °C. Electrolytes were produced by mixing EC and EMC at a 3:7 ratio by mass and subsequently adding this solvent mixture to a pre-weighed mass of LiPF$_6$ salt in order to achieve a solution volume corresponding to 1 M concentration. Solvent water content was measured at below 10 ppm using Karl-Fisher titration.

Dielectric relaxation spectroscopy (DRS) was performed in glass vials at 21 °C using a coaxial probe (Keysight N1501A) and vector network analyzer (Keysight P9375A) over a frequency (f) range from 0.5 to 26.5 GHz. Three-point calibration was performed using air, water, and tetrahydrofuran prior to each set of measurements. Two independent measurements were made on each sample using independent calibrations for each measurement series. In DRS of electrolytes, the experimentally accessible quantity is the total dielectric response η. While the real part of the permittivity ε' is equal to the real part of the response η', the imaginary part of the permittivity ε'' requires subtraction of the

---

J. Self
Department of Chemical Engineering, Polytechnique Montreal, Montreal, QC H3T 1J4, Canada
J. Self, K. A. Persson
Department of Materials Science and Engineering, University of California, Berkeley, CA 94720, USA
Energy Technologies Area, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
E-mail: kapersson@lbl.gov
N. T. Hahn
Material, Physical and Chemical Sciences Center, Sandia National Laboratories, Albuquerque, NM 87185, USA

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/eem2.12494.

DOI: 10.1002/eem2.12494

conductivity σ contribution to the imaginary dielectric response η'' as follows:[9,36]

$$\varepsilon'' = \eta'' - \sigma/(2\pi f \varepsilon_0) \tag{1}$$

In order to fit these spectra, two Debye relaxations[37] were used for the neat solvent case (3:7 EC:EMC) while three Debye relaxations were used for the 1 M $LiPF_6$ in EC:EMC 3:7 system. The expressions for the three Debye relaxations for ε' and ε'', where the symbols have their typical significance,[37] are as follows:

$$\varepsilon' = \frac{\varepsilon_1}{1+(f/f_1)^2} + \frac{\varepsilon_2}{1+(f/f_2)^2} + \frac{\varepsilon_3}{1+(f/f_3)^2} + \varepsilon_\infty \tag{2}$$

$$\varepsilon'' = \varepsilon_1 \frac{(f/f_1)}{1 + (f/f_1)^2} + \varepsilon_2 \frac{(f/f_2)}{1 + (f/f_2)^2} + \varepsilon_3 \frac{(f/f_3)}{1+(f/f_3)^2} \tag{3}$$

During the iterative fitting procedure, each parameter was treated as adjustable, including the ionic conductivity value. For the neat solvent mixture, the parameters were first fit to the ε'' spectra and the remaining ε_∞ parameter was fit to the ε' spectra. For the 1 M electrolyte, the ε' spectra were fit first, and the resulting parameters were then used to fit for the conductivity as verified against the ε'' spectra. The non-linear curve fitting of the DRS spectra was undertaken using the trust region reflective algorithm in the SciPy Python package.[38] The in-house curve fitting Python code is available at: https://github.com/JSelf42/DielectricRelaxation.

In 1 M $LiPF_6$, the ε'' values became unphysical at low frequencies due to the high ionic conductivity. In accordance with similar established methods,[39] ε'' values measured below 1 GHz were excluded from the fitting procedure in order to enable simultaneous agreement with ε'. Two sources of error were considered here, one from reproducibility and one from the uncertainty of the fits. From analysis of duplicate runs, the former proved negligible, while the latter proved significant. Thus, we herein report the fits from the data of averaged duplicate runs, where the uncertainties come from the fit. We use the standard error returned from the non-linear curve fitting procedure for the reported parameter uncertainties, noting that although the errors on the parameters may not come from an underlying normal distribution, the effective standard error is nonetheless a relevant measure of uncertainty. For the neat solvent mixture, a constraint of EMC frequency below 20 GHz was used, while for the 1 M solution a constraint of EMC amplitude below 1.0 was used (see Appendix S1, Supporting Information, for further details). In both cases, we note that removal of the constraints did not significantly impact ε_s but did yield physically unlikely parameters for the main EMC dipolar mode contribution.

Figure 1 (left) shows the dielectric spectra as a function of concentration for neat EC:EMC 3:7 at 21 °C. For the neat binary solvent mixture, one significant peak (pink) is seen for the (very polar) EC solvent contribution, while a much smaller peak is seen for the linear carbonate. The total value of the dielectric constant, 18.7, is consistent with a previous reported value, measured via (lower frequency) impedance spectroscopy.[16] The relevant parameters for the two employed Debye relaxations are shown in **Table 1**. There are no literature data for neat liquid EC at 21 °C since EC is solid at this temperature but the relaxation time is of the right order of magnitude when compared with values measured for liquid EC at higher temperatures.[40] Similarly, no literature data could be found for neat EMC; however, literature data show that a similar dialkyl carbonate solvent, dimethyl carbonate, has a relaxation frequency of 22 GHz[41] which led us to constrain the EMC relaxation frequency to < 20 GHz in the EC:EMC mixture. Furthermore, dialkyl carbonates have been shown to exhibit a non-Debye absorption process in the far IR region that may cause deviation in the high-frequency dielectric response.[41,42] Understandably, the error bars are quite high for the EMC frequency, reflecting the difficulty of precisely fitting this minor component in the studied mixtures.

Figure 1 (right) shows the dielectric spectra for 1.0 M $LiPF_6$ in EC:EMC 3:7. Here, three Debye relaxations are used: one for the EC solvent (pink), EMC solvent (black), and associated salt (blue). The relevant parameters for the three employed Debye relaxations are shown in Table 1. Here, the amplitude ε_1 of the EC solvent contribution to the permittivity is reduced from 14.1 to 5.3 due to the loss of free EC to the solvation shell of Li^+. It should be noted that the frequency of the EC relaxation f_1 decreases significantly after the addition of 1 M $LiPF_6$, which arises from the viscosity increase of factor ~ 3.[43] We include the difference between the fits and the experimental data in the Appendix S1, Supporting Information, where the absolute differences are smaller than 0.4 for the spectra studied herein.

The apparent permittivity contribution ε_2 from EMC does not significantly decrease after 1 M of $LiPF_6$ is added to the solution. Although this suggests that EMC does not interact strongly with the Li^+, the small amplitude and large uncertainty in relaxation frequency for EMC cloud such interpretations. Thus, any definitive claim on the inference of preferential solvation of EC over EMC is left to more detailed analysis in an upcoming publication.

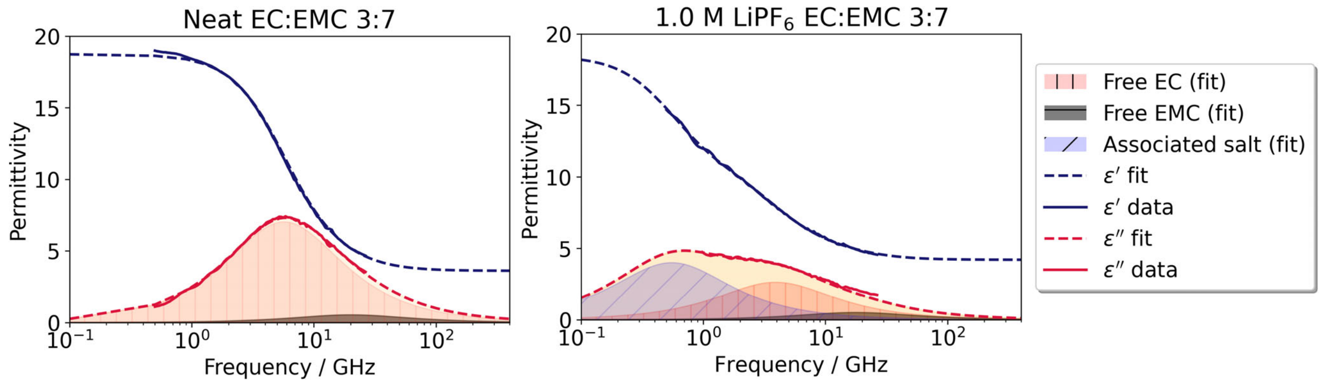

Figure 1. Neat EC:EMC 3:7 dielectric spectra (left) and 1 M $LiPF_6$ EC:EMC 3:7 dielectric spectra (right).

Table 1. Fit parameters from DRS data (21 °C).

	Neat EC:EMC 3:7		1.0 M $LiPF_6$ EC:EMC 3:7	
Total dielectric constant	$\varepsilon_s = 18.7 \pm 0.4$	–	$\varepsilon_s = 18.5 \pm 0.5$	–
Free EC	$\varepsilon_1 = 14.1 \pm 0.3$	$f_1 = 5.7 \pm 0.1$ GHz	$\varepsilon_1 = 5.3 \pm 0.2$	$f_1 = 3.9 \pm 0.2$ GHz
Free EMC	$\varepsilon_2 = 1.1 \pm 0.2$	$f_2 = 20 \pm 7$ GHz[a)]	$\varepsilon_2 = 1.0 \pm 0.2$[b)]	$f_2 = 18 \pm 8$ GHz
Associated salt	–	–	$\varepsilon_3 = 8.0 \pm 0.3$	$f_3 = 0.55 \pm 0.04$ GHz
Electronic component	$\varepsilon_\infty = 3.6 \pm 0.1$	–	$\varepsilon_\infty = 4.2 \pm 0.3$	–
Conductivity	–	–	$\sigma_{fit} = 7.7 \pm 0.2$ mS cm^{-1}	$\sigma_{meas} = 8.6$ mS cm^{-1}[c)]

[a)] Constraint $f_2 \leq 20$ GHz.
[b)] Constraint $\varepsilon_2 \leq 1.0$.
[c)] 24 °C.

The associated salt species in solution exhibits a characteristic relaxation frequency of 0.5 GHz, and its permittivity contribution ε_3 is 8.0, representing the largest contribution to the overall dielectric constant. Previous DRS studies[19,21,22] on other electrolytes have identified peaks in similar frequency ranges as either solvent-separated ion pairs (SSIPs)[27] or contact ion pairs (CIPs).[24] We note that although one functional form is fit to the associated salt feature to avoid overfitting, we do not discount the possibility of presence of two or more types of associated salt species in solution (e.g. SSIPs or CIPs). Summing the various contributions to the total permittivity, including the high-frequency term ε_∞, the permittivity of the 1 M $LiPF_6$ electrolyte is 18.5, compared to 18.7 for the neat binary solvent system. Here, the loss of the free EC permittivity contribution due to Li^+ solvation is almost completely balanced by the positive contribution of the associated $LiPF_6$ salt, demonstrating that a significant quantity of ion pairs exists (either as SSIPs or CIPs). Previous scholarship has sometimes overlooked the importance of ion-pairing[28,44,45] in describing the solvation environment of Li^+ in solution. The herein measured value of ε_s=18.5 is likely fairly close to values that would be observed if a different linear carbonate was used (e.g. dimethyl carbonate or diethyl carbonate), or if small weight percentages of additives are added to the bulk solution, as is typical for state-of-the-art electrolytes.[2] Thus, we believe the value of $\varepsilon_s \simeq 19$ to be representative of Li-ion carbonate-blend electrolytes generally used for Li-ion cells.

Acknowledgements

This work was intellectually led by the Battery Materials Research program under the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, Contract DE-AC02-05CH11231. This work was also supported by the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Keywords

batteries, dielectric relaxation spectroscopy, electrolytes

Received: June 24, 2022
Revised: July 26, 2022
Published online: August 3, 2022

[1] K. Xu, *Chem. Rev.* **2004**, *104*, 4303.
[2] K. Xu, *Chem. Rev.* **2014**, *114*, 11503.
[3] J. Self, N. T. Hahn, K. D. Fong, S. A. McClary, K. R. Zavadil, K. A. Persson, *J. Phys. Chem. Lett.* **2020**, *11*, 2046.
[4] J. Vincze, M. Valiskó, D. Boda, *J. Chem. Phys.* **2010**, *133*, 154507.
[5] I. Y. Shilov, A. K. Lyashchenko, *J. Phys. Chem. B* **2015**, *119*, 10087.
[6] B. Maribo-Mogensen, G. M. Kontogeorgis, K. Thomsen, *Ind. Eng. Chem. Res.* **2012**, *51*, 5353.
[7] J.-P. Simonin, O. Bernard, L. Blum, *J. Phys. Chem. B* **1998**, *102*, 4411.
[8] K. L. Gering, *Electrochim. Acta* **2017**, *225*, 175.
[9] Y. Marcus, G. Hefter, *Chem. Rev.* **2006**, *106*, 4585.
[10] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999.
[11] E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032.
[12] S. A. Delp, O. Borodin, M. Olguin, C. G. Eisner, J. L. Allen, T. R. Jow, *Electrochim. Acta* **2016**, *209*, 498.
[13] P. Jankowski, W. Wieczorek, P. Johansson, *J. Mol. Model.* **2017**, *23*(1), 6.
[14] R. L. Wang, C. Buhrmester, J. R. Dahn, *J. Electrochem. Soc.* **2006**, *153*, A445.
[15] X. Qu, A. Jain, N. N. Rajput, L. Cheng, Y. Zhang, S. P. Ong, M. Brafman, E. Maginn, L. A. Curtiss, K. A. Persson, *Comput. Mater. Sci.* **2015**, *103*, 56.
[16] D. S. Hall, J. Self, J. R. Dahn, *J. Phys. Chem. C* **2015**, *119*, 22322.
[17] E. R. Logan, E. M. Tonita, K. L. Gering, L. Ma, M. K. G. Bauer, J. Li, L. Y. Beaulieu, J. R. Dahn, *J. Electrochem. Soc.* **2018**, *165*, A705.
[18] N. Yao, X. Chen, X. Shen, R. Zhang, Z. Fu, X. Ma, X. Zhang, B. Li, Q. Zhang, *Angew. Chem. Int. Ed.* **2021**, *60*, 21473.
[19] S. Hwang, D.-H. Kim, J. H. Shin, J. E. Jang, K. H. Ahn, C. Lee, H. Lee, *J. Phys. Chem. C* **2018**, *122*, 19438.
[20] T. Yamaguchi, M. Hayakawa, T. Matsuoka, S. Koda, *J. Phys. Chem. B* **2009**, *113*, 11988.
[21] M. Delsignore, H. Farber, S. Petrucci, *J. Phys. Chem.* **1985**, *89*, 4968.

[22] H. Lee, S. Hwang, M. Kim, K. Kwak, J. Lee, Y.-K. Han, H. Lee, *J. Phys. Chem. Lett.* **2020**, *11*, 10382.

[23] M. Ue, *J. Electrochem. Soc.* **1995**, *142*, 2577.

[24] A. J. Ringsby, K. D. Fong, J. Self, H. K. Bergstrom, B. D. McCloskey, K. A. Persson, *J. Electrochem. Soc.* **2021**, *168*, 80501.

[25] M. Nie, D. P. Abraham, D. M. Seo, Y. Chen, A. Bose, B. L. Lucht, *J. Phys. Chem. C* **2013**, *117*, 25381.

[26] K. Kondo, M. Sano, A. Hiwara, T. Omi, M. Fujita, A. Kuwae, M. Iida, K. Mogi, H. Yokoyama, *J. Phys. Chem. B* **2000**, *104*, 5040.

[27] D. M. Seo, S. Reininger, M. Kutcher, K. Redmond, W. B. Euler, B. L. Lucht, *J. Phys. Chem. C* **2015**, *119*, 14038.

[28] X. Bogle, R. Vazquez, S. Greenbaum, A. v. W. Cresce, K. Xu, *J. Phys. Chem. Lett.* **2013**, *4*, 1664.

[29] M. Castriota, E. Cazzanelli, I. Nicotera, L. Coppola, C. Oliviero, G. A. Ranieri, *J. Chem. Phys.* **2003**, *118*, 5537.

[30] M. Morita, Y. Asai, N. Yoshimoto, M. Ishikawa, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 3451.

[31] B. Jiang, V. Ponnuchamy, Y. Shen, X. Yang, K. Yuan, V. Vetere, S. Mossa, I. Skarmoutsos, Y. Zhang, J. Zheng, *J. Phys. Chem. Lett.* **2016**, *7*, 3554.

[32] I. Skarmoutsos, V. Ponnuchamy, V. Vetere, S. Mossa, *J. Phys. Chem. C* **2015**, *119*, 4502.

[33] J. Self, K. D. Fong, K. A. Persson, *ACS Energy Lett.* **2019**, *4*, 2843.

[34] Y. Zhang, M. Su, X. Yu, Y. Zhou, J. Wang, R. Cao, W. Xu, C. Wang, D. R. Baer, O. Borodin, K. Xu, Y. Wang, X.-L. Wang, Z. Xu, F. Wang, Z. Zhu, *Anal. Chem.* **2018**, *90*, 3341.

[35] O. Borodin, M. Olguin, P. Ganesh, P. R. C. Kent, J. L. Allen, W. A. Henderson, *Phys. Chem. Chem. Phys.* **2016**, *18*(1), 164.

[36] R. Buchner, G. Hefter, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8984.

[37] F. Kremer, A. Schönhals (Eds), *Broadband Dielectric Spectroscopy*, Springer, Berlin, Heidelberg **2003**.

[38] P. Virtanen, R. Gommers, T. E. Oliphant, M. Haberland, T. Reddy, D. Cournapeau, E. Burovski, P. Peterson, W. Weckesser, J. Bright, S. J. van der Walt, M. Brett, J. Wilson, K. J. Millman, N. Mayorov, A. R. J. Nelson, E. Jones, R. Kern, E. Larson, C. J. Carey, İ. Polat, Y. Feng, E. W. Moore, J. VanderPlas, D. Laxalde, J. Perktold, R. Cimrman, I. Henriksen, E. A. Quintero, C. R. Harris, A. M. Archibald, A. H. Ribeiro, F. Pedregosa, P. van Mulbregt, SciPy 1.0 Contributors, A. Vijaykumar, A. P. Bardelli, A. Rothberg, A. Hilboll, A. Kloeckner, A. Scopatz, A. Lee, A. Rokem, C. N. Woods, C. Fulton, C. Masson, C. Häggström, C. Fitzgerald, D. A. Nicholson, D. R. Hagen, D. V. Pasechnik, E. Olivetti, E. Martin, E. Wieser, F. Silva, F. Lenders, F. Wilhelm, G. Young, G. A. Price, G.-L. Ingold, G. E. Allen, G. R. Lee, H. Audren, I. Probst, J. P. Dietrich, J. Silterra, J. T. Webber, J. Slavič, J. Nothman, J. Buchner, J. Kulick, J. L. Schönberger, J. V. de Miranda Cardoso, J. Reimer, J. Harrington, J. L. C. Rodríguez, J. Nunez-Iglesias, J. Kuczynski, K. Tritz, M. Thoma, M. Newville, M. Kümmerer, M. Bolingbroke, M. Tartre, M. Pak, N. J. Smith, N. Nowaczyk, N. Shebanov, O. Pavlyk, P. A. Brodtkorb, P. Lee, R. T. McGibbon, R. Feldbauer, S. Lewis, S. Tygier, S. Sievert, S. Vigna, S. Peterson, S. More, T. Pudlik, T. Oshima, T. J. Pingel, T. P. Robitaille, T. Spura, T. R. Jones, T. Cera, T. Leslie, T. Zito, T. Krauss, U. Upadhyay, Y. O. Halchenko, Y. Vázquez-Baeza, *Nat. Methods* **2020**, *17*, 261.

[39] R. Buchner, G. T. Hefter, P. M. May, *J. Phys. Chem. A* **1999**, *103*(1), 1.

[40] R. Payne, I. E. Theodorou, *J. Phys. Chem.* **1972**, *76*, 2892.

[41] D. Saar, J. Brauner, H. Farber, S. Petrucci, *J. Phys. Chem.* **1978**, *82*, 2531.

[42] M. W. Evans, M. N. Afsar, *Chem. Phys. Lett.* **1977**, *52*, 6.

[43] E. R. Logan, E. M. Tonita, K. L. Gering, J. Li, X. Ma, L. Y. Beaulieu, J. R. Dahn, *J. Electrochem. Soc.* **2018**, *165*, A21.

[44] K. D. Fulfer, D. G. Kuroda, *J. Phys. Chem. C* **2016**, *120*, 24011.

[45] A. von Wald Cresce, M. Gobet, O. Borodin, J. Peng, S. M. Russell, E. Wikner, A. Fu, L. Hu, H.-S. Lee, Z. Zhang, X.-Q. Yang, S. Greenbaum, K. Amine, K. Xu, *J. Phys. Chem. C* **2015**, *119*, 27255.