Supplementary of the manuscript:

Effect of vinylene carbonate on SEI formation on  $LiMn_2O_4$  in carbonate-based electrolytes

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Figure S1: The scheme of electrochemical experiments on the LMO cathode using a three-electrode beaker cell.



Figure S2: (a) Analysed F1s and (b) Mn2p XPS spectra of counter electrode, Li foil, after electrochemical reaction until 3.8V vs Li+/Li in an electrolyte solution of 1.1 M LiPF<sub>6</sub> in DEC/EC/PC (70/25/5, v/v). As seen in the left figure, two peaks appeared in the F1s region, which could be assigned to LiF (685.3 eV) and Li<sub>x</sub>PO<sub>y</sub>F<sub>z</sub> (687.2 eV). No peak appeared in the Mn2P region showing the absence of MnF<sub>2</sub> (right figure).



Figure S3: (a) Raman spectra of the pristine  $LiMn_2O_4$  (LMO) (grey line), the soaked LMO in the VC-free electrolyte (blue line), and the LMO cathode after the electrochemical reaction until E2 employing the VC-free electrolyte (green line). The peaks at 483, 580, 625, and 658 cm<sup>-1</sup> were corresponding to LMO thin film [Ref. C. V. Ramana et al., Surf. Interface Anal. 37 (2005) 412–416]. The insertion is the enlarge figure of the range 200 – 400 cm<sup>-1</sup> Raman shift. (b) A comparison of corresponding F1s spectra of the pristine LMO, the soaking and E2 samples using the VC-free electrolyte.



Figure S4: Mn3s XPS spectra of pristine  $LiMn_2O_4$  surface and the  $LiMn_2O_4$  after soaking in VC-free electrolyte and VC-added electrolyte.



Figure S5: F1s spectra of supplied commercial LMO cathode after the pretreatment process employing VC-added electrolyte as received and after argon etching for 5 minutes.



Figure S6: Lattice orientation of LMO in (a) the (111) plane and (b) (110) plane, in which blue polyhedron are  $MnO_4$ , green spheres are oxygen sites, and orange spheres are lithium sites.