

OPEN ACCESS

Quantitative Determination of Carbon Dioxide Content in Organic Electrolytes by Infrared Spectroscopy

To cite this article: H. Yu and M. N. Obrovac 2019 *J. Electrochem. Soc.* **166** A2467

View the [article online](#) for updates and enhancements.



ECS Membership = Connection

ECS membership connects you to the electrochemical community:

- Facilitate your research and discovery through ECS meetings which convene scientists from around the world;
- Access professional support through your lifetime career;
- Open up mentorship opportunities across the stages of your career;
- Build relationships that nurture partnership, teamwork—and success!

Join ECS!

Visit electrochem.org/join





Quantitative Determination of Carbon Dioxide Content in Organic Electrolytes by Infrared Spectroscopy

H. Yu¹ and M. N. Obrovac^{1,2,*}

¹Department of Chemistry, Dalhousie University, Halifax, N.S. B3H 4R2, Canada

²Department of Physics and Atmospheric Science, Dalhousie University, Halifax, N.S. B3H 4R2, Canada

CO₂ has been shown to be an effective additive to improve the cycling characteristics of silicon negative electrodes for Li-ion batteries. However, a quantitative technique for measuring the CO₂ content in electrolyte is not readily available. Here, FTIR was used to accurately determine the CO₂ content of various carbonate-based Li-ion battery electrolytes. The accuracy of this method was validated with the weight variation method. Using this method, it was found that in EC/DEC electrolytes with 1M LiPF₆ and LiTFSI salts, CO₂ was found to have a maximum solubility of 0.37 wt% when the LiPF₆:LiTFSI molar ratio is 3:1. In 1M LiPF₆ solutions, CO₂ solubility is in the order of PC ≈ EMC > DEC for the pure solvents. Mixed non-polar solvents are also favorable for CO₂ dissolution. When used in silicon alloy cells, electrolytes saturated with CO₂ (0.33% CO₂ in EC/DEC) resulted in the best cycling stability.

© The Author(s) 2019. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, <http://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits non-commercial reuse, distribution, and reproduction in any medium, provided the original work is not changed in any way and is properly cited. For permission for commercial reuse, please email: oa@electrochem.org. [DOI: 10.1149/2.0291912jes]



Manuscript submitted April 1, 2019; revised manuscript received June 14, 2019. Published July 9, 2019.

Graphite is the most commonly used negative electrode material for lithium-ion batteries, having a theoretical capacity of 372 mAh/g or 764 Ah/L.¹ On the other hand, Silicon has a theoretical capacity of 3578 mAh/g or 2194 Ah/L. However, during lithiation/delithiation, silicon alloy undergoes a 280% volume expansion. This can result in the loss of electrical connection between silicon particles, particle fracture, and disruption of the SEI layer, all resulting in cell fade.² In order to overcome capacity loss in Si based electrodes, a variety of electrolyte additives have been used.^{3,4} Fluoroethylene carbonate (FEC) is the most commonly used additive for Si based electrodes to reduce capacity fade. Despite non-unanimous views on the exact mechanism of how FEC provides this benefit, the most accepted point is that the decomposition of FEC results in the formation of a relatively stable SEI layer which includes LiF, Li₂CO₃ and other organic compounds.⁵ This passivating SEI layer inhibits further reaction between Si alloys and electrolytes, resulting in improved cycling performance.⁶ However, FEC is continually consumed during the cycling of cells containing Si based electrodes.⁷ After all of the FEC is consumed, cells undergo sudden failure. Improved additives are needed to enable Si-based negative electrodes, especially those that are less costly.

CO₂ has been shown as an effective additive for establishing a stable solid electrolyte interphase on graphite electrodes.⁸ Recently, Krause et al. have shown that by incorporating CO₂ in the electrolyte of cells with Si-based negative electrode materials, considerable improvements in cycling performance can be achieved.⁹ Subsequently, Solchenback et al. showed that lithium oxalate can be added to the positive electrode that decomposes as an in-situ source of carbon dioxide during cell operation, resulting in cycling enhancement of Si electrodes.¹⁰ However, as with FEC, the CO₂ is continually consumed and higher amounts of CO₂ in the electrolyte result in longer cycle life. Since the electrolyte has limited solubility for CO₂, it may not be able to accommodate large amounts of CO₂, resulting, in the case of Krause et al., the bulging of pouch cells. For practical implementation of CO₂ as an additive, a better understanding of its consumption during cycling is needed. Furthermore, new electrolytes that can dissolve larger amounts of CO₂ would be advantageous to increase cycle life and reduce cell gassing.

In order to study the effect of CO₂ as an additive and to develop new electrolytes with increased CO₂ solubility, the CO₂ content in electrolytes must be quantitatively determined. However, this is not easily done. Methods used for quantitative CO₂ determination in solution include weighing methods, the vapor equilibrium method,¹¹

chemical absorption rate and gas chromatography–mass spectrometry (GC-MS). However, these methods have unavoidable drawbacks such as either being time consuming, destructive, or requiring a large electrolyte sample. Here, it is shown that Fourier transform infrared spectroscopy (FTIR) can be used a quick and accurate method for quantitative CO₂ determination in organic Li-ion battery electrolytes.

Experimental

CO₂ was added to solvent and electrolyte samples without air exposure at 15°C using the procedure and apparatus shown in the Supplementary Materials section. Propylene carbonate (PC) was obtained from BASF (battery grade). A standard electrolyte solution was prepared by dissolving 1 M LiPF₆ (BASF 98%) in ethylene carbonate (EC), diethyl carbonate (DEC) (1:2 v/v, <50ppm H₂O, BASF) by volume in an agron-filled glove box. Working electrodes consisted of V6 silicon alloy (3M), carbon black (CB, Super C65, Imerys Graphite and Carbon), and LiPAA {(lithium polyacrylate from a 10 wt% aqueous solution made by neutralizing a PAA solution (Sigma-Aldrich, average molecular weight ~250,000 g/mole, 35 wt% in H₂O) with LiOH·H₂O (Sigma Aldrich, 98%) in distilled water¹²)} in a weight ratio of 88:2:10. 3M V6 alloy is “an active/inactive alloy where the Si domains and the inactive domains are less than 15 nm and evenly distributed throughout a micron size particle.”¹³ It has a reversible capacity of ~900 mAh/g (1550 Ah/L), corresponding to a 105% volume expansion and a high initial coulombic efficiency of about 87%.¹⁴ In our own experiments we have measured the capacity of V6 alloy to be 930–950 mAh/g. Excellent cycling characteristics have been demonstrated for this alloy, making it a good standard material for electrolyte evaluation studies. Further information regarding the electrochemical properties of this alloy can be found in References 13 and 14. These components and additional distilled water were thoroughly mixed with three half-inch diameter tungsten carbide balls in a Retsch PM200 rotary mill (100 rpm, 60 min.) to create a uniform slurry. The slurry was then coated onto copper foil (Furukawa) and dried at 120°C in air for 1h. Following the drying process, coatings were punched into circular electrodes with an area of 1.3 cm² and dried under vacuum for 2h to remove excessive moisture.

FTIR characterization and weight variation method.—FTIR spectra were collected using a Bruker Alpha FTIR equipped with a standard quartz liquid sample holder. The sample holder was loaded with liquid samples in an Ar-filled glove box and sealed with a cap, so that FTIR measurements could be conducted without sample air

*Electrochemical Society Member.

[†]E-mail: mnobrovac@dal.ca

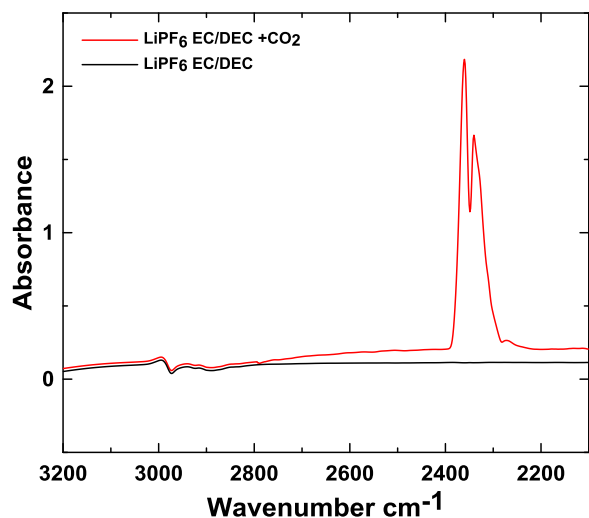


Figure 1. IR spectra of 1M LiPF₆ in EC/DEC solutions without CO₂ and saturated with CO₂.

exposure. The volume of sample in the holder was 3.8 mL. The scanning range of the FTIR spectrum is 3000 cm⁻¹ to 500 cm⁻¹. Thirteen scans were conducted for each background and sample measurement and the spectra were analyzed using Omnic software. For the weight variation method, the mass of electrolyte was measured before and after bubbling CO₂ in the sample. The volume of electrolyte used for weight variation measurements was 5 mL.

Electrochemical characterization.—Coin half cells (2325 type) were assembled in an Ar-glove box with V6/SFG6L working electrodes, lithium metal reference/counter electrodes, two Celgard 2300 separators (to avoid cell shorts from possible imperfections in hand-made electrode coatings), and about 100 μL of electrolyte. Cells were tested at 30.0 ± 0.1°C using a Neware battery testing system at 0.1C for the first cycle and 0.2C for subsequent cycles in a voltage range of 5 mV - 0.9 V. Here C-rate is defined as the current required to fully lithiate the V6/SFG6L in the electrode based on a theoretical capacity of 950 mAh/g and 360 mAh/g for V6 and SFG6L, respectively.

Results and Discussion

Figure 1 shows FTIR spectra of 1 M LiPF₆ in 1:2 EC:DEC (v:v) electrolyte saturated with CO₂ and without CO₂. There are two large peaks present in the CO₂-containing electrolyte at 2340 cm⁻¹ and 2360 cm⁻¹, whereas no features are present in this region for the electrolyte without CO₂. These peaks have been observed previously and assigned to CO₂ by Yang et al.¹⁵ Since they appear in a region where the pure electrolyte has no features, these peaks are excellent candidates for the quantification of CO₂ content. According to FTIR quantification theory, the integrated peak area has a linear relationship with the concentration of dissolved species.¹⁶ Therefore, the area of the spectrum near the 2350cm⁻¹ region can indicate the exact amount of CO₂ in the electrolyte.

To establish a quantitative FTIR method, PC was chosen as a standard solution because it has a low vapor pressure and is able to dissolve more CO₂ than other electrolyte solvents.¹⁷ The weight change of a PC sample before and after bubbling with CO₂ at 5°C was measured and FTIR spectra were also collected. The concentration of CO₂ in PC after bubbling CO₂ for 100 minutes at 5°C was 0.74 wt% as determined by weight difference, which agrees well with the solubility limit measured by Blanchard et al.¹⁷ at this temperature, verifying our weight difference analysis. This 5°C saturated 0.74 wt% CO₂ solution was used as a standard solution in following measurements and will be referred to as the “standard solution”. To take into account any vari-

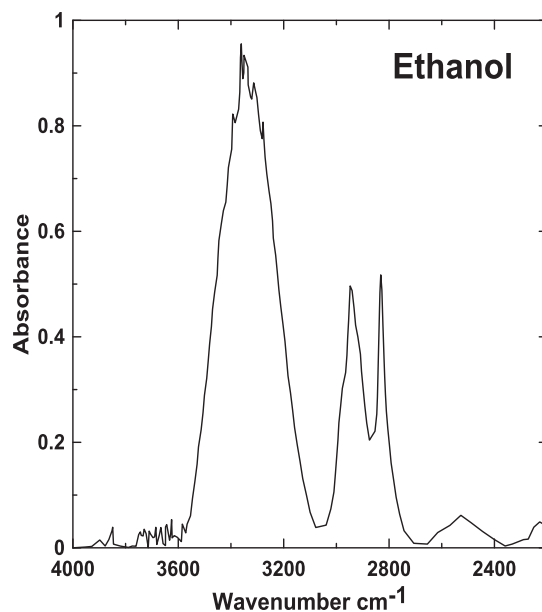


Figure 2. IR spectrum of ethanol.

ations caused by sample loading or changes in the FTIR light source intensity over time, anhydrous 100% ethanol (100% Alfa) was used as an intensity standard. As shown in Figure 2, the ethanol FTIR spectrum has three distinct peaks that do not interfere with peaks from CO₂. Using the area under these peaks, the CO₂ concentration in electrolytes can be determined by:

$$\left(\frac{A_{CO_2, sample}^o}{A_{EtOH}^o} \right) / \left(\frac{A_{CO_2, standard}^1}{A_{EtOH}^1} \right) = C_{CO_2, sample} / C_{CO_2, standard} \quad [1]$$

Where $A_{CO_2, sample}^o$ and $A_{CO_2, standard}^o$ are the areas of the 2350 cm⁻¹ CO₂ peaks in the electrolyte sample to be measured and the standard solution, respectively, A_{EtOH}^1 is total area of the three ethanol peaks in a sample of pure ethanol measured directly after the electrolyte sample FTIR measurement and A_{EtOH}^2 is total area of the three ethanol peaks in a sample of pure ethanol measured directly after the standard solution FTIR measurement. The CO₂ absorption peaks are not regular, so trapezoidal integration was used to calculate the area under peaks using Omnic analysis software. The integral region was fixed from 2400 cm⁻¹ to 2280 cm⁻¹.

In order to test the validity of our FTIR quantitative method, measurements were made of CO₂ solubility after different CO₂ bubbling times in PC at 5°C using both the weight variation and FTIR methods. As shown in Figure 3, both measurements agree closely and show that the CO₂ content increases roughly linearly with bubbling time. The variation between the weight and FTIR methods is ± 0.007 wt% or ±3% of the total CO₂ content measured in the sample. The experiment was also repeated for a EC:PC 1:1 (v:v) solution. For this solution, there is less CO₂ solubility and a correspondingly larger error between the FTIR results and the weight variation method. Nevertheless, the error between the two methods at these low CO₂ concentrations is ±0.01 wt% or ± 7% of the total CO₂ content measured in the sample. These experiments demonstrate that the FTIR method can be used for the quantitative measurement of CO₂ in electrolytes for CO₂ concentrations at least within the concentration ranges measured in this study: i.e. above about 0.1 wt%. However, it is possible that the method could be extended to the analysis of solutions with lower CO₂ content.

In order to demonstrate the utility of the FTIR method, measurements of CO₂ solubility in EC/DEC 1:2 v/v solvent containing 1M of LiPF₆/LiTFSI salt blends was investigated. The solubility of CO₂ in these electrolytes is shown in Figure 4. As the LiTFSI content is increased, the CO₂ solubility also decreases, until the LiTFSI content is

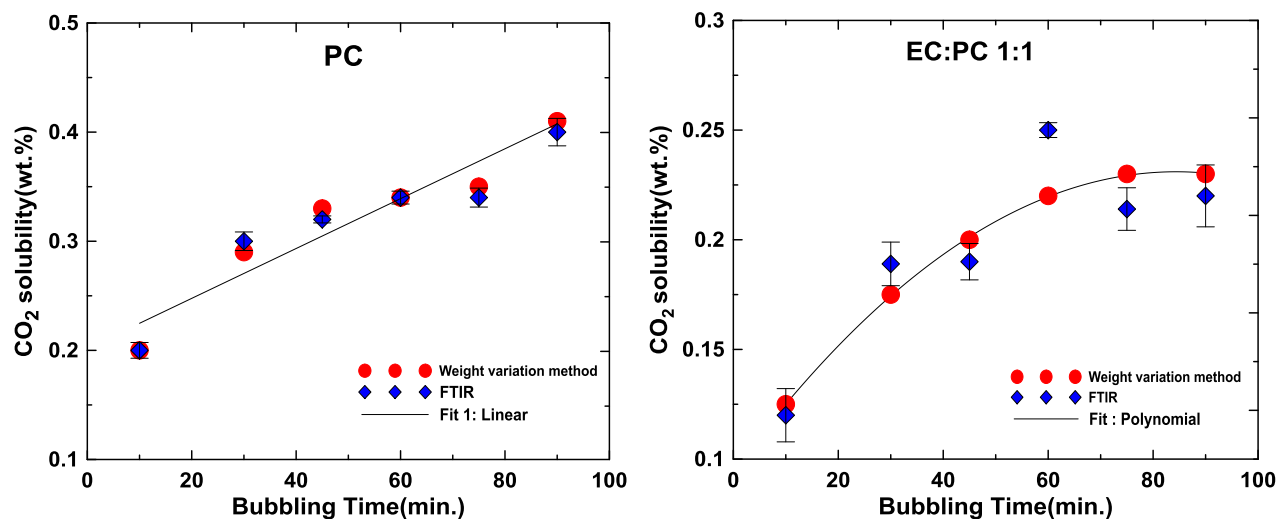


Figure 3. CO₂ solubility results from FTIR and weight variation methods in (a) PC and (b) EC:PC 1:1, respectively. Fitted trendlines are added as a guide to the eye.

50 mole%. Further additions of LiTFSI result in an increased CO₂ solubility, until a maximum solubility of 0.37 wt% is reached for a 75 at.% LiTFSI and 25 at.% LiPF₆ salt blend. These results show that the CO₂ solubility can have a complex dependence on the electrolyte composition and, furthermore, that the salt anion can significantly affect CO₂ solubility. The CO₂ solubility of 1M LiPF₆ dissolved in different solvents was also measured and is summarized in the Table I. These results show that for 1M LiPF₆ solutions, CO₂ solubility is in the order of PC ≈ EMC > DEC for the pure solvents. In contrast Blanchard et al. found that the solubility of CO₂ in pure DEC was higher than that of pure PC, while Dougassa et al. found that the solubility of CO₂ in 1M LiPF₆ in DEC was also higher than that of 1M LiPF₆ in PC.^{17,18} However, Blanchard et al. studied pure solvents that contained no salts and the measurements of Dougassa et al. were made for electrolytes saturated with CO₂ at 25°C, whereas the electrolytes studied here were saturated at 5°C. In any case, all of the solubilities measured here for 1M LiPF₆ in pure solvents were very similar (within 8% of each other). Given this similarity and the complexity of the factors contributing to CO₂ solubility, it is difficult to ascribe the data in Table I with any meaningful trend. For mixed solvents with EC, the largest solubility

of CO₂ occurs for EC/DMC, which has nearly the same CO₂ solubility as PC. Thus EC/DMC blends might be beneficial when high CO₂ contents are desired. We are now investigating the dependence of CO₂ solubility on many electrolyte systems in detail.

To demonstrate the importance of CO₂ as an electrolyte component, the cycling performance of 3M V6 alloy half-cells was measured in 1M LiPF₆ electrolytes with EC/DEC 1:2 v/v solvent with and without CO₂ and FEC additives. The cycling performance of these cells is shown in Figure 5. The cell with no CO₂ or FEC additives fades quickly after 20 cycles. This is typical of alloy cells that require special additives to reduce electrolyte consumption due to the disruption of the SEI layer during alloy volume expansion. The addition of 0.25 wt% CO₂ to the electrolyte has little effect on the cycling performance. Increasing the CO₂ content to 0.33 wt% results in cells with little fade over the 50 cycles tested. This is in agreement with the recent results of Krause et al., who showed that higher CO₂ contents result in more improved cycling.⁹ Cycling performance is also improved with the addition of 10 vol.% FEC to the electrolyte, however, the improvement is not as great as for 0.33 wt% CO₂. Electrolytes with even higher CO₂ contents may result in even longer cycle life. Therefore, studies of the CO₂ content in electrolyte are important. We believe the FTIR method presented here is well adapted to the rapid evaluation of CO₂ solubility in different electrolyte systems.

Conclusions

It was shown that CO₂ concentration can be accurately determined in electrolyte solutions using FTIR. This method is much more convenient than weighing methods and much smaller electrolyte volumes are required. Using this method, it was shown that the CO₂ solubility in EC/DEC 1:2 v/v solutions containing 1M Li⁺ depends significantly

Table I. Solubility of CO₂ in different solvents with 1M LiPF₆ electrolyte.

Electrolyte (1M LiPF ₆)	CO ₂ solubility(wt%)
PC	0.40
EC/PC 1:1	0.22
EC/DEC 1:2	0.33
EMC	0.39
DEC	0.35
EC/DMC 1:1	0.39

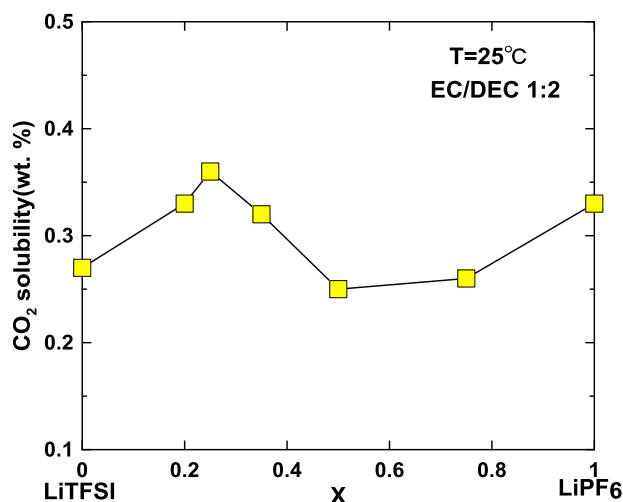


Figure 4. CO₂ solubility in EC/DEC 1:2 solvent with LiTFSI and LiPF₆ salt mixtures (1M total salt concentration), where x is the mole fraction of LiPF₆.

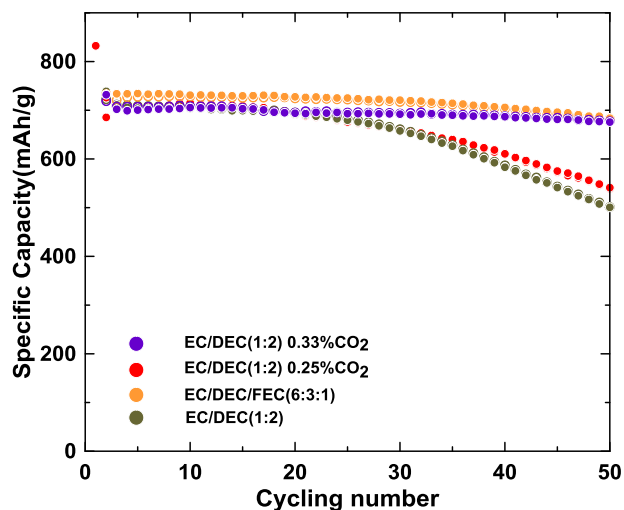


Figure 5. Cycling performance of V6 Electrodes in 1M LiPF₆ in EC:DEC electrolytes saturated with CO₂ and without CO₂. Cells with FEC additives are also shown for comparison.

on the salt anion and in a complicated manner. The cycling performance of Si alloy cells was also shown to depend significantly on the CO₂ content in the electrolyte. We believe the FTIR method presented here is well adapted to the rapid evaluation of CO₂ solubility in different electrolyte systems. This can help gain an understanding of CO₂ solubility and allow for the rapid development of high performance electrolytes for lithium-ion batteries with Si-based negative electrode materials.

ORCID

M. N. Obrovac  <https://orcid.org/0000-0001-5509-3185>

References

1. J. R. Dahn, T. Zheng, Y. Liu, and J. S. Xue, *Science*, **270**, 590 (1995).
2. M. N. Obrovac and V. L. Chevrier, *Chem. Rev.*, **114**, 11444 (2014).
3. S. Seko, H. Nara, M. Jeong, T. Yokoshima, T. Momma, and T. Osaka, *Electrochimica Acta*, **243**, 65 (2017).
4. F. Lindgren, C. Xu, L. Niedzicki, M. Marcinek, T. Gustafsson, F. Björefors, K. Edström, and R. Younesi, *ACS Appl. Mater. and Interfaces*, **8**, 15758 (2016).
5. J. Xu, W. H. Yao, Y. W. Yao, Z. C. Wang, and Y. Yang, *Wuli Huaxue Xuebao/Acta Physico-Chimica Sinica*, **25**, 201 (2009).
6. K. Schroder, J. Alvarado, T. A. Yersak, J. Li, N. Dudney, L. J. Webb, Y. S. Meng, and K. J. Stevenson, *Chem. Mater.*, **27**, 5531 (2015).
7. R. Jung, M. Metzger, D. Haering, S. Solchenbach, C. Marino, N. Tsiouvaras, C. Stinner, and H. A. Gasteiger, *J. Electrochem. Soc.*, **163**, A1705 (2016).
8. B. Strehle, S. Solchenbach, M. Metzger, K. U. Schwenke, and H. A. Gasteiger, *J. Electrochem. Soc.*, **164**, A2513 (2017).
9. L. J. Krause, V. L. Chevrier, L. D. Jensen, and T. Brandt, *J. Electrochem. Soc.*, **164**, A2527 (2017).
10. S. Solchenbach, M. Wetjen, D. Pritzl, K. U. Schwenke, and H. A. Gasteiger, *J. Electrochem. Soc.*, **165**, A512 (2018).
11. M. Anouti, Y. R. Dougassa, C. Tessier, L. El Ouatani, and J. Jacquemin, *J. Chem. Thermodyn.*, **50**, 71 (2012).
12. J. Li, Z. Du, R. E. Ruther, S. J. An, L. A. David, K. Hays, M. Wood, N. D. Phillip, Y. Sheng, and C. Mao, *JOM*, **69**, 1484 (2017).
13. V. L. Chevrier et al., *J. Electrochem. Soc.*, **161**, A783 (2014).
14. R. A. Dunlap, Z. Du, and M. N. Obrovac, *J. Electrochem. Soc.*, **161**, A1698 (2014).
15. J. Yang, N. Solomatin, A. Kraysberg, and Y. Ein-Eli, *ChemistrySelect*, **1**, 572 (2016).
16. S. Heinze, B. Vuillemin, and P. Giroux, *Analysis*, **27**, 549 (1999).
17. F. Blanchard, B. Carré, F. Bonhomme, P. Biensan, and D. Lemordant, *Can. J. Chem.*, **81**, 385 (2003).
18. Y. R. Dougassa, J. Jacquemin, L. El Ouatani, C. Tessier, and M. Anouti, *J. Phys. Chem. B*, **118**, 3973 (2014).