

Experiment Report Form



Experiment title:
Study of Interfacial Mechanisms of SiO₂ Anodes for Lithium-ion Batteries

Experiment number:
 A25-2-1043

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Report:

The goal of this experiment was to perform a depth profile study on the nanometric solid electrolyte interphase layer (SEI) formed at the surface of SiO₂ anodes for Lithium-ion batteries since a precise control of its chemical composition and structure is critical to overcome performance issues related to initial capacity loss, cycle life and rate capability of the anode material. Anodes having different salt (LiPF₆ and LiFSI) and different electrolyte additives (FEC, VC and FEC+VC), were subjected to 4 electrochemical cycles until a stable SEI was formed (**Fig.1a**). Cycled anodes were prepared for HAXPES characterization (**Fig.1b**) inside a glovebox.

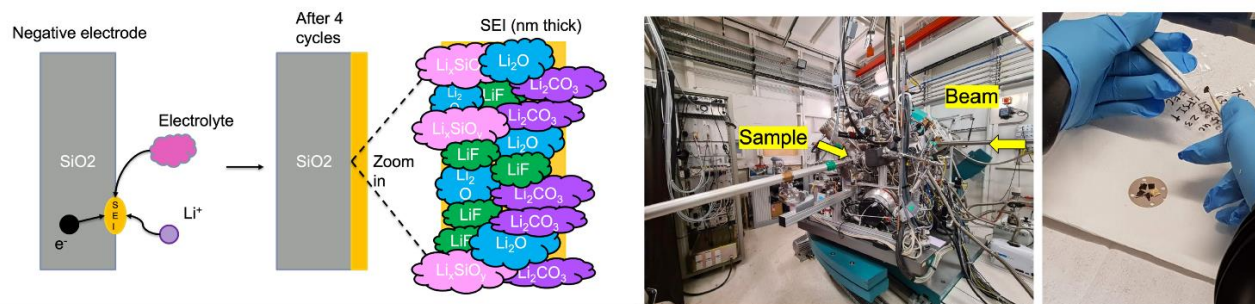


Fig. 1- a) Schemed of SEI formed at the surface of SiO₂ negative electrode, **b)** Mounting of the sample at SpLine

HAXPES measurements were performed at two excitation energies: 7 keV and 12 keV, in order to investigate the entire SEI. For electrodes cycled with LiPF₆, spectra of Si 1s, F 1s, O 1s, C 1s and Si 2p electrons were collected. For samples cycled with LiFSI, spectra of Si 1s, F 1s, O 1s, C 1s, Si 2p, S 2p and N 1s were acquired. The experiment was successful and a preliminary analysis of the experimental data is presented in the following.

In all cases, the SEI was found to be composed of electrolyte decomposition products and silicon-containing species. However, the specific components of the SEI vary depending on the electrolyte used. The C1s spectra with FEC for both LiPF₆ and LiFSI contain Li₂CO₃ together with lithium ethylene dicarbonate (LEDC) and poly(VC), indicated by the broad shoulder of C—O—C and O—C—O at 12 keV. The sample with pure LiPF₆ has a very different curve at 12 keV, compared to the curve with LiPF₆+FEC. For the curve with additive we see a clear shoulder from the CO₃ signal. According to literature, the additive FEC would increase the Li₂CO₃ content generated at the SEI [1], which agrees with our results. When comparing with the cells that had VC as additive, the CO₃ peak is a bit less intense than with the FEC additive. Here the peak is flattened, which can indicate that there are more signal from the species at lower binding energies, that can indicate there are more poly(VC) with the addition of VC than FEC. The electrochemical performance was better for the samples with FEC than VC additives, this is maybe caused by the increased amount of poly(VC) in the VC SEI. Poly(VC) is described of being a poorly ion conducting polymer, which leads to high cell impedance, and a lower electrochemical performance [2]. The additive VC have also been reported to inhibit the reduction of EC, therefore decreasing the generation of LEDC and ethylene[3]. This could be the case of what we see in the HAXPES spectra with VC, since there is a lower intensity of the O—C—O shoulder.

One of the main difference in the SEI with the different electrolytes is related to the LiF component. One major differences between FEC and VC is the additional fluorine atom, and therefore more LiF should be found in the anode cycled with FEC additive. Another thing to report is that the LiPF₆ salt is known for the formation of LiF, which regarding the common use of this salt must be an important component of the SEI [3]. In the spectra LiF is present in all the samples. For both samples without additives a peak or shoulder at higher binding energy corresponding to F-S and F-P is observed, which indicates the presence of LiFSI and LiPF₆ salt respectively. The spectrum of LiPF₆ shows that the peak corresponding to the F-P bond is the strongest, which can indicate

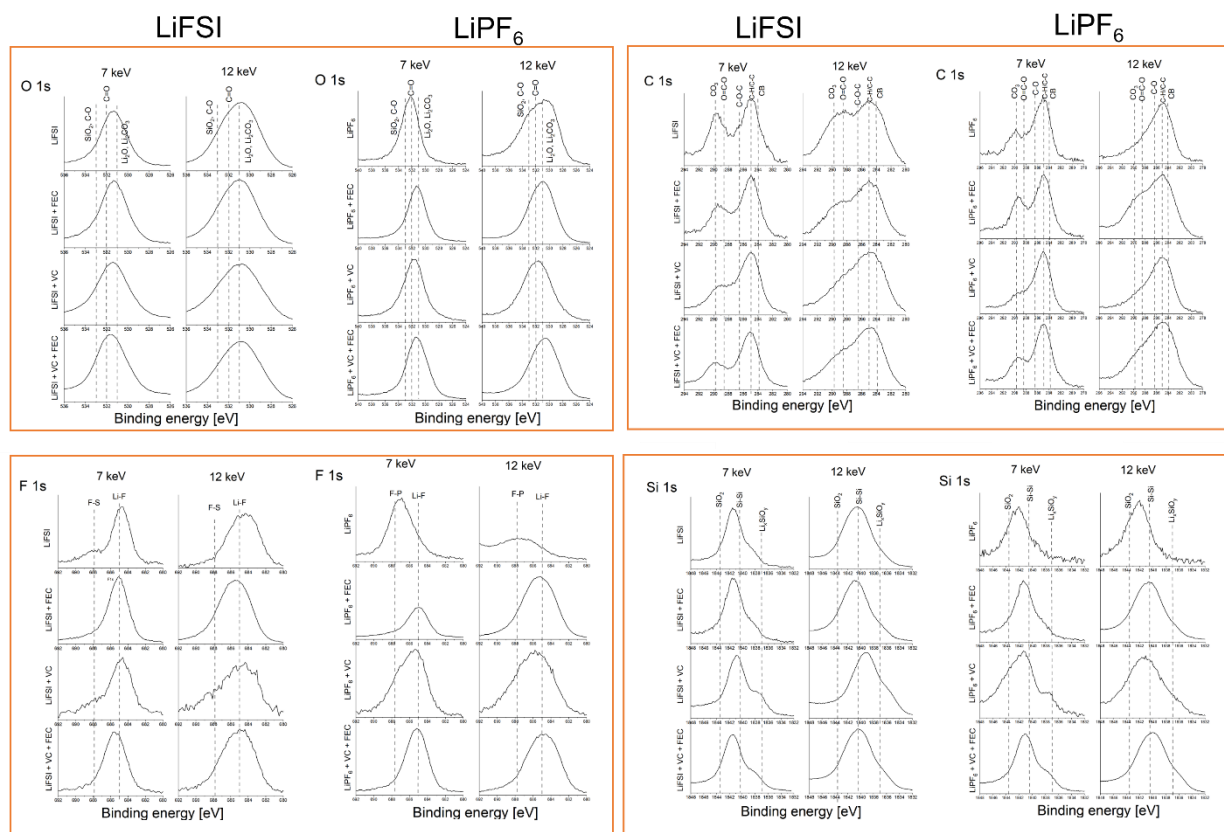


Fig. 2- Spectra of O1s, C1s, F1s and Si1s of electrodes cycled with different electrolyte formulations.

incomplete removal of the electrolyte when washed with DMC. All electrodes cycled with additives display a shoulder on the Si1s spectra corresponding to lithium silicates (Li_xSiO_y). Such shoulder is more distinct for the sample with VC as additive, but the reason for this is unclear. It is possible that the SEI is thinner with VC than with FEC, therefore increasing the Li_xSiO_y signal. In some cases, the presence of unreacted SiO₂ can also be observed. Quantitative analysis of the acquired datasets is under progress.

References: [1] Qian Sun, Bing Zhang, and Zheng-Wen Fu. Lithium electrochemistry of SiO₂ thin film electrode for lithium-ion batteries, Appl. Surf. Science 254.13 (2008), 3774–3779. [2] Bo Zhang. Role of 1,3-Propane Sultone and Vinylene Carbonate in Solid Electrolyte Interface Formation and Gas Generation. J. Phys. Chem.C 119.21 (2015). [3] Mengyun Nie and Brett L. Lucht. Role of Lithium Salt on Solid Electrolyte Interface (SEI) Formation and Structure in Lithium Ion Batteries, J. Electrochem. Soc. A1001 (2014).