**Supporting Information**

# Influence of carbonate solvents on SEI composition over Si electrode monitored by *in situ* and *ex situ* spectroscopies

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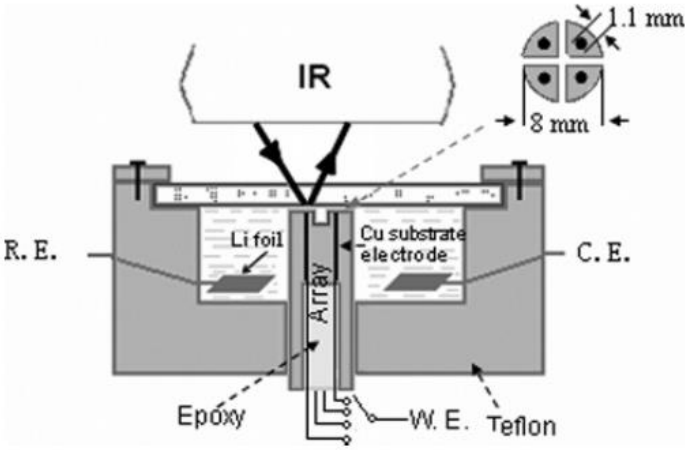


Figure S1 Schematic diagram of *in situ* three-electrode microscope FTIRS cell

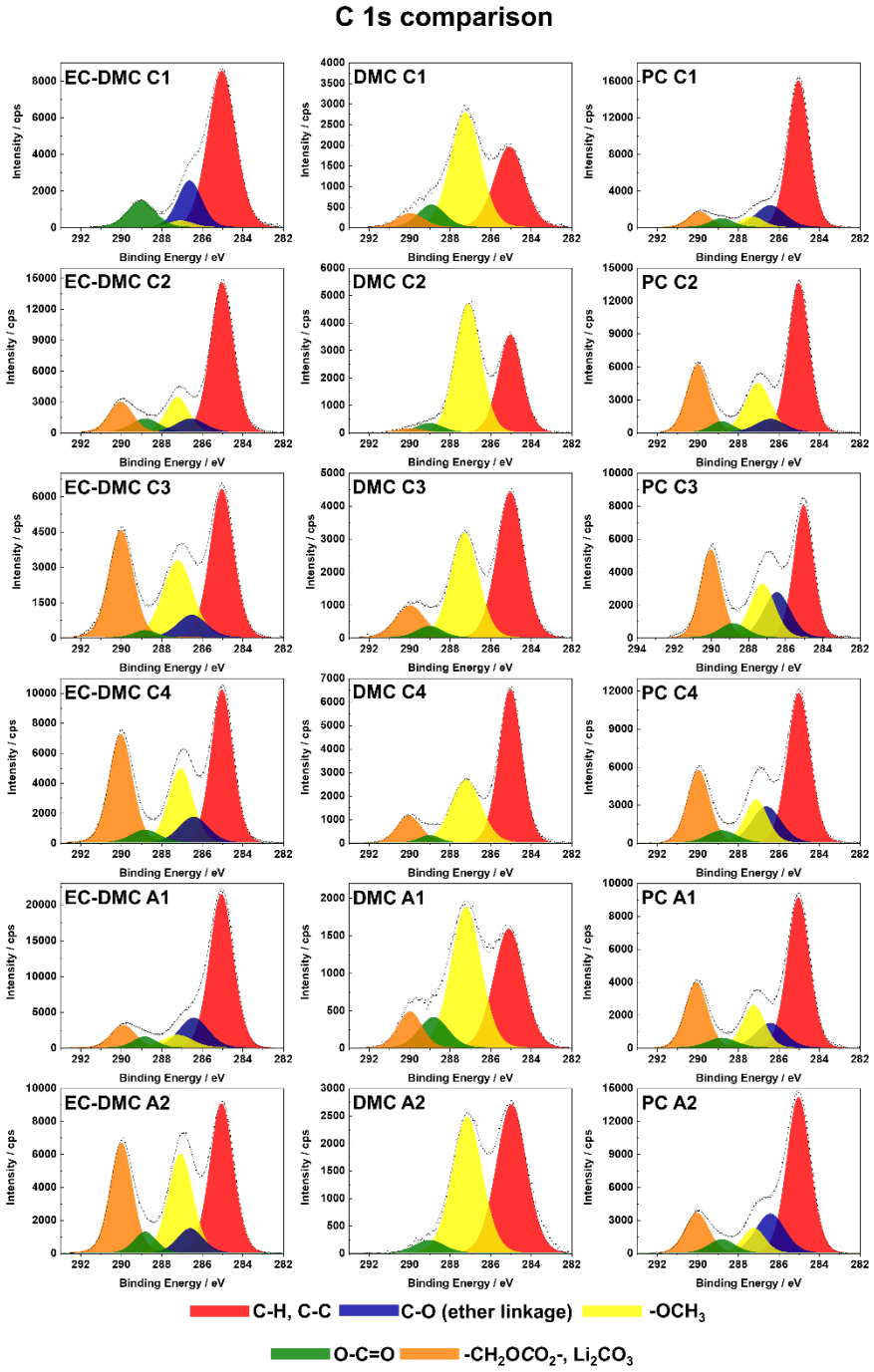


Figure S2 High resolution C 1s core level spectra obtained for Si electrodes at different states during the first CV cycle in three different electrolytes (1M $LiPF_6$/EC-DMC, 1M $LiPF_6$/DMC and 1M $LiPF_6$/PC).

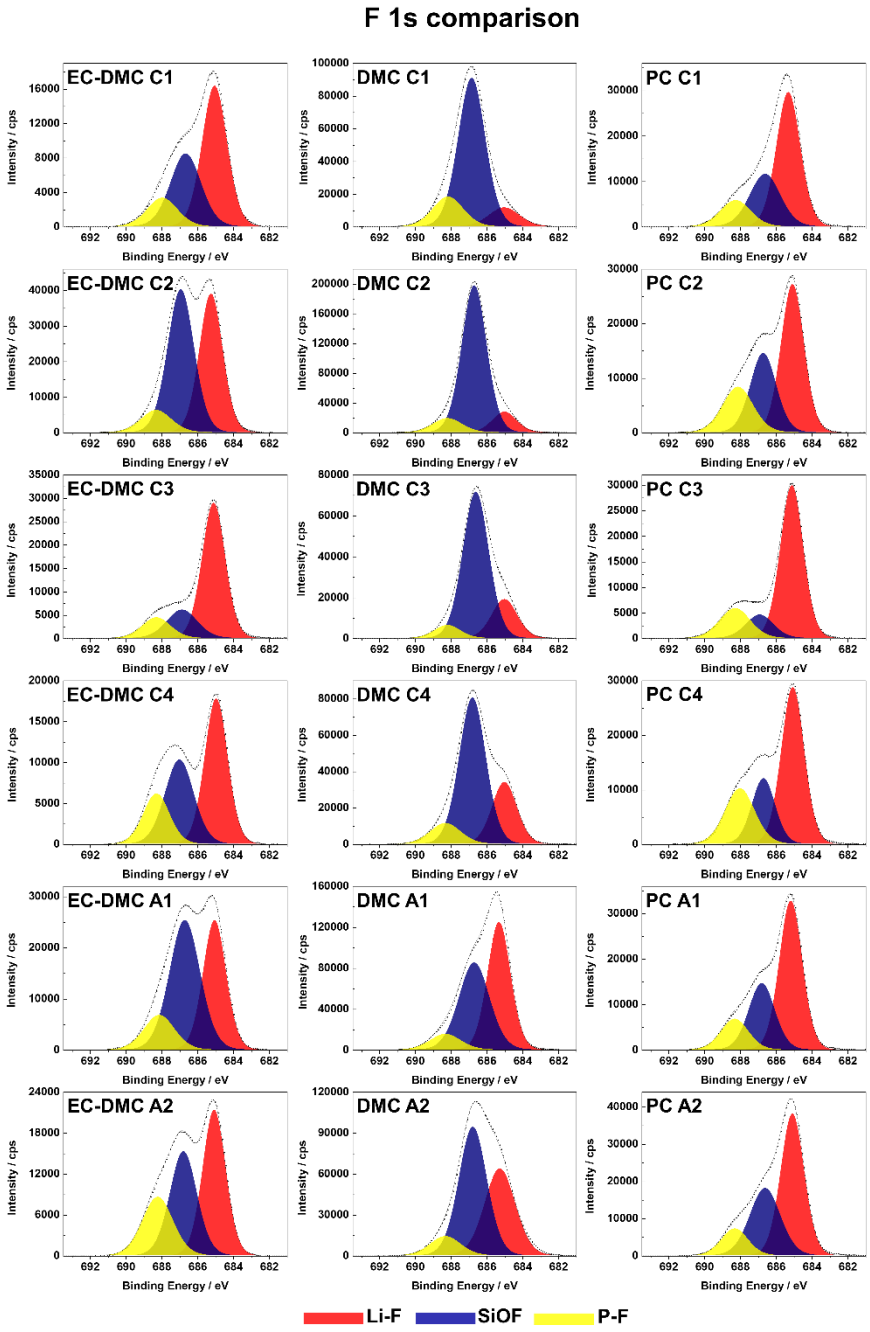


Figure S3 High resolution F 1s core level spectra obtained for Si electrodes at different states during the first CV cycle in three different electrolytes (1M $LiPF_6$/EC-DMC, 1M $LiPF_6$/DMC and 1M $LiPF_6$/PC).

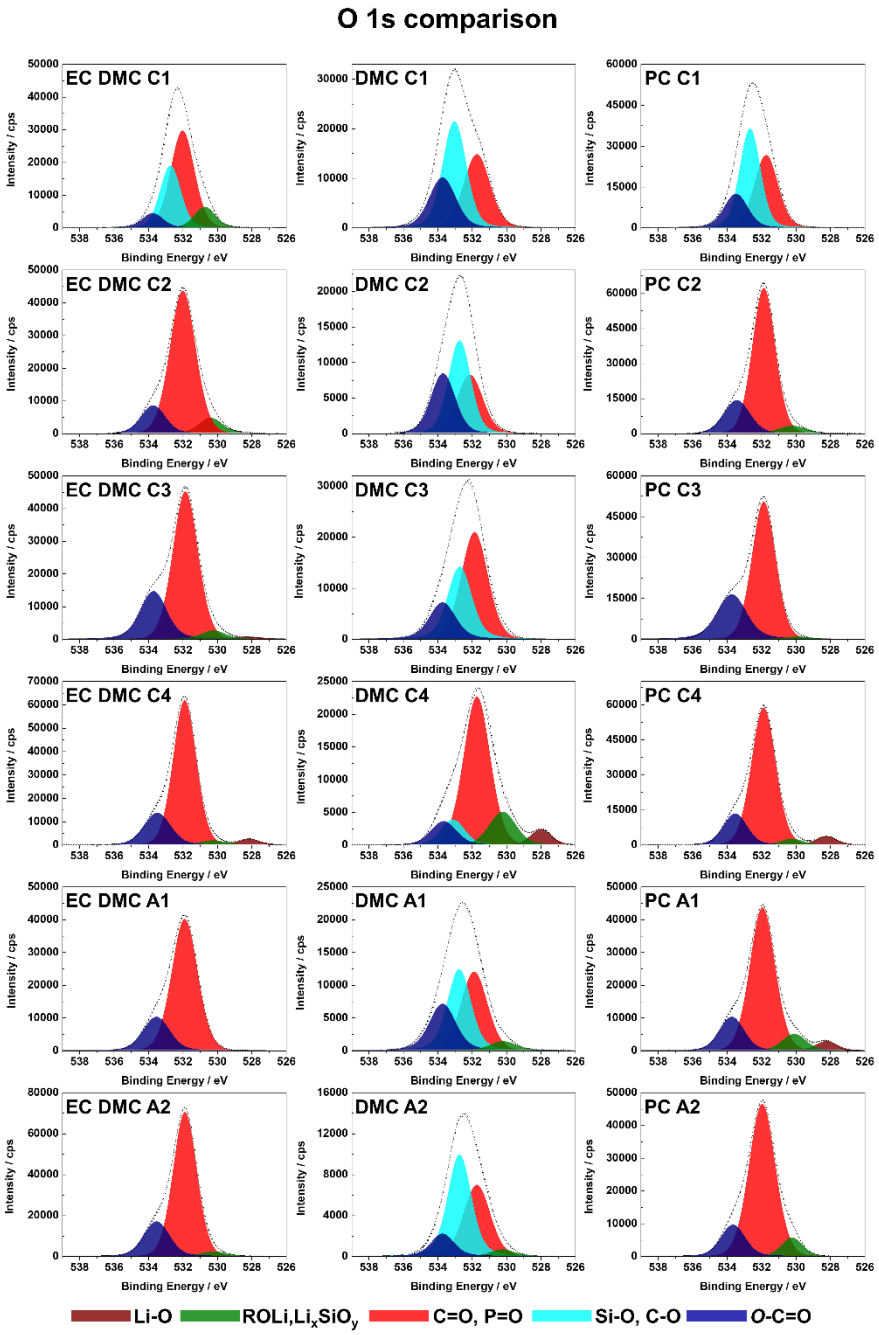


Figure S4 High resolution O 1s core level spectra obtained for Si electrodes at different states during the first CV cycle in three different electrolytes (1M $LiPF_6$/EC-DMC, 1M $LiPF_6$/DMC and 1M $LiPF_6$/PC).

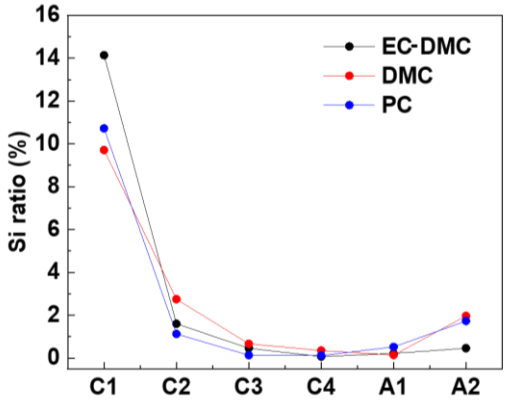


Figure S5 Evolution of Si quantity (in atomic %) at the surface of Si thin film electrode at different stages of lithiation and delithiation performed in different electrolytes.

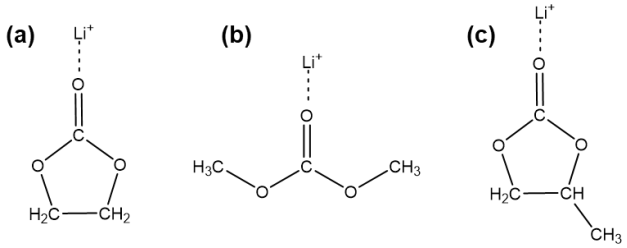


Figure S6 Schematic molecular structure of (a) EC, (b) DMC and (c) PC solvated with lithium ion.

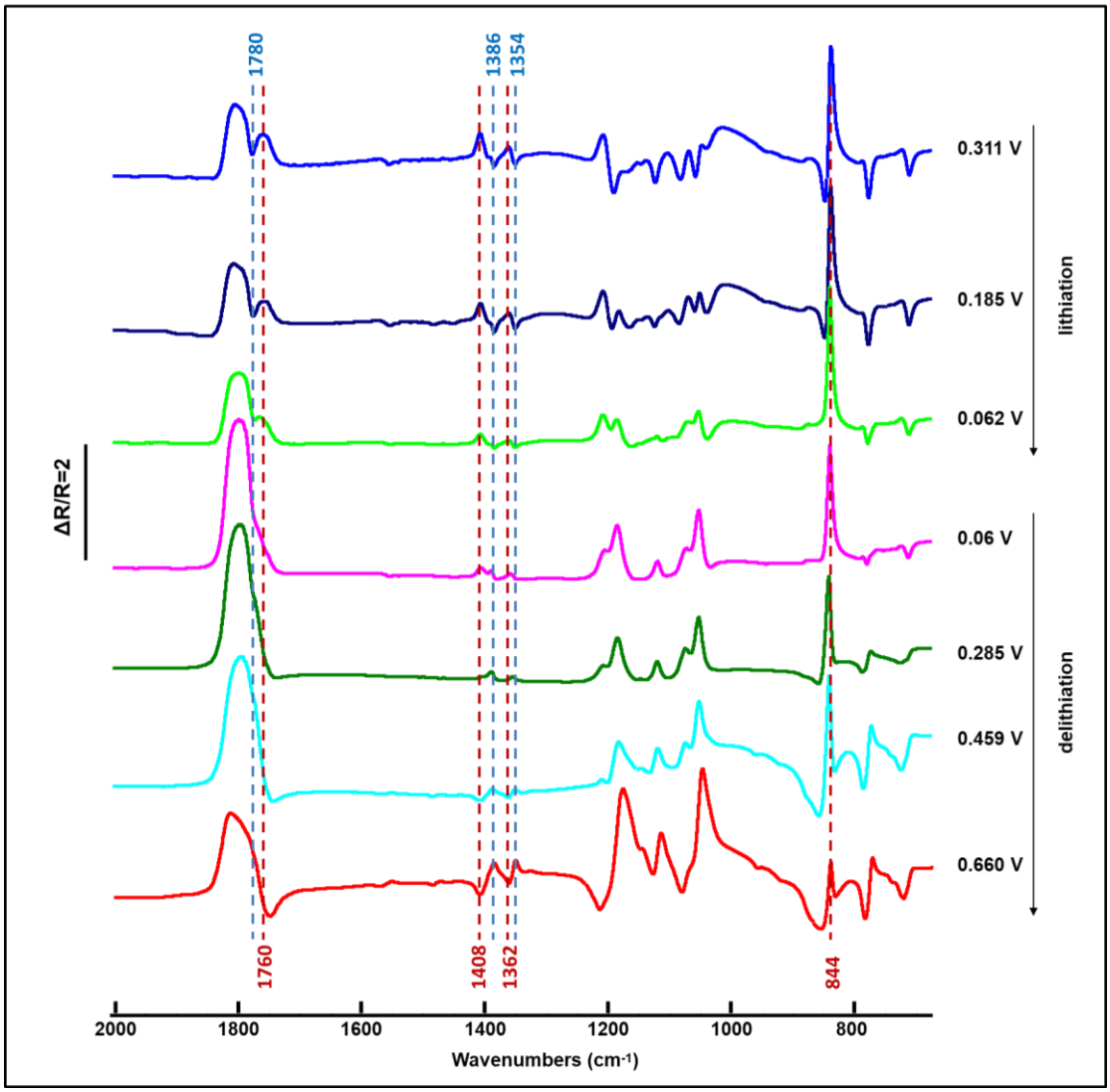


Figure S7 *In situ* MFTIR spectra of Si electrode in 1 M $LiPF_6$/PC during the first lithiation and delithiation process. All spectra were calculated by setting 0.611 V as reference potential.

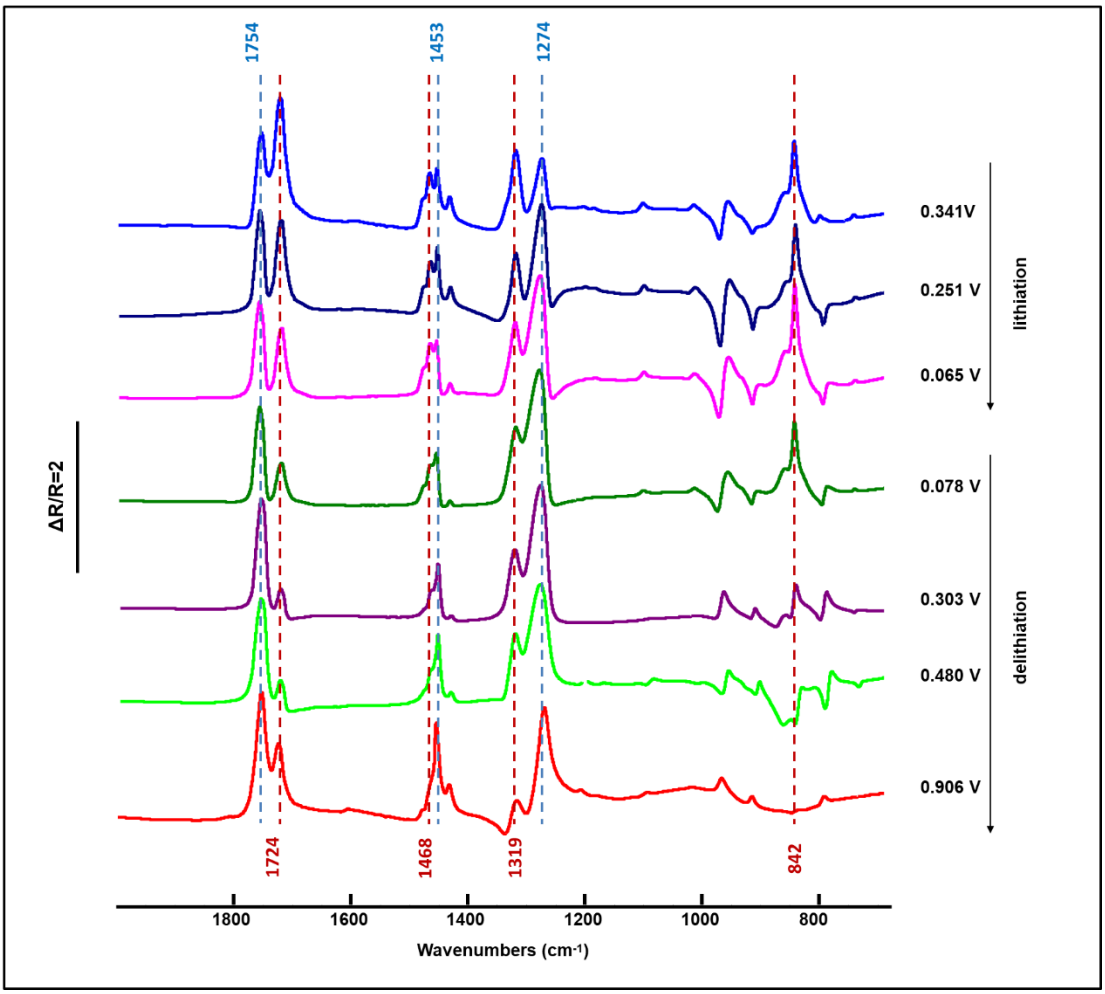


Figure S8 *In situ* MFTIR spectra of Si electrode in 1 M $LiPF_6$/DMC during the first lithiation and delithiation process. All spectra were calculated by setting 0.59 V as reference potential.

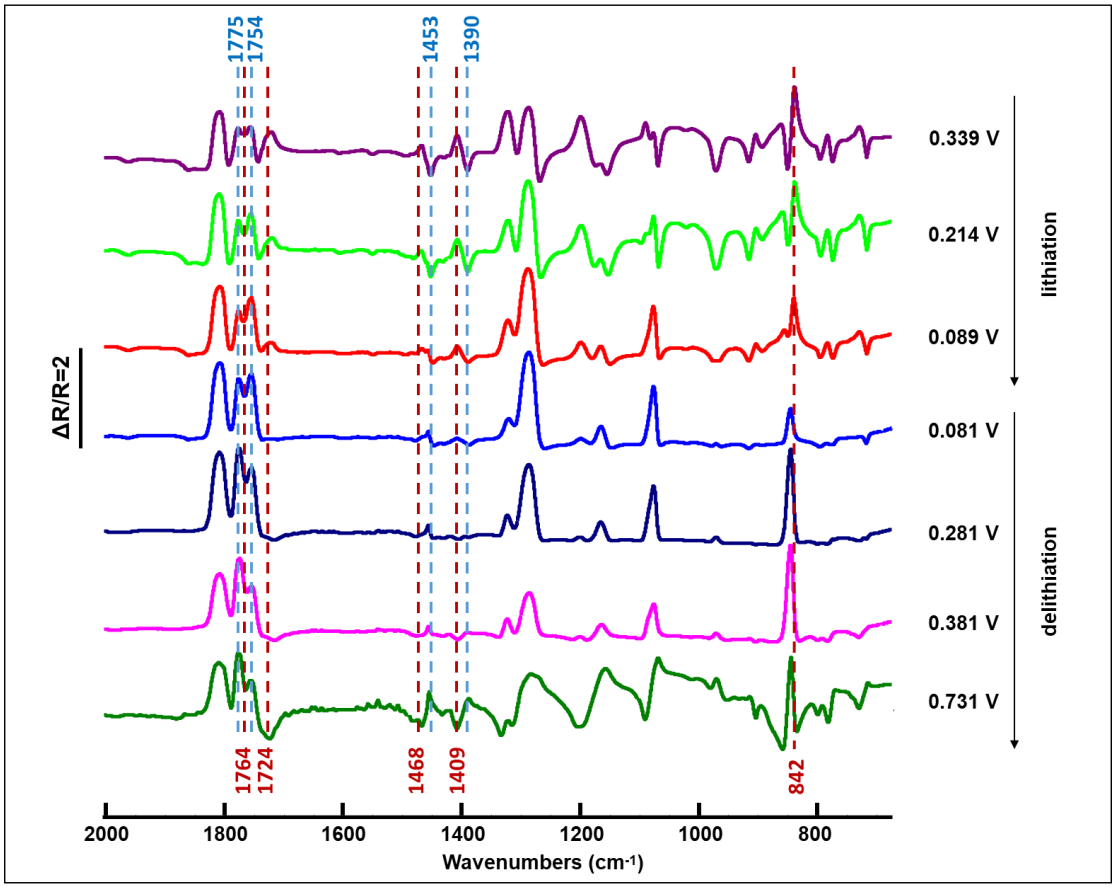


Figure S9 *In situ* MFTIR spectra of Si electrode in 1 M $LiPF_6$/EC-DMC (1:1) during the first lithiation and delithiation process. All spectra were calculated by setting 0.671 V as reference potential.

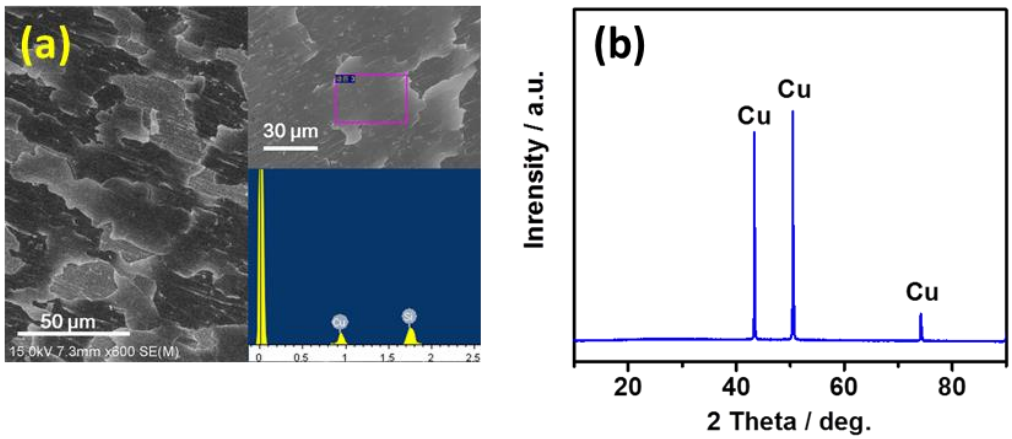


Figure S10 (a) Top-view SEM image of Si thin film electrode. The inserts are the high magnification image (top right) and the EDS of Si thin film electrode (bottom right). (b) XRD pattern of Si thin film electrode.

Figure S10 (a) presents the SEM micrograph of pristine Si thin film electrode. It exhibits a flake-like structure on the Cu substrate. The EDS of the Si thin film inserted to Figure S10(a) confirms the existence of Si and copper. The existence of copper attributes to the Cu current collector. Figure S10(b) displays the XRD pattern of Si thin film electrode, all reflections of this sample are assignable to standard copper (JCPDS No. 48-1550), and no peak matches with crystalline Si indicating the present of amorphous Si on the Cu current collector.