Supporting Information

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

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Experimental

Electrode Preparation

Electrodes were prepared by casting a water-based slurry containing 63 wt.% Si nanoparticles (<100 nm, ≥98%, Sigma-Aldrich), 22 wt.% Super C65 carbon black (Timcal), and 15 wt.% poly(vinyl alcohol) Selvol 425 binder (Sekisui) onto 18 µm-thick Cu foil (Gould Electronics) followed by drying at 80 °C in vacuum for 12 h. The areal loading was around 0.4 mg_{Si} cm^{-2} for the long-term cycling and 0.3 mg_{Si} cm^{-2} for the gas analysis.

Testing and Instrumentation

Coin-type cells were used for long-term cycling, while custom cells with gas inlet and outlet were used for the DEMS-DEIRS measurements. The cells and system were previously described.[1,2] A mass flow controller (F-201CV-020-RAD-33-Z, Bronkhorst) was used to obtain a constant flow of the carrier gas (2.5 mL_{He} min^{-1}, purity 6.0). The gas was analyzed using a mass spectrometer (GSD 320, OmniStar Gas Analysis System, Pfeiffer Vacuum GmbH, Germany) and FTIR spectrophotometer (TENSOR II, Bruker Optik GmbH, Germany). The cells were assembled inside an Ar-filled glovebox (MBraun) by stacking 600 µm-thick Li metal foil (Rockwood Lithium Inc.), glass microfiber separator (GF/D type for long-term cycling, GF/A type for DEMS-DEIRS, GE Healthcare Life Sciences, Whatman), and Si electrode. The electrodes and the separator used for the DEMS-DEIRS measurements had a diameter of 40 mm and 42 mm, respectively. In the coin-type cells, the electrodes had a diameter of 13 mm and the separator of 17 mm. Both LP57 (1 M $LiPF_6$ in EC:EMC, 3:7 by wt.) and EMC were provided by BASF SE. The FEC-containing electrolyte was prepared by mixing 1 M $LiPF_6$ in a 1:1 wt. mixture of FEC (Solvay) and EMC. The water content in both LP57 and EMC was determined to be <10 ppm by Karl-Fischer titration. The producer specified the water content in FEC to be <10 ppm. Electrochemical testing was performed at 25 °C using a MACCOR Series 4000 cycler (Tulsa) for the long-term cycling and a VSP-300 potentiostat (BioLogic) for the DEMS-DEIRS measurements. After the initial formation cycles at rates of C/10 (1st cycle) and C/5 (2nd to 4th cycles) in the voltage range between 1000 mV and 10 mV were completed (1C = 4008 mA g_{Si}^{-1}), the cells were cycled at C/5 charge (alloying) and discharge (dealloying) between 600 mV and 30 mV during the subsequently cycles. After each DEMS-DEIRS measurement a calibration gas was introduced in the system to quantify the ion currents and the IR absorption data in terms of molar ppm values.

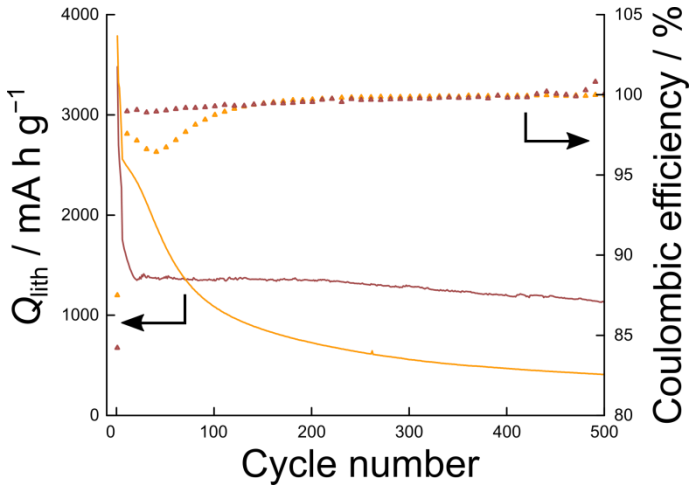

Figure S1. Specific lithiation capacities and Coulombic efficiencies for a Si half-cell with higher loading (~0.8 mg_{Si} cm^{-2}) using 1 M $LiPF_6$ in EC:EMC (orange) and FEC:EMC (red).

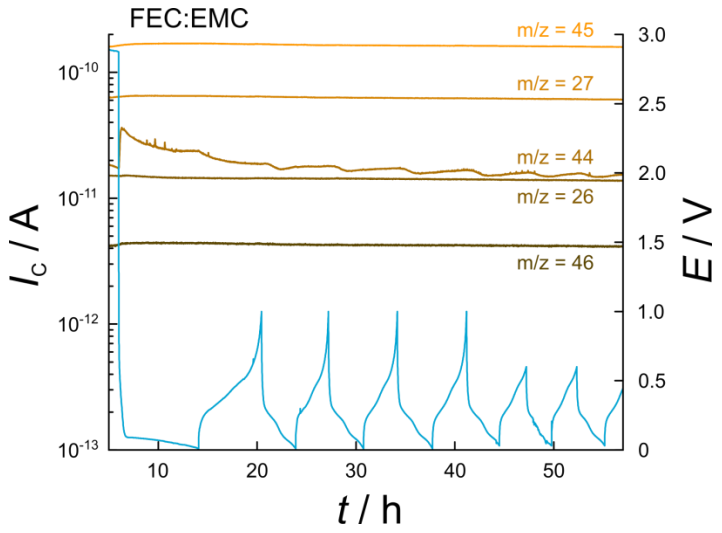

Figure S2. Charge-discharge profiles (blue) for the first seven cycles of a Si half-cell using 1 M $LiPF_6$ in FEC:EMC with the corresponding ion currents (orange/brown) for the main fragments of C_2H_3F.

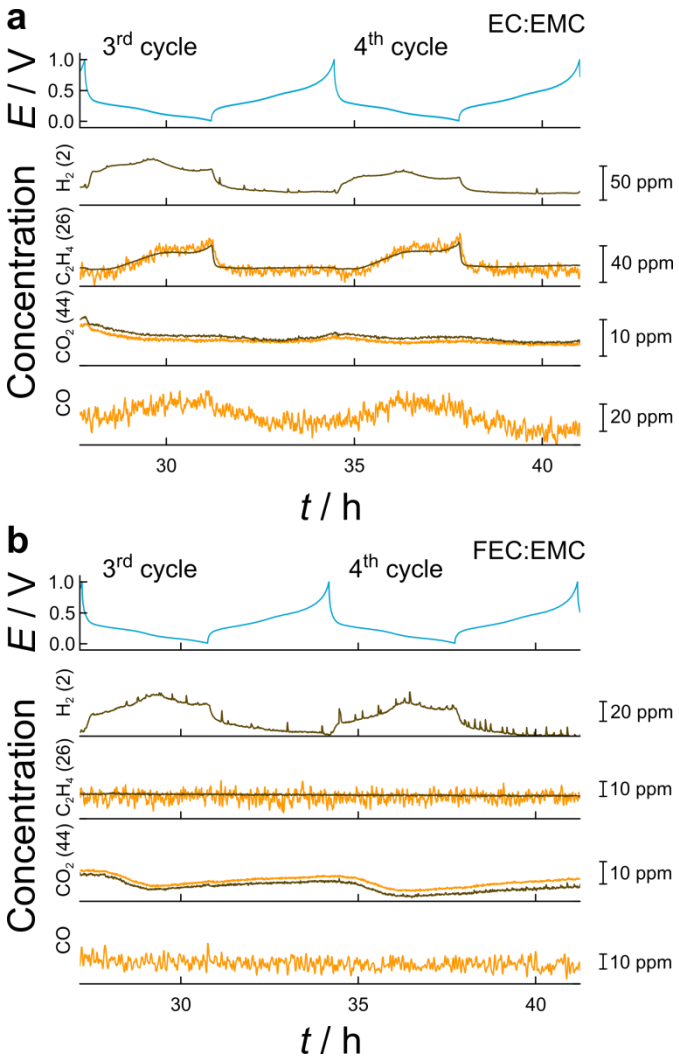

Figure S3. Charge-discharge profiles (blue) for the 3rd and 4th cycles of Si half-cells using (a) 1 M $LiPF_6$ in EC:EMC and (b) FEC:EMC with the corresponding mass signals (brown) m/z = 2 (H_2), 26 (C_2H_4), and 44 (CO_2), and IR absorption curves (orange) for C_2H_4, CO_2, and CO.

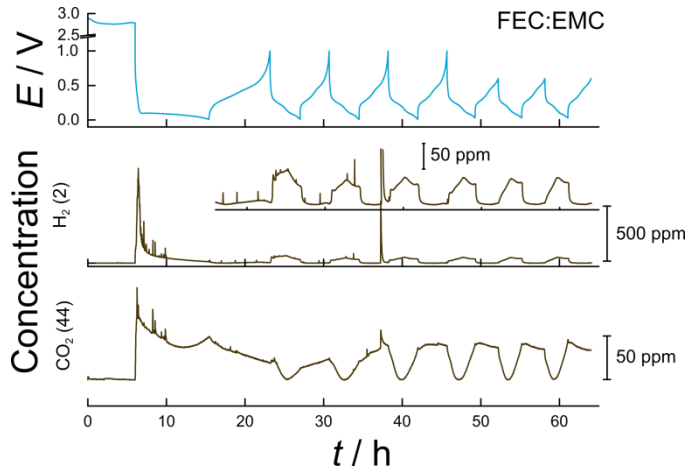

Figure S4. Charge-discharge profiles (blue) for the first seven cycles of a Si half-cell with higher loading (~0.4 mg_{Si} cm^{-2}) using 1 M $LiPF_6$ in FEC:EMC with the corresponding background corrected mass signals (brown) *m*/*z* = 2 (H_2) and 44 (CO_2).

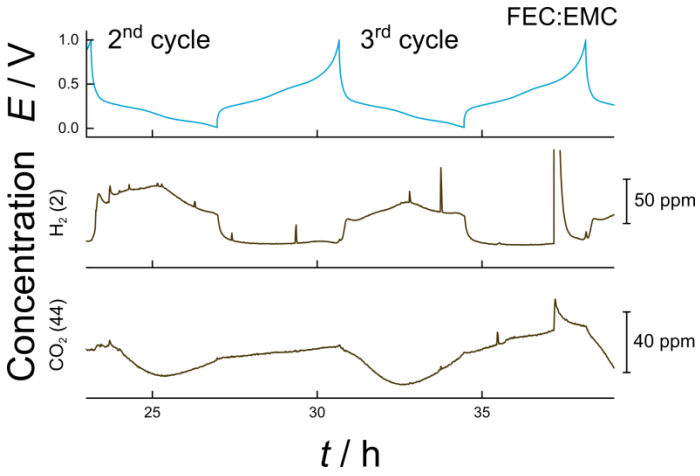

Figure S5. Charge-discharge profiles (blue) for the 2nd and 3rd cycles of a Si half-cell with higher loading (~0.4 mg_{Si} cm^{-2}) using 1 M $LiPF_6$ in FEC:EMC with the corresponding background corrected mass signals (brown) *m*/*z* = 2 (H_2) and 44 (CO_2).

(1) Berkes, B. B.; Jozwiuk, A.; Sommer, H.; Brezesinski, T.; Janek, J. Simultaneous Acquisition of Differential Electrochemical Mass Spectrometry and Infrared Spectroscopy Data for In Situ Characterization of Gas Evolution Reactions in Lithium-Ion Batteries. *Electrochem. Commun.* **2015**, *60*, 64–69.

(2) Berkes, B. B.; Jozwiuk, A.; Vračar, M.; Sommer, H.; Brezesinski, T.; Janek, J. Online Continuous Flow Differential Electrochemical Mass Spectrometry with a Realistic Battery Setup for High-Precision, Long-Term Cycling Tests. *Anal. Chem.* **2015**, *87*, 5878–5883.