| Title          | Effect of Anion Species in Early Stage of SEI Formation Process |
|---------------|---------------------------------------------------------------|
| Author(s)     | Sonoki, Hidetoshi / Matsui, Masaki / Imanishi, Nobuyuki       |
| Citation      | Journal of The Electrochemical Society, 166(15): A3593-A3598 |
| Issue date    | 2019-10-23                                                    |
| Resource Type | Journal Article / 学術雑誌論文                                |
| Resource Version | publisher                                                   |
| Rights        | © The Author(s) 2019. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. |
| DOI           | 10.1149/2.0191915jes                                         |
| URL           | http://www.lib.kobe-u.ac.jp/handle_kernel/90006506           |

PDF issue: 2020-05-07
Lithium-ion batteries are widely used energy storage devices because of their long cycle life and high specific energy. With the spread of their applications from portable electronics through large electric supply stations, the demands for high-energy rechargeable batteries have been continuously increasing.1−3 A typical strategy to develop high-energy rechargeable batteries is using high-capacity anodes, such as lithium metal and lithium alloys.4−6 There remains a lot of problems to utilize lithium metal or alloys as battery anodes, for the widespread applications.

The lithium metal electrodes suffer from the unavoidable dendritic deposition of lithium metal during the charging process. The lithium dendrite leads the internal short circuit of the cell, resulting in safety incidents. The inhomogeneous solid electrolyte interphase (SEI), on the lithium metal anode causes dendritic growth.6,8−11 To suppress the dendritic growth, researchers have tried physical protection of lithium anode using solid electrolytes12 and forming stable SEI layer using various electrolyte component materials, such as electrolyte salts,13 solvents,14−17 and additives.18,19 We previously reported that fluoroethylene carbonate (FEC) stabilizes the surface layer, and a solvate liquid delays the dendrite formation.16,17 However, the dendrite formation still remains as a fundamental challenge on the lithium metal anodes.18−20

In the case of the alloy/internmetallic anodes, the volume expansion and shrinkage of the active material leads pulverization of the particles during the charging and discharging processes. The pulverized particles are isolated from the electronic/ionic conduction paths and deteriorate the cycle life.21 Many researchers have attempted to suppress the deterioration using nano-sized and structure-controlled active materials.22−26 Strong adhesive binders,27,28 and electrolyte additives.29−31 Some film forming additives, such as vinylene carbonate (VC) and FEC, improve the cycling performance of lithium−silicon alloy anodes.32,33 The VC forms polymerized surface film and reduces the formation of lithium fluoride (LiF) in the SEI layer.34 The FEC produces an SEI layer with low charge-transfer resistance, and improves the cycling performance of a lithium−silicon composite anode.35 Among the above studies, the surface film suppresses further decomposition of the electrolyte and physically protects the electrode surface. Therefore the formation of stable and flexible surface film becomes one of the major strategies to improve the cycling performance of the high-capacity anodes.

On the other hand, we recently found that an electrolyte solution containing lithium borohydride (LiBH4) remarkably improve the cycling performance of a lithium−bismuth intermetallic anode.31 Since the LiBH4 is a strong reducing agent, the SEI formation is significantly suppressed in the LiBH4 solution, as a consequence, we think the suppression of the SEI layer is an effective strategy to utilize the high capacity anodes. There remains a question, however, whether an SEI layer exists in the LiBH4 solution or not, because the in situ FTIR spectra also detect the structural changes of the electrolyte solution at the vicinity of the electrode. Hence, we need to explore other methodology to characterize the SEI layer in the LiBH4 solution. Variety of analytical techniques, such as electrochemical quartz crystal microbalance (EQCM),32,33 X-ray photoelectron spectroscopy (XPS),34−36 FTIR37−39 electrochemical impedance spectroscopy (EIS),40,41 and atomic force microscopy (AFM)42,43 have also been employed to characterize the SEI layer. Among these techniques, the EQCM is a powerful technique to quantify the amount of the SEI layer.

In the present study, we attempted to characterize and quantify the SEI layer produced in electrolyte solutions containing various electrolyte salts, using EQCM and XPS, mainly focusing on the early stage of the SEI formation process. Firstly we confirmed that the LiBH4-based electrolyte forms a pseudo-SEI-free interphase. We also investigate how the conventional anion species, such as hexafluoroarsenate (PF6−) anion and bis(trifluoromethanesulfonyl)amide anion (TFSA−) affects to early stage of the SEI layer formation process.

Experimental

We conducted a comparative study of the SEI formation process using four electrolyte solutions: 2.0 mol L−1 LiBH4 in THF (LiBH4/THF), 1.0 mol L−1 LiPF6 in ethylene carbonate−diethyl carbonate (50:50 vol%) (LiPF6/EC−DEC), 1.0 mol L−1 LiTFSA in EC−DEC (50:50 vol%) (LiTFSA/EC−DEC), and 1.0 mol L−1 LiTFSA in diethylene glycol dimethyl ether (LigTFSA/diglyme). LiBH4/THF (Sigma-Aldrich, MO) and LiPF6/EC−DEC (lithium battery grade (LBG), Kishida Chemical, Japan) was used as received. The LiTFSA/EC−DEC and the LiTFSA/diglyme were prepared according to the following procedure: a LiTFSA (Wako Pure Chemical Industries, Japan) was dried under vacuum at 150°C for 8 h before usage; an EC−DEC (50:50 vol%, LBG, Kishida Chemical, Japan) and a diglyme (99.5%, Sigma-Aldrich, MO) were dried over an activated molecular sieve (Nacala Tesque, Japan); the dried LiTFSA was dissolved in the solvents and stirred for 24 h to obtain the desired solutions. The electrolyte solutions were stored and handled in

**E-mail: matsui@godzilla.kobe-u.ac.jp
a dried and argon-filled glove box. The water content in the solutions except for LiBH₄/THF was estimated to be <20 ppm with a Karl Fischer moisture titrator (MKC-510, Kyoto Electronics Manufacturing, Japan).

We conducted the EQCM measurements using a potentiostat/galvanostat (ECstat-301, EC Frontier, Japan) with a QCM system (QCM922A, Seiko EG&G, Japan). An AT-cut 9.04 MHz quartz crystal with copper electrode (QA-A9M-CU, Seiko EG&G, Japan) was employed as the working electrode in a three-electrode EQCM cell. Lithium foil (Honjo Metal, Japan) was used as the counter and the reference electrode. We performed EQCM cyclic voltammetry at a scan rate of 10 mV s⁻¹ between open circuit potential and 0.1 V vs. Li to investigate the surface layer formation behavior under ambient temperature in the argon-filled glove box. The mass change per unit surface area of the working electrode Δm/A, which represents the amount of the SEI layer, was estimated by Sauerbrey equation.

Potentiostatic measurements were performed at 0.5 or 1.5 V vs. Li for 24 h to prepare the surface layer for the XPS analyses. A copper foil (99.9+%, Nilaco, Japan) was employed as the working electrode in a conventional three-electrode cell. A lithium foil (Honjo Metal, Japan) was used as the counter and the reference electrode. After the measurement, the copper electrode was rinsed with a 1,2-dimethoxyethane (LBG, Kishida Chemical, Japan) for the electrode. We performed EQCM cyclic voltammetry at a scan rate of 10 mV s⁻¹ between open circuit potential and 0.1 V vs. Li to investigate the surface layer formation behavior under ambient temperature in the argon-filled glove box. The mass change per unit surface area of the working electrode Δm/A, which represents the amount of the SEI layer, was estimated by Sauerbrey equation.

Results and Discussion

At first, we performed EQCM cyclic voltammetry to examine the surface layer formation behavior in the electrolyte solutions. Figure 1 shows cyclic voltammograms (top), differential mass change–potential graphs at the first cathodic sweep (middle), and mass change–potential graphs (bottom) in the four electrolyte solutions. The darker color of the charts represents the earlier cycle of the EQCM cyclic voltammetry. In all cases, the significant increases in electrode mass are observed with the cathodic current peaks during the first cycle, and the mass changes are mostly irreversible. The irreversible mass change, the value of Δm/A at the end of each cycle, decreases as cycled. The cyclic voltammograms after the second cycle show better reversibility, and the peak positions are different from those in the first cycle. Therefore, we suspect the surface layer is mostly formed in the first cycle.

As we expected, the LiBH₄/THF solution forms the smallest amount of the surface layer. As seen in Figure 1a, Δm/A gradually decreases at the beginning of the first cycle, because the LiBH₄, which is typically used as the reduction agent, reduces the native oxide layer of the copper electrode. The first mass increase simultaneously appears with the cathodic current at 1.2 V vs. Li. We observe differential mass change peaks at the same potentials where the cathodic peaks are observed. The irreversible mass change at the first cycle was 0.02 μg cm⁻². The amount of the surface layer in LiBH₄/THF is on hundred times smaller compared with the other three electrolyte solutions. Furthermore, the mass change–potential graph after the second cycle also shows reversible behavior. Thus, we conclude that LiBH₄/THF is effective to suppress the surface layer formation and might achieve to form a pseudo-SEI-free interphase. The EQCM result of the LiBH₄ solution quantitatively proves the pseudo-SEI-free model, which we proposed in our previous paper.

In the case of LiPF₆/EC–DEC, the mass increase of the copper electrode begins at a surprisingly high electrode potential of 2.3 V vs. Li during the initial cathodic sweep. The mass increase of the electrode is observed at the same electrode potential we identify the cathodic current peak. As shown in Figures 1b and 1c, the first significant irreversible increase in mass is observed from 2.3 to 1.7 V vs. Li in LiPF₆/EC–DEC, whereas Δm/A began to increase at 1.2 V vs. Li in LiTFSA/EC–DEC. Even though LiPF₆ and the LiTFSA are dissolved

---

**Figure 1.** EQCM measurement results for the four electrolyte solutions; Cyclic voltammograms (top), differential mass change–potential graphs at the first cathodic sweep (middle), and mass change–potential graphs (bottom) in (a) 2.0 mol L⁻¹ LiBH₄ in THF, (b) 1.0 mol L⁻¹ LiPF₆ in EC–DEC, (c) 1.0 mol L⁻¹ LiTFSA in EC–DEC, and (d) 1.0 mol L⁻¹ LiTFSA in diglyme.
in the same solvent, EC–DEC (50:50 vol%), the onset potentials have a large gap. Thus, we think the cathodic current and the increase in mass above 1.2 V vs. Li in LiPF6/EC–DEC could be corresponding to the reductive decomposition of PF6− anions and the surface layer formation. The irreversible mass change at the first cycle was 3.07 μg cm−2, which is higher than that in the other three electrolyte solutions. Though the current observed in the cyclic voltammogram after the second cycle is almost negligible, the Δm/A continuously increases. Accordingly, a relatively large amount of surface layer is formed in LiPF6/EC–DEC.

The electrochemical behaviors of the LiTFSA/EC–DEC and the LiTFSA/diglyme are similar to each other. The electrode mass increases at 1.2 V vs. Li and below, which the cathodic current peak appears, as shown in Figures 1c and 1d. The current density is higher than that at the same potential in LiPF6/EC–DEC. Hence, most of the cathodic current and the increase in Δm/A could be assigned to the reductive decomposition of TFSA− anions and surface layer formation. After the second cycle, some cathodic peaks, not observed in LiPF6/EC–DEC, appear at 0.6, 1.4, 1.8, and 2.3 V vs. Li. We calculated mass per mole of the electron from two potential ranges, 0.4–0.8 V vs. Li and 1.2–1.6 V vs. Li, as μgc m−2. The closer this value is to 1, the higher the reversibility. Again, the results are also strongly dependent upon anions in the electrolyte solutions. The LiBH4/THF shows excellent reversibility over the entire cycle. It suggests that almost no SEI layer was formed and only adsorption state changes of ions were observed as the mass change during the cyclic voltammetry. On the other hand, −Δm/Δm cathodic in LiPF6/EC–DEC shows negative values because the Δm increases even in the anodic scan. The surface layer continuously grows during the CV cycles. As for the LiTFSA-based electrolyte solutions, the reversibility gradually improves with cycling; suggesting that the stable SEI layer formed in the initial cycles prevents further decomposition of the electrolyte solution. Therefore, we suspect that the reversible peaks and mass change during the cyclic voltammetry (Figures 1c and 1d) are corresponding to adsorption/desorption of ions and solvent molecules. This trend supports the fact that LiTFSA is a functional additive for lithium-ion batteries.  

In order to characterize the surface layer, we also conducted XPS analyses of the electrodes prepared by these four electrolytes. The surface layer was formed on a copper electrode by a potentiostatic method. The electrode potential was maintained at 0.5 V vs. Li in the case of LiBH4/THF. The potential is low enough to form the surface layer since it is lower than where the cathodic current was observed in the EQCM cyclic voltammetry. The electrode potential was maintained at 1.5 V vs. Li in the case of other electrolyte solutions to investigate the early stage of SEI formation process. Figures 3–6 show XPS spectra of these electrodes. Three stacked spectra in each graph represent the argon sputtering process. The spectra at the top of the chart correspond to the electrodes without argon sputtering. The spectra at the middle and bottom and correspond to after the argon sputtering for 10 seconds and 30 seconds respectively. The detected signals are displayed by dotted lines, while the backgrounds, the deconvoluted peaks, and the sums are displayed by solid lines. The peak assignments for the spectra are carried out by referring multiple sources: the spectra we took with reference samples, NIST X-ray Photoelectron Spectroscopy Database, and past reports and listed in Table I. Relative elemental composition is estimated by integration of peak area and listed in Table II. The XPS spectra and the elemental composition for the LiBH4/THF also prove that the LiBH4/THF produces a tiny amount of the surface layer. Figure 3 shows the XPS spectra of the copper electrode treated in the LiBH4/THF. The C 1s spectrum of the surface can be deconvoluted into three components, which derived from hydrocarbon contamination, polyether compounds, lithium alkyl carbonate (ROCO2Li), and lithium metaborate (LiBO2) respectively. The broad peak corresponding to ethers and carbonates immediately decreases by the argon-ion etching. Also, Figure 3d; the peaks at 188.0 eV and 191.5 eV are assigned to LiBH4 and lithium metaborate (LiBO2) respectively. The peak corresponding to residual LiBH4 salts is observed only in the spectrum at the surface of the electrode. Even though the peak corresponding

| Component     | C 1s | O 1s | Li 1s | B 1s | F 1s |
|---------------|------|------|-------|------|------|
| Hydrocarbon   | 284.8|      |       |      |      |
| Polyether     | 285.2–286.7| 533.0|       |      |      |
| ROCO2Li       | 287.2–290.0| 532 | 55    |      |      |
| Li2CO3        | 289.0–290.0| 532 | 55    |      |      |
| Li2O          | 529.5| 53.5 |       |      |      |
| LiBO2         | 530.4| 55   | 191.5 |      |      |
| LiBH4         | 55   |      | 188.0 |      |      |
| LiF           | 56.0 | 684.5–685.5|      |      |      |
| LiPF6         | 56.7 | 686.6|      |      |      |
| LiTFSA        | 55   | 688.7|      |      |      |

Table I. XPS peak assignments for the surface layer which formed on potentiostatic measurements.

The EQCM cyclic voltammograms revealed that the surface layer formation behavior is strongly dependent upon anions in the electrolyte solutions. The LiBH4/THF solution forms a tiny amount of the surface layer because of the excellent reductive stability of LiBH4. In contrast, LiPF6/EC–DEC produces the most significant amount of the surface layer at a relatively high electrode potential. It is said that LiPF6-based electrolyte solution begins to decompose on carbonaceous electrodes below 1.0 V vs. Li. However, several research groups reported that the electrolyte solution is also decomposed above 1.0 V vs. Li to form a surface layer on several substrates. The LiTFSA-based electrolyte solutions produce thinner layer than the LiPF6-based electrolyte. Although LiTFSA/diglyme employed the ether-based solvent as with LiBH4/THF, only the LiBH4-based electrolyte solution showed excellent reversibility in the electrode mass. The SEI formation is generally dominated by the decomposition of the anions and lithium carbonate (Li2CO3). The peak intensity of the C 1s spectrum of the surface layer is significantly higher than that in the other electrolytes.

Figure 2. Reversible mass change during the EQCM cyclic voltammetry for the initial 5 cycles.
Figure 3. (a) C 1s, (b) O 1s, (c) Li 1s, and (d) B 1s XPS spectra of the copper electrode maintained at 0.5 V vs. Li for 24 hours in 2.0 mol L\(^{-1}\) LiBH\(_4\) in THF.

to LiBO\(_2\) remained even after the argon etching, the amount of the LiBO\(_2\) is much smaller than carbon-based species, as shown in Table II. Furthermore, the atomic concentration of Cu for the LiBH\(_4\)/THF is much higher than that for the other three electrolyte solutions. Therefore, we think the XPS results are in good agreement with the EQCM results.

We also conducted the characterization of the surface layer derived from in the electrolyte solutions containing the conventional electrolyte salts. Even though the three samples are prepared at 1.5 V vs. Li, which is high electrode potential, the surface layers are formed on the copper electrodes. Figure 4 shows C 1s XPS spectra of the copper electrodes prepared in (a) LiPF\(_6\)/EC–DEC, (b) LiTFSA/EC–DEC, and (c) LiTFSA/diglyme. The C 1s XPS spectra for the LiPF\(_6\)/EC–DEC show the formation of the polyether-based surface layer; however, the signals immediately got weaker after the argon sputtering. As for the LiTFSA-based solutions, in contrast, the C 1s XPS spectra show that the surface layer containing ROCO\(_2\)Li or Li\(_2\)CO\(_3\) are formed. Since the peaks corresponding to ROCO\(_2\)Li and Li\(_2\)CO\(_3\) remain even after 30 seconds of the argon-ion sputtering, a significant amount of TFSA\(^-\) anions and solvent molecules are reduced during the electrochemical process.

Figure 5 shows F 1s spectra for the three solutions. All the spectra have a peak at 685–686 eV assigned to LiF. The peak intensity of the LiF in the LiPF\(_6\)/EC–DEC is significantly higher than the other two electrolytes, and another peak corresponding to the residual salt is almost negligible. We also confirmed peaks at 56.0 eV, which can be assigned to LiF in Li 1s spectra, as shown in Figure 6. Also, Li and F are the main components of the surface layer in LiPF\(_6\)/EC–DEC, as shown in Table II. The facts indicate that the surface layer mostly consists of LiF.

### Table II. Relative elemental composition based on the integrated peak intensity of the XPS spectra.

| Electrolyte solution | Etching time/s | C 1s | O 1s | Li 1s | B 1s | F 1s | Cu 2p |
|----------------------|---------------|-----|-----|------|-----|-----|------|
| 2.0 mol L\(^{-1}\) LiBH\(_4\) in THF | 0 | 33.3 | 35.3 | 22.7 | 5.9 | 2.8 | |
| | 10 | 9.7 | 35.0 | 33.3 | 5.6 | 16.4 | |
| | 30 | 6.5 | 17.1 | 16.2 | 3.2 | 57.0 | |
| 1.0 mol L\(^{-1}\) LiPF\(_6\) in EC–DEC | 0 | 4.1 | 3.1 | 47.4 | 45.3 | 0.1 | |
| | 10 | 1.5 | 1.1 | 48.8 | 48.5 | 0.1 | |
| | 30 | 1.6 | 1.3 | 47.4 | 49.5 | 0.2 | |
| 1.0 mol L\(^{-1}\) LiTFSA in EC–DEC | 0 | 30.3 | 41.1 | 20.5 | 4.2 | 3.9 | |
| | 10 | 30.9 | 40.5 | 15.6 | 4.0 | 9.0 | |
| | 30 | 24.1 | 38.1 | 25.5 | 3.9 | 8.4 | |
| 1.0 mol L\(^{-1}\) LiTFSA in diglyme | 0 | 28.9 | 36.4 | 24.9 | 1.1 | 8.7 | |
| | 10 | 26.4 | 36.5 | 20.9 | 2.7 | 13.5 | |
| | 30 | 23.8 | 32.0 | 25.8 | 1.7 | 16.7 | |

Downloaded on 2019-11-17 to IP 133.30.52.203 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
Figure 4. C 1s XPS spectra of the copper electrodes maintained at 1.5 V vs. Li in (a) 1.0 mol L$^{-1}$ LiPF$_6$ in EC–DEC, (b) 1.0 mol L$^{-1}$ LiTFSA in EC–DEC, and (c) 1.0 mol L$^{-1}$ LiTFSA in diglyme.

In LiTFSA/EC–DEC, we observe peaks that derived from TFSA$^-$ anion in all the F 1s and Li 1s spectra, as shown in Figures 5b, 5c, 6b and 6c. The salts and decomposition products of the electrolyte seem to turn into layer components concertedly. Since the TFSA$^-$ anion derivatives are continuously detected after the argon sputtering in the case of the LiTFSA/EC–DEC, we assume a relatively porous organic layer is formed, compared with the LiTFSA/diglyme.

The LiF formation as the main component in the LiPF$_6$/EC–DEC is obviously due to the reduction of PF$_6^-$ anions. Hydrofluoric acid (HF), typically contained as an impurity species in the LiPF$_6$/EC–DEC, may also contribute to the formation of the LiF layer. The EQCM measurement suggests that the reduction of the PF$_6^-$ anions take place at the initial cathodic sweep of the cyclic voltammetry. Furthermore, the following cyclic voltammograms prove that the electrode surface is well passivated during the initial cycle. The results indicate that LiPF$_6$ preferably forms a dense LiF layer which suppresses further reductions of the anions and solvent molecules. In contrast, the surface layer formed in the LiTFSA-based solutions contains a significant amount of organic compounds, which is formed by decomposed TFSA$^-$ anions and solvent molecules. Therefore, the surface layer behaves like a polymer electrolyte, and the reversible current peaks are observed in the CV.

According to the XPS spectra, the surface layer characteristics are highly dependent upon the anions in the electrolyte solutions. The trend can be seen in the depth profiles of Cu 2p, as shown in Figure 7. For the LiBH$_4$/THF, the copper substrate immediately appears at the early stage of the argon etching. It shows that the surface layer is extremely thin even at 0.5 V vs. Li. The result is in good agreement with the EQCM findings. In the case of the LiPF$_6$/EC–DEC, the atomic concentration of Cu 2p is lower than 2% until the etching time reached to 60 s. However, it increases up to 75% after 5 minutes of the argon sputtering. Since the Cu 2p content after the sputtering process is close to that for the LiBH$_4$/THF, we think thin and dense LiF layer is formed in LiPF$_6$/EC–DEC. On the other hand, for the LiTFSA-based...
species. We also prove that the LiBH₄-based electrolyte forms pseudo-SEI. The organic surface layer gradually grows during the long-time po-tentialistic process should be done in the future.

Conclusions

In the present study, we investigate the amount and the chemical composition of the surface layer formed in four electrolyte solutions using EQCM and XPS. The EQCM and XPS result quantitatively reveal that negligible amount of surface layer is formed at 0.5 V vs. Li metal. 

Acknowledgment

The present study was financially supported by Japan Science and Technology Agency PRESTO grant Number JPMPJPR13CA, JSPS KAKENHI grant Number JP16H06055, JP19H02816, and Tokyo Ohka Foundation for the Promotion of Science and Technology.

ORCID

Hidetoshi Sonoki  https://orcid.org/0000-0002-3728-361X
Masaki Matsu  https://orcid.org/0000-0003-1499-7457
Nobuyuki Imanishi  https://orcid.org/0000-0003-1424-0729

References

1. B. Scrosati and J. Garche, J. Power Sources, 195, 2419 (2010).
2. T. Horiba, Proc. IEEE, 102, 939 (2014).
3. E. A. Olivetti, G. Ceder, G. G. Guastad, and X. Pa, Joule, 1, 229 (2017).
4. W. Xu, J. Wang, F. Ding, X. Chen, E. Nasybulin, Y. Zhang, and J.-G. Zhang, Energy Environ. Sci., 7, 513 (2014).
5. M. N. Obrovac and V. L. Chevrier, Chem. Rev., 114, 11444 (2014).
6. E. Peled, J. Electrochem. Soc., 126, 2047 (1979).
7. J. G. Thevenin and R. H. Muller, J. Electrochem. Soc., 134, 273 (1987).
8. K. Kanamura, H. Tamura, S. Shiraishi, and Z. Takehara, J. Electrochem. Soc., 142, 340 (1995).
9. K. Kanamura, S. Shiraishi, and Z. Takehara, J. Electrochem. Soc., 143, 2187 (1996).
10. H. Ito, K. Shima, M. Ue, and Y. Yamaki, Electrochim. Acta, 49, 555 (2004).
11. H. Kuwata, H. Sonoki, M. Matsu, Y. Matsuda, and N. Imanishi, Electrochemistry, 84, 854 (2016).
12. H. Wang, M. Matsu, H. Kuwata, H. Sonoki, Y. Matsuda, X. Shang, Y. Takeda, O. Yamamoto, and N. Imanishi, Nat. Commun., 8, 15106 (2017).
13. M. Arakawa, S. Tobishama, Y. Nemoto, M. Ichimura, and Y. Yamaki, J. Power Sources, 43-44, 27 (1993).
14. M. Rosso, C. Brissot, A. Teyssot, M. Dolle, L. Sannier, J.-M. Tarascon, R. Bouchet, and J.-P. Fleurial, Electrochim. Acta, 51, 5334 (2006).
15. J. Becking, A. Grobmeier, M. Keule, U. Rodehorst, Schulze, M. Winter, B. Pieker, and M. C. St. Adv. Mater. Interfaces, 4, 1700166 (2017).
16. U. Kasavajjula, C. Wang, and A. J. Appleby, J. Power Sources, 163, 1003 (2007).
17. H. Li, X. Huang, L. Chen, Z. Wu, and Y. Liang, Electrochim. Solid-State Lett., 2, 547 (2009).
18. L. Hu, H. Wu, S. S. Hong, L. Cui, J. R. McDonough, S. Bohn, and Y. Cui, Chem. Commun., 47, 367 (2011).
19. A. Magasinski, B. Zdyrko, I. Kovalenko, B. Hertzbarg, R. Burtovoy, C. F. Huebner, T. Fuller, I. Luzinov, and G. Yushin, ACS Appl. Mater. Interfaces, 2, 3004 (2010).
20. S. Komaba, K. Shimaguro, Y. Nabuchi, T. Ozeki, H. Yui, and K. Kono, J. Phys. Chem. C, 115, 13487 (2011).
21. L. Chen, K. Wang, X. Xie, and J. Xie, J. Power Sources, 174, 538 (2007).
22. N.-S. Choi, K. H. Yew, K. Y. Lee, M. Sung, H. Kim, and S.-K. Kim, J. Power Sources, 161, 1254 (2006).
23. S. Dalavi, P. Guduru, and B. L. Lucht, J. Electrochem. Soc., 159, A642 (2012).
24. M. T. Friedel, S. Gruegeon, S. Laruelle, H. Hassoun, P. Reale, B. Scrosati, and J.-M. Tarascon, J. Power Sources, 195, 2036 (2010).
25. C. C. Nguyen and B. L. Lucht, J. Electrochem. Soc., 161, A1933 (2014).
26. H. Kuwata, M. Matsu, H. Sonoki, Y. Manabe, N. Imanishi, and M. Mizuha, J. Electrochem. Soc., 165, A1486 (2018).
27. D. Aurbach and A. Zaban, J. Electroanal. Chem., 393, 43 (1995).
28. T. Kawaguchi, K. Shimada, T. Ichiitsu, S. Yagi, and E. Matsubara, J. Power Sources, 271, 431 (2014).
29. K. Kanamura, H. Takezawa, S. Shiraishi, and Z. Takehara, J. Electrochem. Soc., 144, 1900 (1997).
30. R. Derdreyville, S. Laruelle, S. Gruegeon, L. Gireaud, J.-M. Tarascon, and D. Gonbeau, J. Electrochem. Soc., 152, A689 (2005).
31. A. Zaban, E. Zingrad, and D. Aurbach, J. Phys. Chem., 100, 3809 (1996).
32. G. Sauerbrey, Z. Phys., 155, 206 (1959).
33. J. D. Hunter, Comput. Sci. Eng., 9, 90 (2007).
34. W. McKinney, In Proceedings of the 9th Python in Science Conference (SciPy 2010), San Diego, CA, 2010, pp. 113-119.
35. A. Deftar, L. DuPont, P. Poizot, and J.-B. Leriche, J. Electroanal. Chem., 418, A1266 (2001).
36. E. Peled, D. Golodnitsky, C. Menachem, and D. Bar-Tov, J. Electrochem. Soc., 145, 3482 (1998).
37. J. B. Goodenough and Y. Kim, J. Power Sources, 196, 6688 (2011).
38. J. Lee, J.-J. Cho, J. Kim, and H.-J. Kim, J. Electrochem. Soc., 152, A1193 (2005).
39. J. T. Lucas, E. Pollak, and R. Kostecki, Electrochem. Commun., 11, 2157 (2009).
40. L. Martin, H. Martinez, D. Poinot, B. Pecquenard, and F. Le Cras, J. Power Sources, 248, 861 (2014).
41. M. Ayache, S. F. Lux, and R. Kostecki, J. Phys. Chem. Lett., 6, 1126 (2015).
42. E. Peled and M. Menkin, J. Electrochem. Soc., 164, A1703 (2017).
43. D. Aurbach, J. Power Sources, 89, 206 (2000).
44. K. Xu, Chem. Rev., 104, 4303 (2004).
45. V. Sharo, A. Moretti, T. Diemant, A. Varzi, R. J. Behm, and S. Plasserini, J. Power Sources, 375, 43 (2018).
46. T. Eriksson, A. M. Anderson, A. G. Bishop, C. Gejke, T. Gustafsson, and J. O. Thomas, J. Electrochem. Soc., 149, A69 (2002).
47. H. Ota, Y. Sakata, X. Wang, J. Sasahara, and E. Yasukawa, J. Electrochem. Soc., 151, A457 (2004).

Downloaded on 2019-11-17 to IP 133.30.52.203 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).