Electrolyte additives are critical for lithium ion batteries (LIBs) to achieve longer cycle life with enhanced safety. Fluoroethylene carbonate (FEC) and vinylene carbonate (VC) are two of the most widely used additives in LIBs that show obvious performance improvement for high capacity Si and Li metal anodes.\textsuperscript{1} The beneficial effects of FEC/VC are generally attributed to the structure modification of the solid electrolyte interphase (SEI) formed on anodes, which consist of inorganic Li compounds (e.g. LiF, Li$_2$O) and oligomeric/polymeric species. The organic SEI maybe the key component.\textsuperscript{2} However, due to the inherent difficulty to characterize interphacial species, the chemical structures of organic SEI remain elusive.

We have recently reported that FEC fully defluorinates, forming VC and vinoxyl species that results in a branched PEO-type polymer.\textsuperscript{3} In that system, FEC was used as an additive (~10 vol\%) in standard LP30 electrolyte (1 M LiPF$_6$ in ethylene carbonate and dimethyl carbonate). Questions still remain regarding the different functionalities of FEC and VC as well as their decomposition pathways. In this study, we use FEC and VC as the only solvent (1 M LiPF$_6$ in pure FEC and VC) in Si half-cells to understand their degradation process. Pure FEC and VC electrolytes all have smaller irreversible capacity loss than LP30-based electrolytes (Fig.1). The chemical composition of the SEI formed in pure FEC/VC electrolyte has been systematically characterized by solid-state NMR and dynamic nuclear polarization (DNP) NMR. We find that highly cross-linked heterogeneous polymers are formed. After multiple cycling, the organic polymers are covalently bonded to Si surface. A detailed understanding of the polymeric species that form in the stabilized SEI and the nature of their bonding to the active material is important for the rational design of artificial SEI and new electrolyte additives.

![Graph showing capacity loss](image)

**Figure 1** Capacity loss (the difference between lithiation and delithiation capacities) during each cycle (a), and the accumulated capacity loss during cycling (b) of silicon nanowires cycled in standard LP30 electrolyte, LP30+10 % FEC, pure FEC and VC electrolytes.

**References:**