The Critical Role of Fluoroethylene Carbonate in the Gassing of Silicon Anodes for Lithium-Ion Batteries

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ABSTRACT: The use of functionalized electrolytes is effective in mitigating the poor cycling stability of silicon (Si), which has long hindered the implementation of this promising high-capacity anode material in next-generation lithium-ion batteries. In this Letter, we present a comparative study of gaseous byproducts formed by decomposition of fluoroethylene carbonate (FEC)-containing and FEC-free electrolytes using differential electrochemical mass spectrometry and infrared spectroscopy, combined with long-term cycling data of half-cells (Si vs Li). The evolving gaseous species depend strongly on the type of electrolyte; the main products for the FEC-based electrolyte are H2 and CO2, while the FEC-free electrolyte shows predominantly H2, C2H4, and CO. The characteristic shape of the evolution patterns suggests different reactivities of the various LiₓSi alloys, depending on the cell potential. The data acquired for long-term cycling confirm the benefit of using FEC as cosolvent in the electrolyte.

While lithium-ion batteries based on intercalation reactions in lithium metal oxide cathodes and graphite anodes are widely used to address the fast-growing demand for energy storage in portable devices and electric vehicles, the increasing energy density needs in these applications require different storage mechanisms with the possibility to reach either higher potentials or capacities (or both).¹ A promising next-generation negative electrode material is silicon (Si), which conducts an alloying reaction with lithium (Li), thus achieving high theoretical specific capacities based on the extent of lithiation \( \approx 4000 \text{ mA h g}^{-1} \text{ (Li}_{12}\text{Si}_{2}), \approx 3580 \text{ mA h g}^{-1} \text{ (Li}_{15}\text{Si}_{4}) \). These values are about an order of magnitude higher than that of commonly used graphite (372 mA h g⁻¹), which operates in a comparable potential window. The main disadvantage of Si as active material is the pulverization effect resulting from volume changes during charging and discharging.² While volume changes are observed as well for graphite anodes (≈10%),³,⁴ those for Si are significantly larger (up to 300%).⁵,⁶ In particular, the enormous volume contraction during the delithiation (dealloying) process can lead to a reduced electronic contact between the Si particles and cause an increased cell resistance. Some lithium is even trapped because of such loss of electronic contact, resulting in fast capacity fading during cycling.²,⁵ Another mechanism adversely affecting the (Coulombic) efficiency is the so-called solid electrolyte interphase (SEI) formation. The electrochemical alloying of Si and Li occurs at low potential \( E < 0.5 \text{ V vs Li} \), leading to reductive decomposition of electrolyte species on the free electrode surface. Because of the continuous swelling and shrinking of the Si particles during battery operation, the SEI can break locally and fresh, highly reactive surface is again exposed to the electrolyte. This leads to additional decomposition of the electrolyte and lithium loss in every cycle and therefore thickens the SEI while decreasing the efficiency.⁷

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One possibility to mitigate these degradation phenomena is the use of fluorinated electrolyte solvents, e.g., fluoroethylene carbonate (FEC). These can promote the formation of a more flexible SEI (compared with FEC-free electrolytes), thereby leading to a more stable capacity retention.\textsuperscript{11–15} Nguyen and Lucht\textsuperscript{11} used attenuated total reflection infrared spectroscopy (ATR-IR) to demonstrate that the amount of polymerized FEC on the electrode surface increases with increasing concentration of FEC in the electrolyte. Xu et al.\textsuperscript{10} used X-ray photoelectron spectroscopy (XPS) to show that the main reduction products are LiF and −CHF−OCO\textsubscript{2}−type compounds. Both studies agreed that FEC supports the preservation of the electrode structure, among others, by decreasing the amount of cracks. In a recent work on the decomposition of FEC, Michan et al.\textsuperscript{15} suggest that it is reduced to form LiF and vinylene carbonate (VC). VC is a common additive used in many electrolyte compositions (especially for graphite-based cells) and is apparently further reduced to produce HCO\textsubscript{2}Li, LiC\textsubscript{2}O\textsubscript{4}, and Li\textsubscript{2}CO\textsubscript{3}.\textsuperscript{13} These findings are supported by first-principle calculations, which confirm that the carbon–fluorine bond of FEC is broken first, leading to the formation of LiF.\textsuperscript{14} From investigations on the gassing behavior of lithium iron phosphate (LiFePO\textsubscript{4})/Si–C cells by online electrochemical mass spectrometry (OEMS) combined with \textsuperscript{19}F nuclear magnetic resonance (NMR) spectroscopy and cycling for up to 450 cycles, Jung et al. concluded that FEC is continuously consumed in a four-electron process, leading to CO\textsubscript{2} formation. In addition, they showed that sudden cell failure occurs when FEC is depleted.\textsuperscript{15} These OEMS measurements were carried out during the first lithiation step, but no in situ gassing analysis for multiple cycles is reported until now to the best of our knowledge.

In this Letter, we compare the gassing behavior of Si half-cells (Si vs Li) with two different electrolytes over seven cycles. LP\textsubscript{57} (1 M LiPF\textsubscript{6} in 3:7 by weight ethylene carbonate [EC]:ethyl methyl carbonate [EMC]) was used as reference electrolyte and compared with an electrolyte which contained FEC instead of EC as cosolvent. The gas evolution was investigated using a differential electrochemical mass spectrometry-differential electrochemical infrared spectroscopy (DEIMS-DEIRS) setup described in earlier works.\textsuperscript{16,17} The measurements were supplemented by long-term cycling experiments, resulting in about 2.5 times higher specific capacity of Si for the FEC-containing electrolyte after 400 cycles.

Coin-type Si half-cells were assembled with different electrolytes (1 M LiPF\textsubscript{6} in EC:EMC or FEC:EMC) for long-term cycling studies. Representative charge–discharge profiles and the corresponding specific capacities and Coulombic efficiencies are shown in Figure 1a–c. The lithiation capacity for the cell with FEC-containing electrolyte drops from initially around 4000 mA h g\textsubscript{Si}\textsuperscript{−1} to 2000 mA h g\textsubscript{Si}\textsuperscript{−1} within 20 cycles and is nearly stable during the following 380 cycles. This can be explained with a prolonged SEI formation over multiple cycles, which was also observed by Tokranov et al.\textsuperscript{18} According to a two-phase model, the SEI consists of an “organic” SEI which forms at voltages of 0.3–1.2 V vs Li and an inorganic part forming at potentials <0.3 V. During the prolonged SEI formation, the composition changes, resulting in lower resistance after several cycles. The decrease in resistance is caused by the formation of the inorganic part, which is responsible for a faster Li ion transport. The number of cycles required to achieve a stable SEI resistance depends on the cycling procedure and varied between 5 and 20 cycles, which is in agreement with the measurements presented here. However, it should also be noted that the upper and lower cutoff potentials were decreased and increased, respectively, after the initial formation cycles (for stability reasons) and the C-rate was changed from C/10 to C/5 in the second cycle. In addition, deleterious side reactions such as lithium consumption due to conversion of the native oxide layer on the Si particles are most pronounced in the first couple of cycles.\textsuperscript{19,20} Nevertheless, the capacity reaches stable values after a dense and flexible SEI is
built. In contrast, the cell with FEC-free electrolyte (LP57) loses capacity continuously, demonstrating the importance of FEC in the formation of a stable SEI. The significant difference in the capacity retention between the two systems results in higher specific capacity of the FEC-containing cell after about the 50th cycle. After 400 cycles, the FEC-containing cell delivers a specific capacity around 2.5 times higher than that of the cell with LP57 (1880 mA h gSi \(^{-1}\) vs 760 mA h gSi \(^{-1}\)). Also, the Coulombic efficiency stabilizes much earlier above 98% (after 3 vs 80 cycles) when FEC is used as cosolvent in the electrolyte, and it is even higher than 99.5% after 160 cycles. The efficiency in the first cycle is around 87% and 81% for FEC-free and FEC-containing cells, respectively, indicating more irreversible side reactions during SEI formation in the case of the FEC-based electrolyte. The same general trends are also valid for cells with higher Si loading, as is evident from Figure S1. Overall, these measurements clearly demonstrate the enhanced cycling performance of FEC-containing electrolytes compared with EC-based electrolytes.

The low first cycle efficiency is (among others) a major showstopper for the application of pure Si anodes in lithium-ion batteries because it lowers the practical energy density of the cell. Much work is currently being done to overcome this problem, e.g., by using prelithiated Si.\(^{21-24}\) Nevertheless, the low efficiency can be exploited to improve the energy density of commercial cells by blending small amounts of Si into the graphite anode. Si acts as lithium scavenger and thus helps to reduce the amount of graphite that is typically needed for properly balancing the anode and cathode (in terms of Coulombic efficiency).

To determine the influence of FEC on the gassing behavior, Si half-cells were assembled with either LP57 or 1 M LiPF\(_6\) in FEC:EMC and investigated by DEMS-DEIRS. The cycling was performed under identical conditions, but using custom cells. The charge-discharge profiles and the in situ gas characteristics for the first seven cycles are depicted in Figure 2a,b. The evolution characteristics of H\(_2\) (m/z = 2) are similar for the FEC-free and FEC-containing cells. The main evolution takes place when the Si potential steeply decreases in the beginning of the first lithiation cycle. This evolution is mainly associated with trace water reduction. The evolution rate decreases steadily during the initial cycle until the second lithiation cycle. Thereafter, H\(_2\) evolution could stem from electrolyte decomposition or further water reduction. The similar evolution patterns found for FEC-containing and FEC-free cells suggest that either EMC or water (or both) is the source of H\(_2\). In a study by Seo et al., lithium naphthalenide was used as one-electron reducing agent to examine the decomposition of various organic carbonates.\(^{25}\) Interestingly, no H\(_2\) evolution was observed. Thus, we assume that water residues or certain decomposition products are the major source for H\(_2\) evolution. The characteristics of C\(_2\)H\(_4\) (m/z = 26), CO\(_2\) (m/z = 44), and CO depend strongly on the electrolyte used. In the case of LP57 (Figure 2a), C\(_2\)H\(_4\) evolution is observed during each cycle with consistent detection by both mass spectrometry and IR absorption. C\(_2\)H\(_4\) is a well-known product of reductive decomposition of EC on graphite anodes.\(^{26}\) Because Si and graphite operate in a comparable potential window, we assume that a similar decomposition mechanism takes place.\(^{27}\) The C\(_2\)H\(_4\) evolution starts in the first cycle directly after the alloying reaction starts, and its rate reaches a stable value in the voltage range between 130 and 80 mV. When the potential is further decreased, the evolution rate increases to a maximum value at the lower cutoff potential. During the following delithiation, the rate decreases to a minimum at E \(
less\approx\) 400 mV. In the following cycles, C\(_2\)H\(_4\) evolution takes place only during lithiation and abruptly stops after the lower cutoff potential is reached. The CO\(_2\) evolution characteristics during the first cycle partly resemble the C\(_2\)H\(_4\) evolution. The maximum value is reached at the lower cutoff potential. In contrast to C\(_2\)H\(_4\), CO\(_2\) shows a stable evolution rate during delithiation, which does not drop until the upper cutoff potential is reached. In the later cycles, only very small amounts of CO\(_2\) were detected. CO evolution was detected at about 80 mV using IR spectroscopy. The starting value coincides with an enhancement in C\(_2\)H\(_4\) evolution. The CO evolution rate increases nearly linearly until the middle of the second lithiation cycle. The evolution characteristics of CO, C\(_2\)H\(_4\), and H\(_2\) during further cycling are similar for all cycles and are described in detail below.

The gassing behavior is strongly electrolyte-dependent, which is reflected in different gas evolution characteristics in the case of the FEC-containing electrolyte. During the entire measurement, neither C\(_2\)H\(_4\) nor CO evolution was detected. One might expect that C\(_2\)H\(_3\)F evolves, which we examined by recording its main fragments at m/z = 26, 27, 44, 45, and 46. As depicted in Figure S2, all of these mass signals remained constant during cycling except for m/z = 44, which is also
associated with CO$_2$. The comparison of the acquired mass signal $m/z = 44$ and the IR curves for CO$_2$ clearly shows that the changes in $m/z = 44$ are caused by CO$_2$ evolution (Figure 2b). These results are in agreement with computational modeling predictions of FEC molecular decomposition mechanisms by Leung et al.$^{28}$ The decomposition of FEC was experimentally investigated by Streich et al.$^{29}$ in high-energy lithium nickel cobalt manganese oxide ($x$Li$_2$MnO$_3$ × (1−$x$)LiMO$_2$, M = Ni, Co or Mn; $x ≈ 0.5$)-based cells and by Jung et al.$^{15}$ in LiFePO$_4$/Si cells using OEMS. In both studies, the main gaseous decomposition product found was CO$_2$. Because of the large volume change during cycling, the SEI on the Si particles is not stable, at least during the first seven cycles as the presented gas evolution demonstrates, and CO$_2$ is detected during each cycle (the potential-dependent description of the CO$_2$ gassing follows in the next paragraph).

The evolution rates for the main characteristic gases are depicted magnified in Figure 3b (EC:EMC, H$_2$ and C$_2$H$_4$) and d (FEC:EMC, H$_2$ and CO$_2$) for the third and fourth cycles together with the charge−discharge profiles and their derivatives in Figure 3a,c. The lithiation profile shows two plateaus, which are also clearly visible in the derivative curves (or more rigorously, the transition, as local extremum, between the plateaus). According to Loveridge et al.$^{30}$ the first sloping plateau at ∼280 mV can be associated with the alloying reaction for amorphous (α-) silicon, a-Si $\rightarrow$ a-Li$_{1.5}$Si, while the second plateau at ∼90 mV describes the transition from a-Li$_{1.5}$Si $\rightarrow$ a-Li$_{2}$Si. The evolution characteristics for H$_2$ are similar for both electrolytes. The evolution rate rises rapidly in the beginning of the lithiation cycle, where the potential decreases fast until the first plateau, and it changes slope (marked with $\bullet$ at 290−250 mV) at the same time the evolution of C$_2$H$_4$ starts for LP57. The maximum value of the H$_2$ evolution (marked with $\blacksquare$) is reached at the beginning of the second alloying plateau, where the C$_2$H$_4$ evolution rate reaches a stable value (at 130−120 mV). The evolution of C$_2$H$_4$ remains constant until $E < 60$ mV. At a potential of around 50 mV, the formation of crystalline Li$_{3.75}$Si takes place.$^{30,31}$ The increase in C$_2$H$_4$ evolution might be related with the structural change resulting in higher reactivity. The evolution of both H$_2$ and C$_2$H$_4$ stops abruptly when the direction of the current flow changes at the lower cutoff potential (marked with $\blacktriangle$). In contrast to H$_2$ and C$_2$H$_4$, the CO evolution rate (see Figure S3) simply fluctuates in a sinusoidal manner with no special characteristics. The evolution starts together with C$_2$H$_4$ evolution and reaches a maximum at the same potential as H$_2$. Afterward the rate decreases without notable features at the lower cutoff potential. Because the characteristic features of the H$_2$ and C$_2$H$_4$ evolution coincide, there might be structural changes (nonlinear volume expansion of Si) or different reactivities of the various Li$_x$Si alloys leading to different decomposition rates. Furthermore, the measurements suggest that no electrolyte decomposition takes places during the volume contraction upon delithiation.

As already mentioned, the H$_2$ evolution characteristics are similar for both electrolytes, but for the FEC-containing electrolyte mainly CO$_2$ evolution takes place. The starting point of the CO$_2$ evolution coincides with the H$_2$ maximum (marked with $\blacktriangle$ at 130−120 mV). The CO$_2$ evolution rate increases rather linearly during the second half of the lithiation cycle and throughout the entire delithiation cycle, finally reaching a maximum at the upper cutoff potential. Afterward the rate decreases during the first half of the lithiation cycle. Hence, in contrast to the LP57 electrolyte, FEC is also decomposed to some extent during delithiation. In the literature, a complex SEI on Si particles consisting of different layers was discussed.$^{18,32,33}$ Tokranov et al., for example, suggest an organic SEI, which is formed at potentials higher than 0.3 V on the Si surface, while an inorganic SEI forms below 0.3 V.$^{18}$ The latter consists, among others, of Li$_2$CO$_3$, Li$_2$O, and LiF. Additional investigations on the growth and mechanical properties of the SEI on Si anodes were performed by Breitung et al. using in situ atomic force microscopy (AFM).$^{34}$ The largest changes in electrode height occurred in the initial lithiation cycle. During the following delithiation and in the second cycle, there were only minor changes detectable.

One apparent difference between the different electrolytes used is that CO$_2$ evolution is detected even during delithiation for FEC-containing electrolyte, while C$_2$H$_4$ evolution was detected only during lithiation for FEC-free electrolyte. This implies that SEI is also formed during delithiation for the FEC-containing electrolyte, as the CO$_2$ evolution is likely accompanied by solid decomposition products contributing to the SEI (e.g., LiF, CHF$_2$OCO$_2$-type compounds, etc.).$^{10}$ Such contribution is favorable because Si particles are subjected to large tensile stresses during delithiation, which promotes
initiation and propagation of microcracks.\textsuperscript{5,35} According to ab initio calculations by Okuno et al.,\textsuperscript{36} LiF shows a "glue effect" via bond formation between the lithium in the lithiated Si and fluorine in the LiF of the SEI. Therefore, generation of LiF, which is probably accompanying CO\textsubscript{2} evolution during delithiation, might interfere with crack formation, thus leading to smaller and fewer cracks. An additional measurement on a Si half-cell with higher loading and the same cycling protocol is depicted in Figures S4 and S5. Notably, a different slope of CO\textsubscript{2} evolution is observed upon lithiation and delithiation. In the second and third cycles, the slope during delithiation is slightly lower than during lithiation. In the following cycles, a nearly constant and slightly decreasing CO\textsubscript{2} evolution was detected during delithiation. Summarizing these measurements, it is possible that different decomposition mechanisms of FEC take place upon alloying and dealloying, yet the detailed mechanism needs further study.

In this work, both the electrochemical performance and gassing behavior of Si half-cells using 1 M LiPF\textsubscript{6} in EC:EMC (LP57) or FEC:EMC were analyzed using long-term cycling and DEMS-DEIRS measurements. The cycling performance revealed significant differences. While the capacity for the cells with FEC-containing electrolyte was nearly stable after an initial drop during the first 20 cycles, the capacity of the cells with EC-containing electrolyte dropped continuously during 400 cycles. After 400 cycles, the cells with FEC-containing electrolyte exhibit about 2.5 times higher capacity than the cells with EC-based electrolyte. Besides the difference in capacities, the gassing behavior is also strongly electrolyte-dependent. While the main decomposition products of LP57 are H\textsubscript{2}, CH\textsubscript{4}, and CO, the FEC-containing electrolyte leads to H\textsubscript{2} and CO\textsubscript{2} formation. The evolution patterns showed different features, which were analyzed in detail. One main difference between the two investigated electrolytes is that CH\textsubscript{4} (decomposition of EC) and H\textsubscript{2} evolution takes place only during the lithiation cycle, while FEC is decomposed also during delithiation. This might suppress crack formation upon delithiation because of the "glue effect" of LiF and partially explain the improved cycling performance of cells with FEC-containing electrolyte.

\section{ASSOCIATED CONTENT}

\subsection{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.7b00619.

Details of experimental procedures, cycling data for higher loading Si half-cells, and additional DEMS-DEIRS results (PDF)

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Notes

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