OPEN ACCESS

Improved Performance of Li-metal∣LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ Cells with High-Loading Cathodes and Small Amounts of Electrolyte Solutions Containing Fluorinated Carbonates at 30 °C–55 °C

To cite this article: Elena Markevich et al 2020 J. Electrochem. Soc. 167 070509

View the article online for updates and enhancements.
High energy density is one of the most essential features required from advanced rechargeable battery technology. At the present time lithium ion batteries can be considered as a leading energy storage from advanced rechargeable battery technology. At the present time lithium ion batteries can be considered as a leading energy storage and conversion technology, ensuring very promising combination of high energy and power densities and prolonged cycle life.1,2 Nowadays, the worldwide efforts for further performance improvements of advanced secondary batteries include the challenge of maximizing the energy content.3 The use of positive and negative electrodes which possess high specific capacity is critical for elaboration of high energy density secondary Li batteries. Among anode materials for Li batteries, Li metal anode possesses the highest theoretical specific capacity (3,860 mAh g\(^{-1}\)) and lowest negative redox potential (−3.040 V vs a standard hydrogen electrode). Thus, Li anodes are considerably superior compared to any other anode materials in term of specific capacity and positive impact on energy density.4 Earlier we reported on very stable cycling performance of Li anodes in symmetric Li|Li cells and full Li metal|NCM cells containing practical amounts (<1.2 μl·mg\(^{-1}\) of electrolyte solutions based on FEC/DMC. The lithium metal anodes were characterized by scanning electron microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and Fourier transform infrared spectroscopy (FTIR). The surface films formed on Li anodes cycled in solutions containing FEC and DFEC are composed mainly of their reduction products. In solutions containing FEC and DFEC the role of the latter is to prevent a fast consumption of FEC, by the formation of surface films enriched with its reduction products. Then, minor FEC surface reactions maintain effective electrodes passivation during prolonged cycling. This work clarifies the important role of fluorinated alkyl carbonate co-solvents in stabilizing high energy density secondary batteries based on Li metal anodes.

© 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. 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: 10.1149/167-070509]

Manuscript submitted November 14, 2019; revised manuscript received December 11, 2019. Published January 15, 2020. This paper is part of the JES Focus Issue on Challenges in Novel Electrolytes, Organic Materials, and Innovative Chemistries for Batteries in Honor of Michel Armand.
without any pretreatment. The NCM 811 (LiNi_{0.3}Co_{0.3}Mn_{0.4}O_2) material was obtained from NEI corporation (USA). Cathodes with an areal capacity of 3.4 mAh cm$^{-2}$ (18.39 mg cm$^{-2}$ of active material, porosity 43%) comprising 90% NCM 811, 5% polyvinylidene fluoride (PVDF) binder and 5% conductive carbon (carbon black Super P) on aluminum current collector were used herein. Polyethylene (PE) separators (Tonen) with porosity 40% were used with EC-based electrolyte solution and polypropylene (PP) separators (Celgard) with porosity 40% were used with FEC-based electrolyte solution and polyethylene (PE) separators (Tonen) with porosity 41% were used herein. Black Super P) on aluminium current collector were used herein.

**Electrolyte solutions Conductivity, mS cm$^{-1}$**

| Electrolyte solutions | Conductivity, mS cm$^{-1}$ |
|-----------------------|--------------------------|
| 1M LiPF$_6$ in FEC/DMC 1:4 | 9.9 |
| 1M LiPF$_6$ in FEC/DMC 1:4 | 8.3 |
| 1M LiPF$_6$ in FEC/DFEC/DMC 1:1:8 | 9.3 |

Characterization of pristine and cycled NCM 811 cathodes.—X-ray diffraction (XRD) patterns were obtained with a D8 Advance system (Bruker Inc.) using Cu K$_\alpha$ radiation operated at 40 mA and 40 kV.

Characterization of Li anodes.—Diffuse reflectance Fourier transform infrared (FTIR) spectra from the Li electrodes were measured using a Magna 860 spectrometer (Nicolet) in a glovebox under H$_2$O- and CO$_2$-free atmosphere and upward looking diffuse reflectance (UpIR) accessory from Pike Technologies (USA). Cycled electrodes were washed four times with pure DMC, dried, and put in hermetically sealed home-made cells with KBr windows. SEM images and EDS data were obtained using an Environmental Scanning Electron Microscope, Ouanta FEIG 250 (FEI). Air sensitive samples were transferred from the Ar filled glove box to the chamber of the microscope with the use of homemade vacuum tight transferring cell.

Analysis of electrolyte solution from cycled cells.—$^{19}$F-NMR spectra of the electrolyte solutions were collected using a Bruker Avance-400 spectrometer (376.5 MHz for $^{19}$F). Cycled cells were disassembled in a glove box and their components rinsed with pure dry DMC. To prevent the reaction of HF with NMR tubes made of glass special Teflon NMR probe tubes, equipped with screw caps (New Era, USA) were used for the measurements. Consumption of F-containing species was established by the integration of the area of the corresponding peaks in the $^{19}$F-NMR spectra. The intensity of the signals was calibrated with the use of specially prepared solutions with known concentration of LiPF$_6$, FEC and DFEC in DMC.

**Results and Discussion**

It is important to note that the limiting factor of all the cells comprising Li metal, Ni rich NCM cathodes at high (fully practical) areal loading and small amounts of electrolyte solutions is not the consumption/degradation of the Li metal anodes, but rather consumption of the electrolyte solution in the absence of sufficient Li anode passivation that can hold very prolonged cycling. Hence, for the goals that we wanted to reach in the work presented herein, we could work with the more convenient thick Li foil anodes. The focus of the work was the solutions composition effect.

Table I demonstrates that the specific conductivity values of the solutions containing the fluorinated carbonates are high, $>8$ mS cm$^{-1}$ at RT. The conductivity of the favorite solution containing both FEC and DFEC is more than 9 mS cm$^{-1}$ at RT.

Galvanostatic cycling results obtained with Li/NCM 811 cells with 1.7 $\mu$m g$^{-1}$ NCM (33 $\mu$L cm$^{-2}$) of FEC, DFEC and mixed FEC + DFEC-based electrolyte solutions are shown in Fig. 1. Figure 1a demonstrates a significantly improved cycling performance observed for the electrolytes containing fluorinated cyclic carbonates compared to EC-based electrolyte solutions. This amount of the electrolyte solution ensures approximately the same cycling life for FEC and DFEC-based electrolyte solutions of about 300 cycles at 30 °C, whereas cells containing mixed FEC + DFEC based solutions outperforms both of these electrolyte solutions (with only one fluorinated co-solvent) and demonstrates longer stable cycling. Cells with mixed FEC + DFEC-based electrolyte solutions exhibit the best behavior at 45 °C as well (Fig. 1b). FEC based electrolyte solution shows somewhat higher rate capability of the cells at current densities of 1–2 mA cm$^{-2}$, at least, in the initial period of cycling (Fig. 1c). This observation is in line with slightly higher capacity of the cells observed in FEC-based electrolyte solution compared to DFEC-based and mixed FEC + DFEC-based ones during initial 100 cycles both at 30 °C and 45 °C at 1 mA cm$^{-2}$ (Figs. 1a and 1b). Voltage profiles measured for Li | NCM 811 cells with mixed FEC + DFEC-based electrolyte solution after 100 cycles at two temperatures are shown in Fig. 1d.

With the aim to increase the energy density of Li/NCM 811 batteries we prepared and tested the cells with lower amount of the electrolyte solution relative to the amount of the active cathode material. In our previous works we demonstrated that the decrease of the volume of FEC-based electrolyte solutions from about 1.7 to 1.2 $\mu$L mg$^{-1}$ NCM leads to deterioration of the cycling performance of both Li/NCM 811 and Li/NCM 622 cells. We showed that with cells containing FEC-based electrolyte solution drastic capacity fading followed by capacity recovery occurs for both types of the cells after several dozens of cycles. This phenomenon is ascribed to the formation of thick resistive surface films on the Li metal anodes in Li/NCM cells with FEC-based electrolyte solutions as a result of detrimental “cross talk” between the Li anode and the NCM cathode that leads to worsening of the passivation of Li metal anodes and consumption of the electrolyte solutions by side reactions. In an effort to avoid this unwanted phenomenon observed with low amount of the electrolyte solutions, we tested cells containing mixed
FEC + DFEC electrolyte solutions in specific amounts lower 1.7 μL mg⁻¹ NCM. Figure 2a demonstrates much more stable behavior of the cells with FEC + DFEC-based solution compared to FEC-based cells when the amount of the electrolyte solution was 1.2 μL mg⁻¹ NCM. It is remarkable, that with the mixed electrolyte solution the fading—recovery occurrence disappeared from the capacity vs cycle number curves, even when using in the cells 1.2 μL mg⁻¹ NCM of electrolyte solution. Nevertheless, the cycling life was extended by about 150 additional stable cycles. Moreover, further decrease in the amount of the electrolyte solution down to 1 and 0.7 μL mg⁻¹ NCM resulted in stable cycling both at ambient (30 °C) and elevated (45 °C–55 °C) temperatures (Figs. 2b–2d). These outstanding cycling results are obviously related to the formation of more effective SEI on the Li anodes in the mixed FEC + DFEC-based electrolyte solutions.

Figure 3 completes the performance presentation, showing typical voltage profiles of cells containing DFEC + FEC based solutions at the beginning of their cycle life and after 250 cycles (chart 3a) and the derivative presentation dQ/dV vs V of the voltage profiles (chart 3b). This comparison demonstrates that the unique stabilization of the cells obtained by the use of solutions containing both FEC and DFEC includes not just capacity, but also voltage. This result is very important because it seems to show that surface stabilization of the NCM cathodes (this is the major effect of the solutions containing the fluorinated carbonates co-solvents) affects also their bulk stabilization. This point deserves a deep consideration and discussion about most appropriate preparation of Ni rich NCM cathode materials and their effective stabilization. In brief, it seems that a key issue is their surface stabilization. A further discussion on that is beyond the scope of this paper.

In order to compare the composition of the surface films formed in EC, FEC, DFEC and mixed FEC + DFEC-based electrolyte solutions we measured FTIR spectra from Li anodes after 25 galvanostatic cycles in Li|NCM 811 cells. The results are presented in Fig. 4. The surface film formed in the EC-based electrolyte solution (black curve) is obviously thicker and contains more PEO-like species, as we reported earlier for the case of Li anodes after 100 galvanostatic cycles (in fact, after failure of the cells).8 We showed that EC-based electrolyte solutions does not enable to obtain cycling conditions in Li|NCM 811 cells with practical parameters. It seems that deterioration of the electrolyte solution due to EC polymerization leads to the failure of the cells. The spectra collected from Li anodes cycled in the FEC-based electrolyte solutions (blue curve) is very similar to the spectra that were published earlier, collected from Li anodes after 100 cycles8 and contains Li₂CO₃, organic lithium alkylcarbonates and polycarbonates, as indicated.17 Spectra measured from the surface of Li anodes cycled with DFEC-based electrolyte solutions (green curve) differ from spectra measured...
with Li anodes cycled in FEC-based solution in the frequency region of 1840–1680 cm$^{-1}$ related to C=O stretching of carbonate/polycarbonate species. The set of the peaks observed in this area for the case of mixed FEC + DFEC-based electrolyte solutions (red curve) obviously presents the superposition of the peaks of FEC- and DFEC-derived carbonate species. Thus, the surface film on Li anodes cycled in the electrolyte solution containing FEC + DFEC is composed mainly of the reduction products of both FEC and DFEC.

Previously we provided possible reaction schemes for FEC reduction on Li-Si electrodes which explain predominant presence of the oxygen-free species in the C 1 s XPS spectra of the Si electrodes cycled in FEC-based electrolyte solutions.18,19 The formation of the oxygen-free polymeric species was supposed to be a result of the polymerization of fluoroethylene, which was formed during the reductive decomposition of FEC. In the case of DFEC the formation of difluoroethylene can be proposed (reaction 2 in Scheme 1).

Another reaction path of the formation of oxygen-free polymeric species during the reduction of FEC was proposed by Shkrob et al.20 The authors assumed that the reduction of FEC yields a vinylexyl radical (reaction 2 in Scheme 1) that can abstract H atoms from FEC molecules, initiating both the chain reaction causing FEC decomposition and radical polymerization with the formation of polyfluorovynilene carbonate. The resulting polymer can further defluorinate, yielding interior radicals that migrate and recombine to produce a

Figure 2. Effect of the amount of electrolyte solution on the performance Li | NCM 811 cells at 30 °C–55 °C. (a) Galvanostatic cycling results obtained with (a) 1.2 μL mg$^{-1}$ NCM of FEC and FEC/DFEC based electrolyte solutions at 30 °C and (b)-(d) with 0.7–1 μL mg$^{-1}$ NCM of FEC/DFEC based electrolyte solutions at 30 °C, 45 °C and 55 °C, respectively. Loading of NCM active material of 3.4 mAh cm$^{-2}$.

Scheme 1. Possible reactions of FEC and DFEC on Li anodes which form reactive intermediates. These further polymerize, thus forming surface films which are comprise flexible polymeric membranes in which ionic Li compounds are embedded.
Due to the unique surface chemistry that can be developed on both kinds of electrodes in solutions containing the fluorinated carbonates.

SEM images of Li anodes cycled 25 times in LiNCM 811 cells containing the four electrolyte solutions, as indicated, and the atomic composition of the surface films on the Li anodes determined by EDAX are shown in Fig. 5. The surface morphology of the Li deposition depends significantly on the electrolyte solution composition. The needle-like Li deposits are characteristic of Li anodes cycled in the EC based electrolyte solution (Fig. 5d). High surface area associated with this morphology results in fast depletion of the electrolyte solution and failure of the cells. In contrast, Li anodes cycled in the electrolyte solutions containing FEC and/or DFEC show a flake-like surface structure after cycling. The surface of Li anodes cycled in the DFEC-containing electrolyte solution is characterized by larger flakes (Figs. 5b and 5c). The distinctive feature of the surface films formed on Li anodes cycled in solutions containing FEC and/or DFEC components is the much higher content of F (19–33 at%) compared to Li anodes cycled in EC based electrolyte solution (5.6 at%). Higher F content was measured in the surface films of cycled Li anodes as the amount of DFEC in the solution was higher. Interestingly, an intermediate value of F content equal to 26.9 at% was obtained in the surface films of Li anodes cycled in solutions containing both FEC and DFEC (10% each). This result proves that despite their somewhat similar structure, each fluorinated co-solvent has a unique contribution to the composition of the surface films formed on lithium. Also, the surface films formed on lithium anodes in the solutions which include the fluorinated carbonates contain more species with phosphorous atoms (1.4–1.6 at%), compared to surface films formed on Li anodes in EC-based electrolyte solutions (0.9 at%). The surface films formed on Li anodes in EC based solutions contain more oxygen atoms than the surface films formed in the solutions containing the fluorinated carbonate co-solvents. This result is in line with the FTIR data revealing PEO-like species as major components in the surface films formed on Li anodes cycled in the EC based solutions.

$^{19}$F-NMR spectra of the electrolyte solutions after 40 galvanostatic cycles of Li/NCM 811 cells with FEC, DFEC, and mixed FEC + DFEC were measured in efforts to estimate the consumption of fluorinated cyclic carbonates and PF$_6^{-}$ anions during cycling with these three electrolyte solutions. For this purpose, the cycled cells were disassembled in a glove box and their components were rinsed with a fixed amount of pure dry DMC. The spectra thus obtained are shown in Fig. 6 and the consumption of F-containing species is presented in Table II. It is seen that approximately equal amount of PF$_6^{-}$ anions was consumed from three electrolyte solutions, but the stability of the two fluorinated cyclic carbonates differs significantly during cycling. As is seen from Table II, after 40 cycles 41% of FEC from FEC-based electrolyte solution and 64% of DFEC from DFEC-based electrolyte solution were converted to solid products predominantly on Li anodes. This result points out to higher rate of DFEC decomposition compared to FEC. It is remarkable, that in the case of mixed FEC + DFEC electrolyte solution almost all the FEC remained in the solution, while DFEC undergoes a severe decomposition of 75% (of its initial content). Obviously, preferential decomposition of DFEC in LiNCM cells prevents the consumption of FEC. The content of FEC in the electrolyte solution remains practically unchanged during cycling, and the protective surface films on Li anodes contain mainly DFEC reduction products. However, small amount of FEC decomposition products are, obviously, present in the surface films which are formed in the mixed electrolyte and ensure more effective protection of the electrodes. Indeed, lower absolute amount of DFEC was consumed from the mixed electrolyte solution compared to DFEC-based electrolyte. Thus, better cycling performance observed with the mixed electrolyte solutions may be explained by the formation of surface films rich with DFEC
decomposition products with small amount of FEC-derived species. One can conclude that in the mixed FEC + DFEC electrolyte solutions, the role of DFEC is to prevent a fast consumption of FEC by the formation of surface films enriched by the DFEC-derived products as a first stage. Then, FEC may act as a healing agent, ensures effective continuous passivation by minor incorporation of its reduction products into the surface films on the Li anodes.

This assumption can be clearly demonstrated by the electrochemical window measurements of the three electrolyte solutions performed with inert glassy carbon electrodes (Fig. 7). In efforts to determine the electrochemical stability of the electrolyte solutions, glassy carbon electrodes were freshly polished before every initial cathodic or anodic sweep. Three consecutive cyclic voltammograms between OCV and 5 V vs Li/Li$^+$ and OCV and 0 V vs Li/Li$^+$ were measured to estimate passivating properties of each electrolyte solution during both anodic and cathodic polarization processes. The three electrolyte solutions demonstrate identical anodic stability up to 5 V. In the first cathodic sweep, DFEC- and FEC-based electrolyte solutions show the onset of the pronounced reduction process at $>2.5$ V and around 2 V vs Li/Li$^+$, respectively (Figs. 7a and 7b). This result is consistent with a previous report wherein the reduction of DFEC occurs before that of FEC owing to the relatively lower LUMO energy of DFEC. Higher cathodic currents measured with DFEC-based electrolyte solutions compared to those measured with FEC-based solutions during the first cathodic polarization points toward the much higher cathodic reactivity of DFEC compared to FEC. This conclusion is strengthened by the fact that the 2nd and 3rd cathodic polarizations of the electrodes in the DFEC containing solutions still result in high cathodic currents at potentials below 1 V vs Li. In turn, the cathodic behavior of the carbon electrodes ion the FEC based solutions reflects less cathodic reactivity and a better passivation (lower cathodic currents during the first polarization and a pronounced decrease in the cathodic currents during the 2nd and 3rd polarizations (compare charts 7a and 7b)). The higher cathodic reactivity of DFEC compared to that of FEC is fully expected, since the fluorin atoms are electron withdrawing. An extra F substituent in DFEC increases its affinity towards reduction and also provides more options for surface reactivity via deprotonation, HF elimination and double bonds formation. The cathodic behavior of the carbon electrodes in the solutions containing both DFEC and FEC (chart 7c) reflects a somewhat intermediate behavior. Lower cathodic currents (compared to those measured in DFEC solutions) point towards a synergistic effect of the presence of both fluorinated co-solvents on the electrodes passivation. These results are in line with a predominance of DFEC reduction products in the surface films.

Table II. Consumption (%) of F-containing components of three electrolyte solutions after 40 galvanostatic cycles of Li | NCM 811 cells with with 1.2 μL mg$^{-1}$ NCM (22 μL cm$^{-2}$) of electrolyte solutions established by $^{19}$F NMR spectroscopy. Loading of NCM active material of 3.4 mAh cm$^{-2}$, current density 1 mA cm$^{-2}$, 30 °C.

| Electrolyte solutions          | PF$_6^-$, % | FEC, % | DFEC, % |
|-------------------------------|-------------|--------|---------|
| 1M LiPF$_6$ in FEC/DMC 1:4    | 23          | 41     | —       |
| 1M LiPF$_6$ in DFEC/DMC 1:4   | 22          | —      | 64      |
| 1M LiPF$_6$ in FEC/DFEC/DMC 1:1:8 | 23       | 7      | 75      |

Figure 4. FTIR spectra of Li electrodes surfaces after 25 galvanostatic cycles in Li|NCM 811 cells at 30 °C in 1M LiPF$_6$ EC/DMC, 1M LiPF$_6$ FEC/DMC, 1M LiPF$_6$ DFEC/DMC and 1M LiPF$_6$ FEC/DFEC/DMC, as indicated.
formed on Li anodes in solutions containing the two fluorinated co-solvents. These results are consistent with the conclusion drawn from the results of the $^{19}$F NMR measurements obtained with the mixed FEC + DFEC-based electrolyte solutions, showing a predominant consumption of DFEC but also involvement of FEC in the surface reactions of the cells.

Thus, an increased cycling stability of Li∣NCM cells observed with the mixed FEC + DFEC-based electrolyte solution stems from a synergistic effect of FEC and DFEC, where DFEC is consumed first in passivation formation side reactions that moderates consumption of FEC. This suggests that the initial massive formation of protecting surface films is obtained by reduction of DFEC. Much more moderate surface reactions of FEC complete the passivation and surface protection. The remaining FEC (reflected by the solutions studies, Fig. 7 and Table II) can act further as a healing agent which repairs the electrodes’ passivation whenever local reactive electrodes’ surface zones are occasionally formed during cycling. It is important to note that the prolonged cycling demonstrated herein is enabled also due to unique stabilization of the cathodes’ surfaces. We conducted post mortem analysis of the cathodes after prolonged cycling in these cells and found (by SEM analysis) that there was no change in their morphology. Their stability was clearly confirmed. We attribute this to surface stabilization; however, the study of their surface chemistry is harder, less conclusive and is beyond the scope of this paper. Moreover, most of the effects described herein, namely, prolonged cycling of these cells with practical loading of several mAh cm$^{-2}$ and very small amounts of electrolyte solutions are determined by the passivation and stabilization of the Li metal anodes.

Figure 5. SEM images of Li anodes cycled in Li|NCM 811 cells for 25 cycles with 1M LiPF$_6$ EC/DMC, 1M LiPF$_6$ FEC/DMC, 1M LiPF$_6$ DFEC/DMC and 1M LiPF$_6$ FEC/DFEC/DMC, as indicated, and atomic composition of the surface films on Li anodes determined by EDS.

Figure 6. $^{19}$F NMR spectra of the electrolyte solutions (as indicated) taken from cycled Li|NCM 811 cells after 40 cycles. The cycled cells were dissembled in a glove box after cycling and the residual electrolyte solutions were extracted by equal amounts of pure DMC. Hence the spectral comparison provides a quantitative analysis (Table II).
Conclusions

Our investigation revealed that the combination of the FEC and DFEC could substantially improve the cycling performance of Li∣NCM 811 cells with Li metal anodes operating with practical loading of 3.4 mAh cm⁻² and small amounts of electrolyte solutions at ambient and elevated temperatures. The use of the mixed FEC + DFEC based electrolyte solutions instead of FEC-based solutions enables to extend stable cycling of these cells up to several hundreds of cycles when the amount of the electrolyte solution comprises 0.7–1.2 μl mg⁻¹ NCM 811. The undesirable phenomenon of a drastic capacity fading of Li metal∣NCM cells during the first dozens of cycles, following by a spontaneous capacity recovery during prolonged cycling at 30 °C is fully prevented by using solutions comprising both fluorinated carbonates. We suggest that the surface reactions of solutions containing both DFEC and FEC has a synergistic effect, leading to a more effective passivation of the Li metal anodes. The passivating surface films on the Li anodes contain reaction products derived from both FEC and DFEC reduction. The spectroscopic and the electrochemical measurements lead to conclude that DFEC decomposition is dominating the surface reactions first, leading to a basic passivation of the Li metal anodes. Then, small scale reactions of FEC upon cycling maintain the electrodes’ passivation, hence acting as a healing agent. This sequence of surface reactions in solutions containing both DFEC and FEC enables a prolong cycling of Li metal∣NCM 811 cells containing very small amounts of electrolyte solutions even at elevated temperatures.

Acknowledgments

A partial support for this work was obtained by the Israel High Committee of High Education and the Prime Ministry office in the framework of INREP (Israel National Research center for Electrochemical Propulsion).

References

1. J. M. Tarascon and M. Armand, Nature, 414, 359 (2001).
2. J. B. Goodenough and K.-S. S. Park, J. Am. Chem. Soc., 135, 1167 (2013).
3. T. Placke, R. Kloebsch, S. Dühnen, and M. Winter, J. Solid State Electrochem., 21, 1939 (2017).
4. X.-B. Cheng, R. Zhang, C.-Z. Zhao, and Q. Zhang, Chem. Rev., 117, 10403 (2017).
5. E. Markevich, G. Salitra, F. Chesneau, M. Schmidt, and D. Aurbach, ACS Energy Lett., 2, 1321 (2017).
6. G. Salitra, E. Markevich, M. Afri, Y. Talyosef, P. Hartmann, J. Kulisch, Y.-K. Sun, and D. Aurbach, ACS Appl. Mater. Interfaces, 10, 19773 (2018).
7. E. Markevich, G. Salitra, Y. Talyosef, U.-H. Kim, H.-H. Ryu, Y.-K. Sun, and D. Aurbach, ACS Appl. Energy Mater., 1, 2600 (2018).
8. E. Markevich, G. Salitra, Y. Talyosef, and D. Aurbach, J. Electrochem. Soc., 166, A2834 (2019).
9. E. Markevich, G. Salitra, Y. Talyosef, and D. Aurbach, J. Electrochem. Soc., 166, A1685 (2019).
10. Y. Gao et al., *Nat. Mater.*, **18**, 384 (2019).
11. S. C. Nagpure, T. R. Tanm, E. J. Dufek, V. V. Viswanathan, A. J. Crawford, S. M. Wood, J. Xiao, C. C. Dickerson, and B. Liaw, *J. Power Sources*, **407**, 53 (2018).
12. D. L. Wood, J. Li, and C. Daniel, *J. Power Sources*, **275**, 234 (2015).
13. J. Shen, H. Chen, L. Yu, D. Huang, and Z. Luo, *J. Electroanal. Chem.*, **834**, 1 (2019).
14. C.-C. Su, M. He, R. Amine, Z. Chen, R. Sahore, N. D. Rago, and K. Amine, *Energy Storage Mat.*, **17**, 284 (2019).
15. C.-C. Su, M. He, P. C. Redfern, L. A. Curtiss, I. A. Shkrob, and Z. Zhang, *Energy Environ. Sci.*, **10**, 900 (2017).
16. D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C. S. Kelley, and J. Affinito, *J. Electrochem. Soc.*, **156**, A694 (2009).
17. P. Verma, P. Maire, and P. Novak, *Electrochim. Acta*, **55**, 6332 (2010).
18. E. Markevich, G. Salitra, and D. Aurbach, *ACS Energy Lett.*, **2**, 1337 (2017).
19. E. Markevich et al., *J. Electrochem. Soc.*, **160**, A1824 (2013).
20. I. A. Shkrob, J. Wishart, and D. Abraham, *J. Phys. Chem. C*, **119**, 14954 (2015).
21. C.-C. Su, M. He, P. C. Redfern, L. A. Curtiss, I. A. Shkrob, and Z. Zhang, *Energy Environ. Sci.*, **10**, 900 (2017).
22. U. Purushotham, N. Takenaka, and M. Nagaoka, *RSC Adv.*, **6**, 65232 (2016).