

**Experiment title:**

Safe and green fluorine-free electrolyte for Li-ion batteries: probing the SEI on Si anodes with operando XRR

Experiment number:

A32-2 842

Beamline: BM32	Date of experiment: from: 22/02/2022 to: 24/02/2022	Date of report: 08/09/2022
Shifts: 12	Local contact(s): 2	<i>Received at ESRF:</i>

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The aim of this experiment is to evidence in real-time the formation and the growth of the SEI layer on silicon electrode by operando X-ray reflectivity and in particular investigate promising fluorine-free electrolyte. Half-cell configuration was used in this experiment with Li foil and N-doped Si wafer as electrodes. In order to investigate the effect of the salt (F-containing LiPF₆ or F-free LiBOB) and the effect of the SEI-forming additive (F-containing FEC or F-free VC), four different electrolyte compositions have been tested in this experiment: 1 M LP57, 1 M LP57 with 2 wt% FEC, 0.7 M LiBOB and 0.7 M LiBOB with 2 wt% VC. They are labeled as LP57, LP57-FEC, LiBOB and LiBOB-VC respectively. The cells were firstly cycle from OCV to 2 V with a rate of 1 mV/s following by a CV cycling from 2 V to 5 mV with a rate of 0.1 mV/s. During the cycling the XRR patterns were measured continuously. A custom-made sample holder assured the XRR measurements of two cells alternately during the cycling. Figure 1 presents a summary of the experimental set-ups.

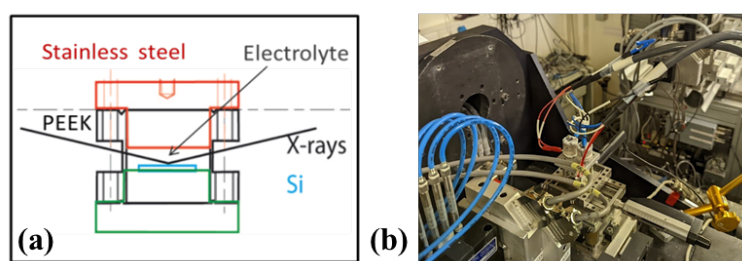


Figure 1. Experimental set-ups operando X-rays reflectivity experiments. (a) Sketch of the cell. The Si wafer is the negative electrode contacted on the bottom stainless steel flange. (b) Custom-made sample holder on the goniometer of Beamline BM32 at ESRF.

The XRR data were recorded during at least 3 cycles of charge and discharge with 4 different electrolytes as mentioned before. The preliminary XRR data as a function of cycling time is shown in Figure 2. The XRR measurements of the samples LP57 and LiBOB are absent during the second cycle due to a beam loss. Drastic evolutions of XRR patterns were observed in the potential range from 0.5 V to 5 mV of the first cycle for all cells. These evolutions indicate the formation and growth of the SEI layers. Furthermore, the evolutions of XRR patterns in the first cycle are different from the ones in the following cycles. The cells with fluorine-free electrolytes also present different XRR evolutions from the cells with fluorinated electrolytes. Specifically, for the cells LiBOB and LiBOB-VC, remarkable Kiessig fringes were observed at low potentials after the first cycle, showing the formation of thick layers, which may be the indication of the lithiation. Further data process is ongoing including XRR fittings which will be correlated with ex-situ XPS analysis in order to identify the thickness, chemical compositions of each layers forming during the cycling.

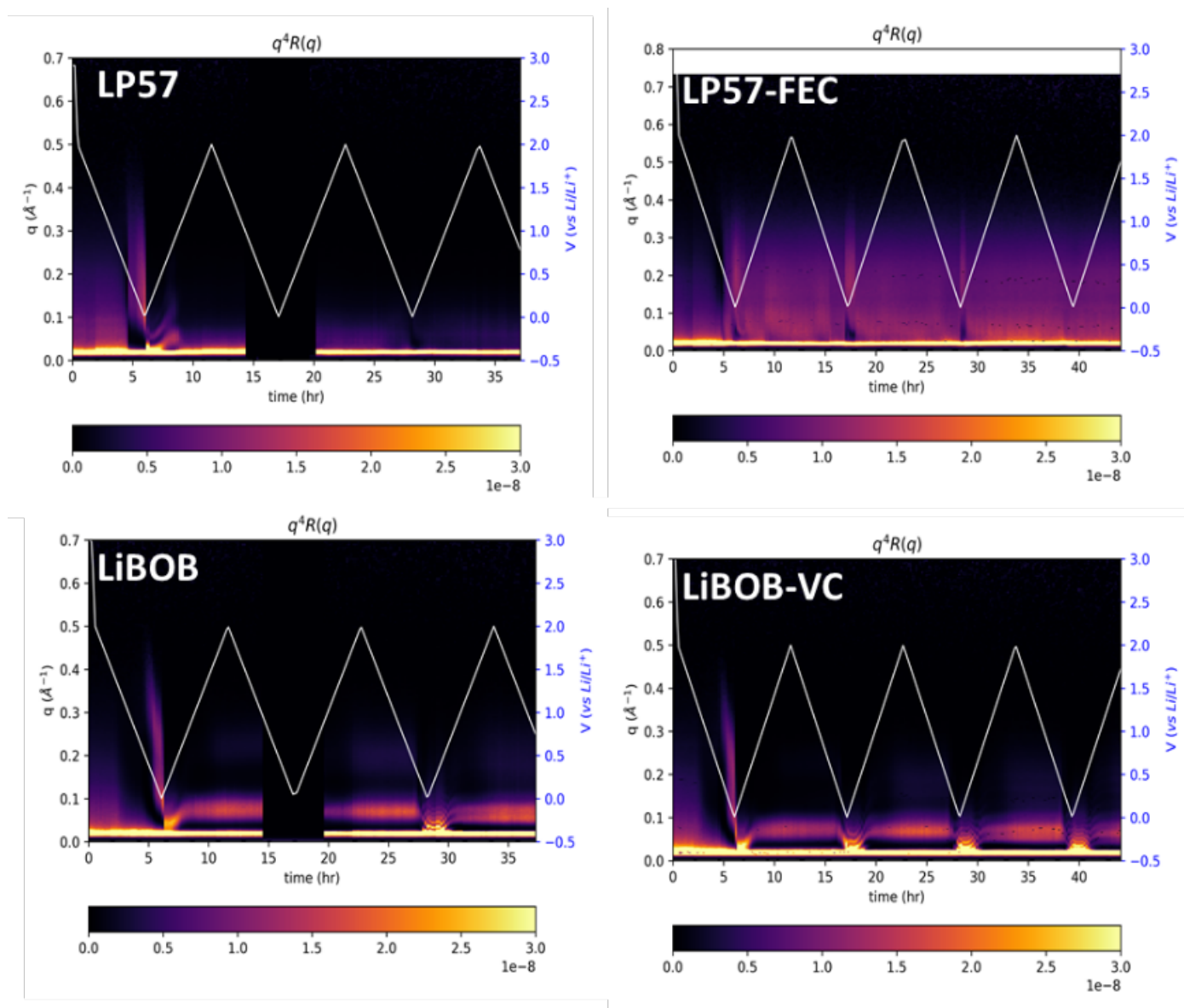


Figure 2. The preliminary XRR data of four cells with different electrolyte compositions.