

Supporting Information to

Elucidating the reactivity of TMSPi and TMSPa additives in carbonate electrolytes - A comparative OEMS study

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S1 Me₃SiF evolution for EC/DEC (3:7, 1M LiPF₆) with 1wt% TMSPi or TMSPa

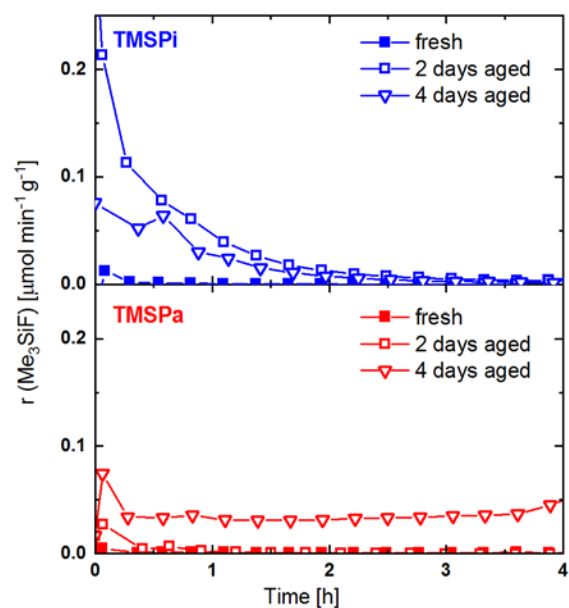


Figure S 1 Influence of the ageing on the Me₃SiF evolution rate during the resting period in Li-rich NCM/graphite full cells containing EC/DEC (3:7, 1M LiPF₆) electrolyte with 1wt% TMSPi or TMSPa.

S2 Potential dependence of POF_3 evolution

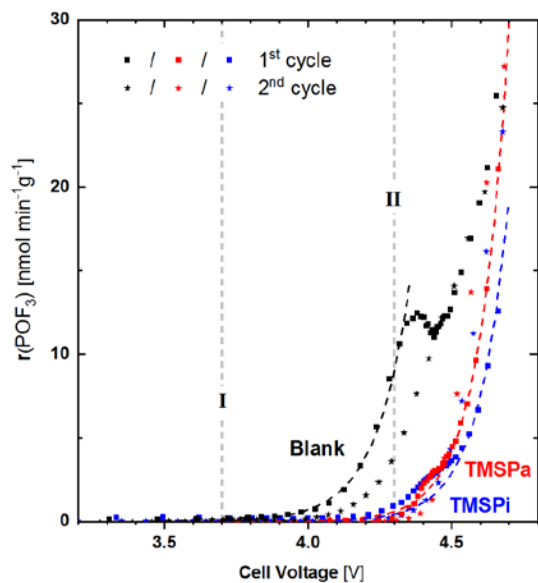


Figure S 2 POF_3 evolution rate as a function of the cell voltage for the 1st and 2nd charge in HENCM/graphite cells with FEC/DEC (12:88, 1M LiPF_6) electrolyte with 0 (blank) and 1 wt% TMSPa or 1wt% TMSPi visualizing the onset voltages of the hydrolysis processes.

S3 XPS data

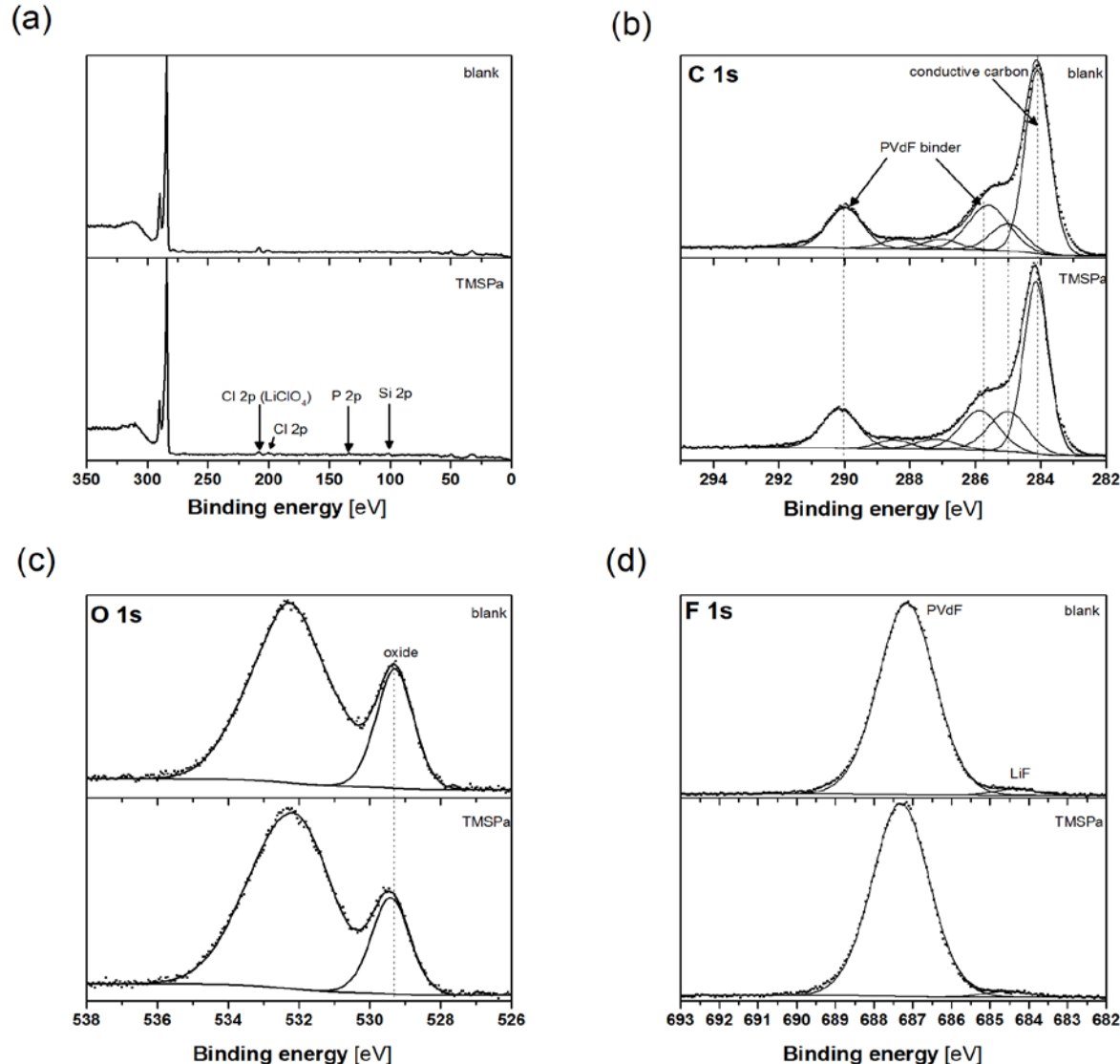


Figure S 3 (a) General survey (0-350 eV), (b) O 1s, (c) C 1s and (d) F 1s XPS spectra collected for HE-NCM electrodes recovered from HE-NCM full cells after 2 cycles at C/10 with EC:DEC (12:88) 1M LiClO₄ electrolyte containing 0 or 1wt% TMSPa additive. After opening the cells, the electrodes were rinsed once with DEC and dried at room temperature. These steps were carried in an Ar-filled glove box and transferred in an airtight transfer chamber to the XPS introduction chamber in order to avoid any air exposure.

Hardly any signal higher than the background level was detected in the binding energy range for P 2p and Si 2p for HE-NCM electrodes cycled in electrolytes with or without TMSPa. No significant difference in O 1s, C 1s and F 1s was observed for electrodes cycled in absence or presence of TMSPa additive as well. This indicates that addition of TMSPa does not affect the interface layer composition after 2 cycles.

S4 Cyclic voltammetry

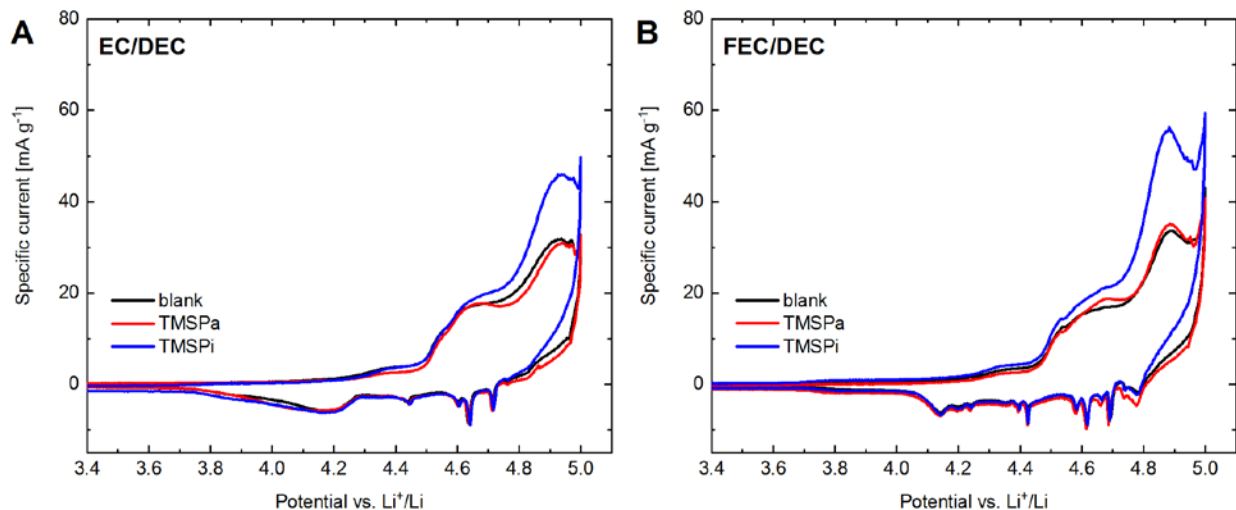


Figure S 4. Specific current for a SC65/SFG6 electrode cycled (working electrode) vs. delithiated LFP (counter-electrode; all potentials were converted to the Li⁺/Li reference electrode by adding 3.45 V) for EC/DEC (12:88, 1M LiPF₆) based electrolytes (A) and FEC/DEC (12:88, 1M LiPF₆) based electrolytes (B).

Carbon-based electrodes composed of 19 wt% graphite SFG6 (Imerys), 38 wt% Super C65 carbon (Imerys) and 43 wt% polyvinylidene fluoride (PVDF Kynar HSV 900, Arkema) were coated on a similar manner on Celgard 2400® (Celgard) monolayer polypropylene (PP). Self-standing LiFePO₄ electrodes were prepared by mixing 80 wt% of LiFePO₄, 5 wt% amorphous carbon Super C65 with 15 wt% polytetrafluoroethylene (PTFE) (Sigma Aldrich) binder in a solution of isopropanol and water (1:1) to form a viscous slurry. The slurry was sonicated and kept under mechanical stirring at 100 °C until evaporation of the solvents and formation of a “dough-like” paste. Electrode sheets were obtained by working the dough with a spatula and mechanical rolling (thickness 200 μm). Electrodes were subsequently punched (20 mm diameter, ~60 mg) and dried (120 °C under dynamic vacuum) before being introduced into an Ar-filled glove-box. FP electrodes were obtained by delithiating LiFePO₄ electrodes vs. Li metal with the reference electrolyte at constant current. Celgard 2400® monolayer PP separator was used as separator (22 mm diameter). Before being introduced into the glove box, the PP separators were dried under vacuum at 80 °C overnight. The carbon electrodes were subjected to cyclic voltammetry (CV) at a scan rate of 0.055 mV/s, starting from open circuit potential (OCP, ~3.2 V) and cycling between 5.0 and 0.5 V vs. Li⁺/Li. All measurements were carried out at room temperature.

S5 EC/Li⁺ ratio and Li⁺ coordination

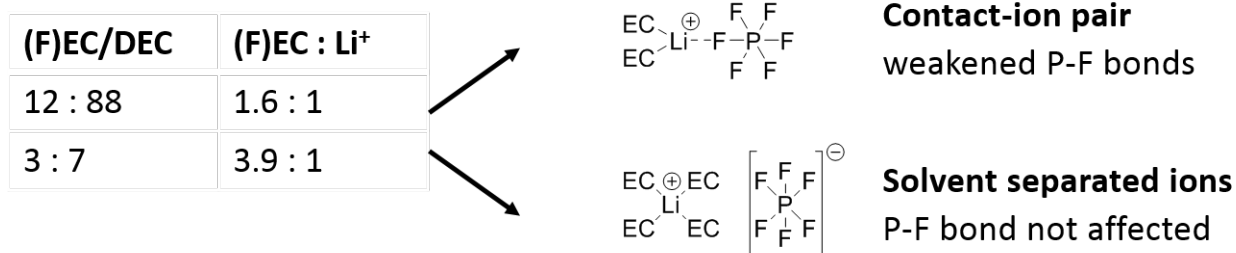


Figure S 5 Estimated (F)EC:Li⁺ ratio (assuming an approximate electrolyte density of 1.15 g cm⁻³) and the resulting coordination models of Li⁺ in solution for (F)EC/DEC based electrolytes with a 12:88 and 3:7 composition.

S6 Enlarged CO₂ evolution profile for EC/DEC (12:88, 1M LiPF₆) with 1wt% TMSPi

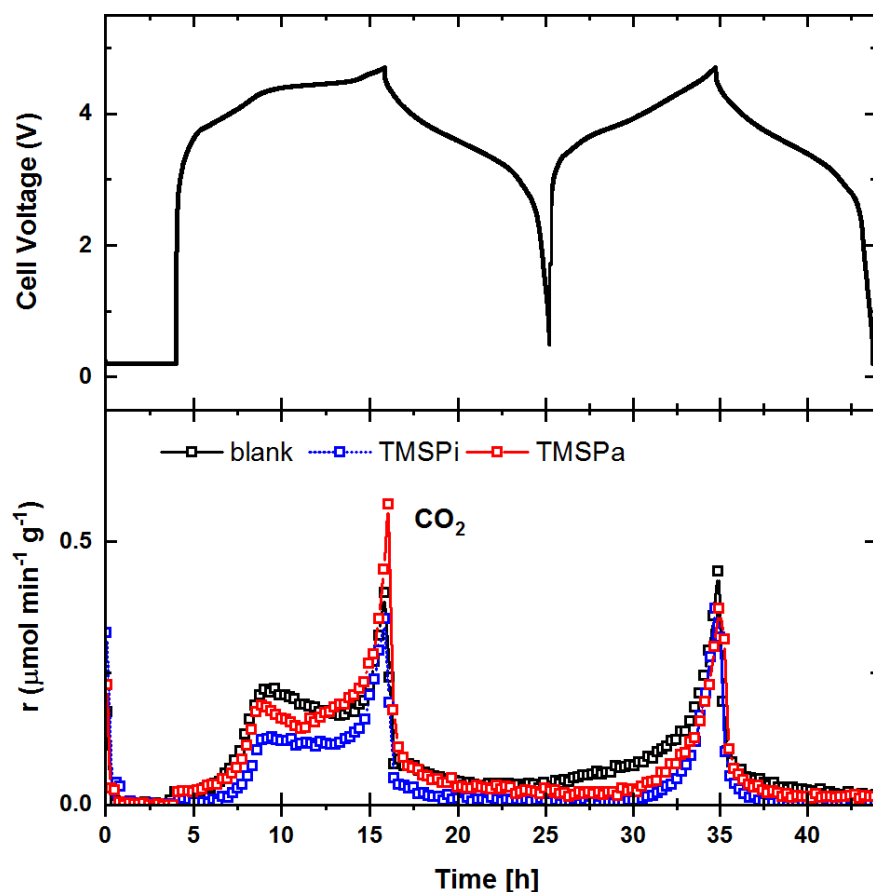


Figure S 6 Gas evolution rate of CO₂ for the two first galvanostatic cycles for HE-NCM electrodes cycled vs. graphite between 0.5 and 4.7 V (C/10) in EC:DEC (12:88, 1M LiPF₆) containing no additive (blank, black), 1 wt% TMSPi (blue) and 1 wt% TMSPa (red).

S7 Longterm cycling of Li-rich NCM/graphite cells

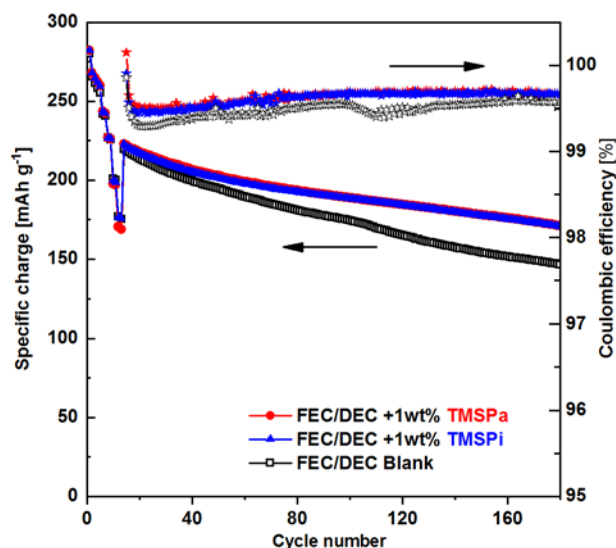


Figure S 7 Cycling performance Specific discharge capacities for HE-NCM vs. graphite full cells based on either 1M LiPF₆ dissolved in 12:88 FEC:DEC electrolytes containing no additive (black), 1wt% TMSPa (red) or 1wt% TMSPi (blue).

Long-term cycling data for HE-NCM electrodes cycled at room temperature vs. graphite were collected by BASF using coin cells 2032. The cycling protocol consisted of a 1st formation cycle followed by C-rate tests (10 cycles, 0.1C/0.1C, 0.1C/0.5C, 1C/0.1C, 2C/0.1C, 3C/0.1C) followed by long-term cycling at C/1 rate.