Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

SEI-Component Formation on Sub 5 nm Sized Silicon Nanoparticles in Li – ion Battery: Role of Electrode Preparation, FEC Addition and Binder

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Table S1. Elemental composition of the pristine silicon electrode in dependency of the binder determined by XPS.

Sample	Si (at.%)	C (at.%)	O (at.%)	F (at.%)
PAA	11.3	68.1	16.9	3.7
CMC/SBR	11.6	66.9	18.8	2.0

Table S2. Elemental composition of the silicon electrode with PAA as binder after 400 times cycling in LP30 with FEC addition in dependency of the washing procedure determined through EDXS. a) fresh electrode, b) washed 3 times in DMC without sonication and c) washed 3 times in DMC with sonication.

Sample	Si (at.%)	C (at.%)	O (at.%)	F (at.%)	P (at.%)
a)	15.73	73.12	6.69	3.08	-
b)	4.92	46.98	32.95	14.75	0.35
c)	9.2	44.18	33.73	12.65	0.23

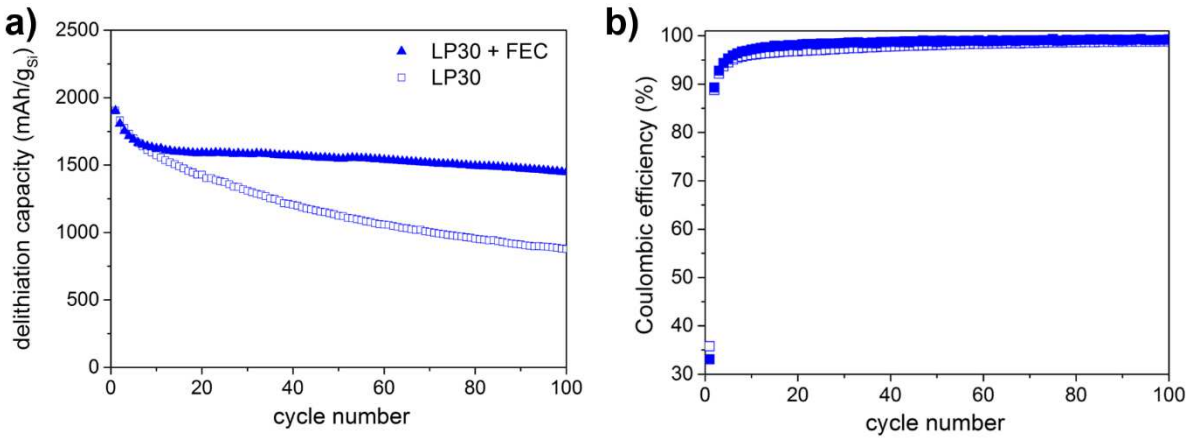

Figure S1. Galvanostatic cycling between 0.01–1.2 V vs. Li/Li$^+$ at 0.5 A/g of the silicon electrode in dependency of FEC addition: a) capacity vs. cycle number and b) Coulombic efficiency vs. cycle number.

Additional electrochemical experiments were carried out to examine the electrolyte decomposition with and without FEC at the anode surface, separated from the lithiation/delithiation reaction. For that purpose, electrodes were repetitively polarized to 0.84 V vs. Li/Li^+. At this potential electrolyte decomposition already occurs, whereas the lithiation of silicon is merely negligible. Moreover, freshly prepared anodes as well as specimens were investigated that had been previously subjected to 100 discharging/charging cycles. The specific charge of the first pulse represents the initial SEI formation. At higher charges, more electrolyte is decomposed as depicted in Figure S2. The electrolyte containing FEC shows a charge flow that is almost 50 % higher than observed for the additive-free electrolyte. This behavior indicates a distinctly stronger electrochemical reaction of the additive-containing mixture, what again confirms the results of the galvanostatic cycling tests (Figure 3). In a sequence of 24 pulses the charge density fades in every step and is thus a direct hint to the formation of a surface layer, which limits further decomposition at the electrode surface with ongoing reaction. The same trend is shown in Figure 2 revealing that the electrochemical system stabilizes during some charging/discharging cycles. In a next step, new electrodes were galvanostatically cycled 100 times and the experiment with the same parameters was performed. In this case the electrodes are covered by a fully formed SEI and as expected the specific charges are remarkably lower compared to pristine electrodes (Figure S2 blue data). This finding is a result of a protective SEI on the surface on all samples and is typical for anode materials in LIB. However, the specific charge of the sample cycled with FEC addition is only about one quarter of the value than measured in the additive-free electrolyte. In both cases the value is constant over various pulses. This behavior evidences that the SEI in presence of FEC has a strong protective effect than without the additive, but causes an initially higher consumption of electrolyte on the pristine electrode.

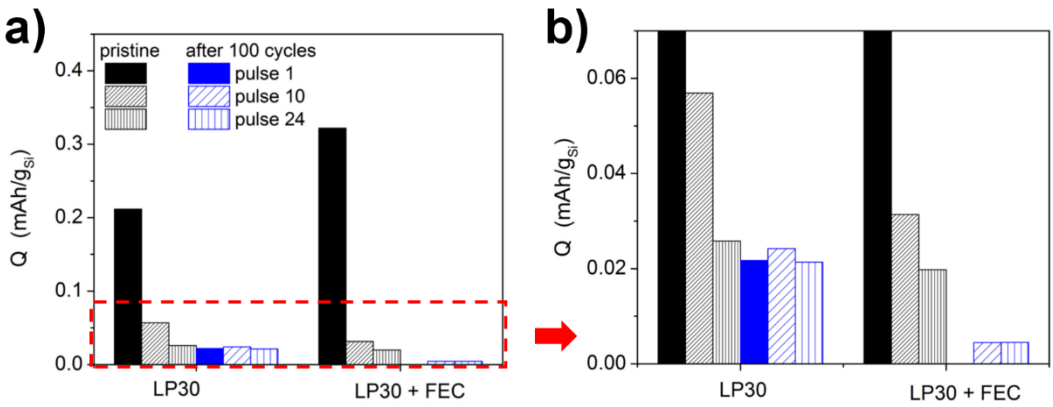

Figure S2. a) Integral specific charge Q of selected potentiostatic pulses in dependency of FEC addition. The charge represents the decomposition of the electrolytes specified in the diagram. b) Integral specific charge Q focused on low specific charge.

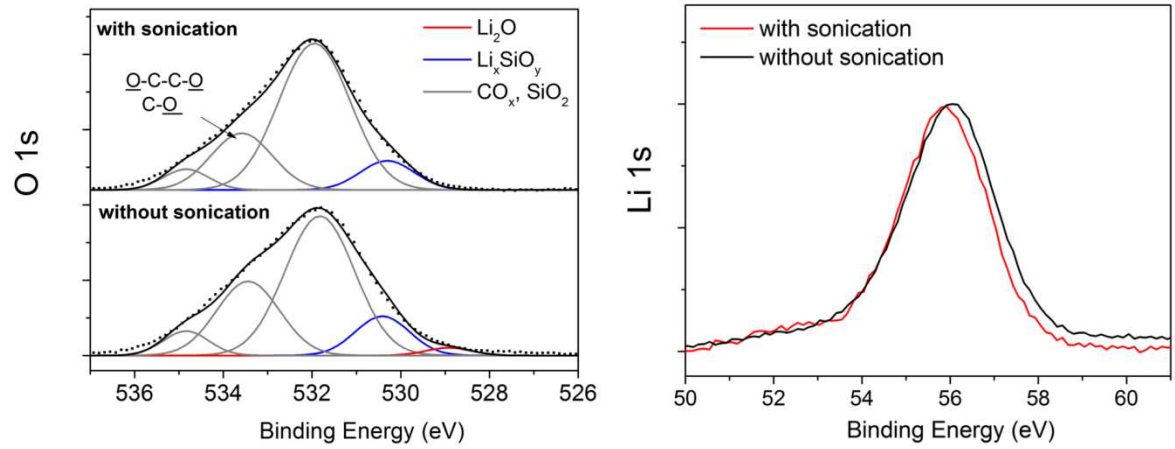

Figure S3. XP spectra of the silicon electrode with PAA as binder cycled 400 times in LP30 + FEC in dependency of sonication.

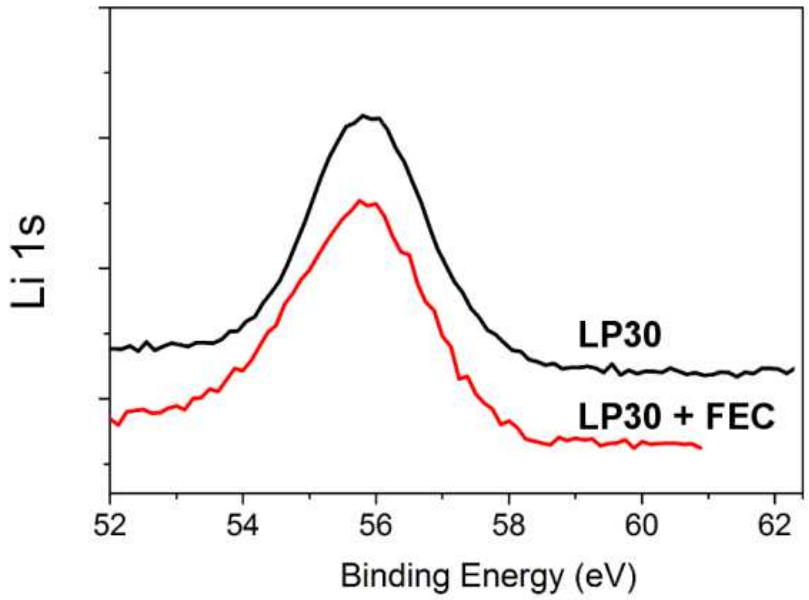

Figure S4. XP spectrum of the silicon electrode with CMC/SBR as binder cycled 400 times in dependency of FEC.

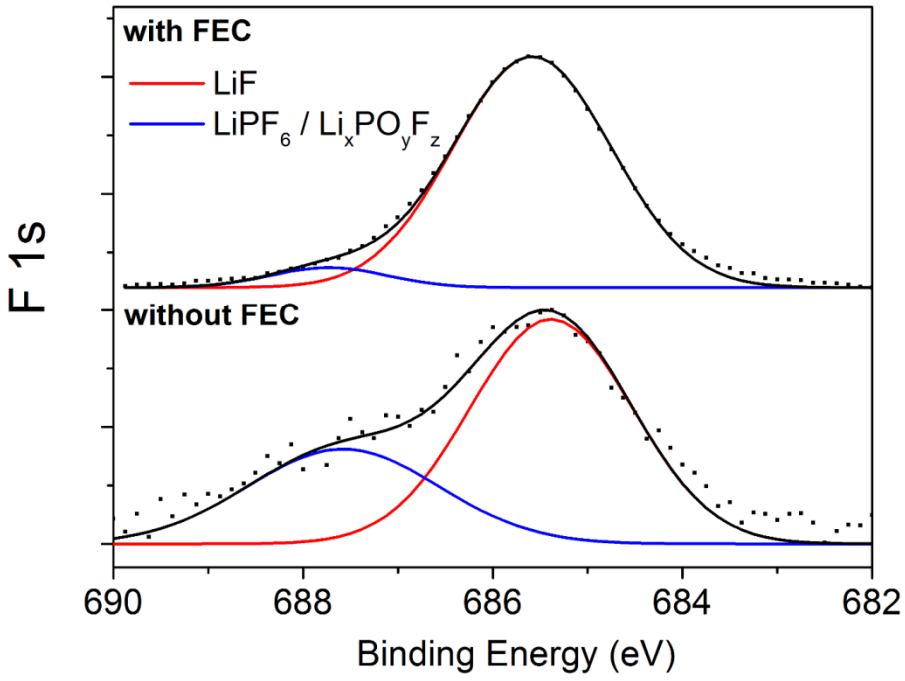

Figure S5. XP spectrum of the silicon electrode with CMC/SBR as binder cycled 400 times in dependency of FEC.