Supporting Information

Beneficial combination of formic acid as processing additive and fluoroethylene carbonate as electrolyte additive for $Li_4Ti_5O_{12}$ lithium-ion anodes

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Keywords: aqueous processing; formic acid; fluoroethylene carbonate; $Li_4Ti_5O_{12}$; lithium battery

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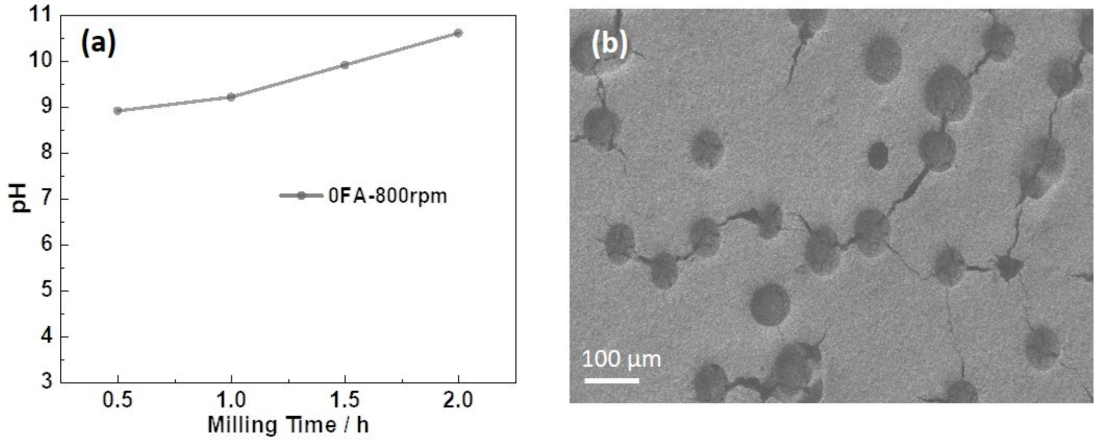

Figure S1. (a) Evolution of the pH value of the LTO electrode slurry in absence of any FA as a function of the ball milling time (milling speed: 800 rpm). (b) SEM micrograph of the resulting LTO electrode.

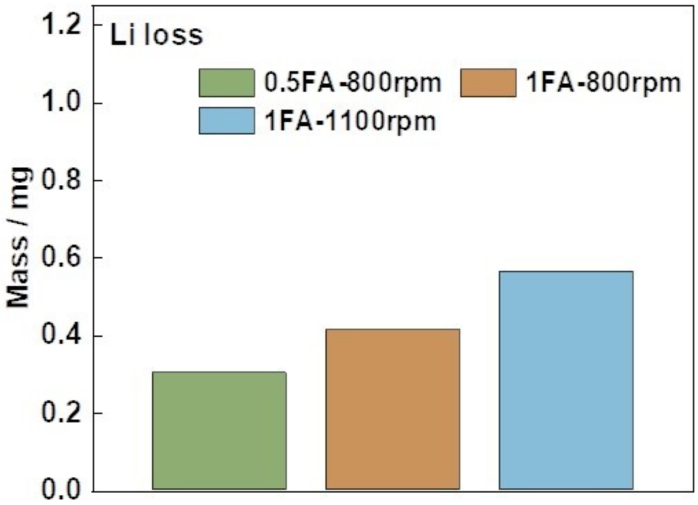

Figure S2. Amount of lithium detected via ICP-OES in the liquid phase after subjecting LTO powder and the indicated amount of FA to ball milling at the given speed.

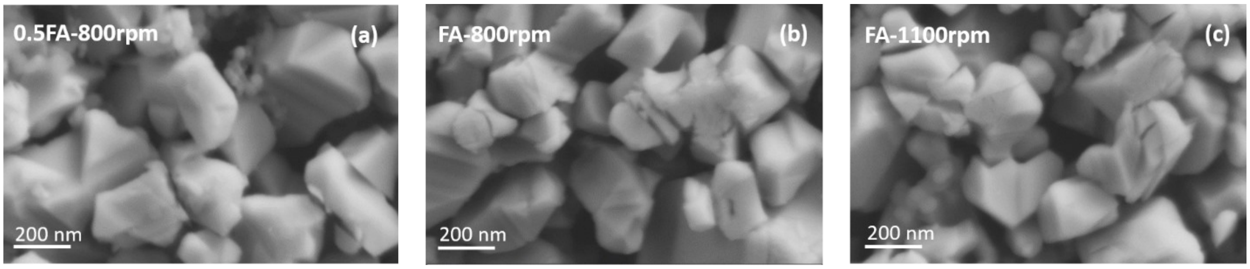

Figure S3. SEM micrographs of the pristine LTO-based electrodes prepared varying amounts of FA and at different milling speeds: (a) 0.5FA-800rpm, (b) 1FA-800rpm, and (c) 1FA-1100rpm.

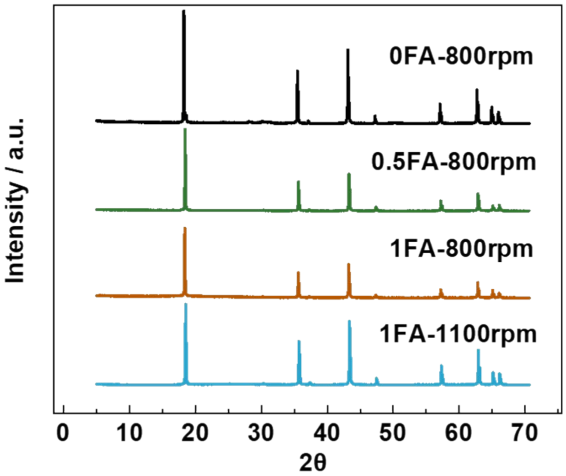

Figure S4. XRD patterns recorded for pristine LTO electrodes prepared with varying amounts FA and different milling speeds, i.e., 0FA-800rpm, 0.5FA-800rpm, 1FA-800rpm, and 1FA-1100rpm (from top to bottom).

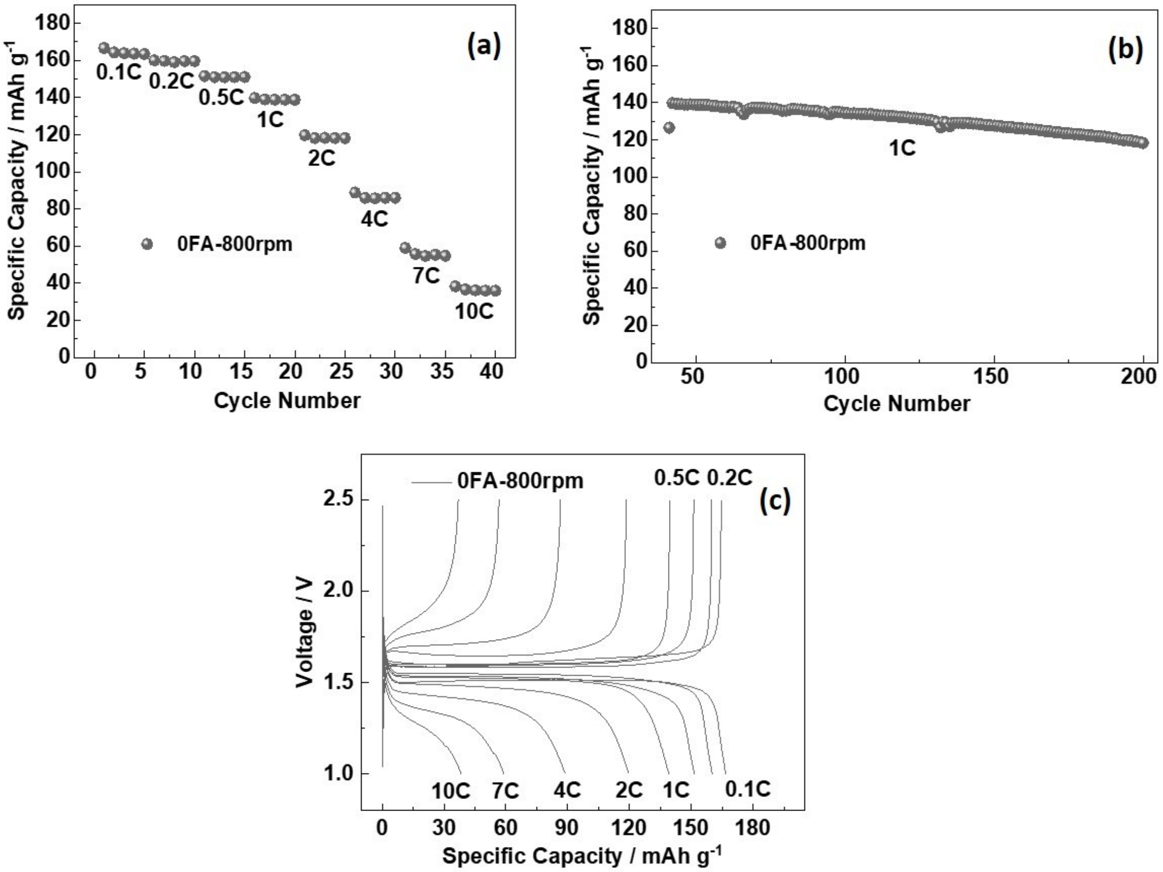

Figure S5. Galvanostatic cycling of a 0FA-800rpm LTO electrode in half-cell configuration: (a) Application of stepwise increasing C rates (each five cycles) and (b) the subsequent constant current cycling at 1C; (c) exemplary dis-/charge profiles for the varying C rates. The cut-off voltages were set to 1.0 and 2.5 V.

Table S1. Comparison of the specific charge capacity at the different C rates applied to the LTO half-cells.

The given capacity values refer to the 1st cycle at the indicated C rate.

	Specific Capacity / mAh g^{-1}							
	0.1C	**0.2C**	**0.5C**	**1C**	**2C**	**4C**	**7C**	**10C**
0FA-800rpm	165	160	151	139	119	87	57	37
0.5FA-800rpm	172	171	167	160	148	125	99	80
1FA-800rpm	171	168	162	150	130	100	65	40
1FA-1100rpm	168	164	156	144	125	95	61	37

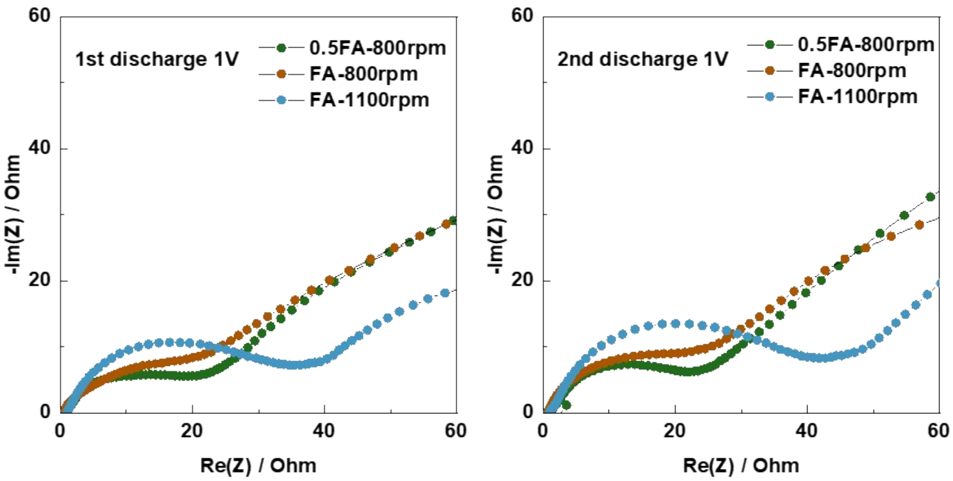

Figure S6. Comparison of the EIS data recorded for half-cells comprising the different LTO-based electrodes (i.e., 0.5FA-800rpm, FA-800rpm and FA-1100rpm) after the first (left) and after the second cycle (right; discharged state).

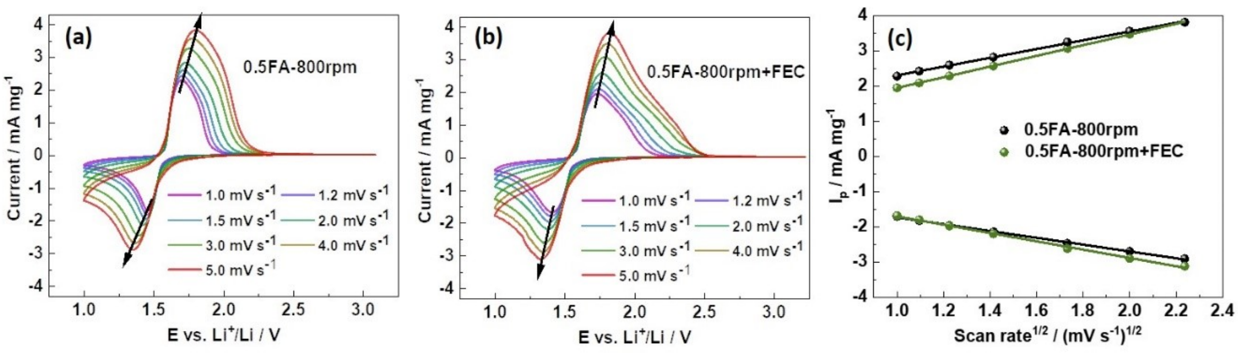

Figure S7. (a,b) Cyclic voltammetry data recorded for 0.5FA-800rpm LTO electrodes in (a) absence and (b) presence of FEC as electrolyte additive. The sweep rate was stepwise increased from 1.0 over 1.2, 1.5, 2.0, 3.0, and 4.0 to 5.0 mV s^{-1}. (c) Analysis of the relationship between the experimentally determined current density I_p and the square root of the applied sweep rate for the two different cells.

The plot of the experimentally determined current density I_p and the square root of the applied sweep rate in **Figure S7c** reveals a linear relationship, indicating a diffusion-controlled charge storage reaction rather than a surface-controlled reaction. Accordingly, the Randles-Sevcik equation is generally suitable for the determination of the apparent Li$^+$ diffusion coefficient D_{Li+}, if considering the limitations mentioned below and focusing on the comparison of the two systems studied herein only:

$$I_p = 2.68 \times 10^5\, n^{3/2} A\, D^{1/2} C\, \omega^{1/2}$$

with n representing the number of transferred electrons, A as the electrode surface area (note that we used simply the geometric electrode area of 1.13 cm^2 here, which is acceptable for a comparative analysis, but not appropriate for the determination of any absolute value for D – apart from the general impact of the experimental setup), D as the (apparent Li$^+$) diffusion coefficient, C as the molar concentration of lithium in LTO, and ω representing the applied sweep rate.

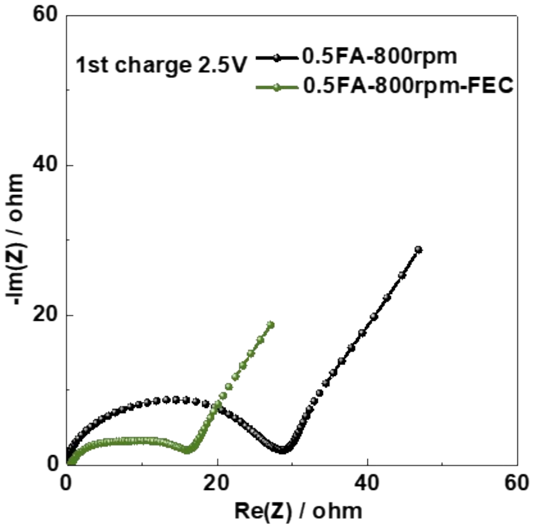

Figure S8. Comparison of the EIS data recorded for LTO (0.5FA-800rpm) half-cells comprising the electrolyte with and without FEC after the 1st cycle (charge state).

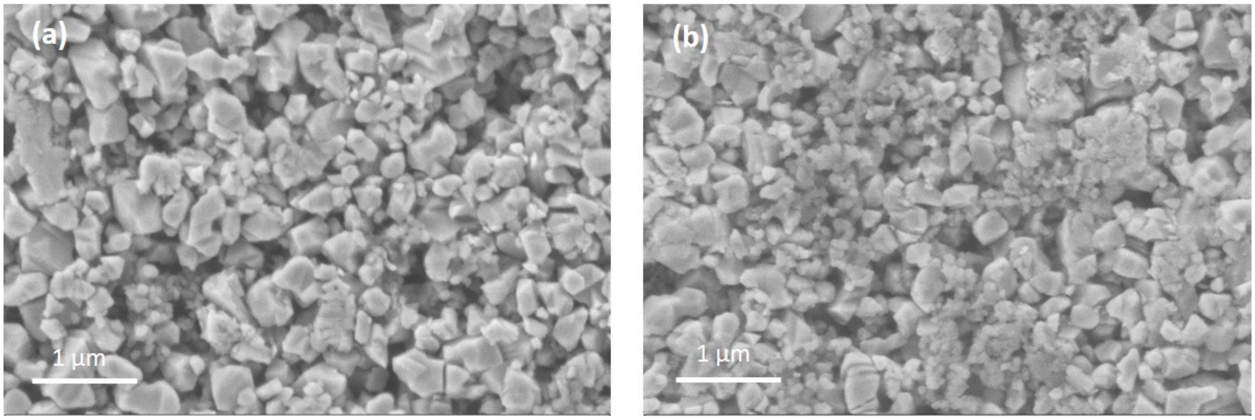

Figure S9. *Ex situ* SEM micrographs of 0.5FA-800rpm LTO electrodes subjected to one full dis-/charge cycle at 0.1C in (a) absence and (b) presence of FEC as electrolyte additive.

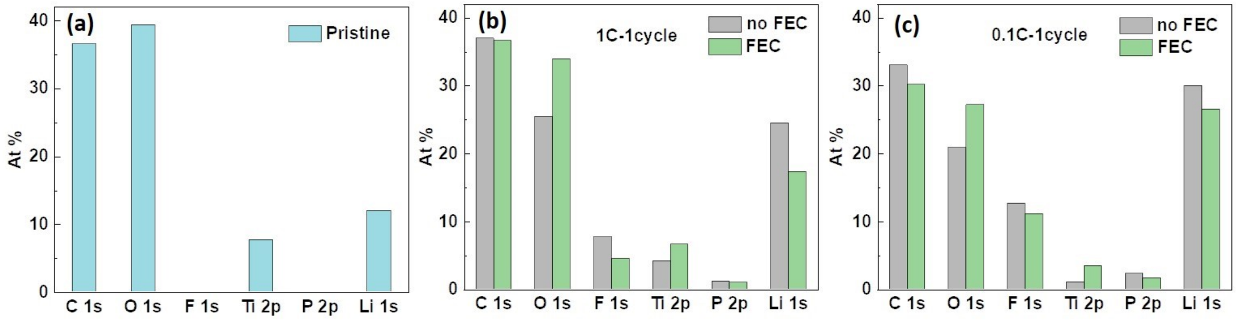

Figure S10. Comparison of the elemental composition, i.e., the atomic percentage of C, O, F, Ti, P, and Li, as observed by XPS analysis (see **Figure 4**) of the (a) pristine and (b,c) cycled 0.5FA-800rpm LTO electrodes after having been subjected to one full dis-/charge cycle at (b) 1C and (c) 0.1C; the results for the LTO electrodes cycled in absence and presence of FEC as electrolyte additive are depicted in grey and green, respectively.