

Supporting information

Operando Investigations of the Solid Electrolyte Interphase in the Lithium Mediated Nitrogen Reduction Reaction

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1 Experimental

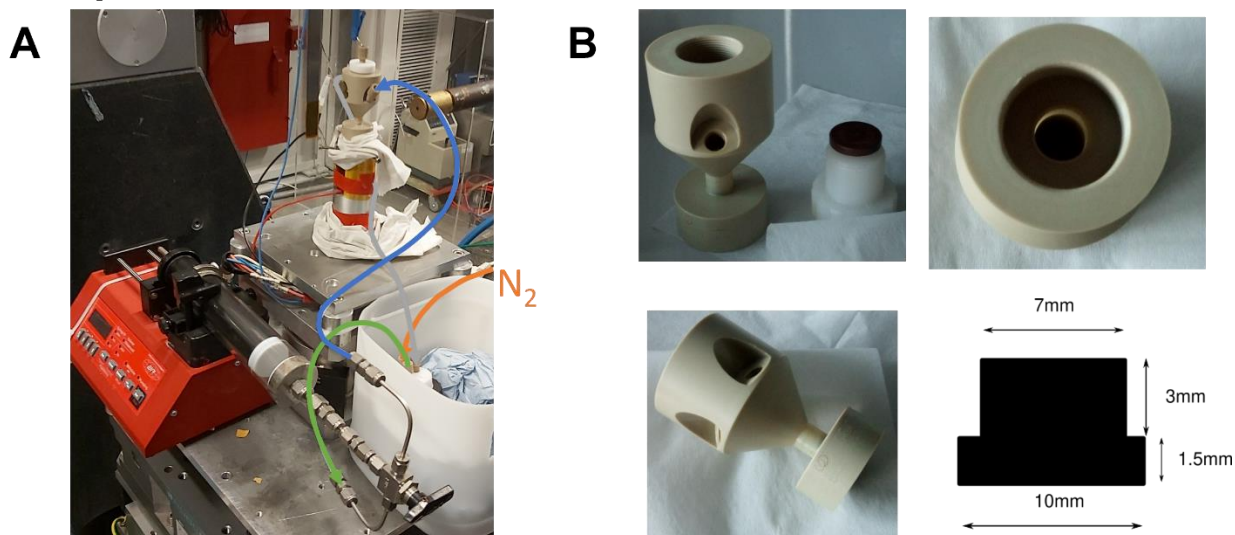


Figure S1: A: Picture of the cell in the synchrotron setup with the bottle in which the electrolyte was saturated and the pump used to transport electrolyte into the cell without miss aligning the cell. B: Pictures of the disassembled cell and schematic of the hat-shape single crystals used.

Electrolyte preparation

All electrolytes were prepared in an Ar-filled glovebox (<0.5 ppm O₂, <0.5 ppm water). LiClO₄ (Sigma Aldrich, 99.99%, anhydrous) and LiBF₄ (Sigma Aldrich, 99.99%, anhydrous) were carefully dissolved in THF (Sigma Aldrich, anhydrous, >99.9%, inhibitor free) and 0 or 1 vol% ethanol (Honeywell, anhydrous) was added.

Single crystal preparation

Before each experiment the Cu (111) single crystals (Mateck, 99.9999%) were prepared prior to cell assembly by annealing in a tube furnace for > 1h at 950 °C in a 1:3 H₂:Ar atmosphere.¹ Afterwards the crystal was cooled down under continued gas flow. Subsequently the tube containing the crystal was closed off and transferred into the glovebox for cell assembly to avoid air exposure.

Cell assembly

For all experiments an airtight, one-compartment cell made from PEEK, shown in Figure S1 was used. To avoid cross-contamination between LiClO_4 and LiBF_4 two fully separate experimental setups (cell, crystals, pipes, syringe pump) were used for the two studied electrolyte cells. Cells were assembled in an Ar-filled glovebox (<0.5 ppm O_2 , <0.5 ppm water). Hat shaped Cu (111) single crystals were used as a working electrode, a Pt-mesh (Goodfellow, 99.99%) as counter electrode and a LFP electrode, prepared as previously described^{2,3} as reference electrode. The Pt mesh counter electrode was annealed in the flame of a butane torch prior to being transferred into the glovebox.

In operando measurements

In-operando experiments were conducted at the ID 31 beamline at the European Synchrotron Radiation Facility (ESRF). The X-ray beam (75 keV) was focused ($3 \times 6 \mu\text{m}^2$, vertical \times horizontal) on the surface of the Cu (111) single crystal working electrode at an angle of 0.05° to perform GI WAXS measurements. The cell was aligned so that the intensity of signals from the Cu (111) single crystal was minimized. After aligning the cell in the beam, electrolyte was introduced into the cell using a syringe pump (World Instruments) with a borosilicate glass syringe and a PTFE plunger (Trajan Scientific and Medical, 100 ml). Subsequently, GI-WAXS measurements were started. Measurements were done on at least two different spots on the working electrode with different time intervals between measurements. On the so called “low dose” spot this interval was more than 1 minute, whereas on other spots the time interval was 5-10

seconds. The recorded 2D WAXS patterns were integrated, resulting in the shown diffraction curves using the pyFAI software package using a CeO₂ standard.⁴ The data was further analyzed using a homemade python program based on software used by Moss *et al.*⁵

Electrochemistry

Electrochemistry experiments were conducted using a Biologic SP150 potentiostat. After introducing electrolyte into the cell, the cell was kept at open circuit voltage (OCV) for >25 min before performing electrochemical measurements. This was to evaluate potential beam effects on the system. The Ohmic resistance was determined by the current interrupt (CI) technique and compensated for, for the following linear sweep voltammetry (LSV). Here the voltage was decreased at a rate of 20 mV s⁻¹ until the current increased to 2 mA cm⁻², indicating the onset of Li plating. The current was kept at 2 mA cm⁻² for 65 min until a total charge of 3 C had been passed. Afterwards the cell was kept at OCV for at least 20 min.

2 Reference Diffractograms

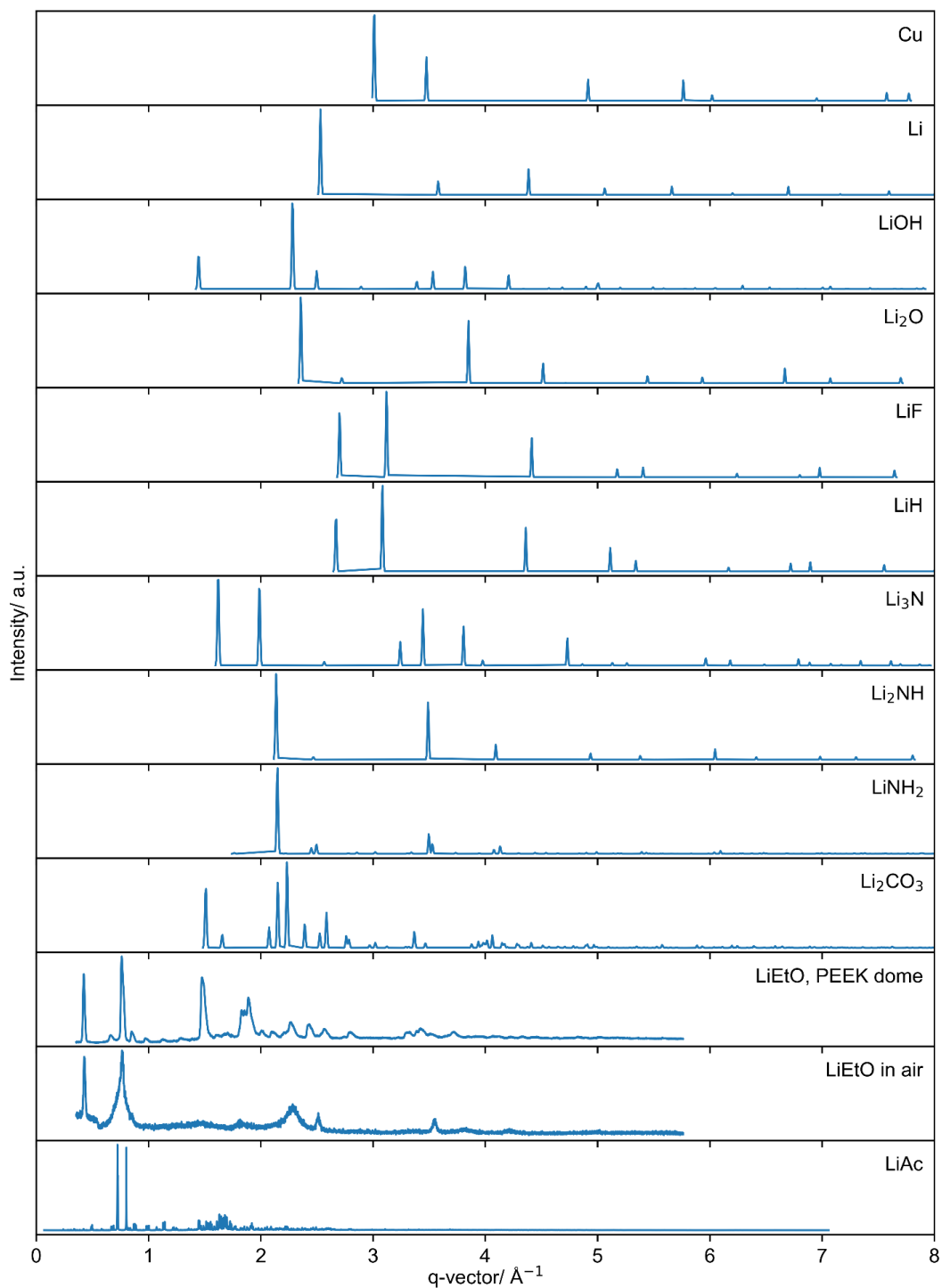


Figure S2: Reference powder XRD patterns. Most patterns were taken from the ICSD database: Cu (#43493), Li (#104737), LiOH (#26892), Li₂O (#257372), LiF (#44879), LiH (#61749), Li₃N (#34280), Li₂NH (#164141), LiNH₂ (#161017), Li₂CO₃ (#66941). The LiEtO patterns were recorded in house using a Malvern Panalytical Empyrean x-ray diffractometer. In the pattern that was recorded using a PEEK dome to avoid air exposure the background from the PEEK dome was subtracted. The pattern recorded in air contains LiOH impurities. The Lithium Acetate (LiAc) pattern was taken from the CCSD database (#802905).

3 1D Diffractograms

3.1 LiBF₄, no EtOH

3.1.1 Experiment 1

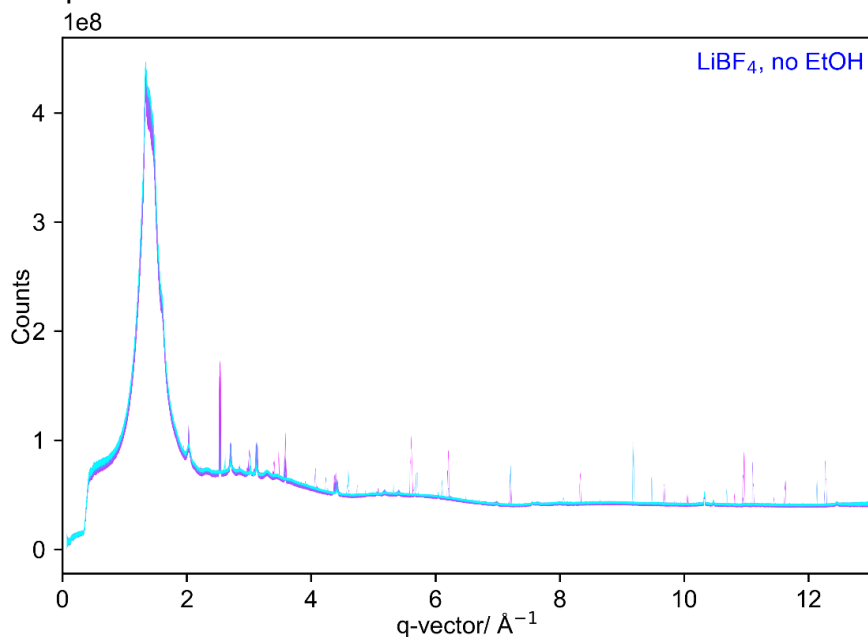


Figure S3: Integrated GI-WAXS pattern. Overview over the full q-range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

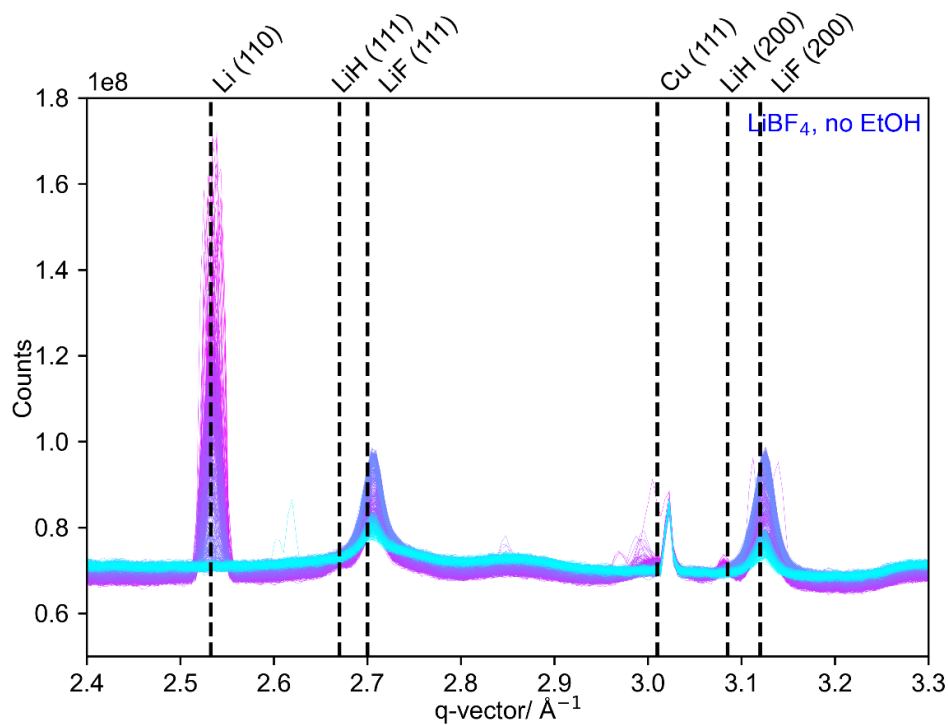


Figure S4: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 Å⁻¹ including Li, LiH, LiF and Cu peaks. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

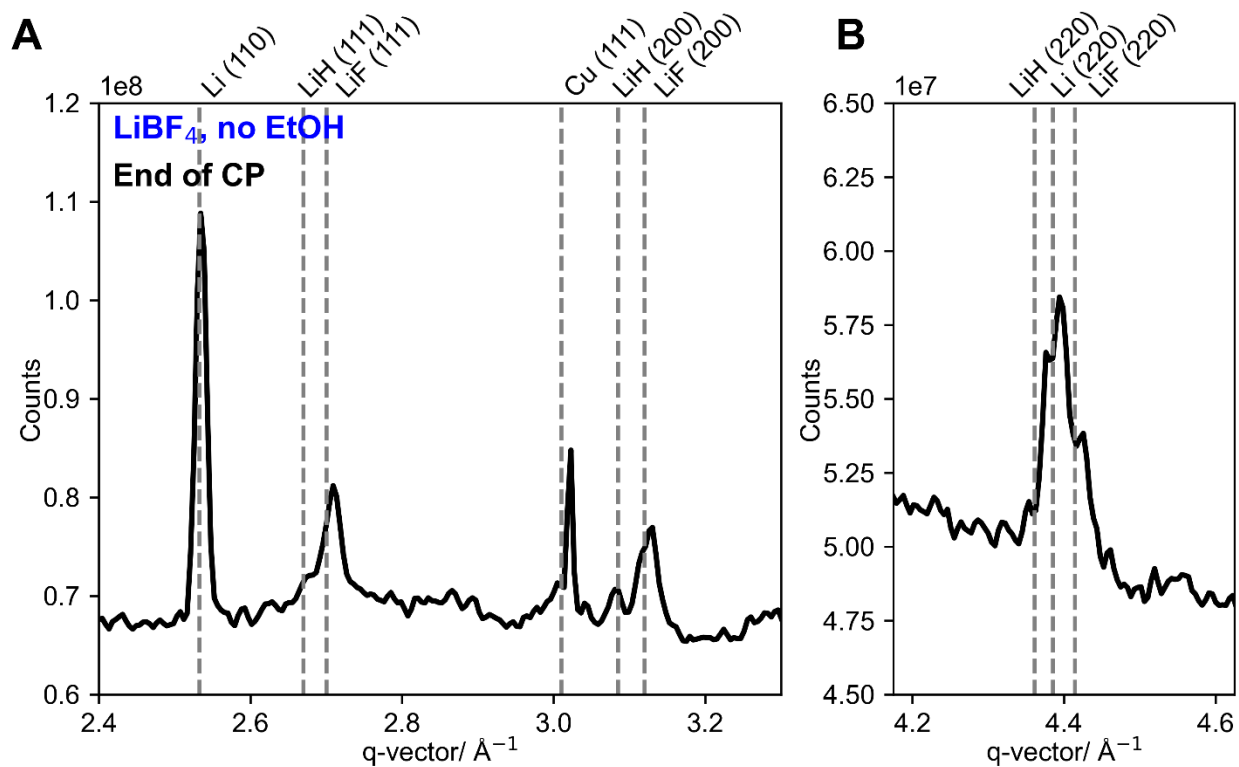


Figure S5: : Integrated GI-WAXS pattern, recorded immediately after the end of CP. Q-range from 2.4-3.3 Å⁻¹ and 4.2-4.6 Å⁻¹ showing LiH peaks overlapping with peaks from Li, LiF and Cu.

3.1.2 Experiment 2

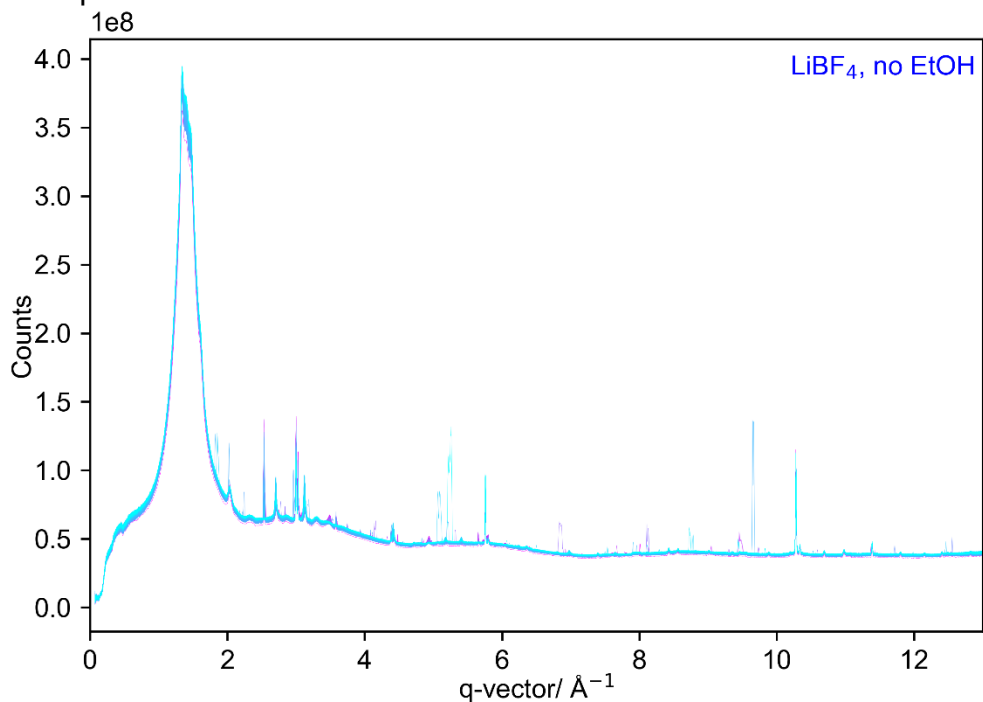


Figure S6: Integrated GI-WAXS pattern. Overview over the full q-range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

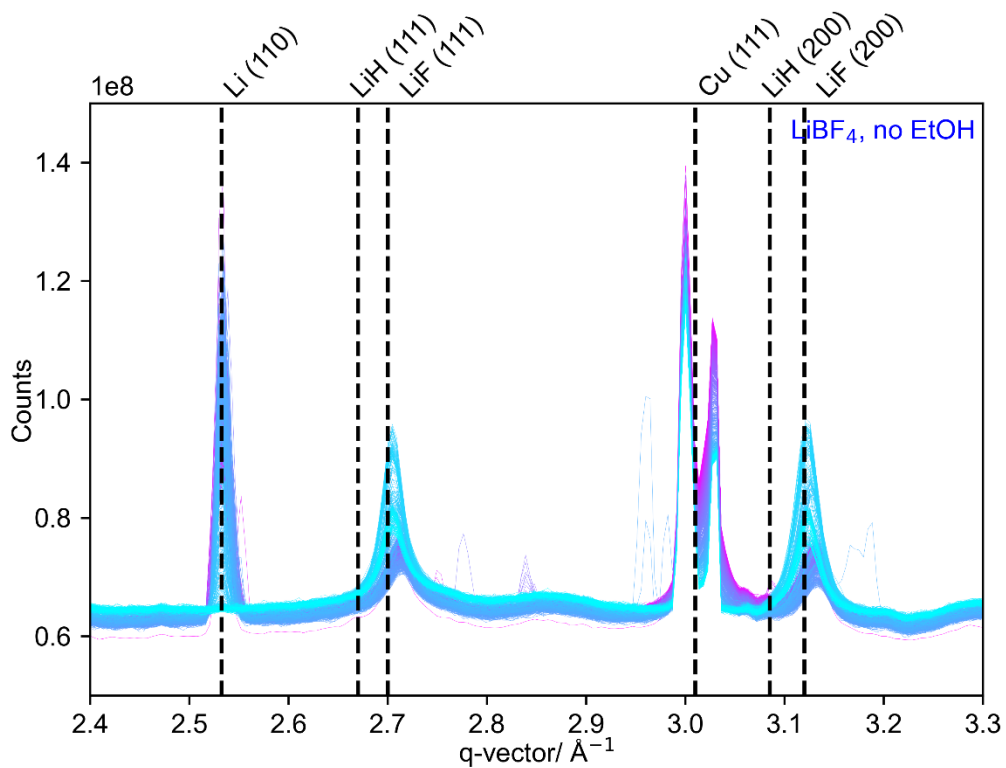


Figure S7: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 \AA^{-1} including Li, LiH, LiF and Cu peaks. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

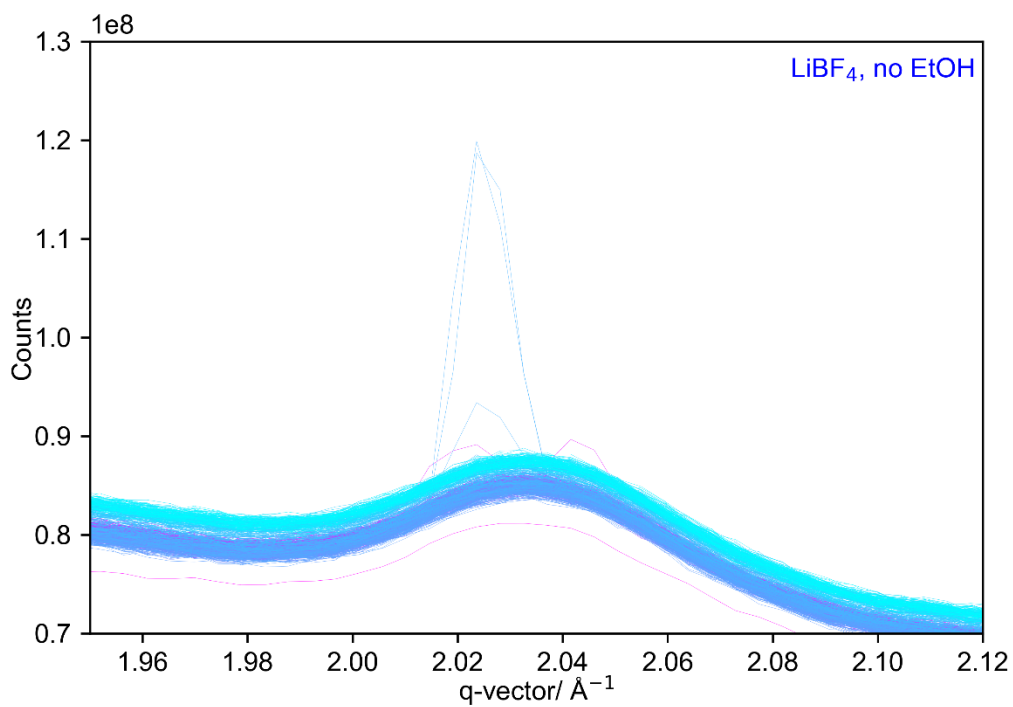


Figure S8: integrated GI-WAXS pattern of an unidentified peak.

3.2 LiBF_4 , 1 vol% EtOH

3.2.1 Experiment 1

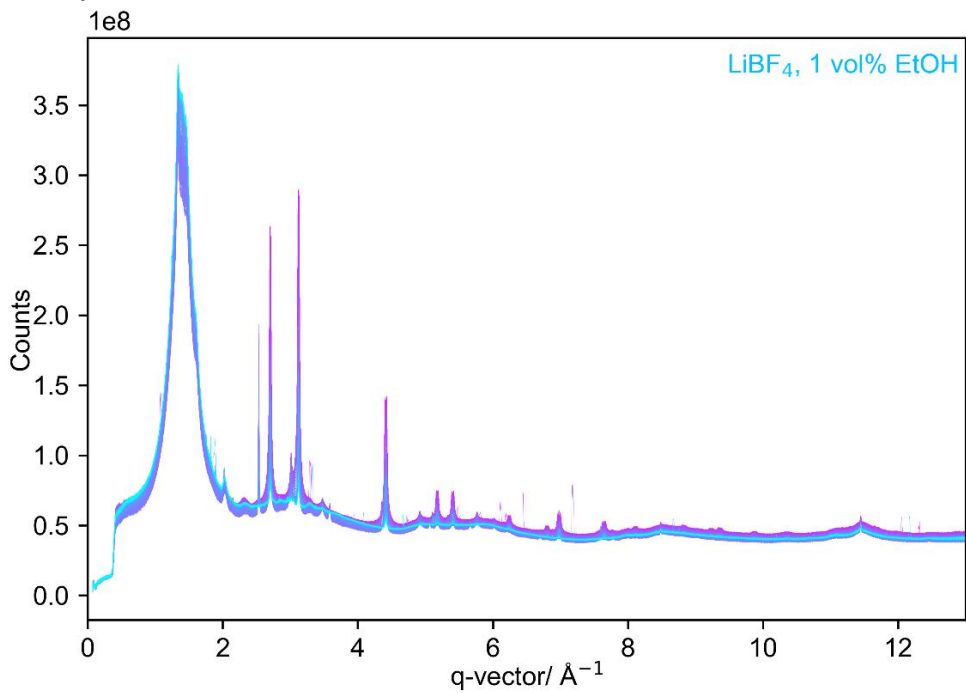


Figure S9: Integrated GI-WAXS pattern. Overview over the full q-range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

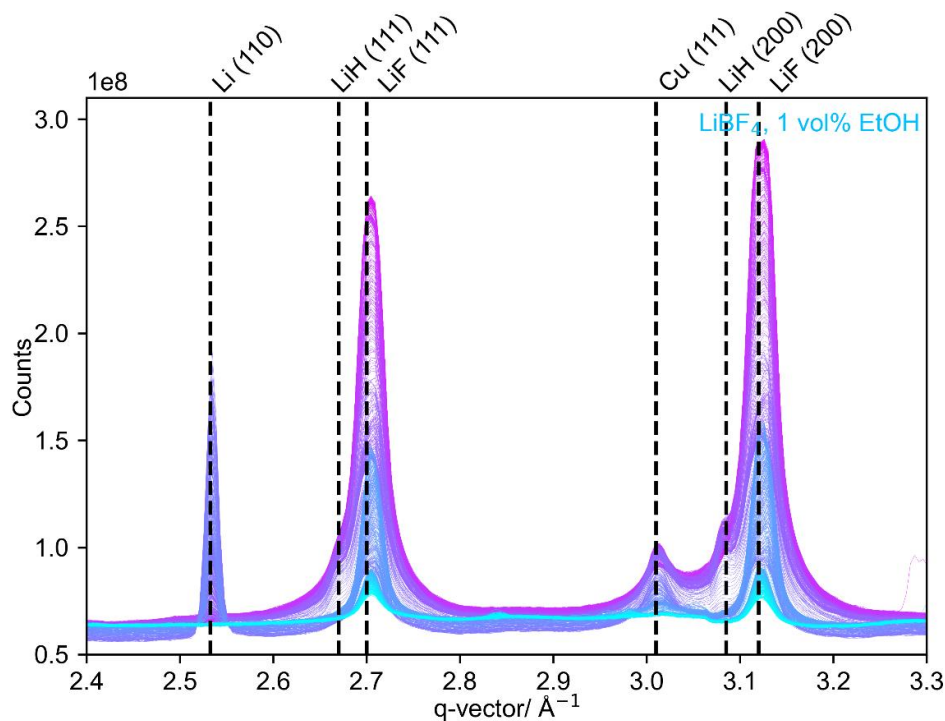


Figure S10: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 \AA^{-1} including Li, LiH, LiF and Cu peaks. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

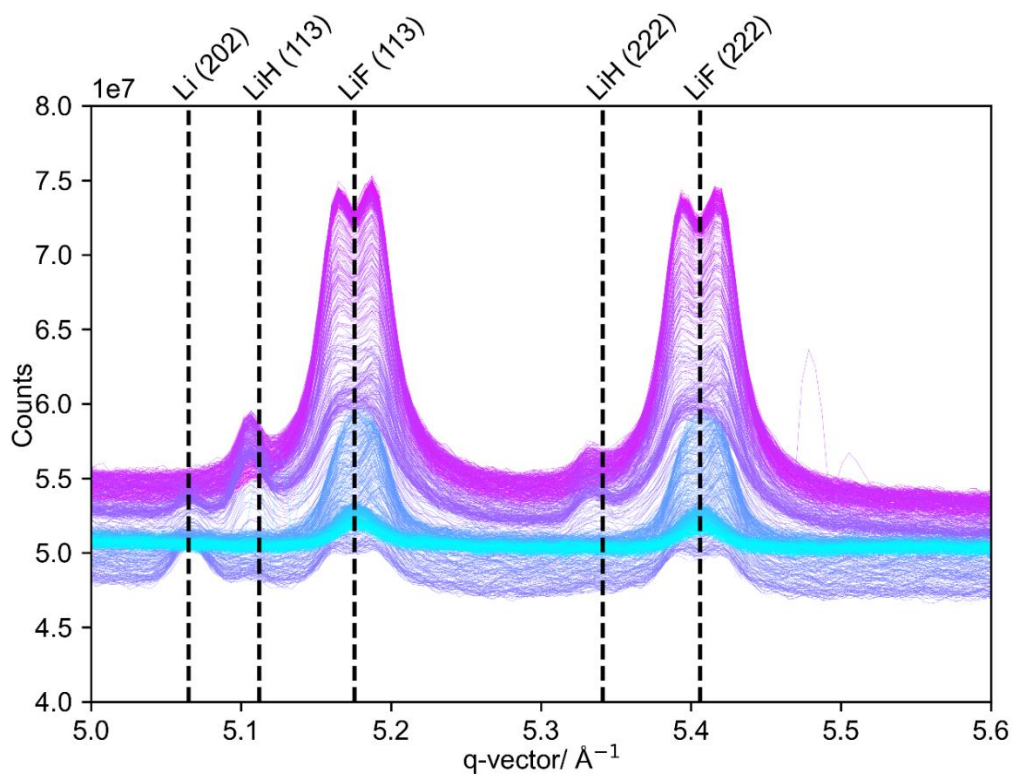


Figure S11: Integrated WAXS patterns. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M solution of LiBF_4 in THF with 1 vol% EtOH was used as electrolyte.

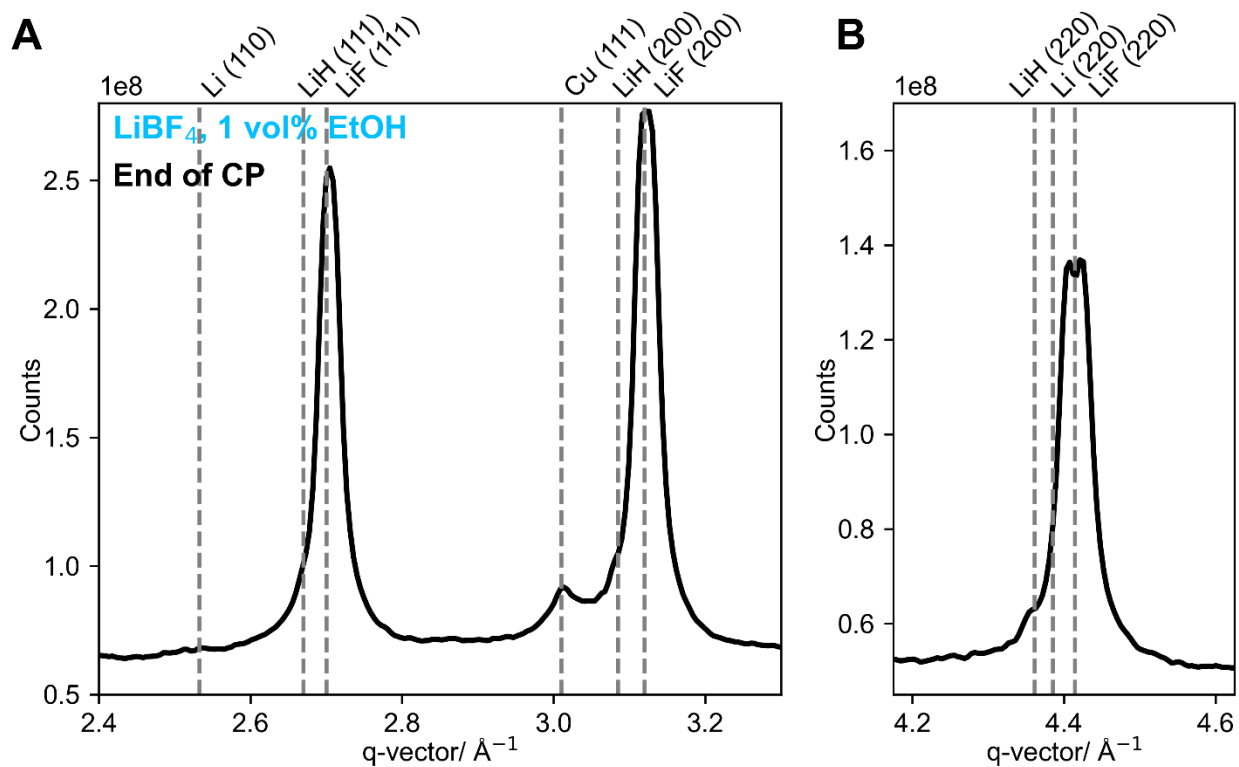


Figure S12: Integrated GI-WAXS pattern, recorded immediately after the end of CP. Q-range from 2.4-3.3 Å⁻¹ and 4.2-4.6 Å⁻¹ showing LiH peaks overlapping with peaks from LiF and Cu.

3.2.2 Experiment 2

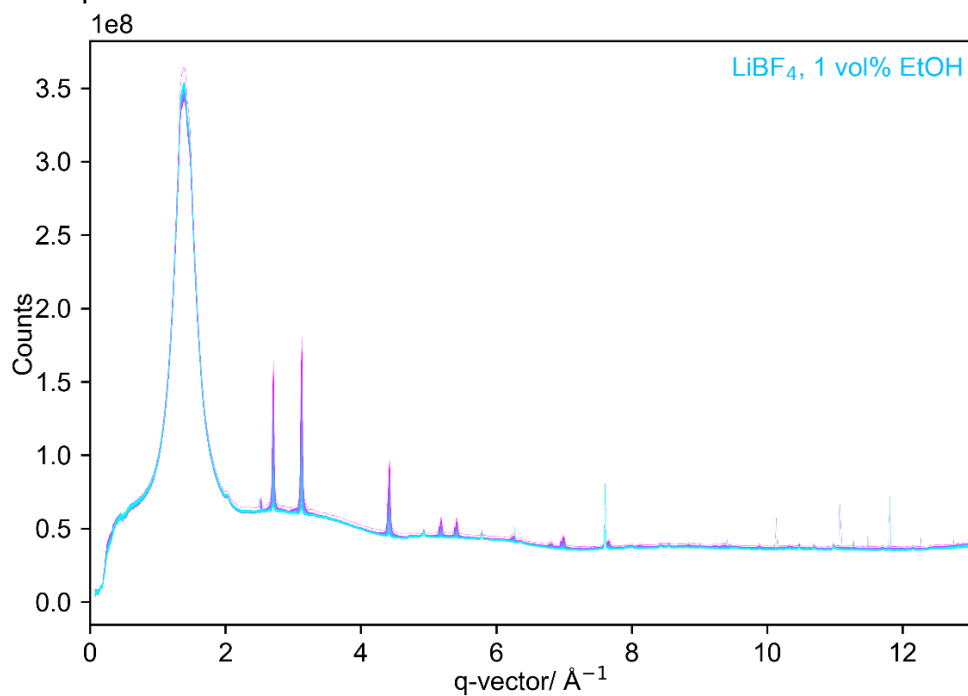


Figure S13: Integrated GI-WAXS pattern. Overview over the full q -range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

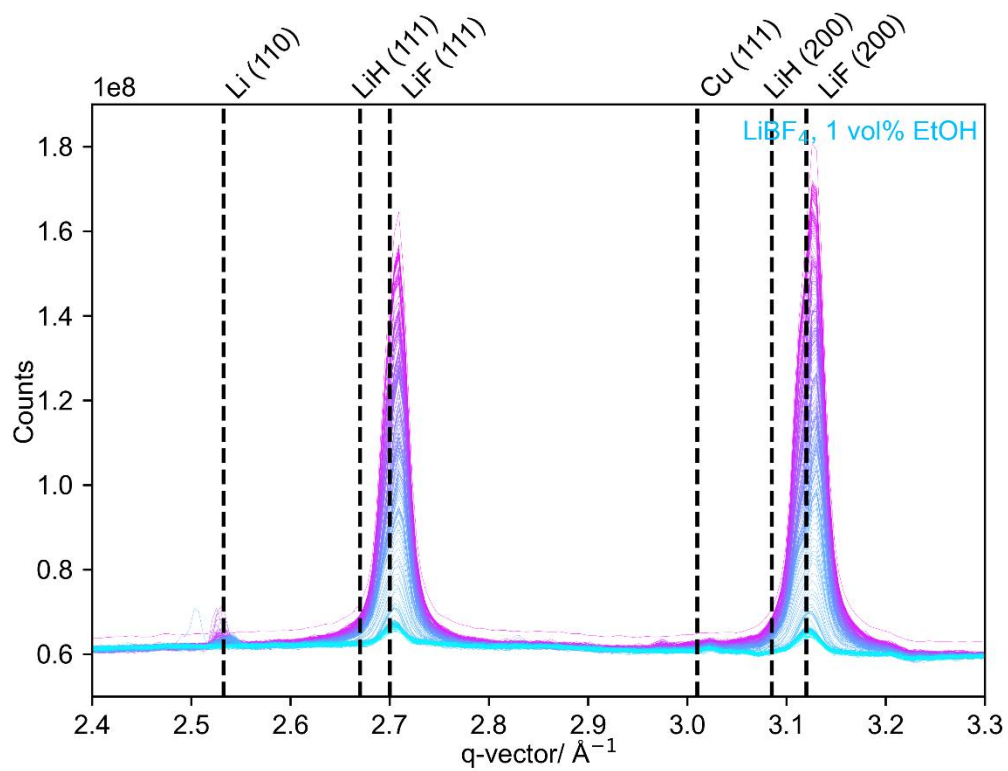


Figure S14: Integrated GI-WAXS pattern. Q -range from 2.4-3.3 \AA^{-1} including Li, LiF and Cu peaks. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

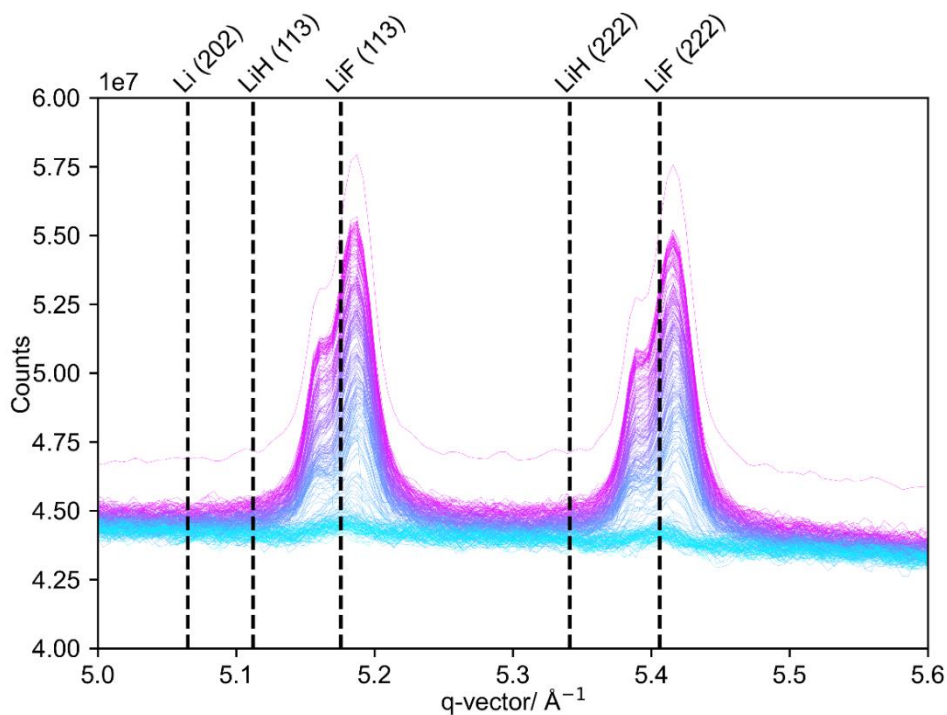


Figure S15: Integrated WAXS patterns. Measurements early in the experiment are drawn in dark colors, whereas light blue colors correspond to measurements later in the experiment. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M solution of LiBF_4 in THF with 1 vol% EtOH was used as electrolyte.

3.3 LiClO_4 , no EtOH

3.3.1 Experiment 1

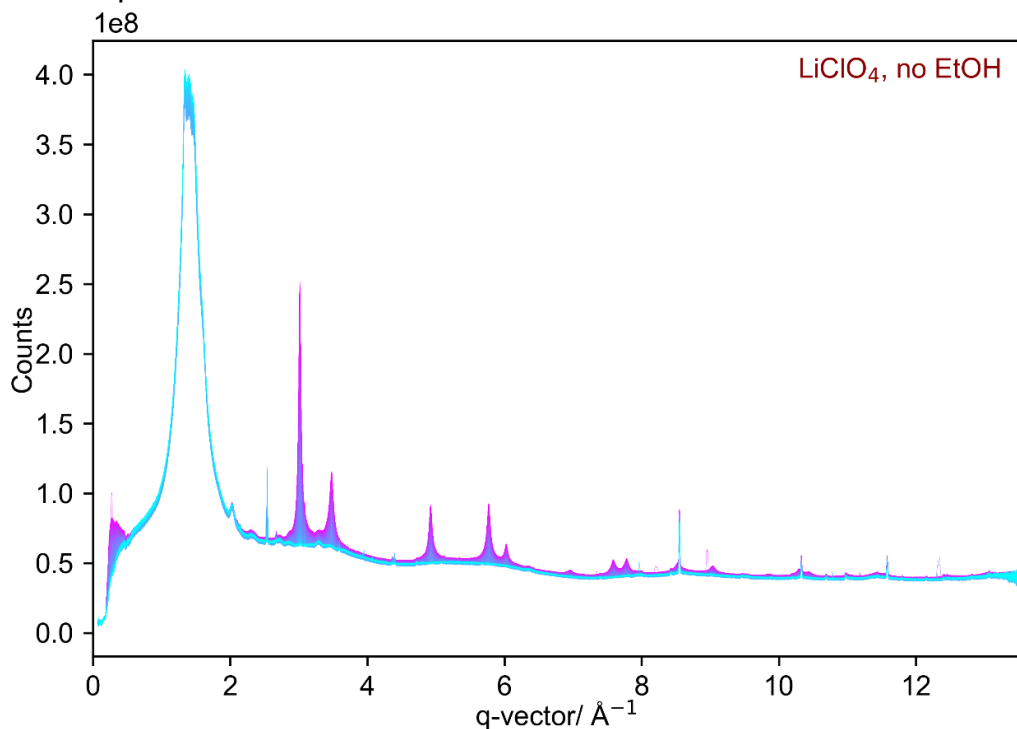


Figure S16: Integrated GI-WAXS pattern. Overview over the full q -range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

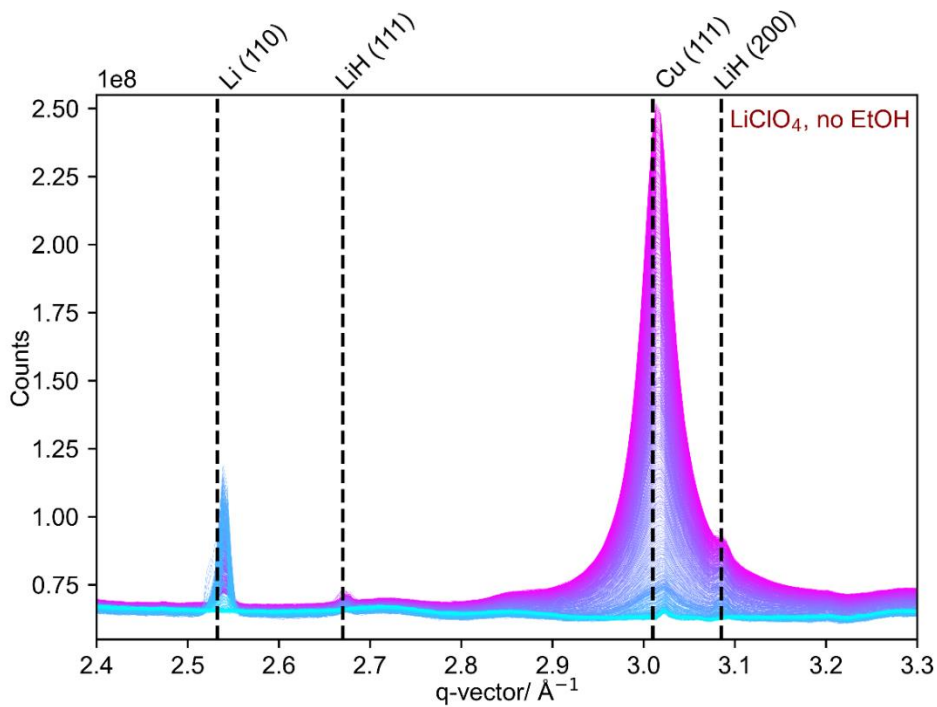


Figure S17: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 \AA^{-1} including Li, LiH and Cu peaks. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

3.3.2 Experiment 2

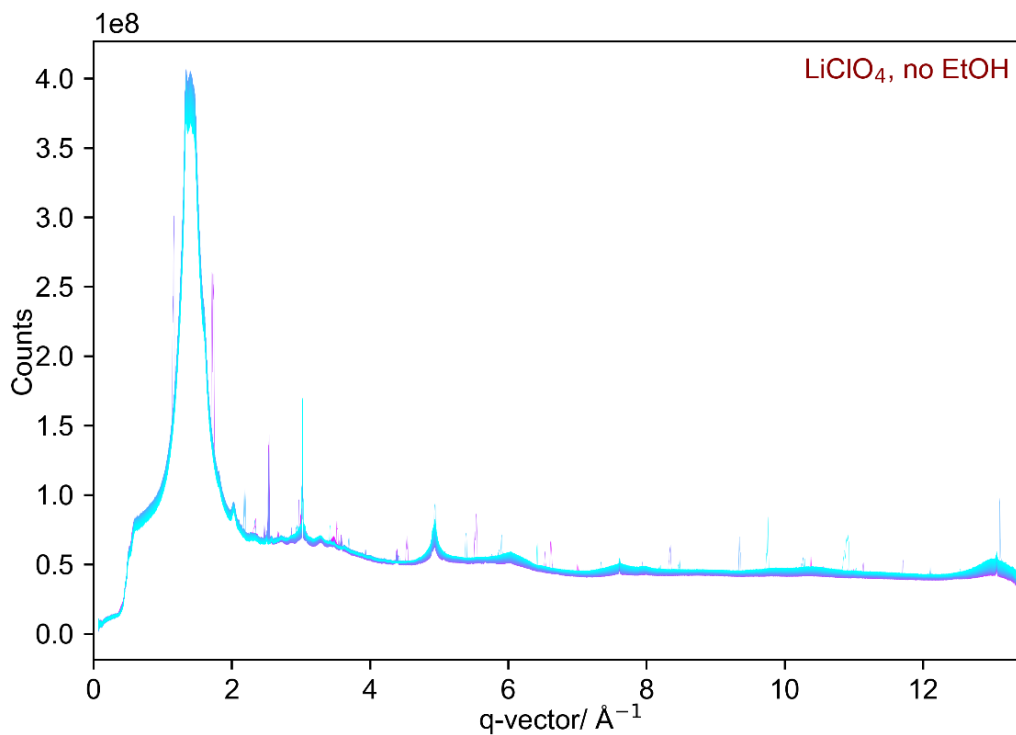


Figure S18: Integrated GI-WAXS pattern. Overview over the full q-range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

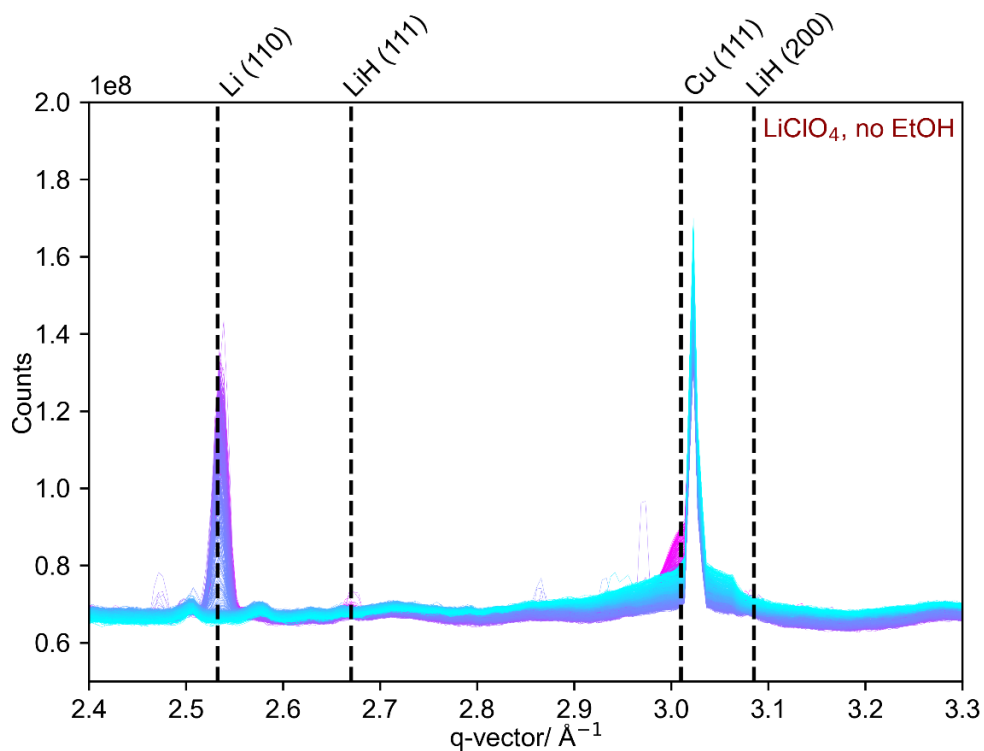


Figure S19: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 \AA^{-1} including Li, LiH and Cu peaks. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

3.4 LiClO₄, 1 vol% EtOH

3.4.1 Experiment 1

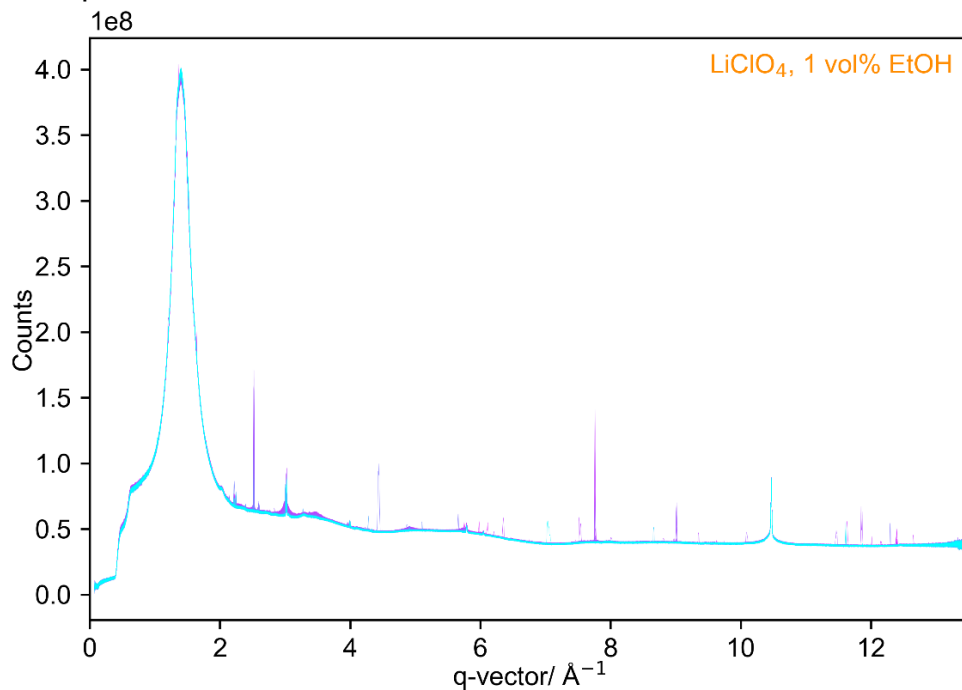


Figure S20: Integrated GI-WAXS pattern. Overview over the full q-range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

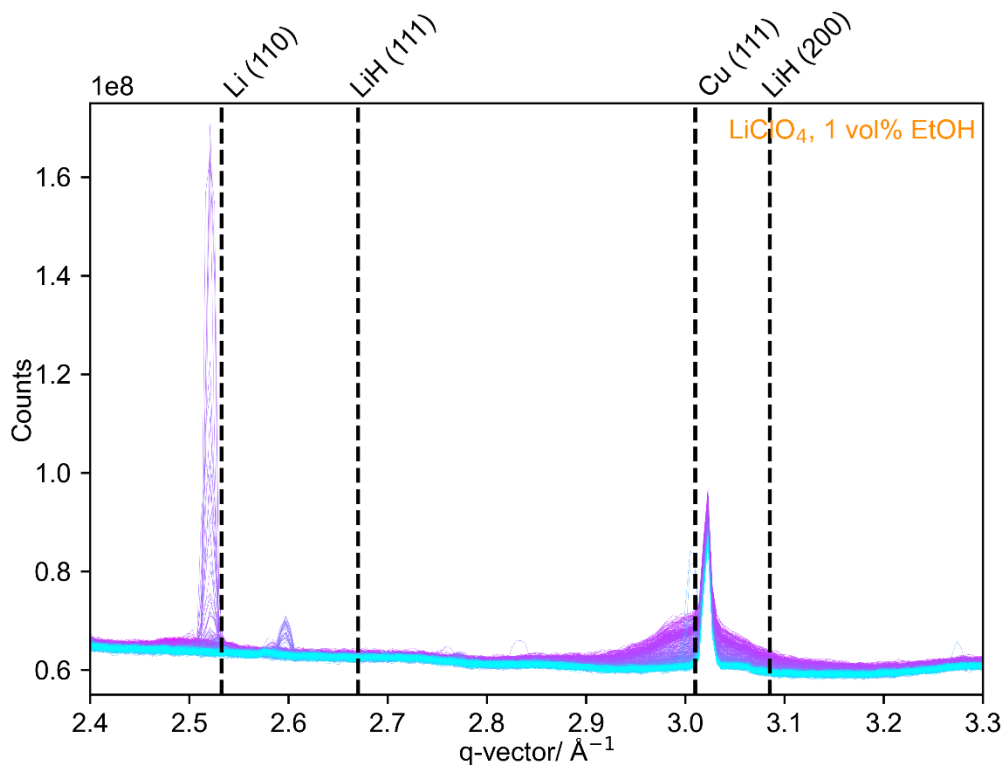


Figure S21: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 \AA^{-1} including Li, and Cu peaks. No LiH was detected. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

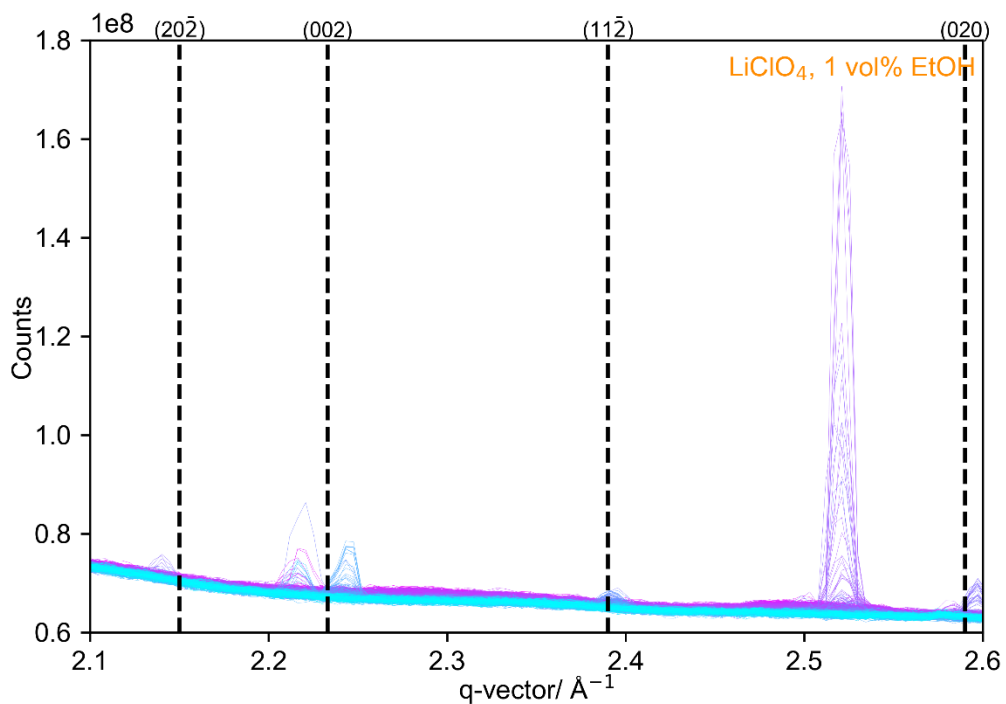


Figure S22: Integrated GI-WAXS pattern. Q-range from 2.1-2.6 \AA^{-1} . Li_2CO_3 reflections are marked. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment.

3.4.2 Experiment 2

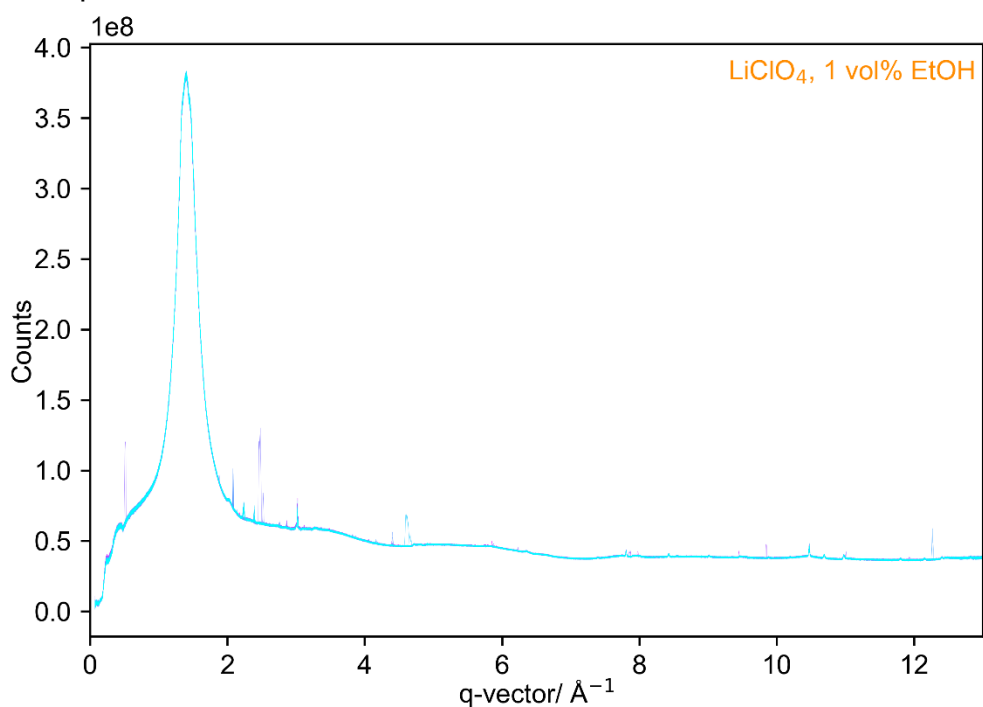


Figure S23: Integrated GI-WAXS pattern. Overview over the full q -range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

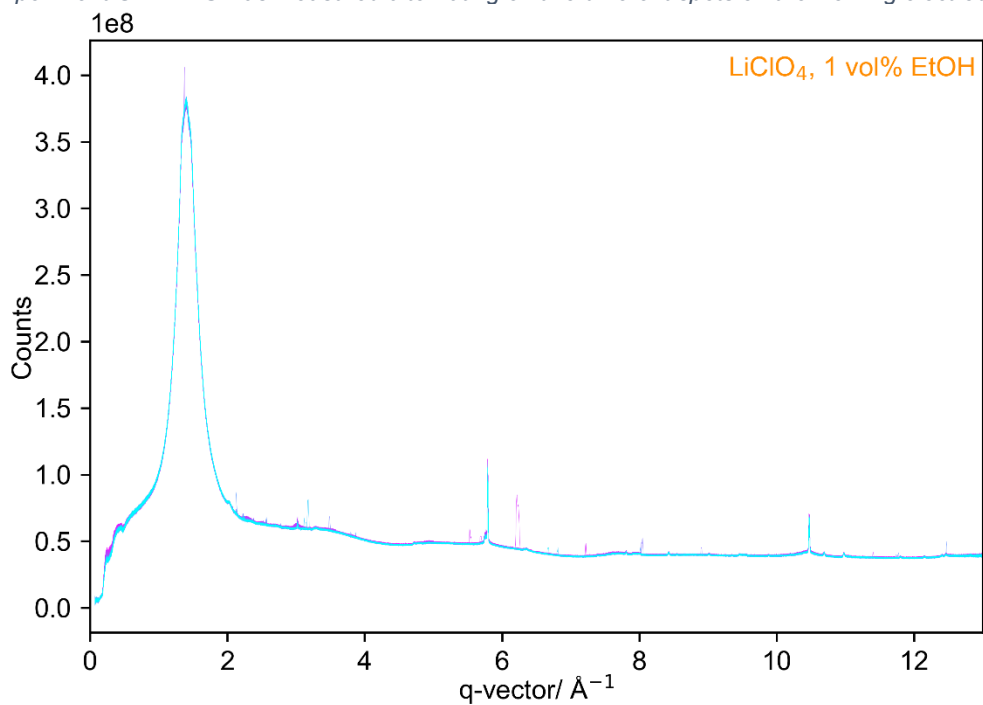


Figure S24: Integrated GI-WAXS pattern. Overview over the full q -range. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

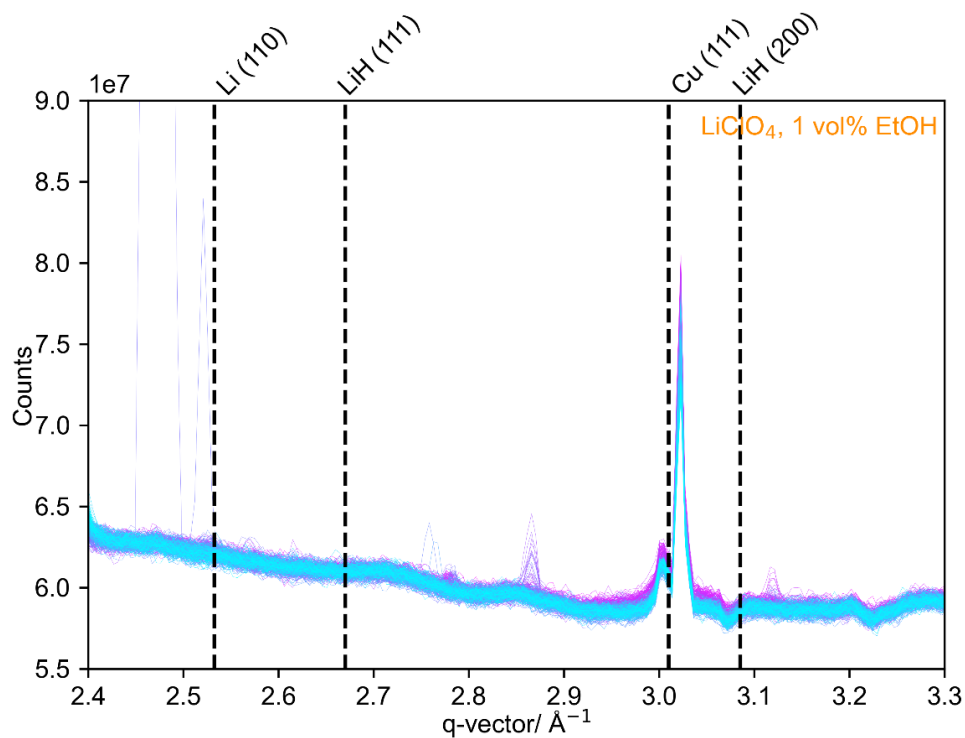


Figure S25: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 \AA^{-1} including Li, and Cu peaks. No LiH was detected. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

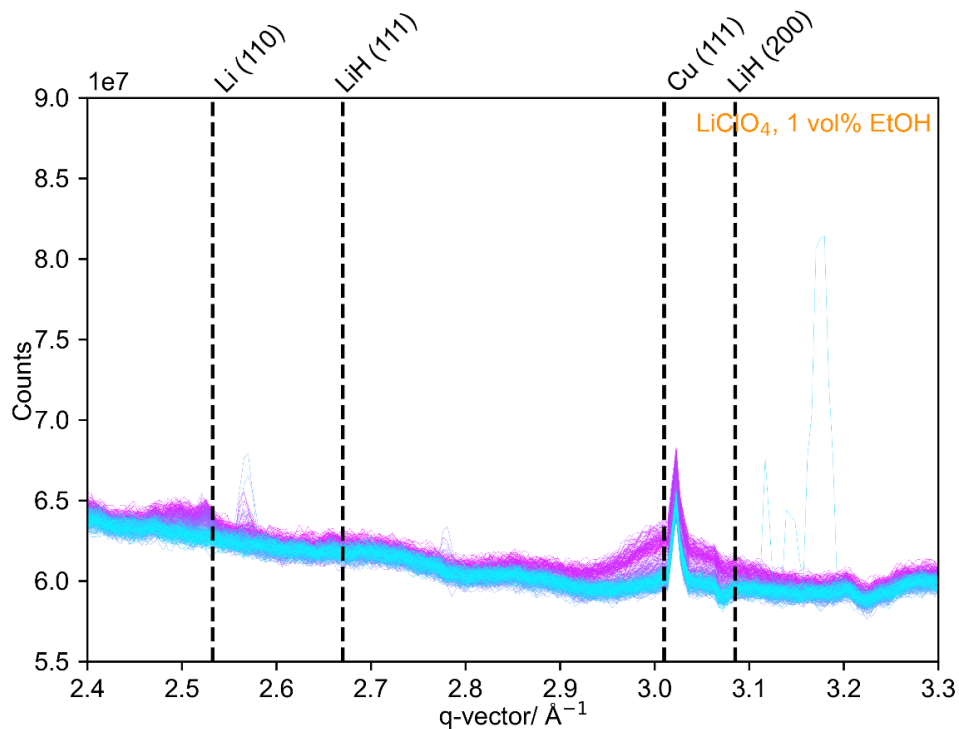


Figure S26: Integrated GI-WAXS pattern. Q-range from 2.4-3.3 \AA^{-1} including Li, and Cu peaks. No LiH was detected. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

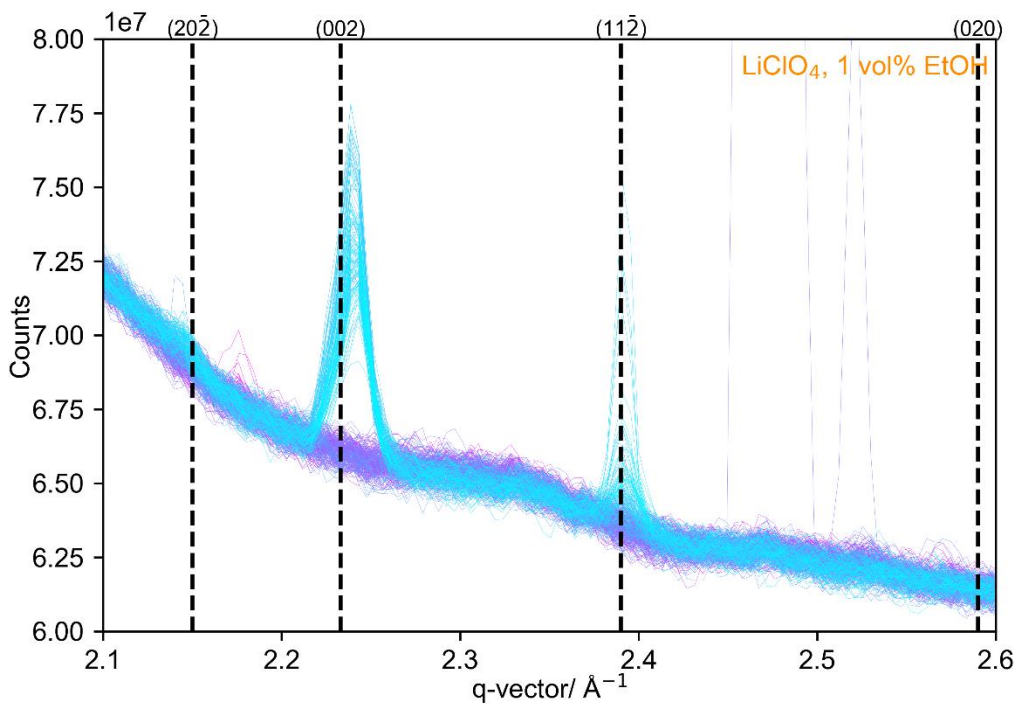


Figure S27: Integrated GI-WAXS pattern. Q-range from 2.1-2.6 \AA^{-1} . Li_2CO_3 reflections are marked. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

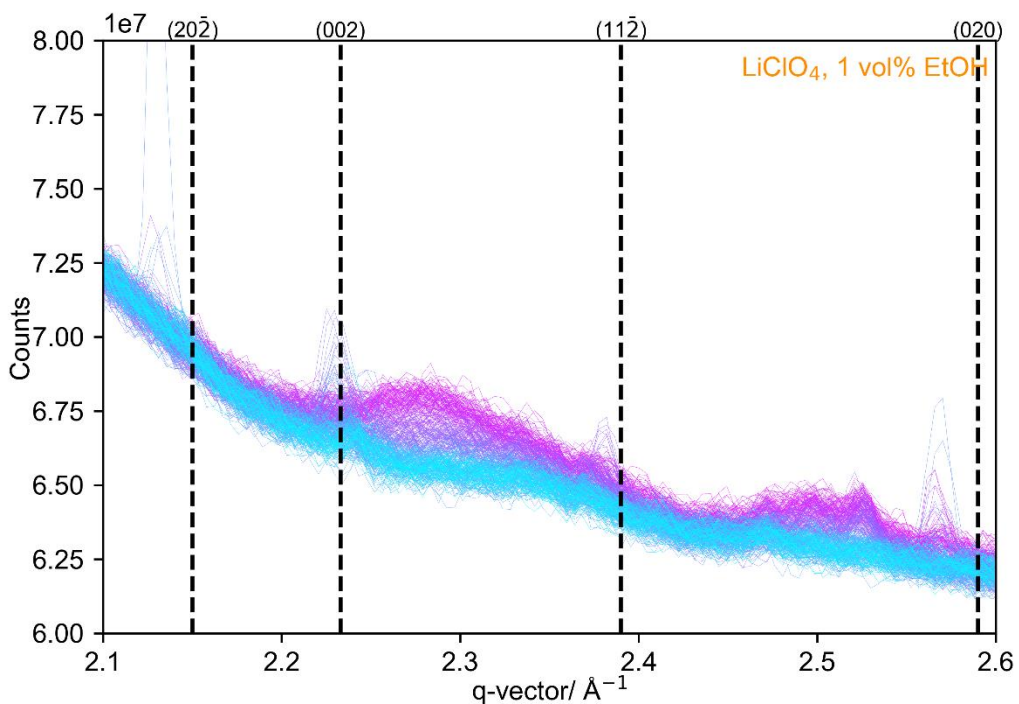


Figure S28: Integrated GI-WAXS pattern. Q-range from 2.1-2.6 \AA^{-1} . Li_2CO_3 reflections are marked. Measurements early in the experiment are drawn in light blue colors, whereas darker, purple colors correspond to measurements later in the experiment. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1) The increase in intensity around 2.3 \AA^{-1} might correspond to the formation of LiOH .

4 Electrochemistry

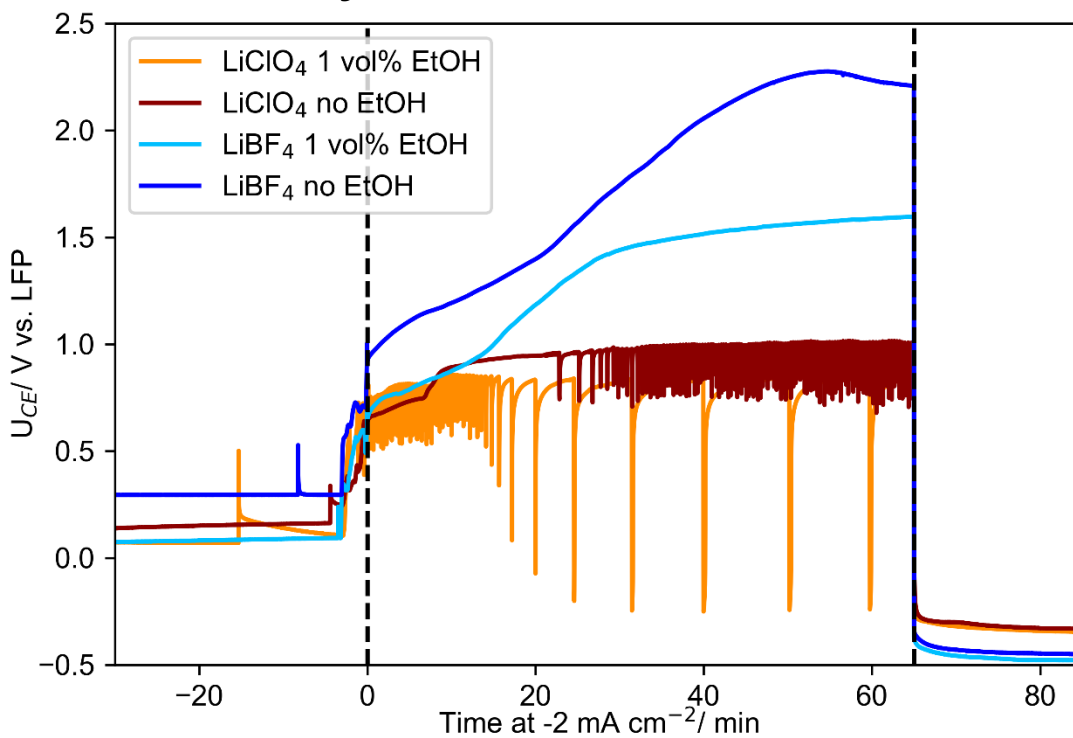


Figure S29: Counter electrode potentials throughout synchrotron experiments.

4.1 LiBF₄, no EtOH

4.1.1 Experiment 1

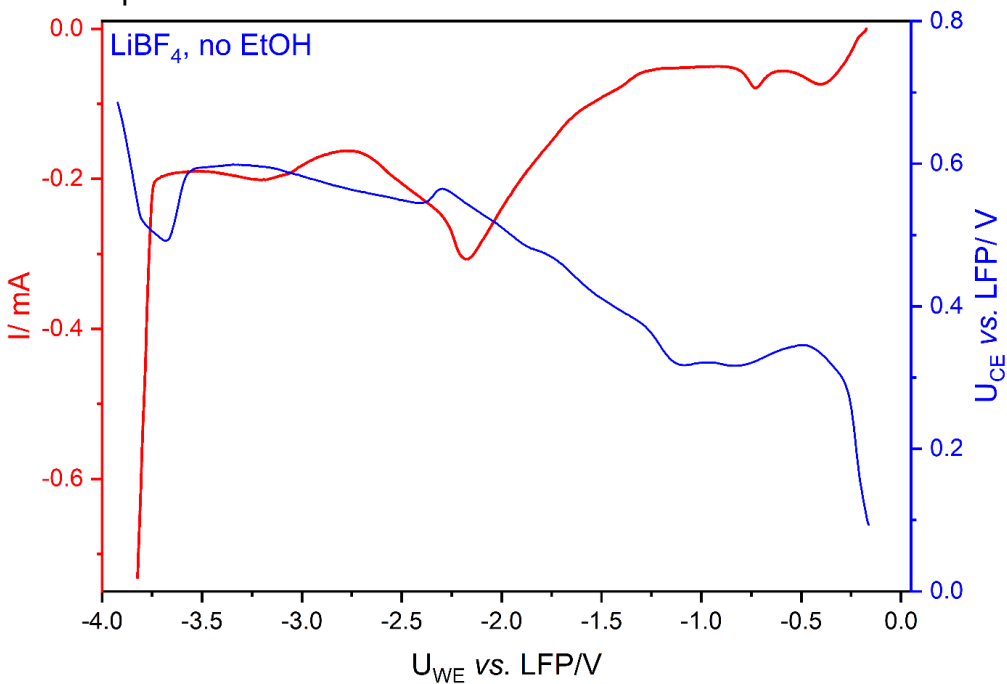


Figure S30: LSV with 20 mv/s from OCV to Li plating potential. A solution of 1 M LiBF₄ in THF with 0 vol% EtOH was used as electrolyte.

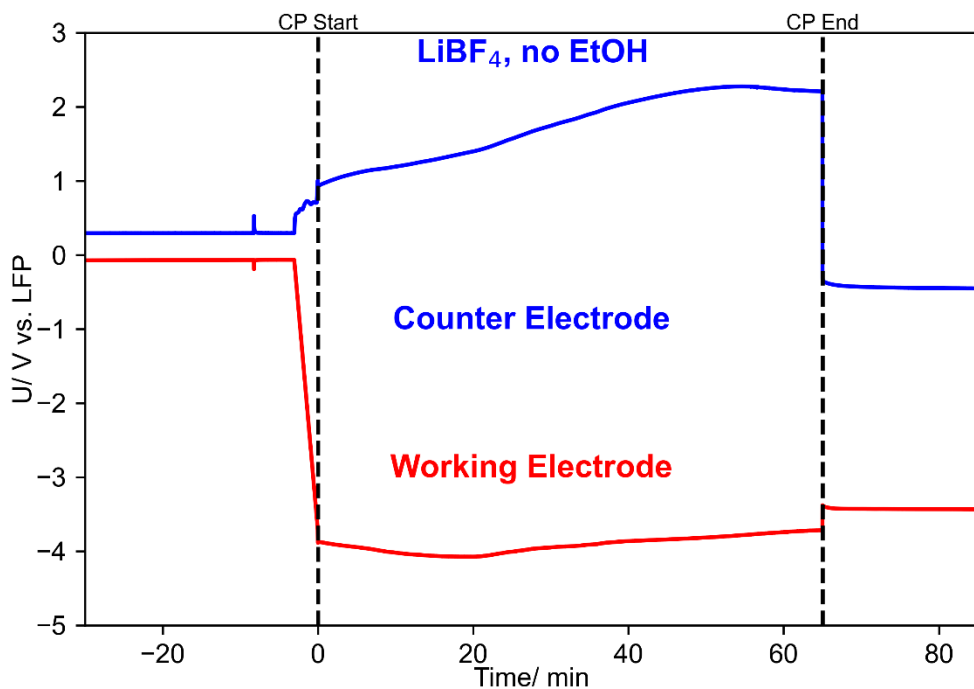


Figure S31: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiBF₄ in THF with no EtOH was used as electrolyte.

4.1.2 Experiment 2

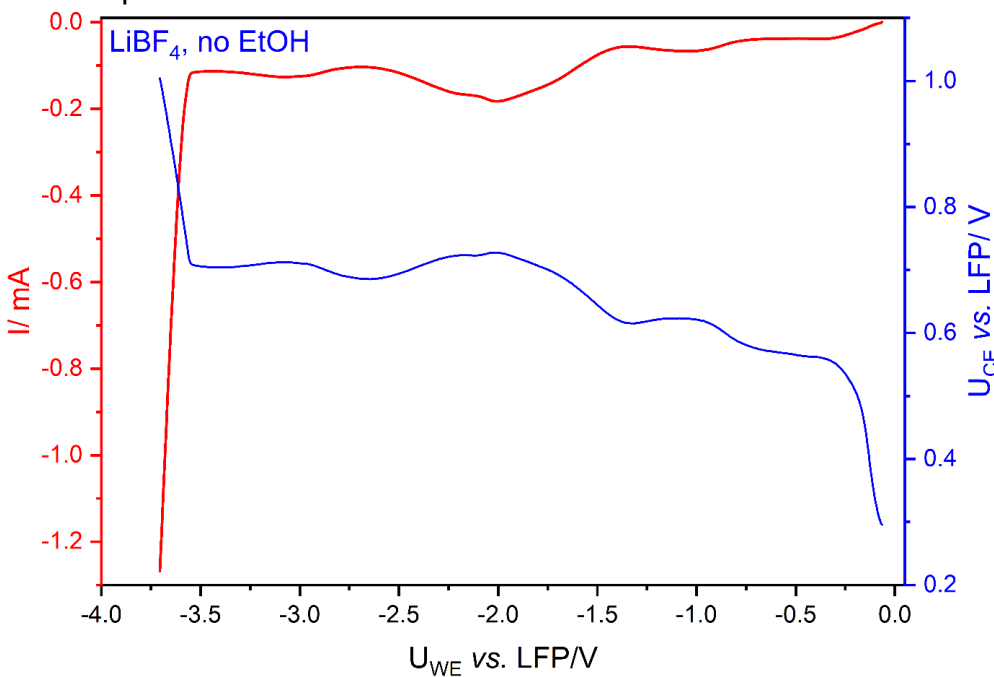


Figure S32: LSV with 20 mv/s from OCV to Li plating potential. A solution of 1 M LiBF₄ in THF with 0 vol% EtOH was used as electrolyte.

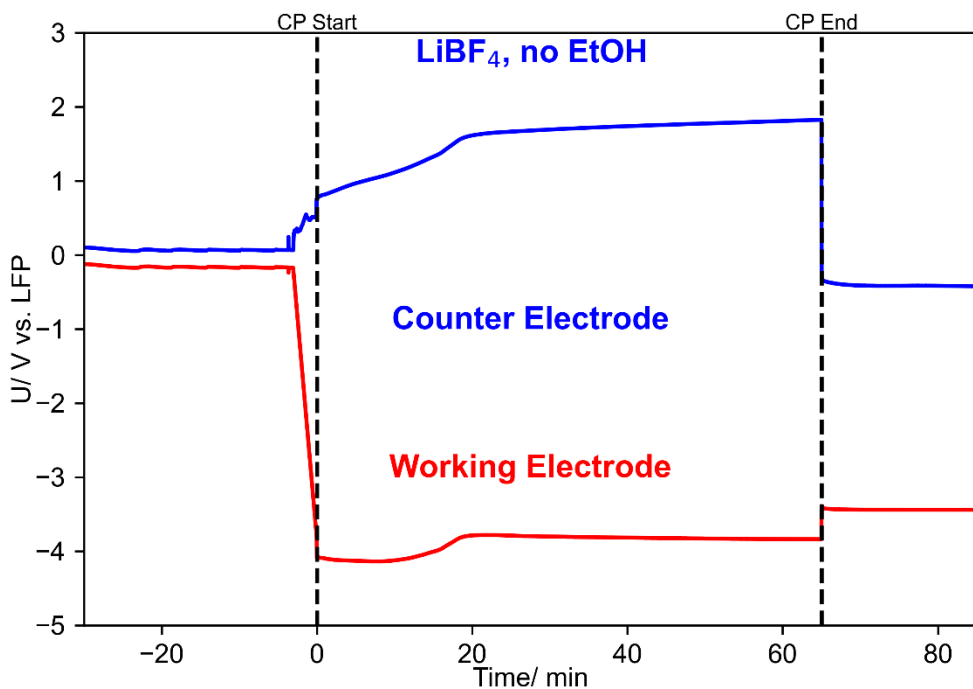


Figure S33: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiBF_4 in THF with no EtOH was used as electrolyte.

4.2 LiBF_4 , 1vol% EtOH

4.2.1 Experiment 1

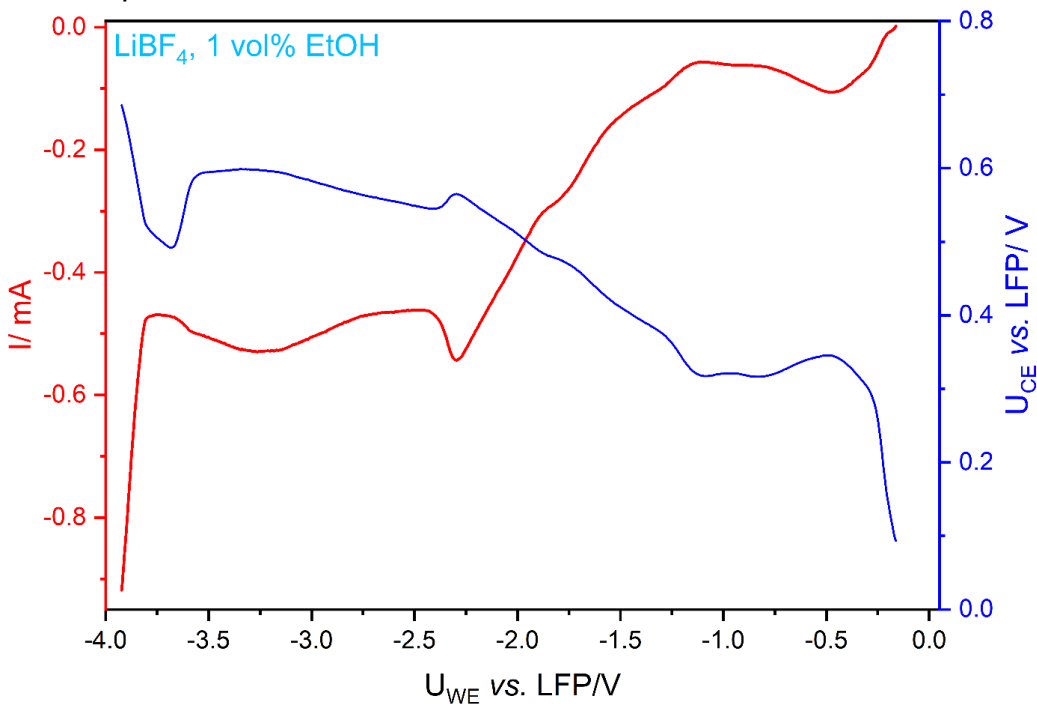


Figure S34: LSV with 20 mv/s from OCV to Li plating potential. A solution of 1 M LiBF_4 in THF with 1 vol% EtOH was used as electrolyte.

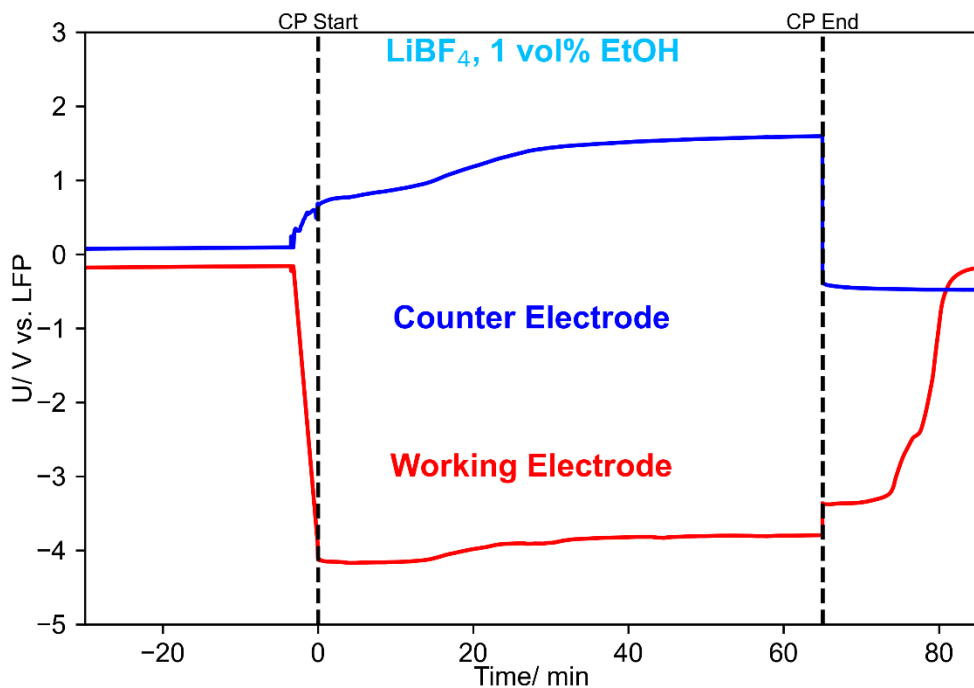


Figure S35: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiBF_4 in THF with 1 vol% EtOH was used as electrolyte.

4.2.2 Experiment 2

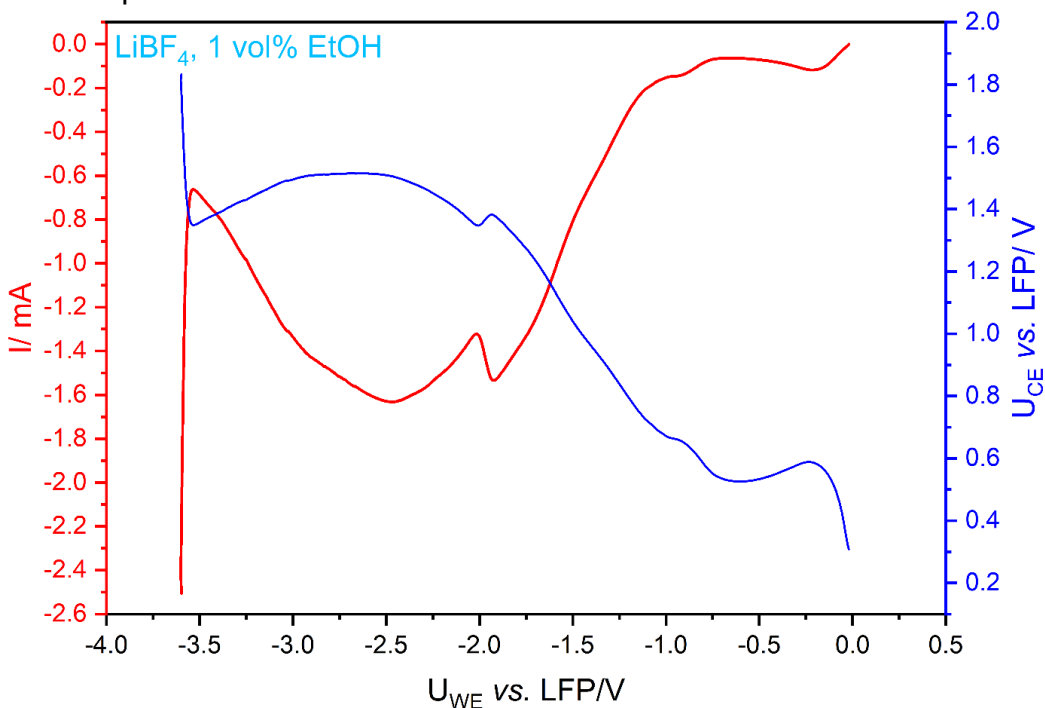


Figure S36: LSV with 20 mv/s from OCV to Li plating potential. A solution of 1 M LiBF_4 in THF with 1 vol% EtOH was used as electrolyte.

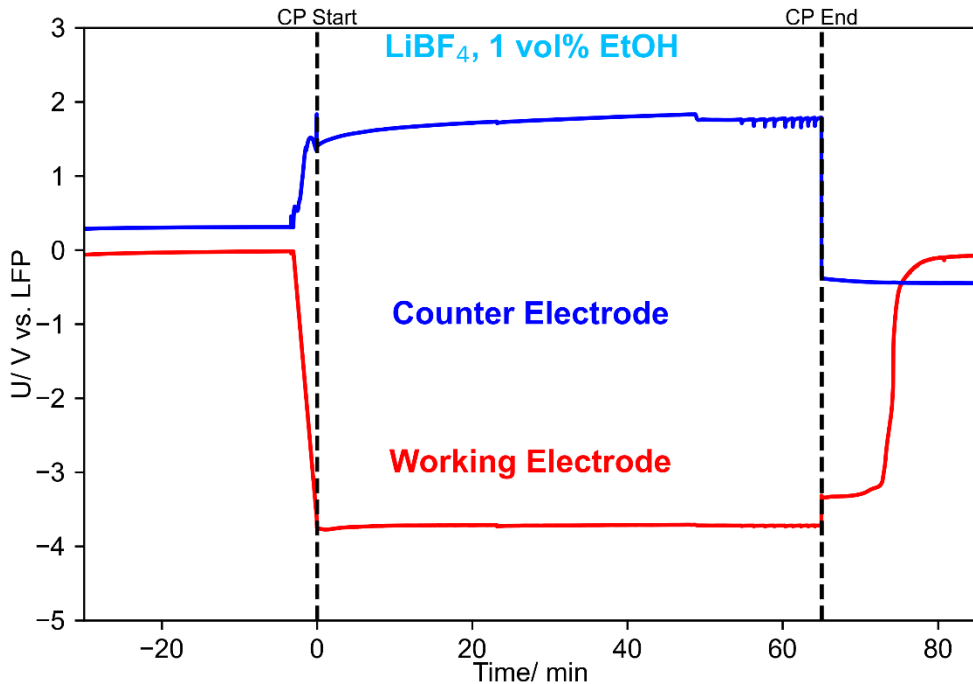


Figure S37: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiBF_4 in THF with 1 vol% EtOH was used as electrolyte.

4.3 LiClO_4 , no EtOH

4.3.1 Experiment 1

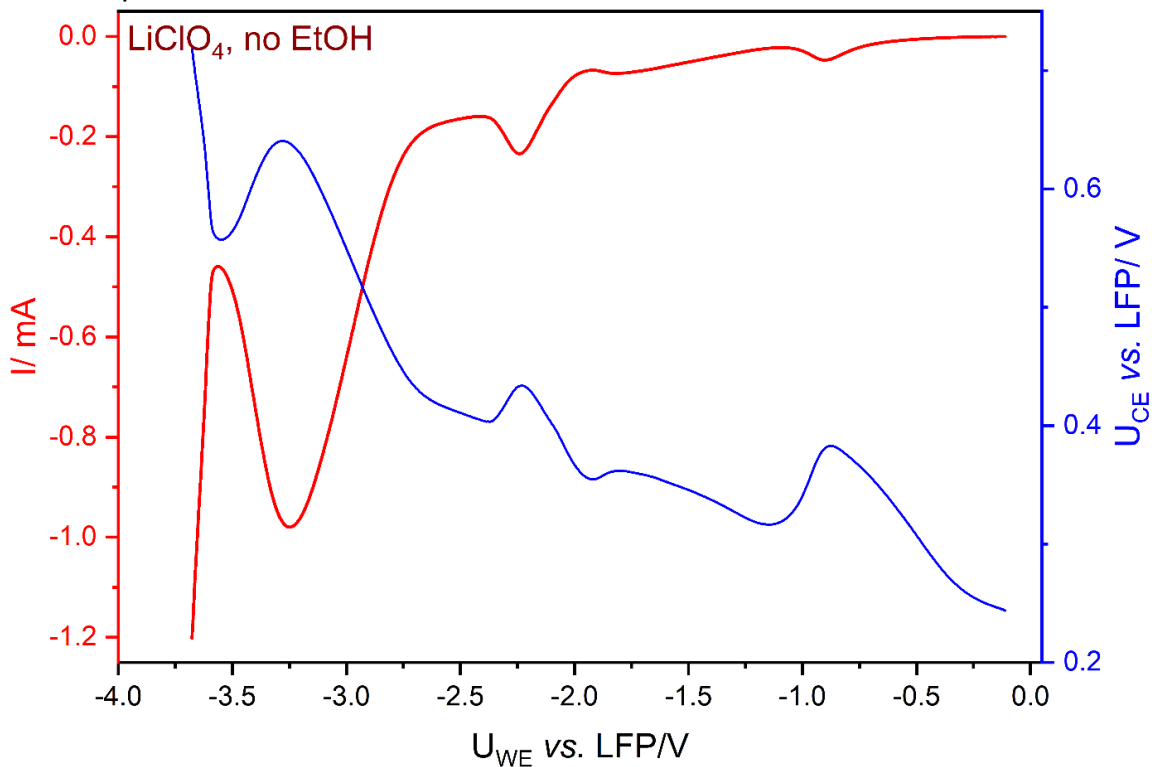


Figure S38: LSV with 20 mv/s from OCV to Li plating potential. A solution of 1 M LiClO_4 in THF with 0 vol% EtOH was used as electrolyte.

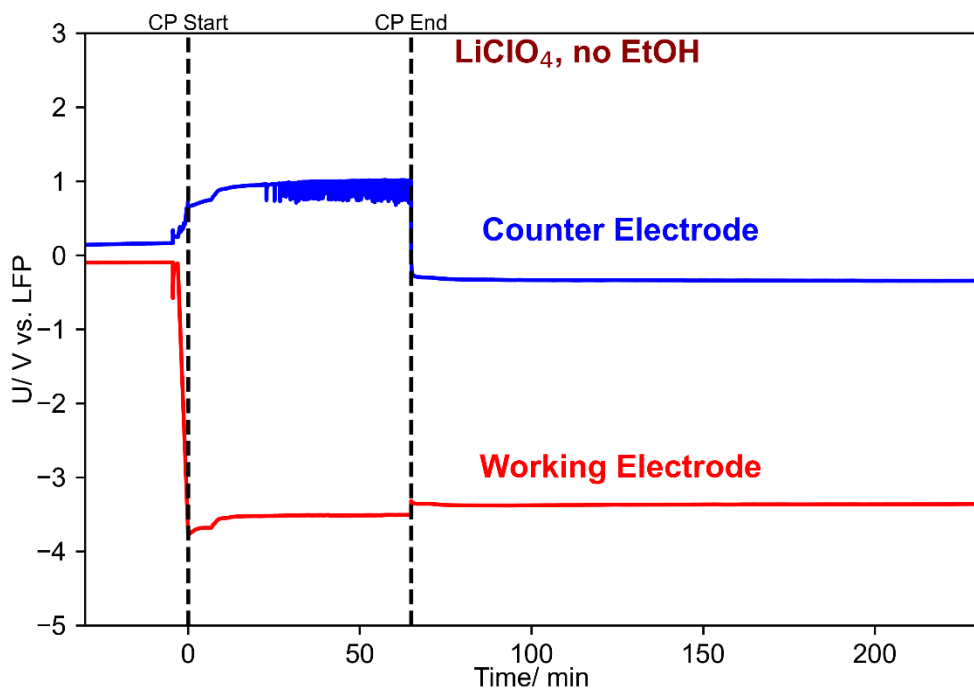


Figure S39: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiClO_4 in THF with 0 vol% EtOH was used as electrolyte.

4.3.2 Experiment 2

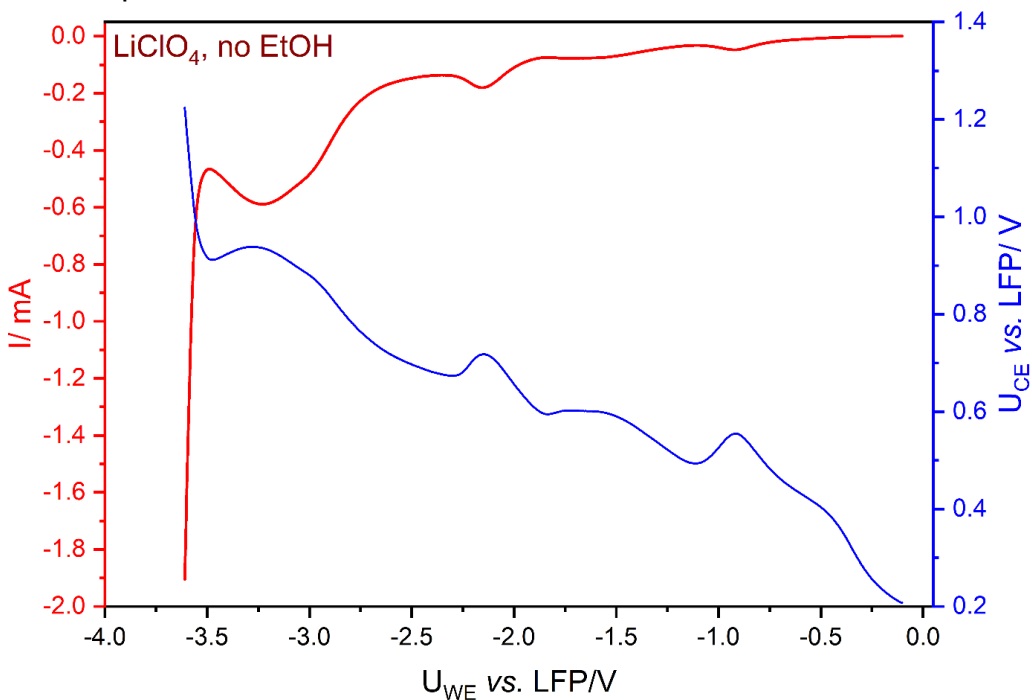


Figure S40: LSV with 20 mv/s from OCV to Li plating potential. A solution of 1 M LiClO_4 in THF with 0 vol% EtOH was used as electrolyte.

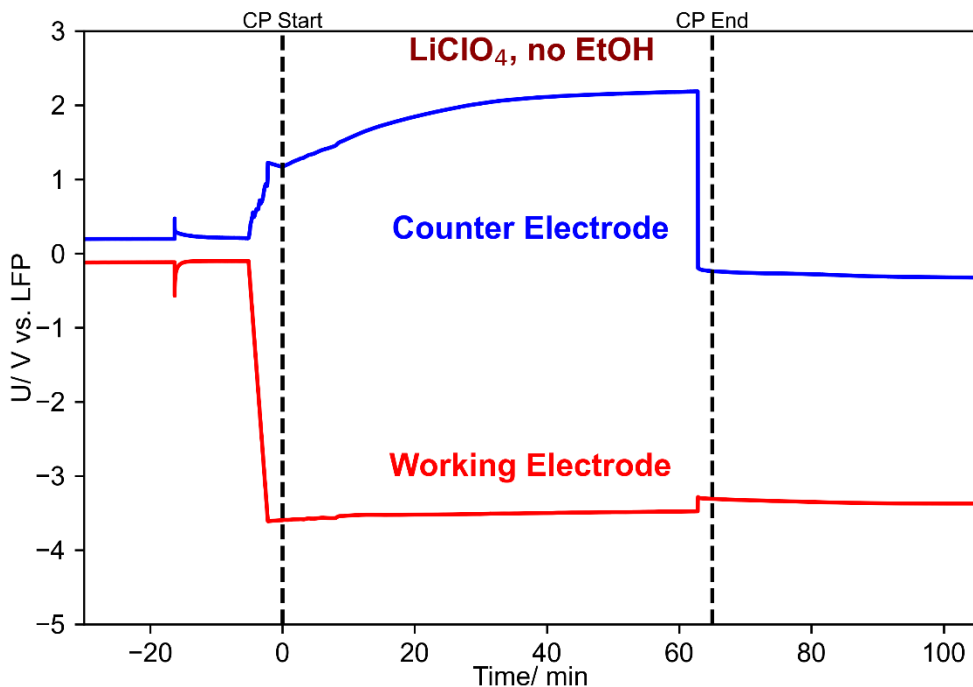


Figure S41: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiClO_4 in THF with 0 vol% EtOH was used as electrolyte.

4.4 LiClO_4 , 1vol% EtOH

4.4.1 Experiment 1

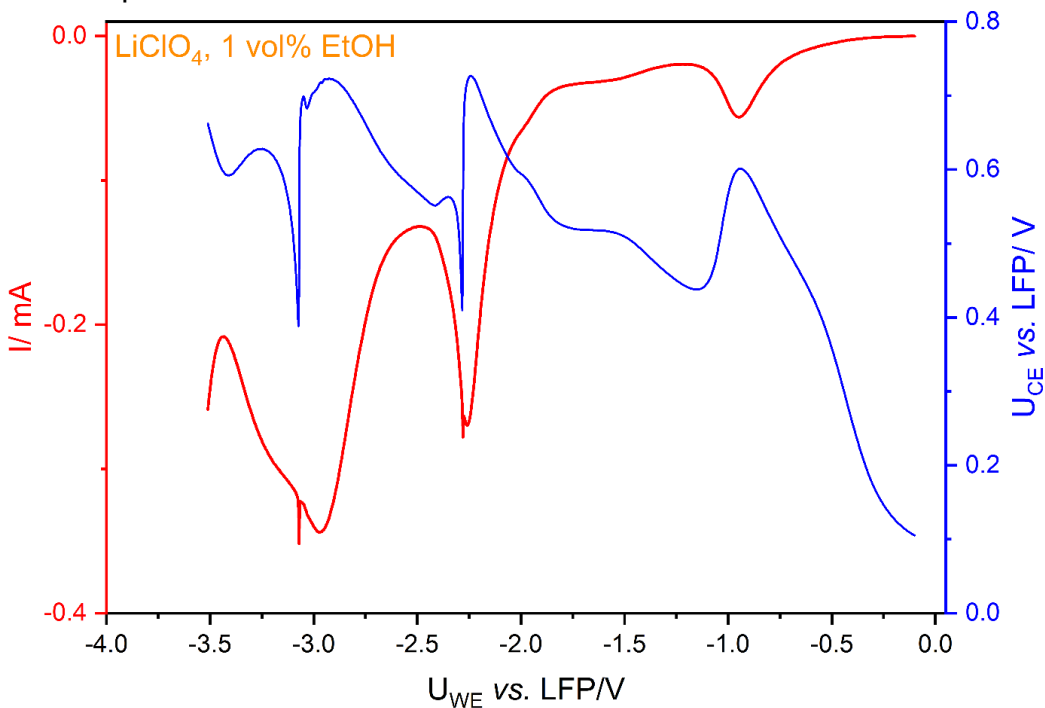


Figure S42: LSV with 20 mV/s from OCV to Li plating potential. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte.

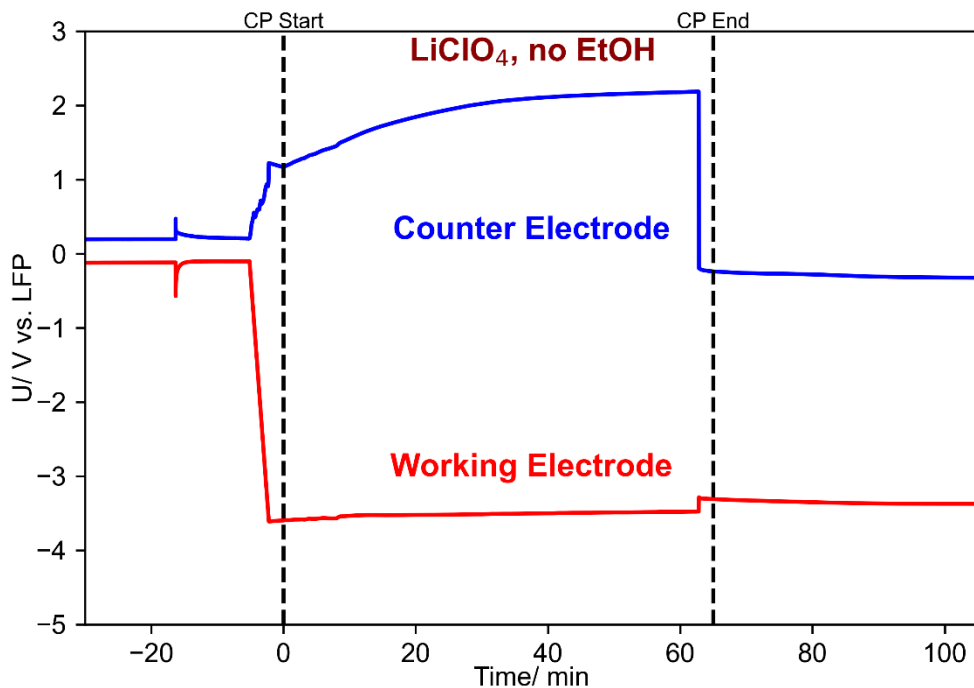


Figure S43: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiClO₄ in THF with 1 vol% EtOH was used as electrolyte.

4.4.2 Experiment 2

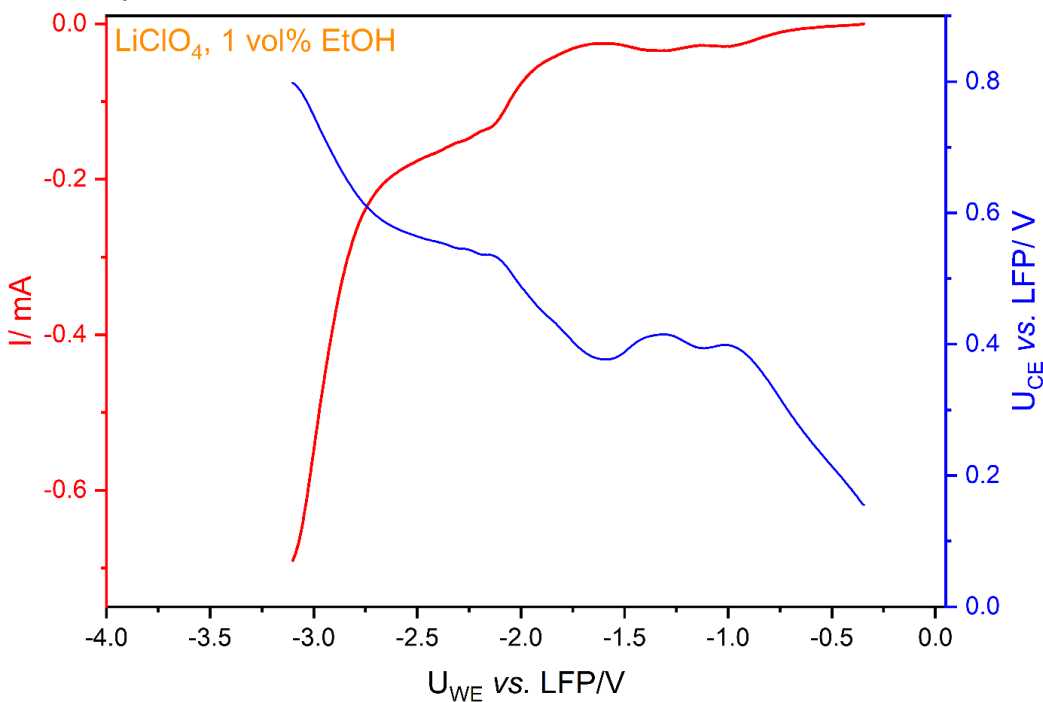


Figure S44: LSV with 20 mv/s from OCV to Li plating potential. A solution of 1 M LiClO₄ in THF with 1 vol% EtOH was used as electrolyte.

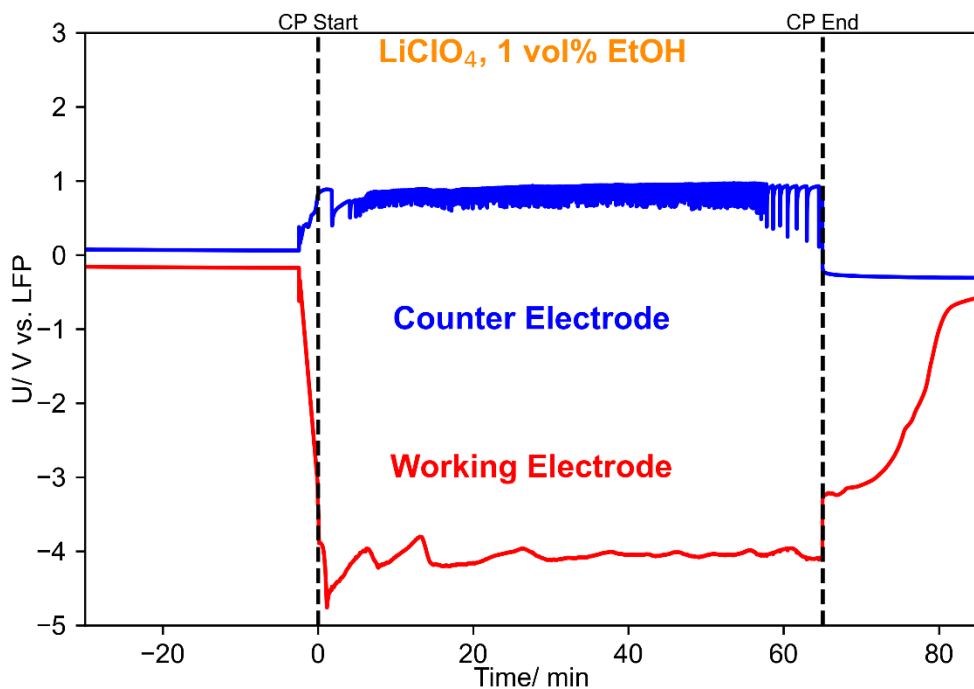


Figure S45: Working and counter electrode potentials during Li-NRR experiment. A solution of 1 M LiClO₄ in THF with 1 vol% EtOH was used as electrolyte.

5 Detector Pixel vs. Time Plots Li

5.1 LiClO₄, no EtOH

5.1.1 Experiment 1

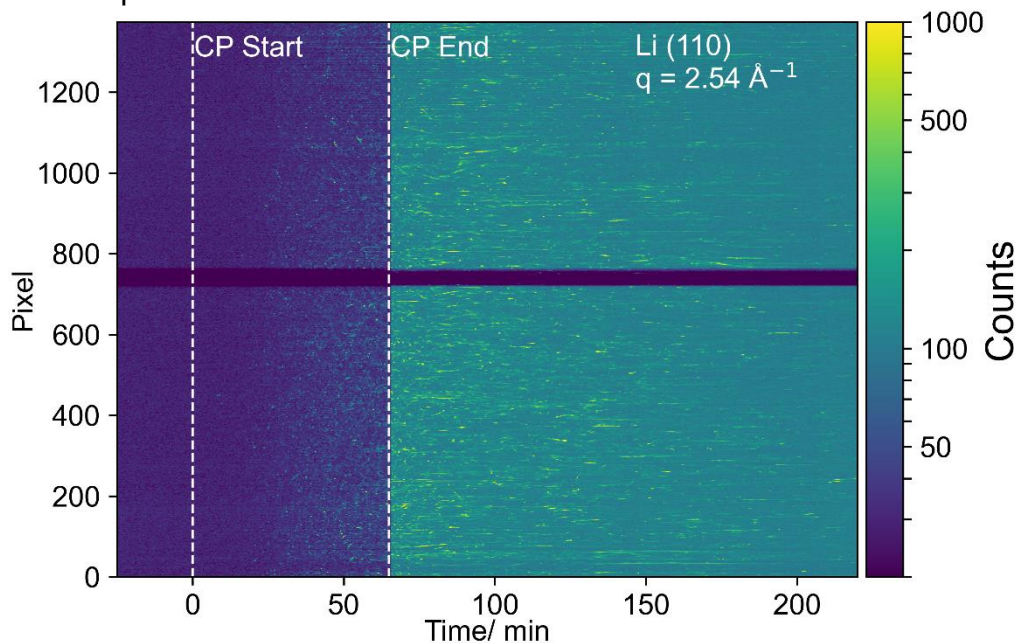


Figure S46: All pixels corresponding to the Li (110) reflection ($q = 2.54 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO₄ in THF with 0 vol% EtOH was used as electrolyte. The increase in intensity after the CP is due to a change in beam attenuation.

5.1.2 Experiment 2

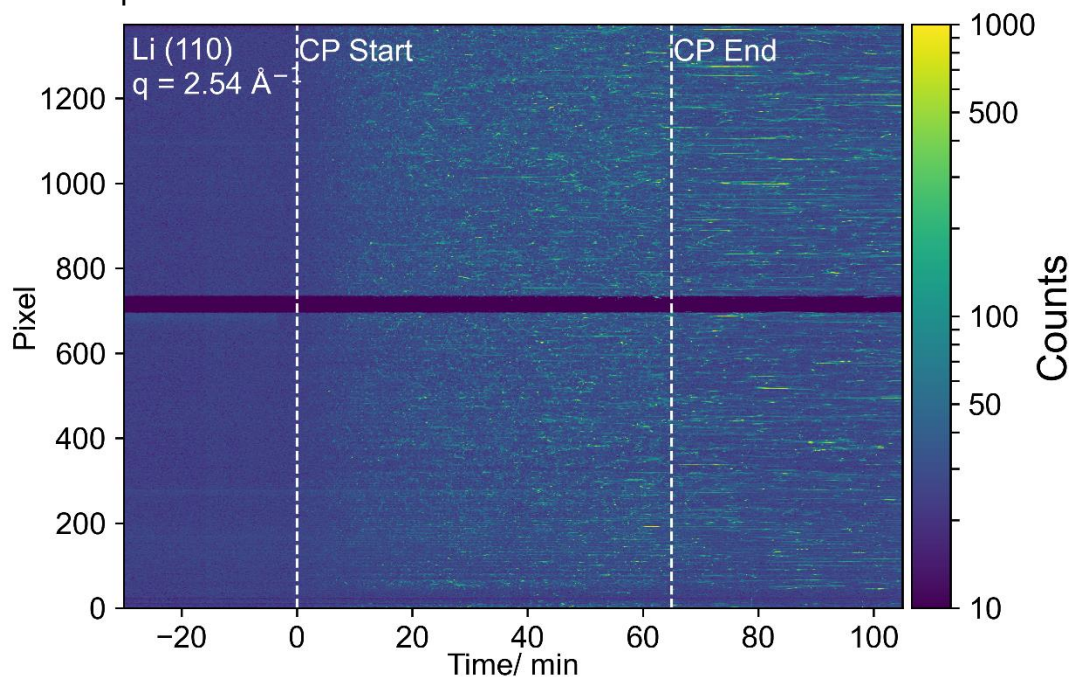


Figure S47: All pixels corresponding to the Li (110) reflection ($q = 2.54 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO₄ in THF with 0 vol% EtOH was used as electrolyte.

5.2 LiClO₄, 1 vol% EtOH

5.2.1 Experiment 1

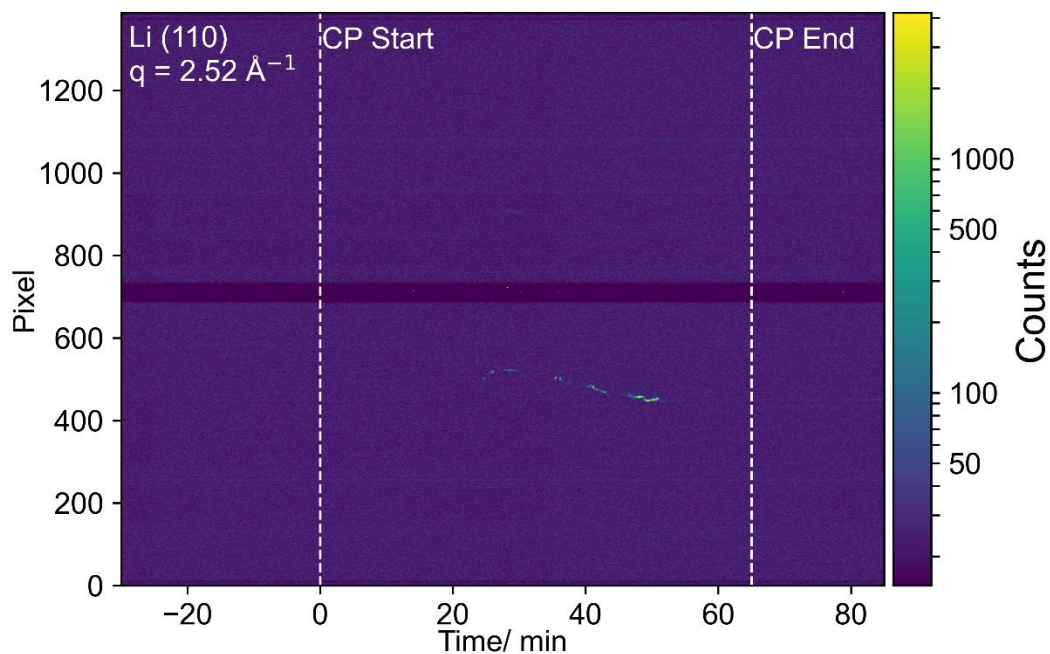


Figure S48: All pixels corresponding to the Li (100) reflection ($q = 2.52 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO₄ in THF with 1 vol% EtOH was used as electrolyte.

5.2.2 Experiment 2

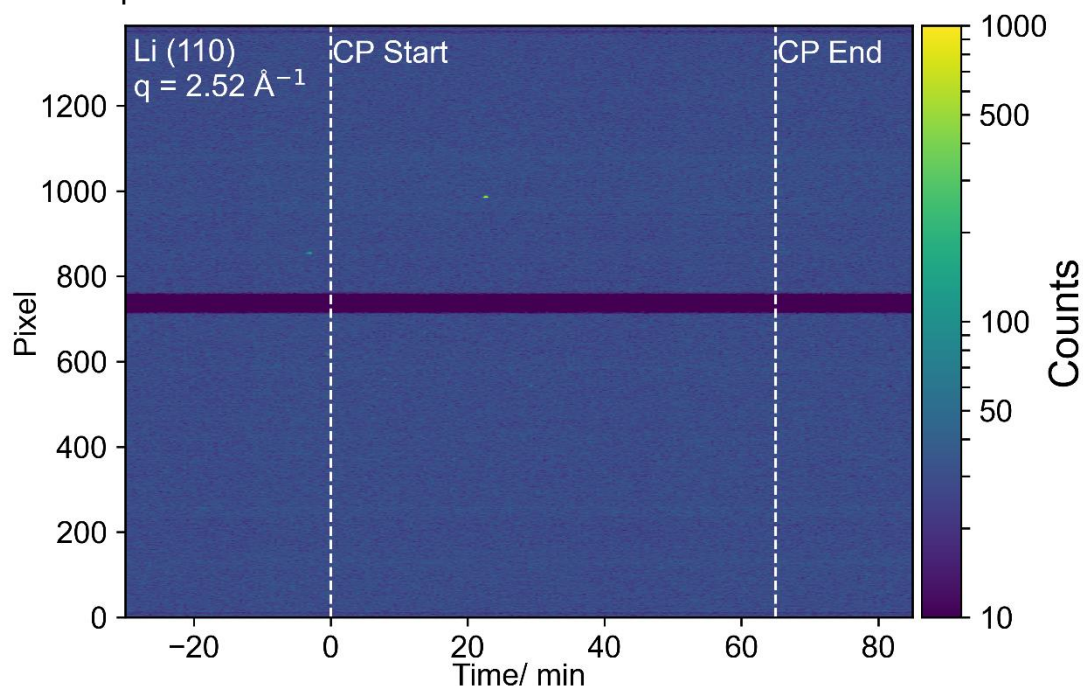


Figure S49: All pixels corresponding to the Li (110) reflection ($q = 2.52 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

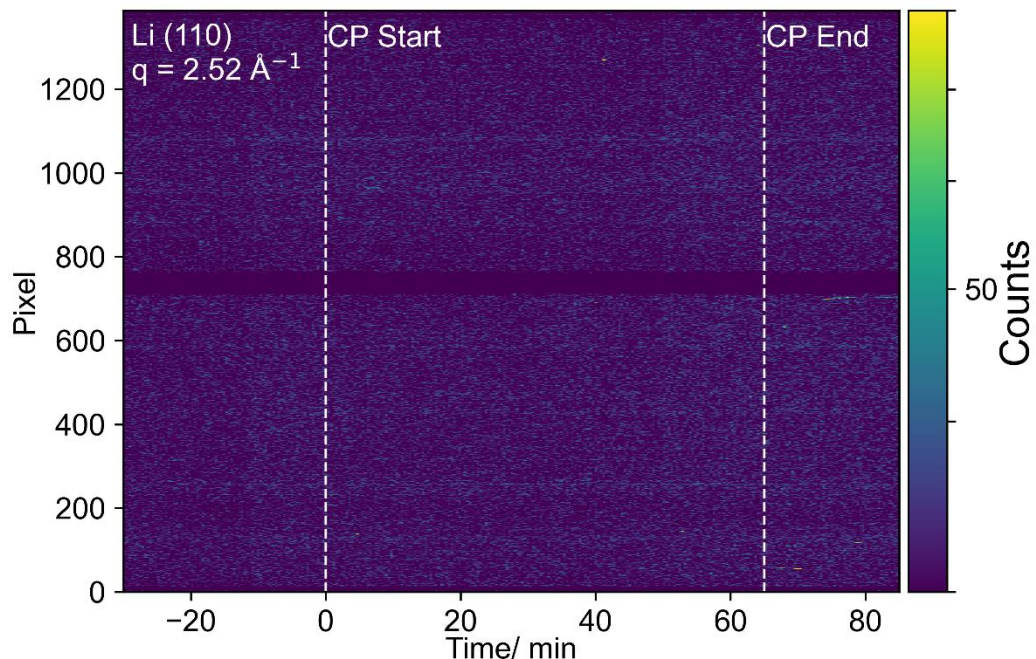


Figure S50: All pixels corresponding to the Li (110) reflection ($q = 2.52 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF_4 in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

5.3 LiBF_4 , no EtOH

5.3.1 Experiment 2

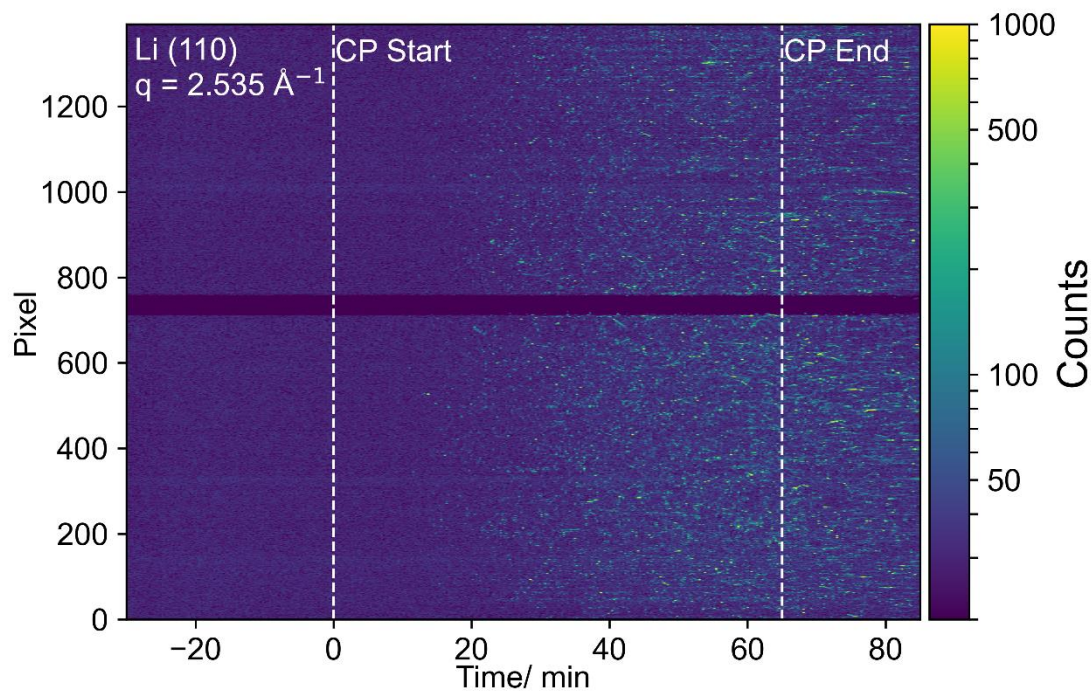


Figure S51: All pixels corresponding to the Li (110) reflection ($q = 2.535 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF_4 in THF with 0 vol% EtOH was used as electrolyte.

5.4 LiBF₄, 1 vol% EtOH

5.4.1 Experiment 1

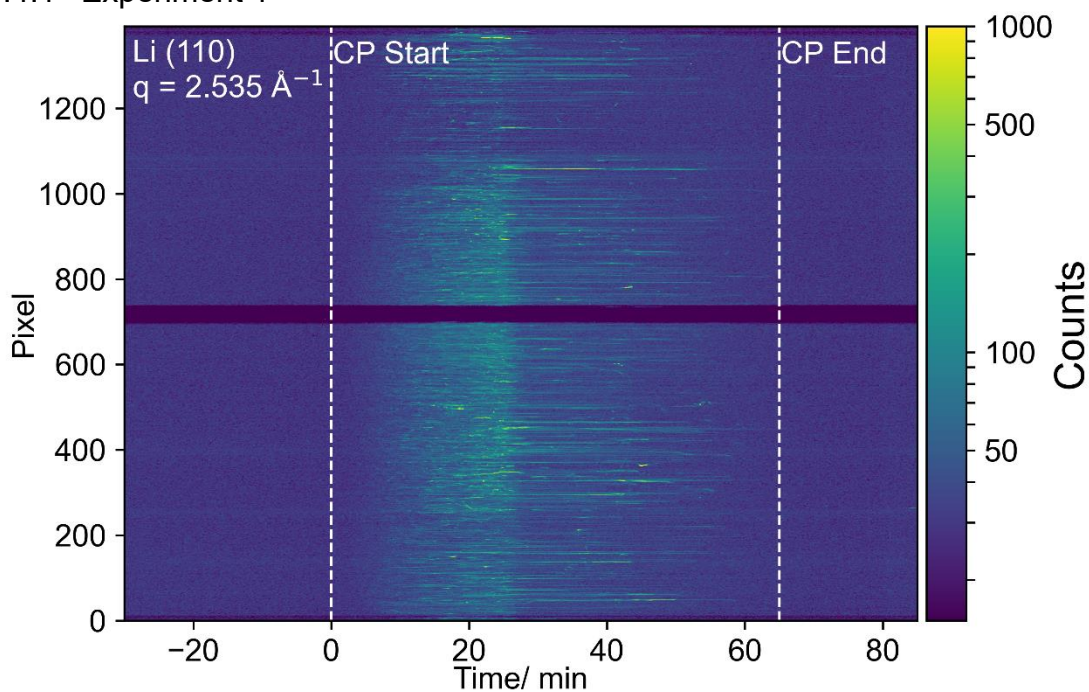


Figure S52: All pixels corresponding to the Li (110) reflection ($q = 2.535 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 1 vol% EtOH was used as electrolyte.

5.4.2 Experiment 2

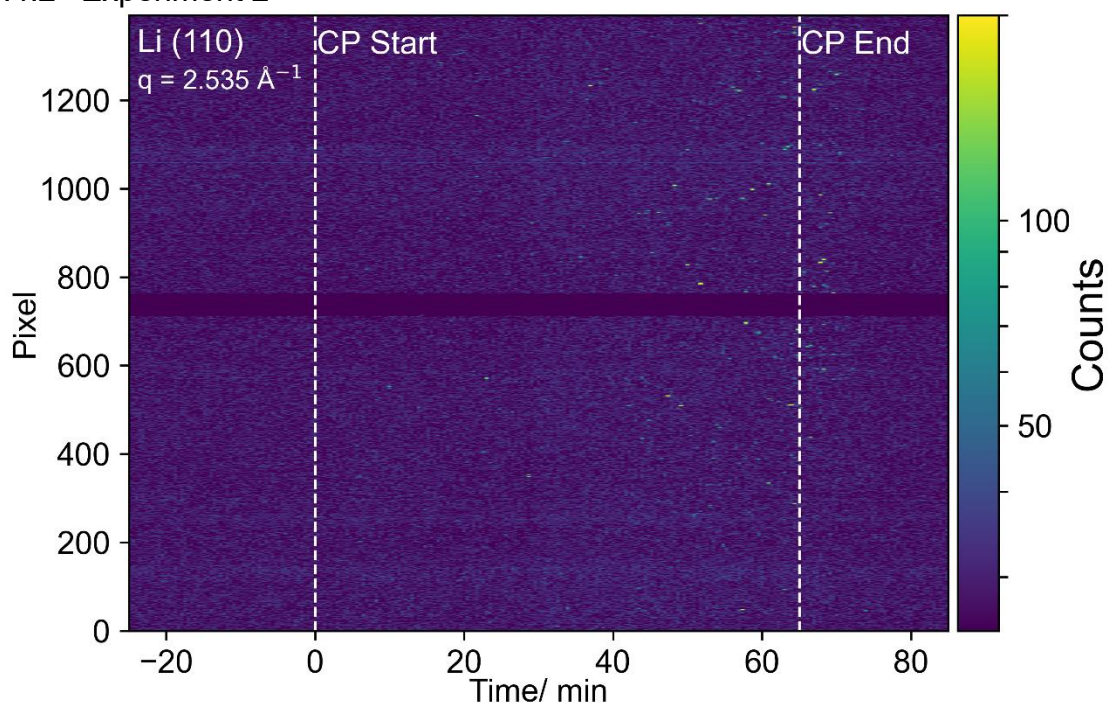


Figure S53: All pixels corresponding to the Li (110) reflection ($q = 2.535 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 1 vol% EtOH was used as electrolyte.

6 Time development plots LiF

6.1 LiBF₄, no EtOH

6.1.1 Experiment 1

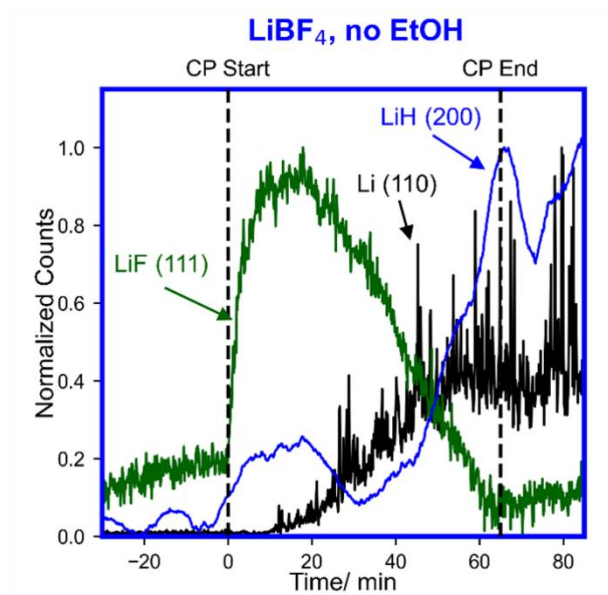


Figure S54: Time development of peak intensities corresponding to the Cu (111), Li (110) and LiF(111) reflections when using LiBF₄ with 0 vol% EtOH in the electrolyte.

6.1.2 Experiment 2

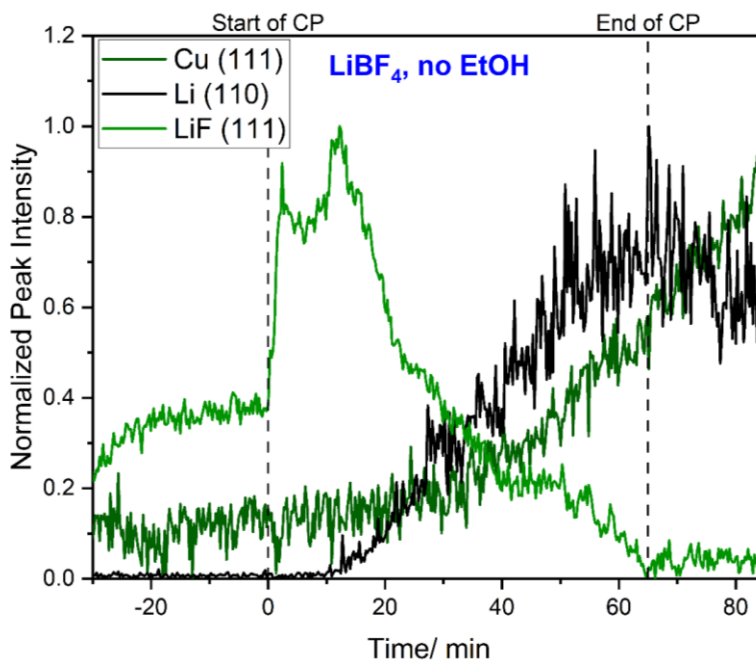


Figure S55: Time development of peak intensities corresponding to the Cu (111), Li (110) and LiF(111) reflections when using LiBF₄ with 0 vol% EtOH in the electrolyte.

6.2 LiBF₄, 1 vol% EtOH

6.2.1 Experiment 1

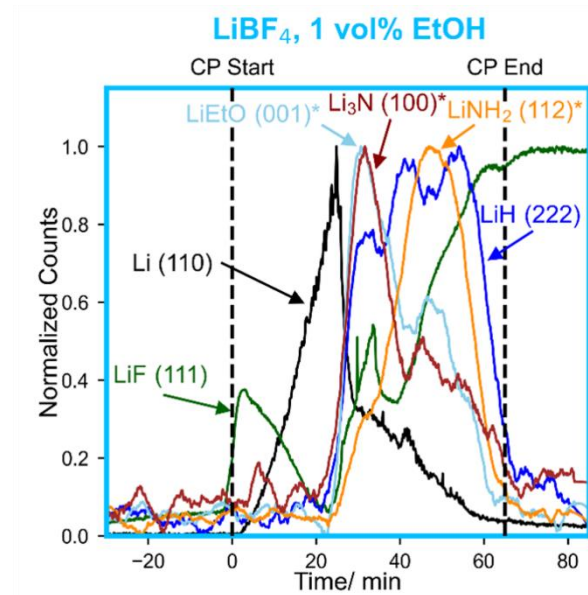


Figure S56: Time development of peak intensities corresponding to observed species and reaction intermediates when using LiBF₄ with 1 vol% EtOH in the electrolyte.

6.2.2 Experiment 2

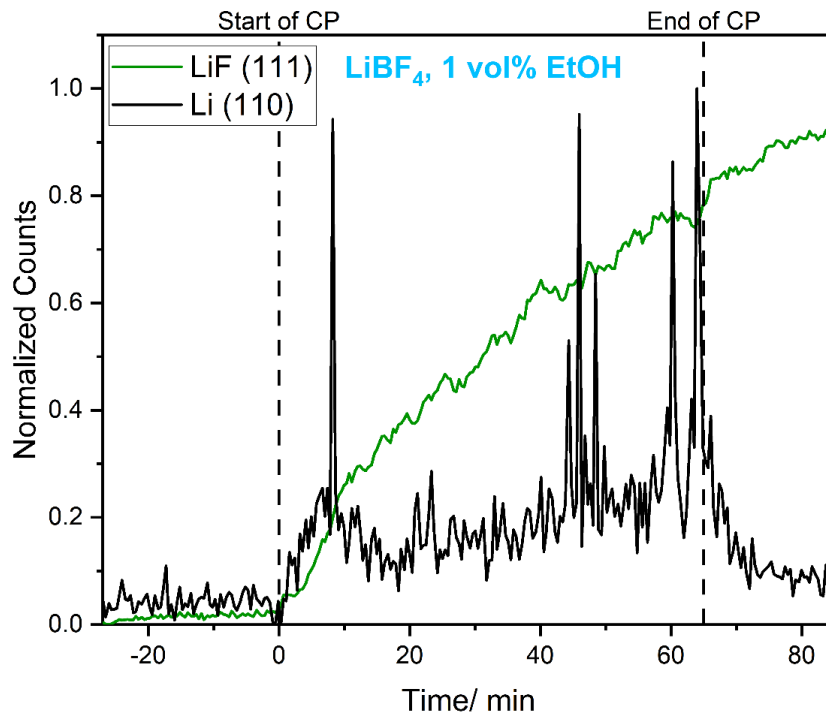


Figure S57: Time development of peak intensities corresponding to observed species and reaction intermediates when using LiBF₄ with 1 vol% EtOH in the electrolyte.

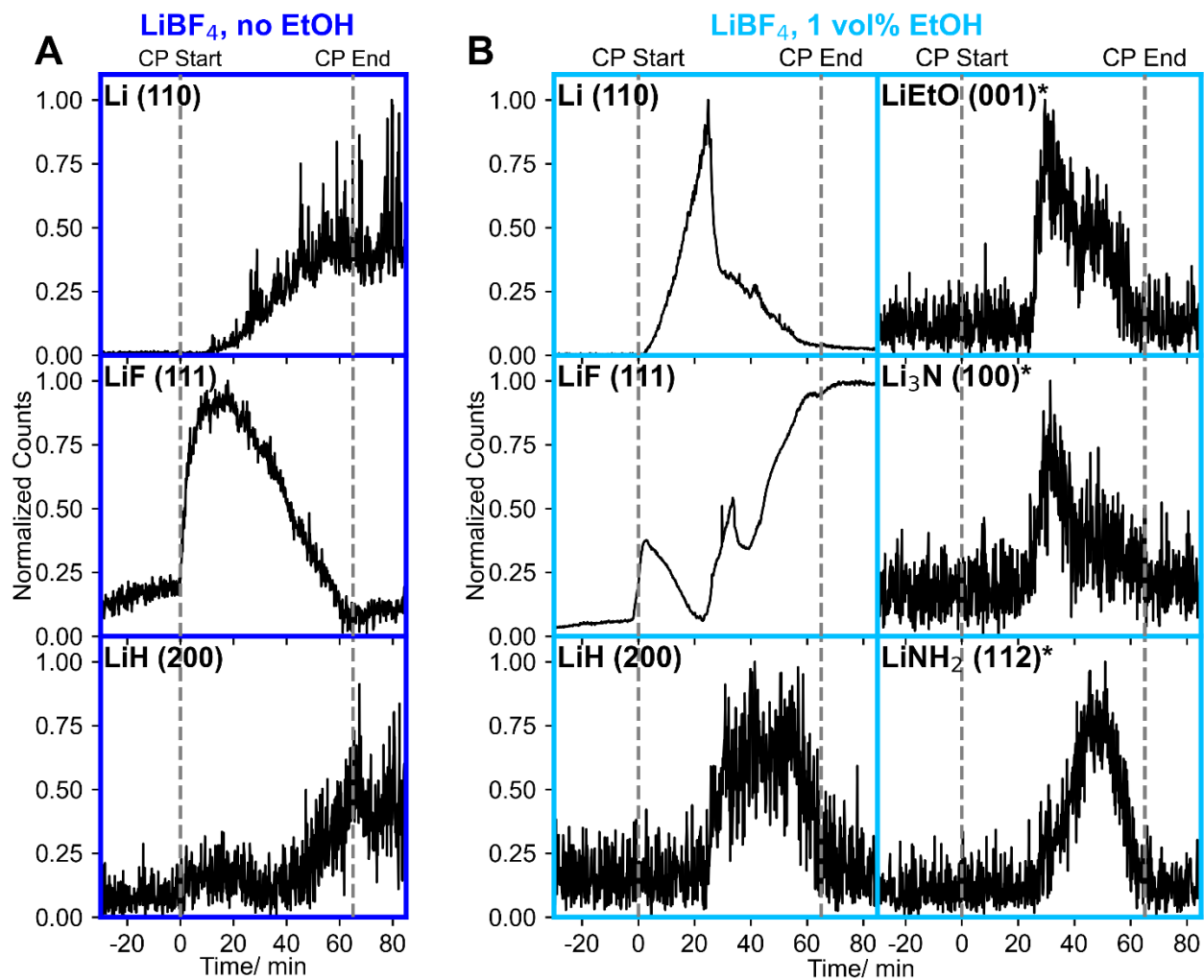


Figure S58: Time development of peak intensities corresponding to observed species and reaction intermediates when using LiBF₄ with 1 vol% EtOH or no EtOH in the electrolyte. Raw data.

7 Detector Pixel vs. Time Plots LiF

7.1 LiBF₄, no EtOH

7.1.1 Experiment 1

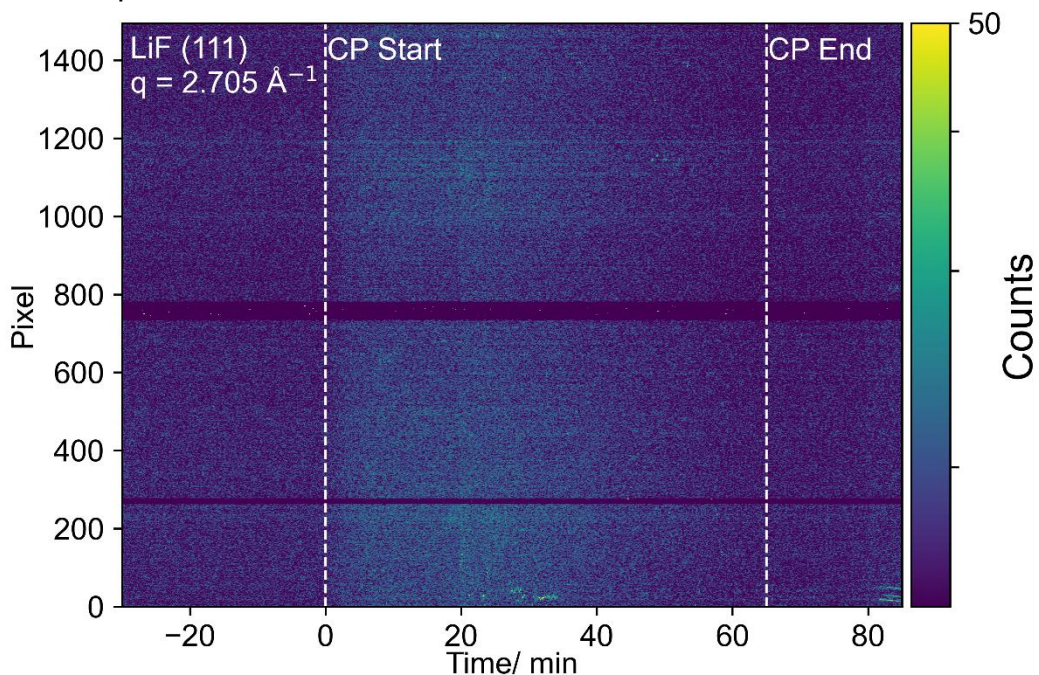


Figure S59: All pixels corresponding to the LiF (111) reflection ($q = 2.705 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 0 vol% EtOH was used as electrolyte.

7.1.2 Experiment 2

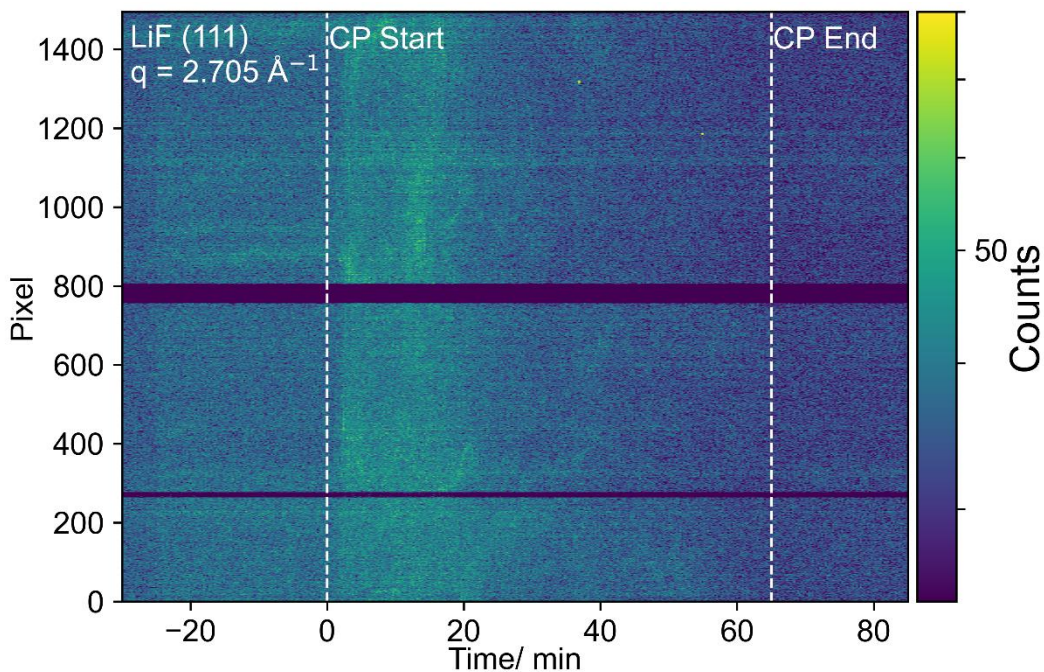


Figure S60: All pixels corresponding to the LiF (111) reflection ($q = 2.705 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 0 vol% EtOH was used as electrolyte.

7.2 LiBF₄, 1 vol% EtOH

7.2.1 Experiment 2

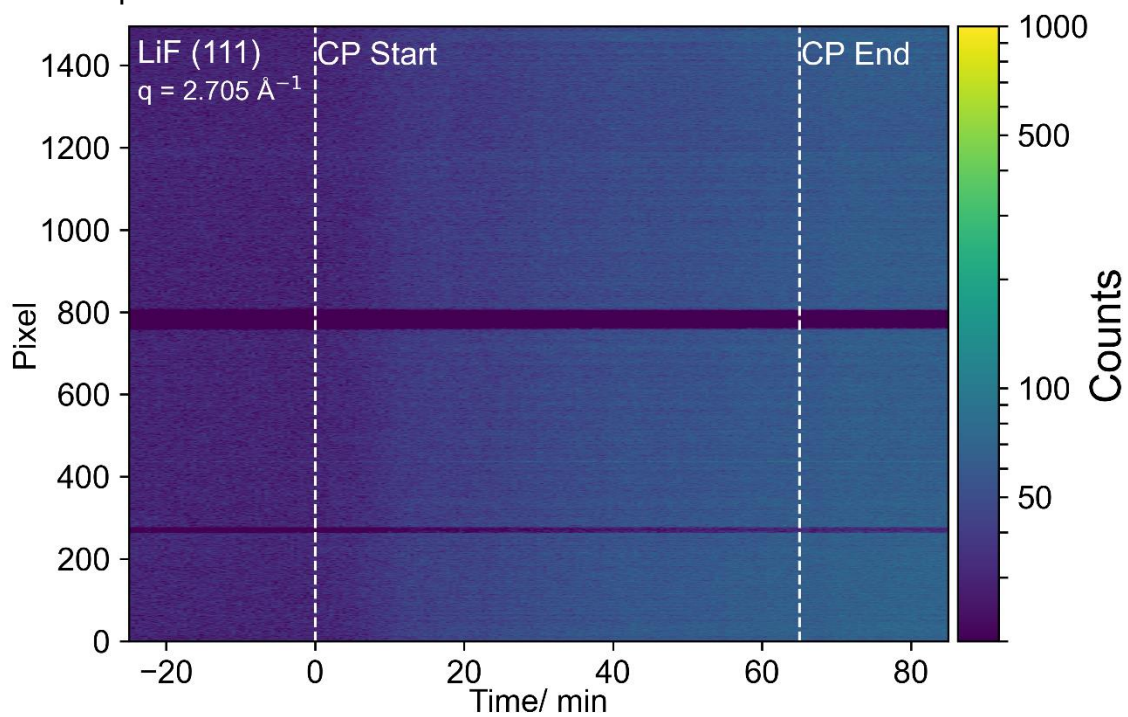


Figure S61: All pixels corresponding to the LiF (111) reflection ($q = 2.705 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 1 vol% EtOH was used as electrolyte.

8 Time development plots LiH

8.1 LiClO₄, no EtOH

8.1.1 Experiment 1

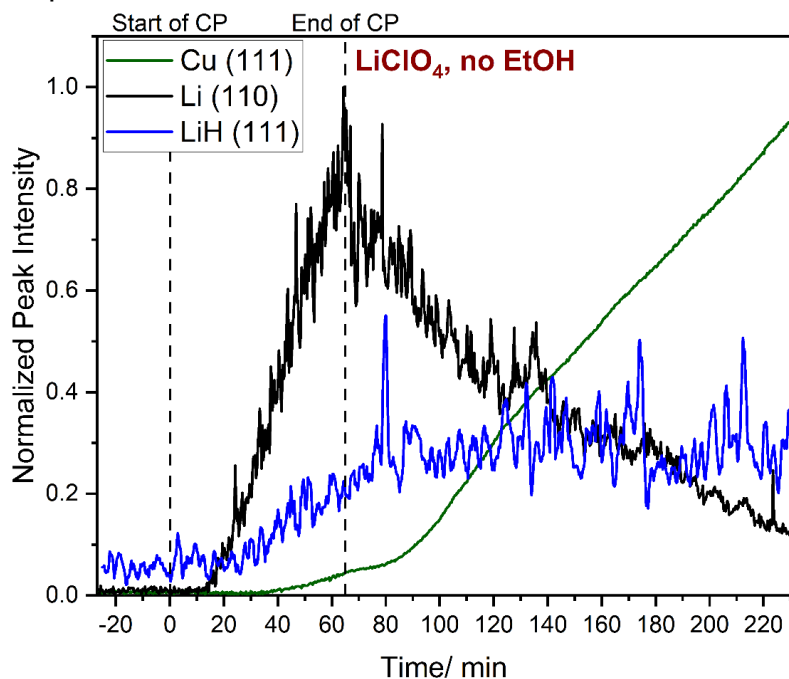


Figure S62: Time development of peak intensities corresponding to the Cu (111), Li (110) and LiH (111) reflections when using LiBF₄ with 0 vol% EtOH in the electrolyte. The LiH trace was smoothed by running averages over 5 values.

8.1.2 Experiment 2

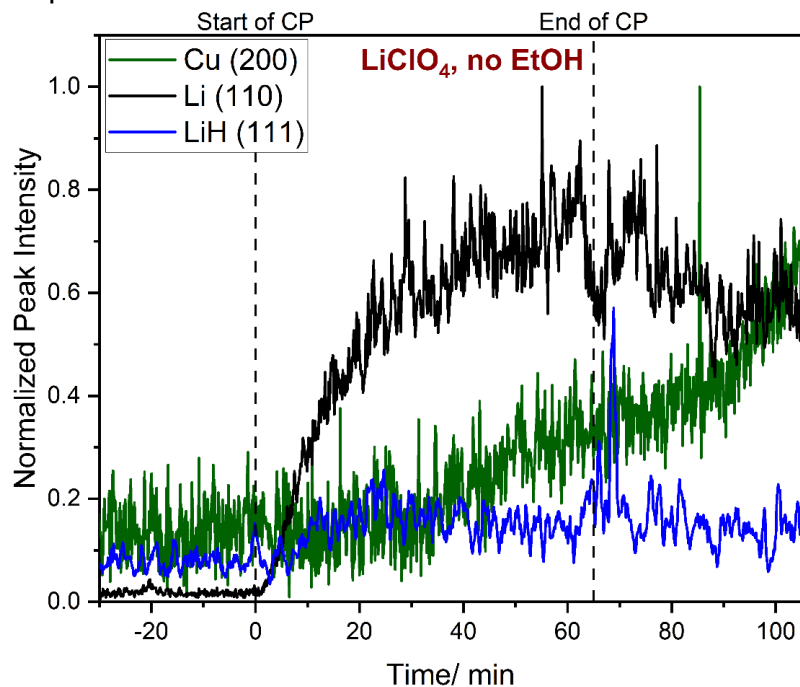


Figure S63: Time development of peak intensities corresponding to the Cu (200), Li (110) and LiH (111) reflections when using LiBF₄ with 0 vol% EtOH in the electrolyte. The LiH trace was smoothed by running averages over 5 values.

9 Discussion of Peak assignment

Lithium Ethoxide (LiEtO)

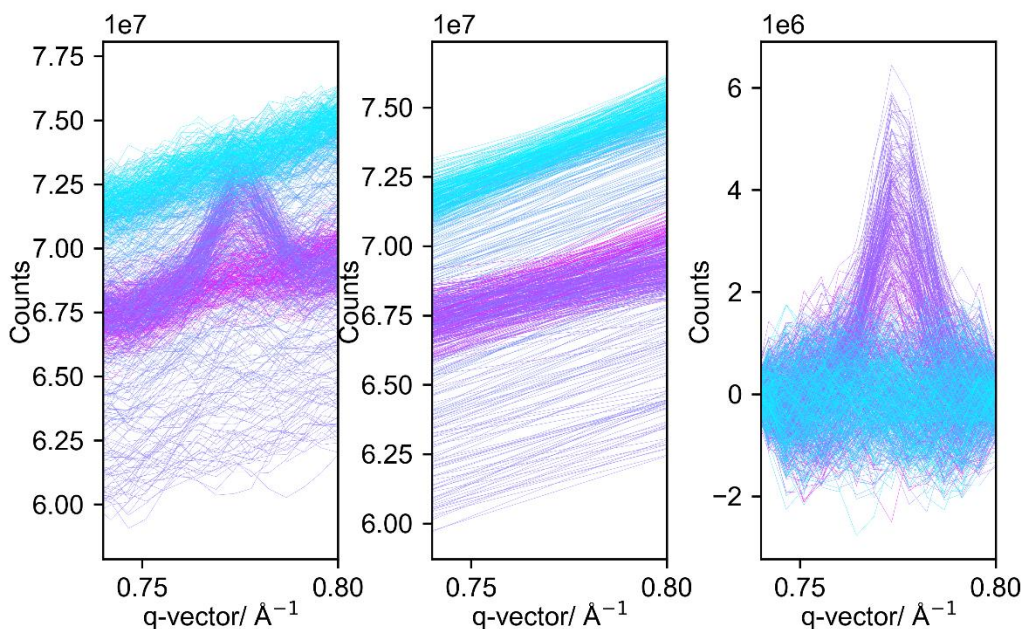


Figure S64: left: GI-WAXS Data. Middle: Approximated linear background that is subtracted from the GI-WAXS Data. Right: Resulting data.

The peak attributed to LiEtO is shown in Figure S64. As the background changes throughout the experiment, it is necessary to subtract a background to evaluate the time development of the actual peak. Therefore, a linear background was approximated by first selecting a q -range around the peak in which the background is roughly linear. Then the first 5 and last 5 data points in that range were averaged and the straight line connecting the resulting point was calculated. This linear background approximation was then subtracted from the raw data. The time development was evaluated on the resulting peak.

In Figure S65, a 2D detector image showing the faint signal at 0.775 \AA^{-1} . However, due to the low intensity it was necessary to sum 30 consecutive measurements to make the signal visible in the image. The signal is visible as a ring and thus suggests that it is coming from a polycrystalline compound. Therefore, other refraction signals with a similar time behavior should be visible. In Figure S2 reference powder XRD patterns are shown. Here a peak at 0.425 \AA^{-1} can be seen. This peak was not detected in the synchrotron experiments as this q -range is covered by the beam stop. In the reference pattern, recorded using a PEEK dome to avoid air exposure, stronger signals are observed at 1.480 \AA^{-1} and 1.889 \AA^{-1} . However, these peaks cannot be seen in the pattern recorded in air, suggesting that in a reactive environment, such as the working electrode during Li-NRR, LiEtO undergoes some phase transition causing the disappearance of these peaks. The peak at 1.480 \AA^{-1} could also be an artifact as it also overlaps with the background of

the PEEK dome. However, the background of the PEEK dome, recorded under the same conditions was subtracted.

Another cause for the signal could be lithium acetate (LiAc). As shown in Figure S2 the LiAc diffractogram has two high intensity peaks around 0.775 \AA^{-1} , that could easily appear as one peak in the synchrotron experiments. However, the formation of LiAc seems unlikely in the LiBF_4 system as no easily available oxygen source is present.

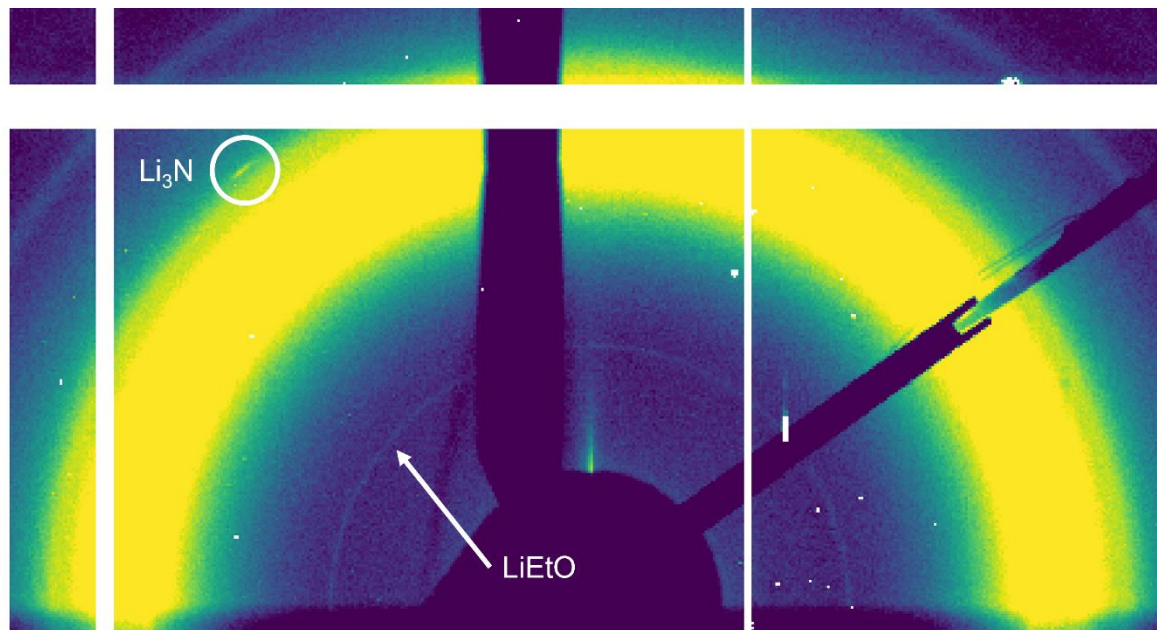


Figure S65: Sum of 30 2D detector images, showing the signals attributed to LiEtO and Li_3N .

Lithium Nitride (Li₃N)

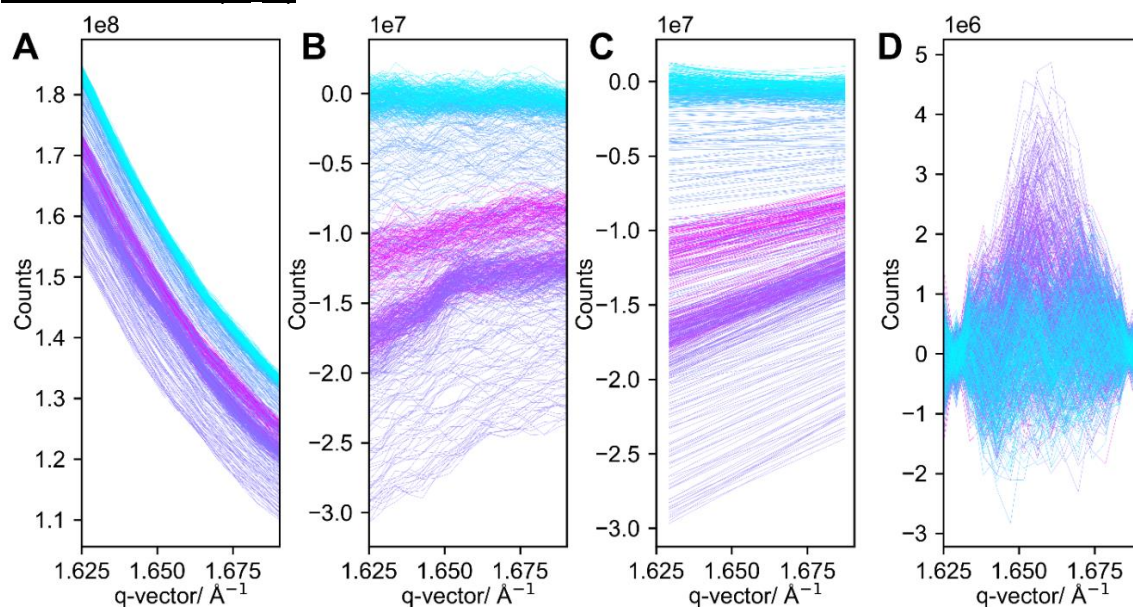


Figure S66: A: Integrated GI-WAXS data. B: Integrated GI-WAXS data with the average of the first 5 frames subtracted. C: Approximated linear background that is subtracted from the GI-WAXS Data. D: Resulting data.

As the peak attributed to Li₃N overlaps with the signal caused by the electrolyte, the average of the first 5 measurements was subtracted from the original data. Due to the changing background, a linear background was then subtracted in the same way described for LiEtO. This procedure is similar to what has been done in previous work, where a peak at this q-vector was attributed to the Li₃N (100) reflection expected at 1.620 \AA^{-1} , stating that the (100) reflection is too low in intensity to be observed.⁶ Figure S65 clearly shows that here the signal attributed to Li₃N arises from only a single spot on the detector, which explains the concurrent absence of other reflections. Another peak shown in Figure S67 was observed during the LSV at 2.023 \AA^{-1} , which is close to the expected q-vector of the (100) reflection of Li₃N. However, the time development of the peak shows that it is only present during the LSV and therefore probably related to a different unidentified species. A peak at the same position was also observed in both experiments using LiBF₄ without EtOH (Fig. S63, S7) but in none of the experiments using LiClO₄.

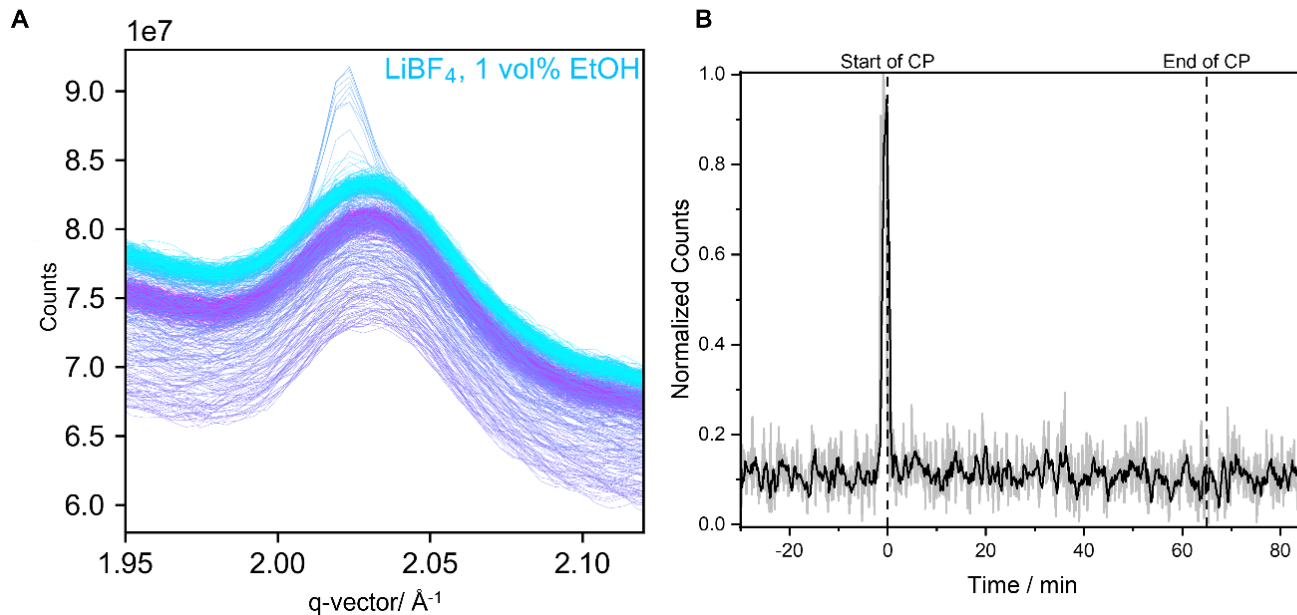


Figure S67: A: Integrated Gi-WAXS data of an unidentified peak. B: Time development of the maximum intensity in the shown q-range, smoothed by running averages over 5 values (black) and raw data (gray).

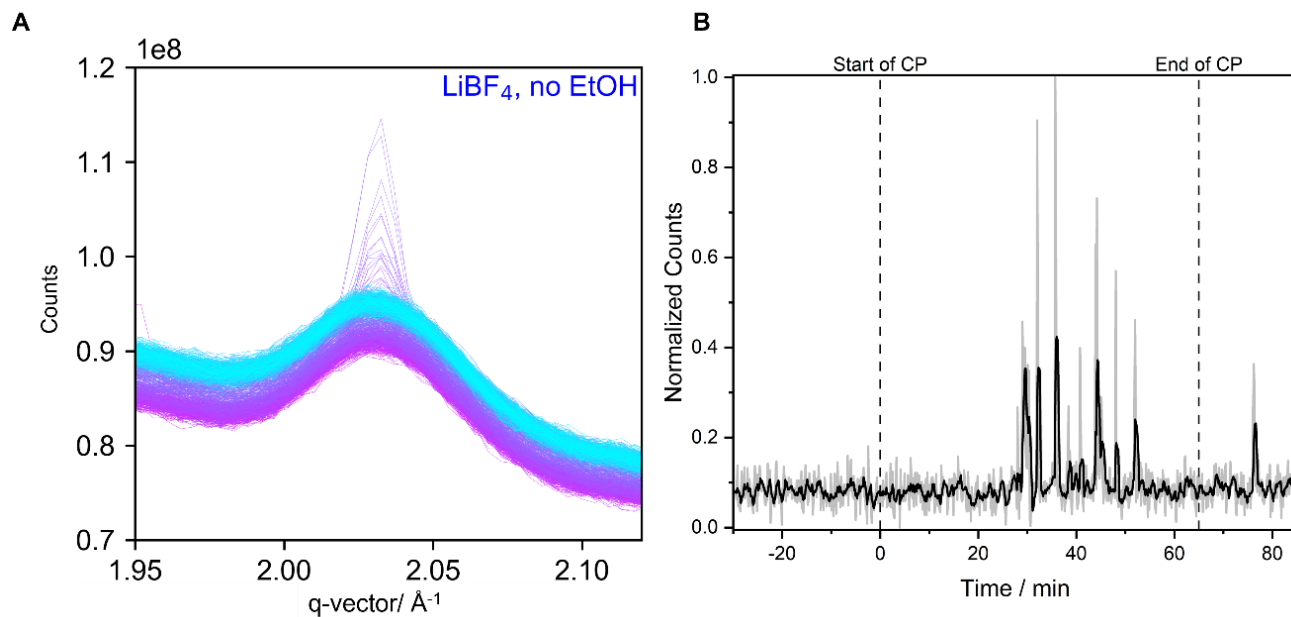


Figure S68: A: Integrated Gi-WAXS data of an unidentified peak. B: Time development of the maximum intensity in the shown q-range, smoothed by running averages over 5 values (black) and raw data (gray).

Lithium Amide (LiNH_2) / Lithium Imide (Li_2NH)

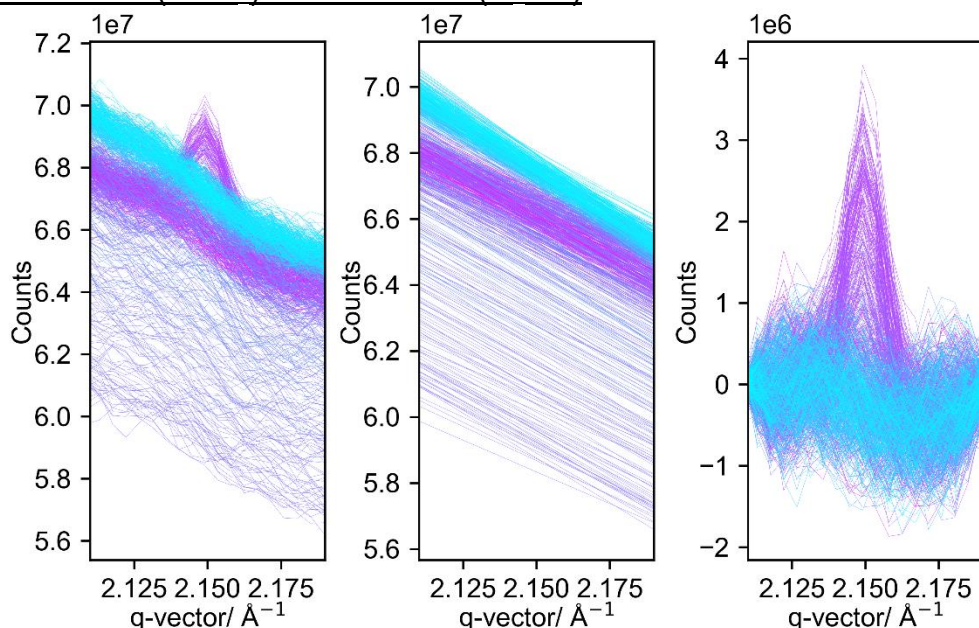


Figure S69: left: GI-WAXS Data. Middle: Approximated linear background that is subtracted from the GI-WAXS Data. Right: Resulting data.

Due to the changing background, a linear background was subtracted in the same way as described for LiEtO .

The peak was attributed to either the (222) reflection of Li_2NH or the (112) reflection of LiNH_2 based on reference spectra shown in Figure S2. As other peaks in the reference spectra have significantly lower intensities than the aforementioned peaks, especially in the case of LiNH_2 , it is reasonable that this is the only peak observed in the experiment. As the observed peak already has a low intensity, other peaks likely have too low intensities to be observed. This also suggests that the signal is caused by LiNH_2 rather than Li_2NH . However, no clear distinction can be made.

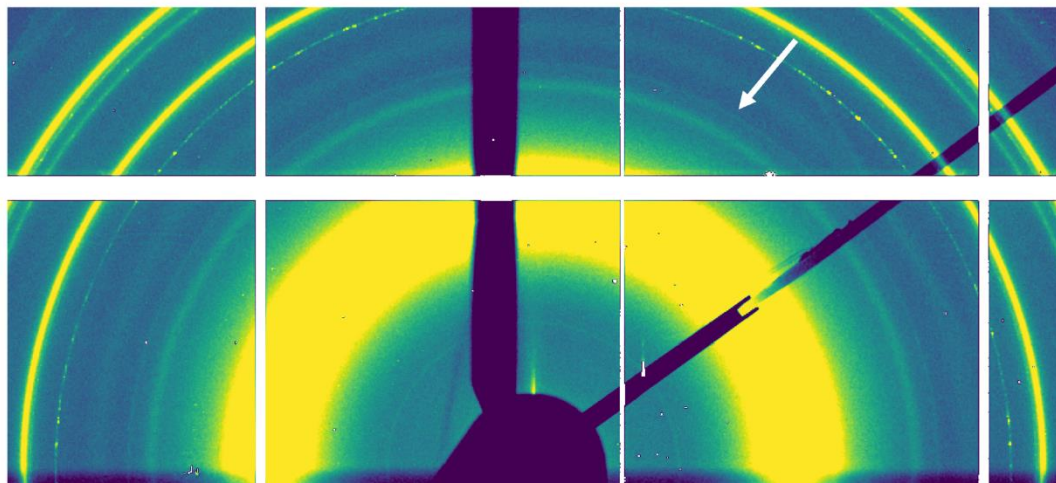


Figure S70: Sum of 30 2D detector images, showing the signal attributed to LiNH_2 .

10 XPS data

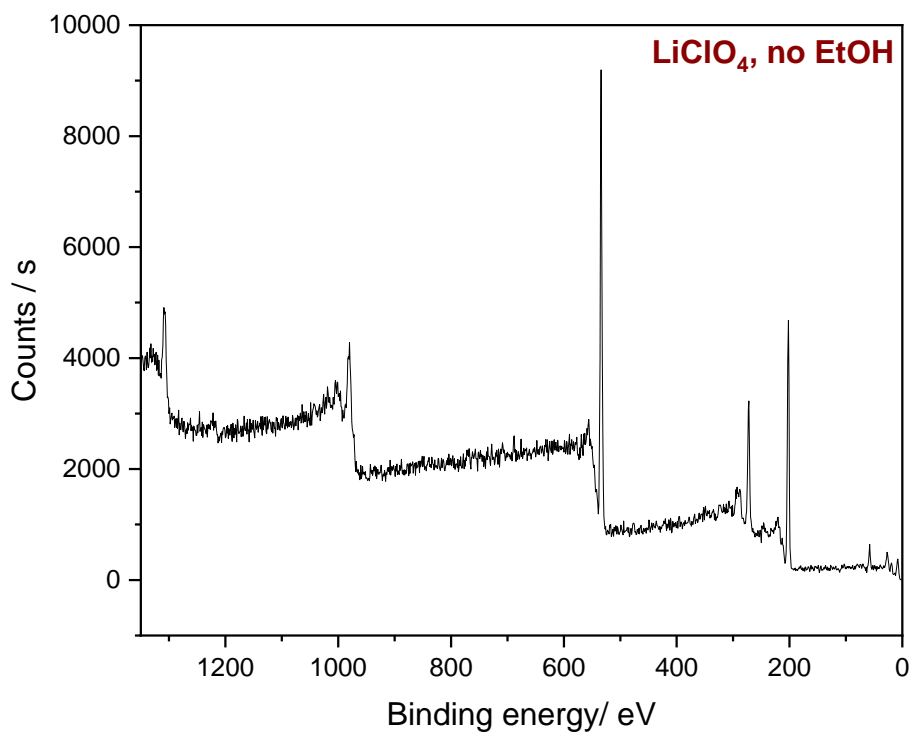


Figure S71: Survey XPS spectrum of the SEI after a Li-NRR experiment. Experiments were run in a glovebox and samples were transferred to the XPS in a transport system described in ⁷ without being exposed to air. A 1 M solution of LiClO₄ in THF with 0 vol% EtOH was used as electrolyte.

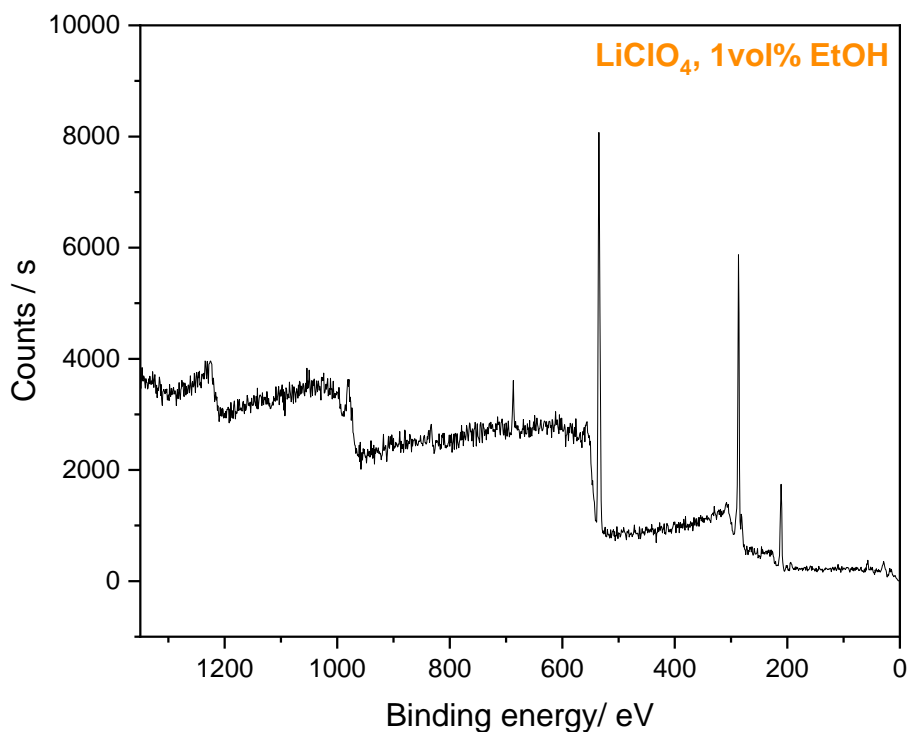


Figure S72: Survey XPS spectrum of the SEI after a Li-NRR experiment. Experiments were run in a glovebox and samples were transferred to the XPS in a transport system described in ⁷ without being exposed to air. A 1 M solution of LiClO₄ in THF with 1 vol% EtOH was used as electrolyte.

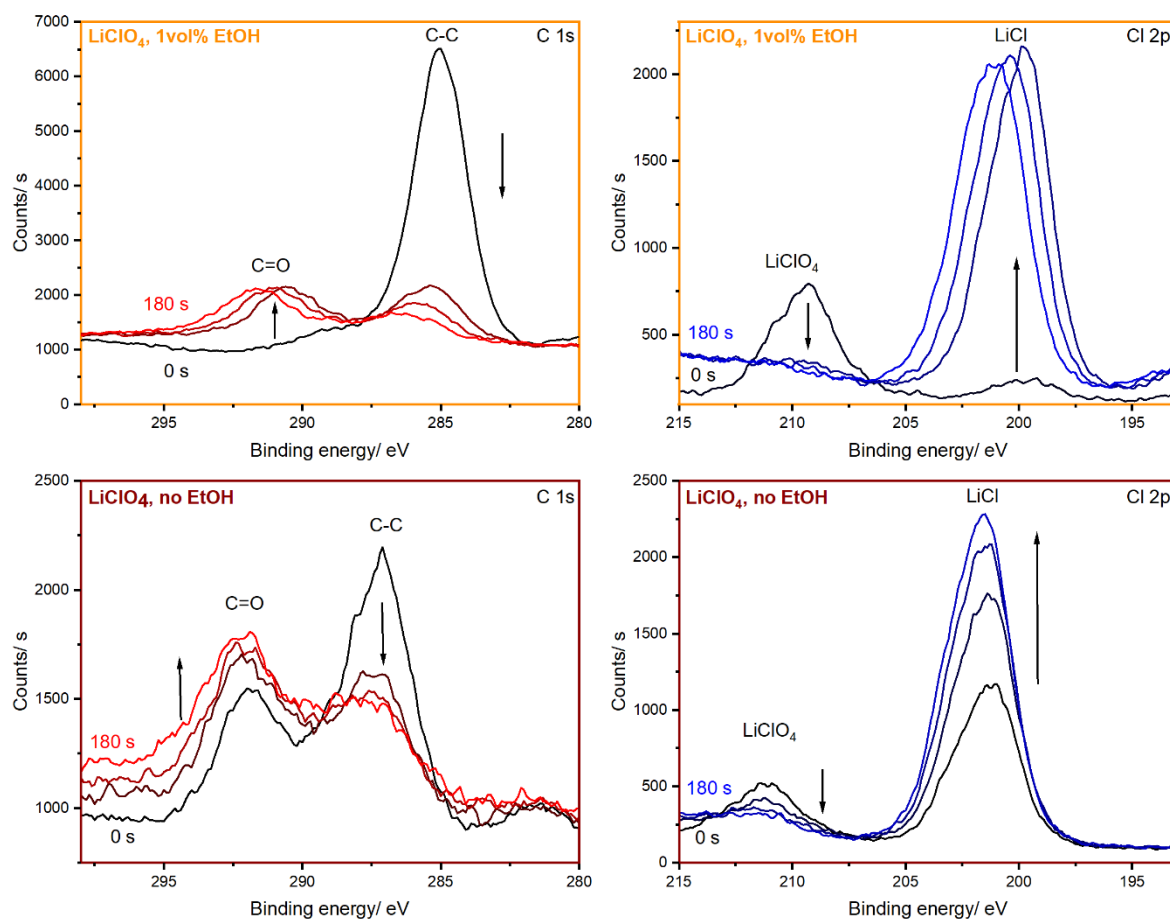


Figure S73: Depth profiling XPS spectra of the SEI after a Li-NRR experiment. Experiments were run in a glovebox and samples were transferred to the XPS in a transport system described in ⁷ without being exposed to air. A 1 M solution of LiClO₄ in THF with or without EtOH was used as electrolyte.

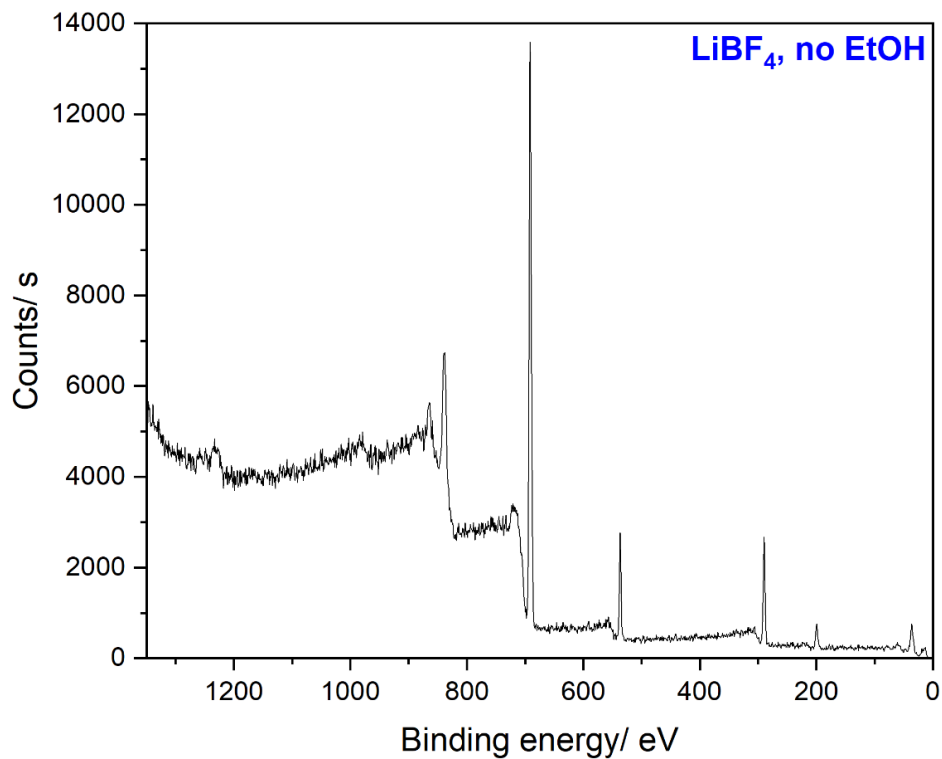


Figure S74: Survey XPS spectrum of the SEI after a Li-NRR experiment. Experiments were run in a glovebox and samples were transferred to the XPS in a transport system described in ⁷ without being exposed to air. A 1 M solution of LiBF₄ in THF with 0 vol% EtOH was used as electrolyte.

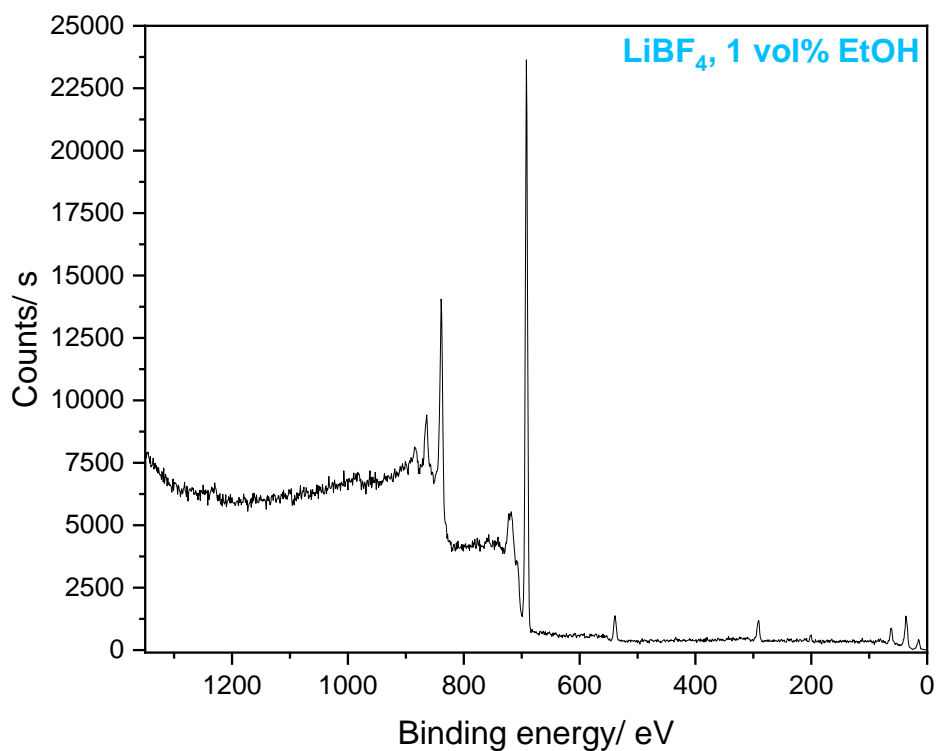


Figure S75: Survey XPS spectrum of the SEI after a Li-NRR experiment. Experiments were run in a glovebox and samples were transferred to the XPS in a transport system described in ⁷ without being exposed to air. A 1 M solution of LiBF₄ in THF with 1 vol% EtOH was used as electrolyte.

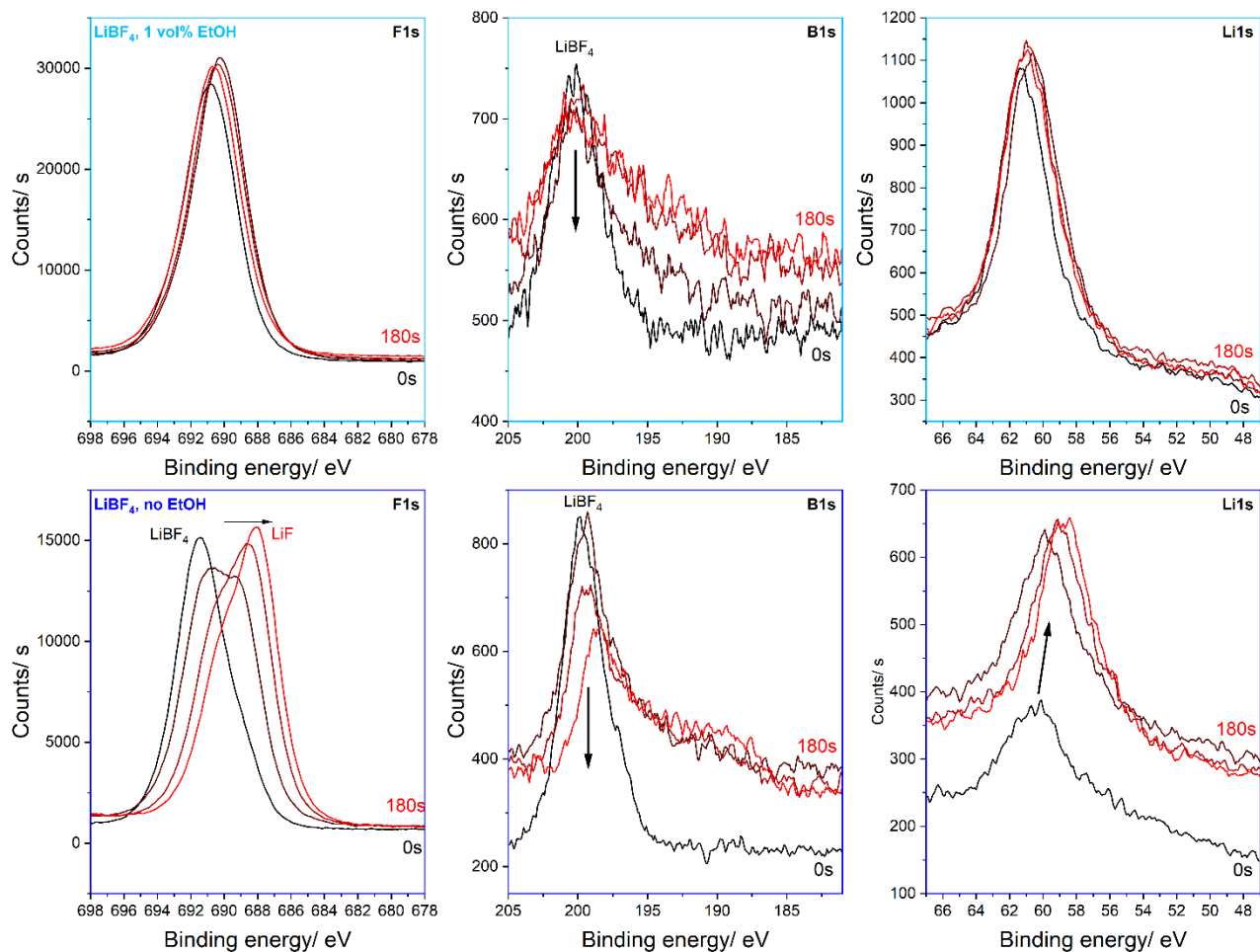


Figure S76: Depth profiling XPS spectra of the SEI after a Li-NRR experiment. Experiments were run in a glovebox and samples were transferred to the XPS in a transport system described in ⁷ without being exposed to air. A 1 M solution of LiBF₄ in THF with or without EtOH was used as electrolyte.

11 Li_2CO_3

11.1 LiClO_4 , 1vol% EtOH

11.1.1 Experiment 1

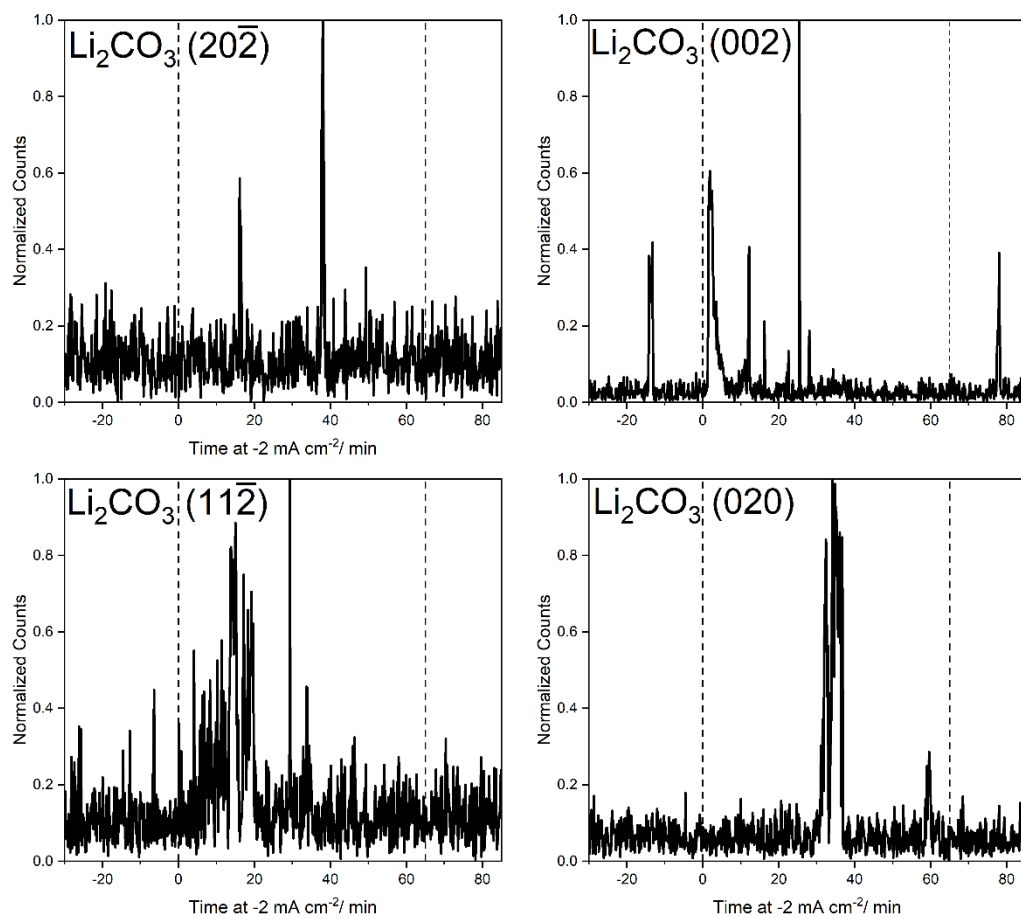


Figure S77: Time development of peak intensities corresponding to the $(20\bar{2})$, (002), $(11\bar{2})$ and (020) reflections of Li_2CO_3 when using LiClO_4 with 1 vol% EtOH in the electrolyte. Raw Data.

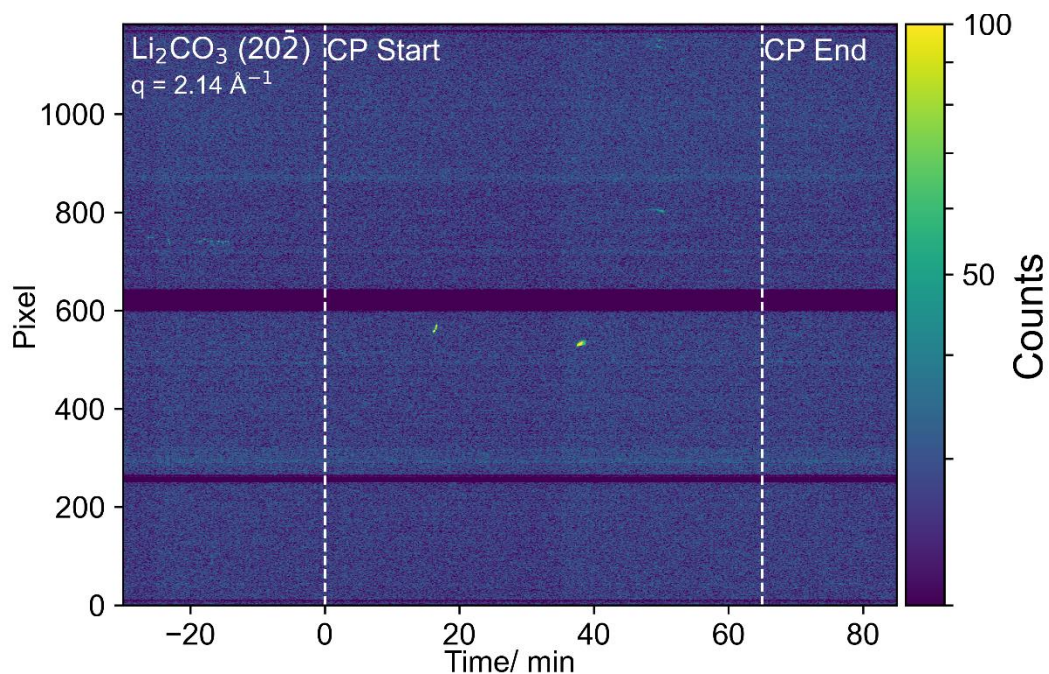


Figure S78: All pixels corresponding to the Li_2CO_3 ($20\bar{2}$) reflection ($q = 2.140 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte.

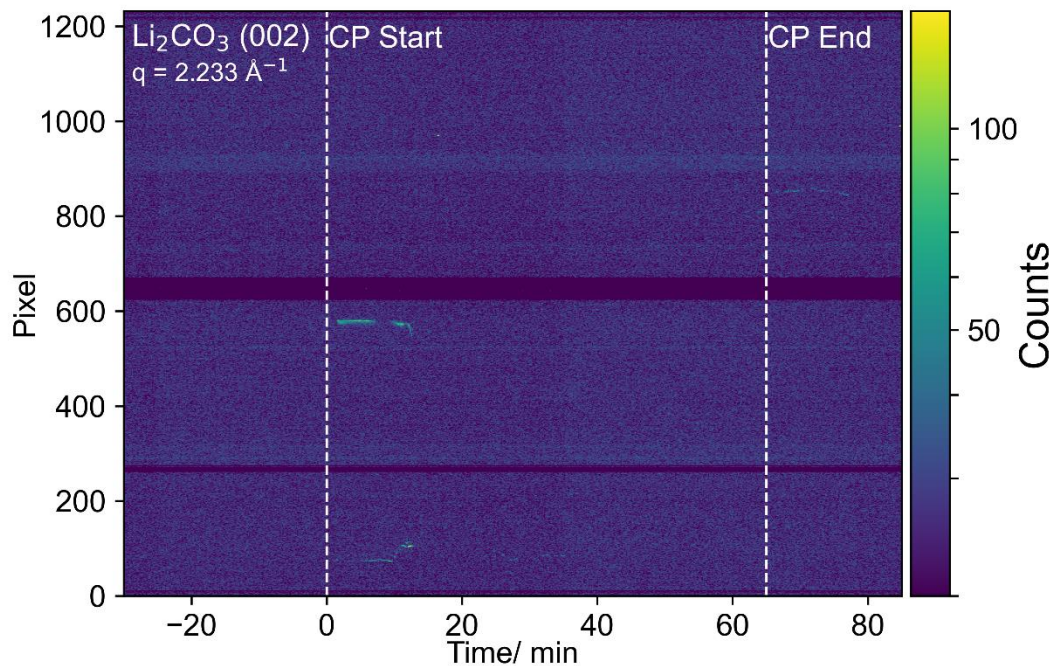


Figure S79: All pixels corresponding to the Li_2CO_3 (002) reflection ($q = 2.233 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte.

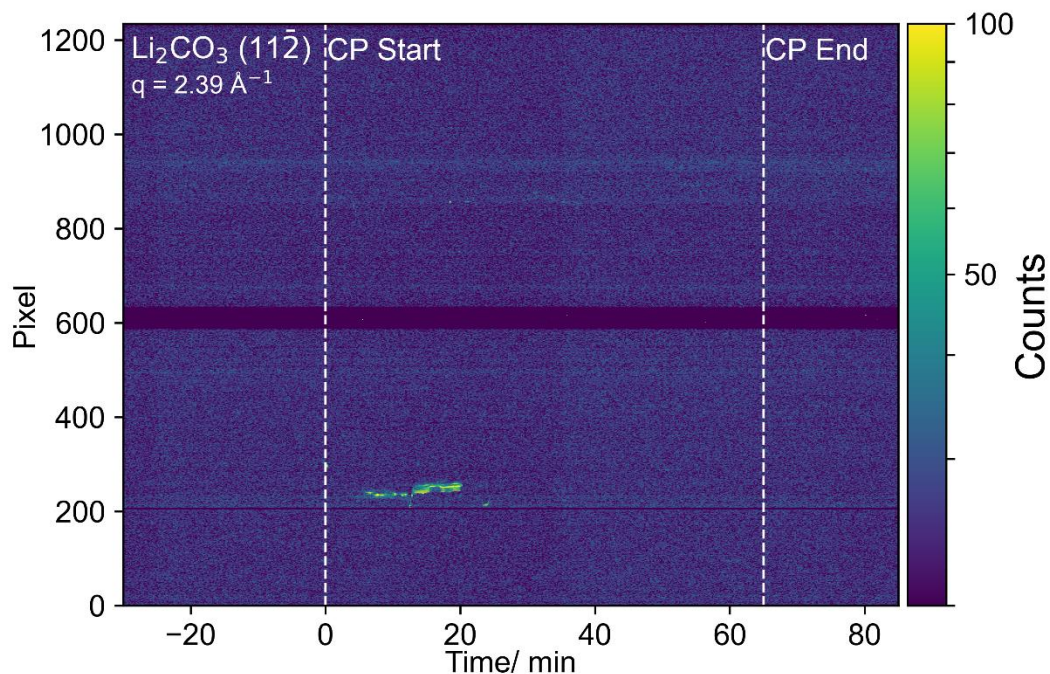


Figure S80: All pixels corresponding to the Li_2CO_3 (112) reflection ($q = 2.390 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte.

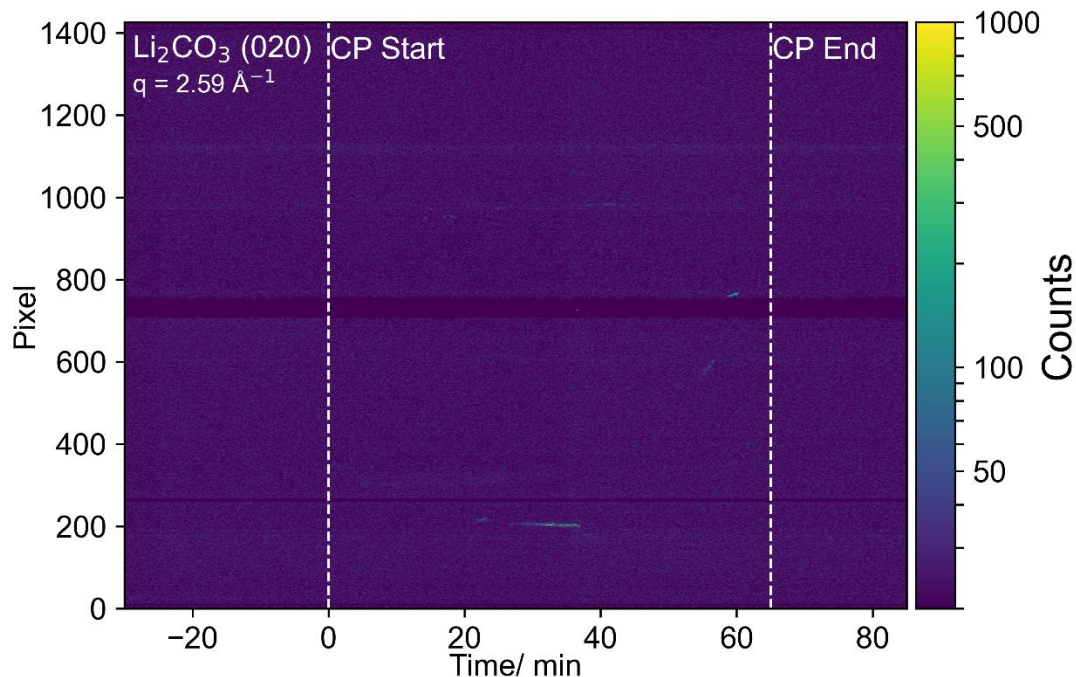


Figure S81: All pixels corresponding to the Li_2CO_3 (020) reflection ($q = 2.590 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte.

11.1.2 Experiment 2

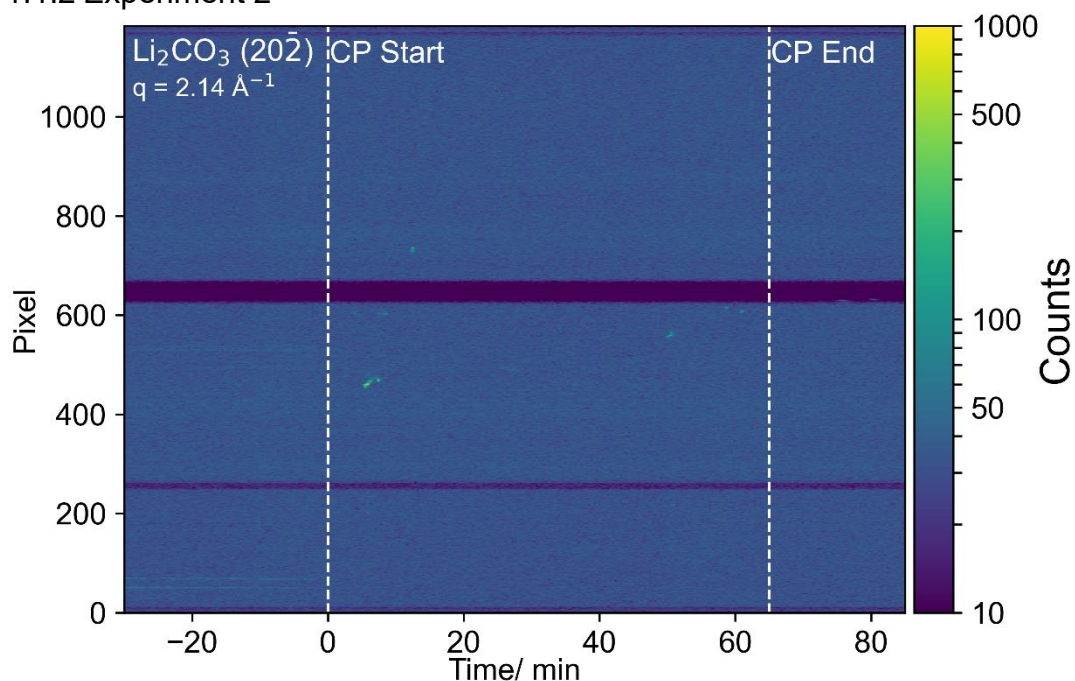


Figure S82: All pixels corresponding to the Li_2CO_3 (202) reflection ($q = 2.140 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

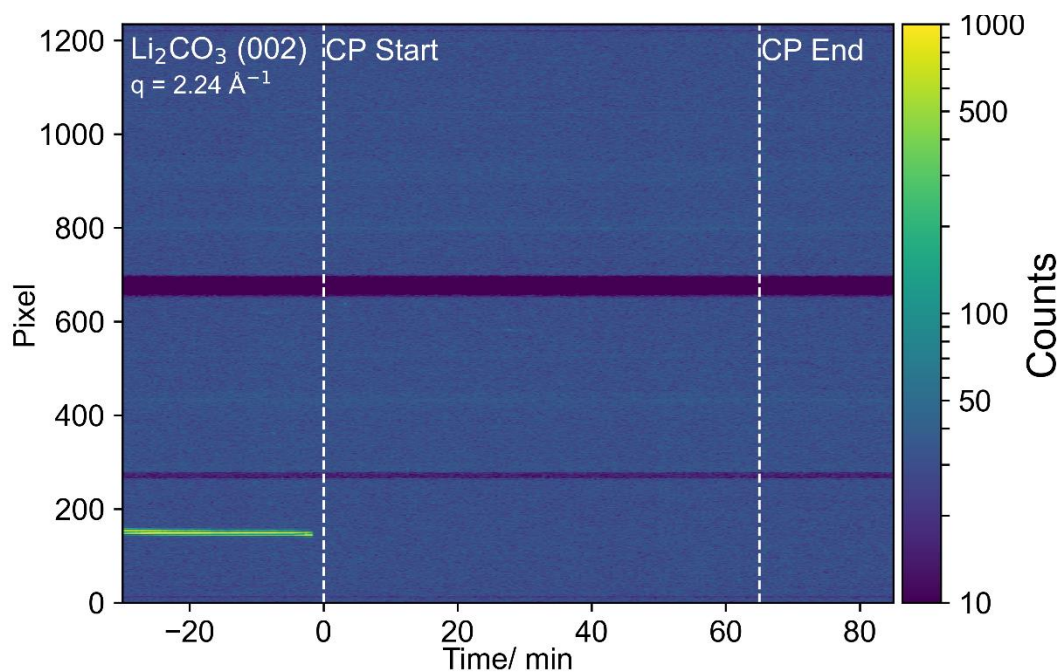


Figure S83: All pixels corresponding to the Li_2CO_3 (002) reflection ($q = 2.24 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

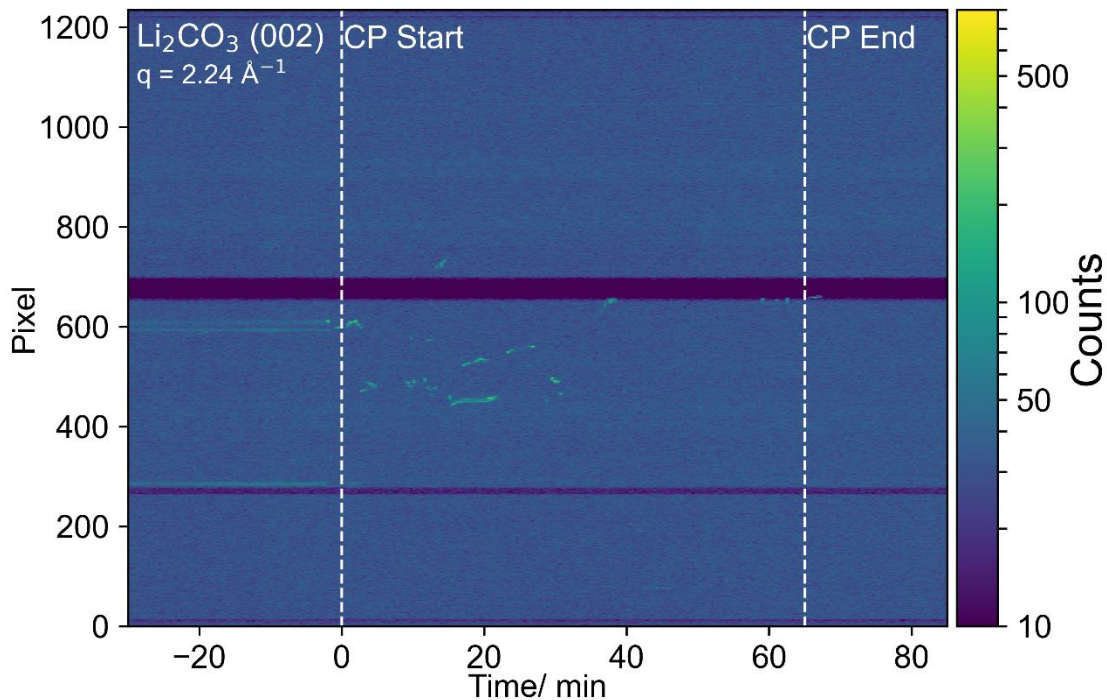


Figure S84: All pixels corresponding to the Li_2CO_3 (002) reflection ($q = 2.24 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

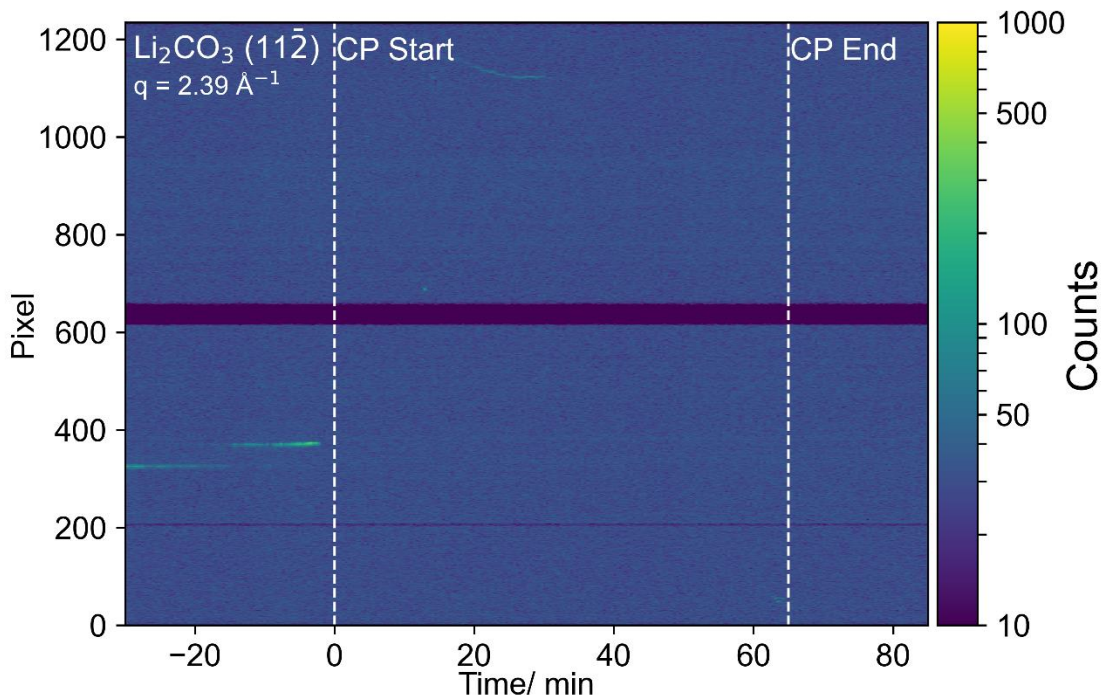


Figure S85: All pixels corresponding to the Li_2CO_3 ($11\bar{2}$) reflection ($q = 2.390 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

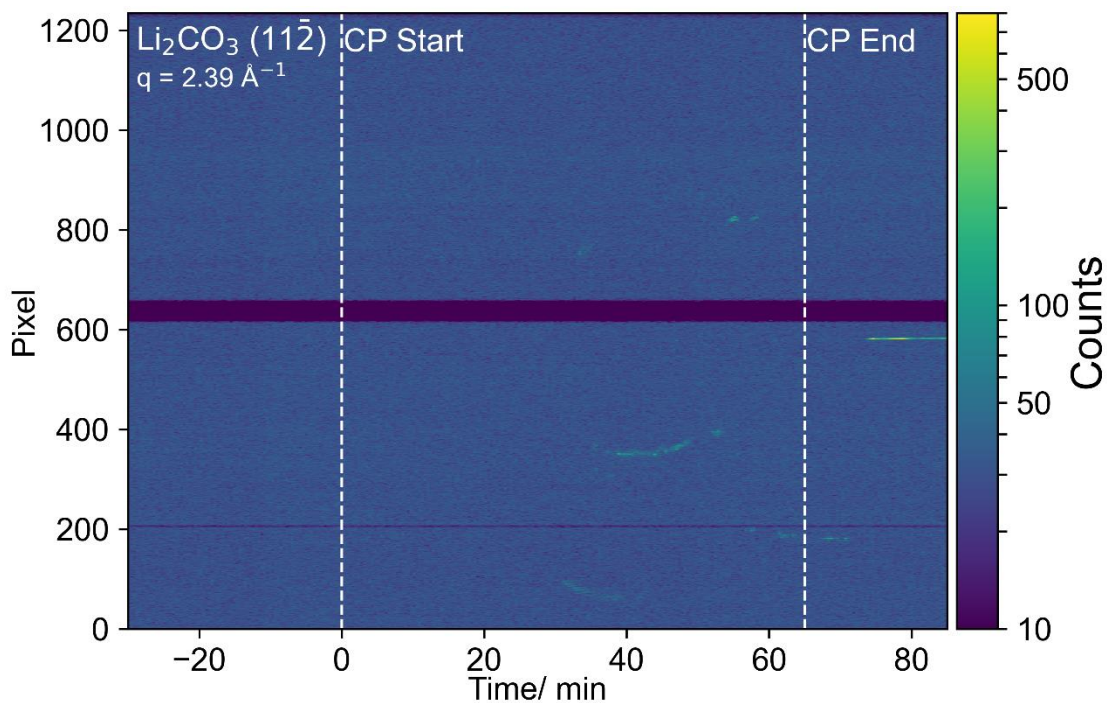


Figure S86: All pixels corresponding to the Li_2CO_3 ($11\bar{2}$) reflection ($q = 2.390 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO_4 in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

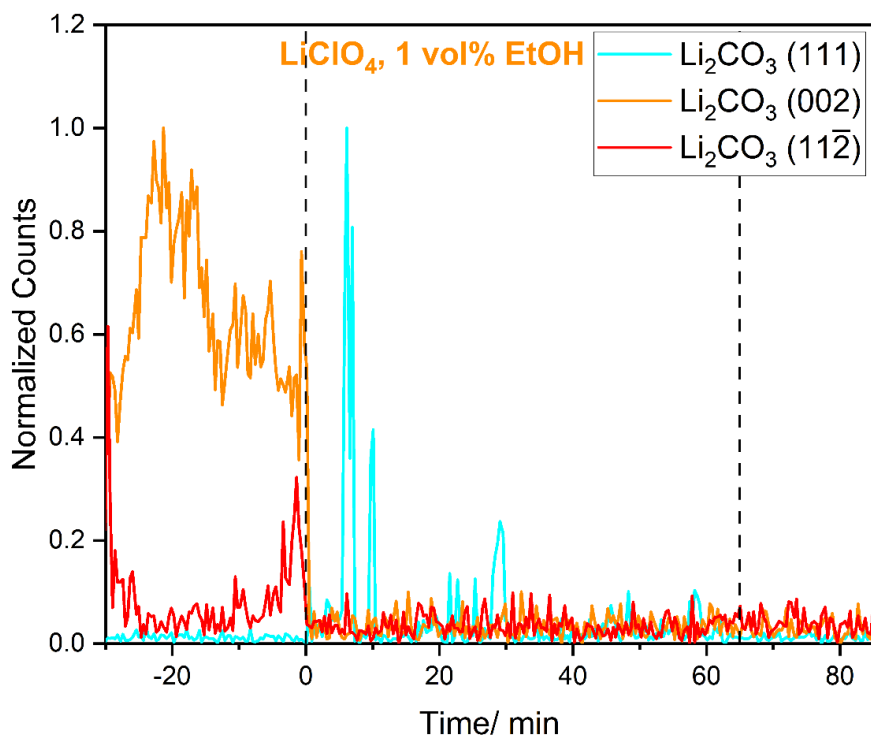


Figure S87: Time development of peak intensities corresponding to the (111), (002) and ($11\bar{2}$) reflections of Li_2CO_3 when using LiClO_4 with 1 vol% EtOH in the electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

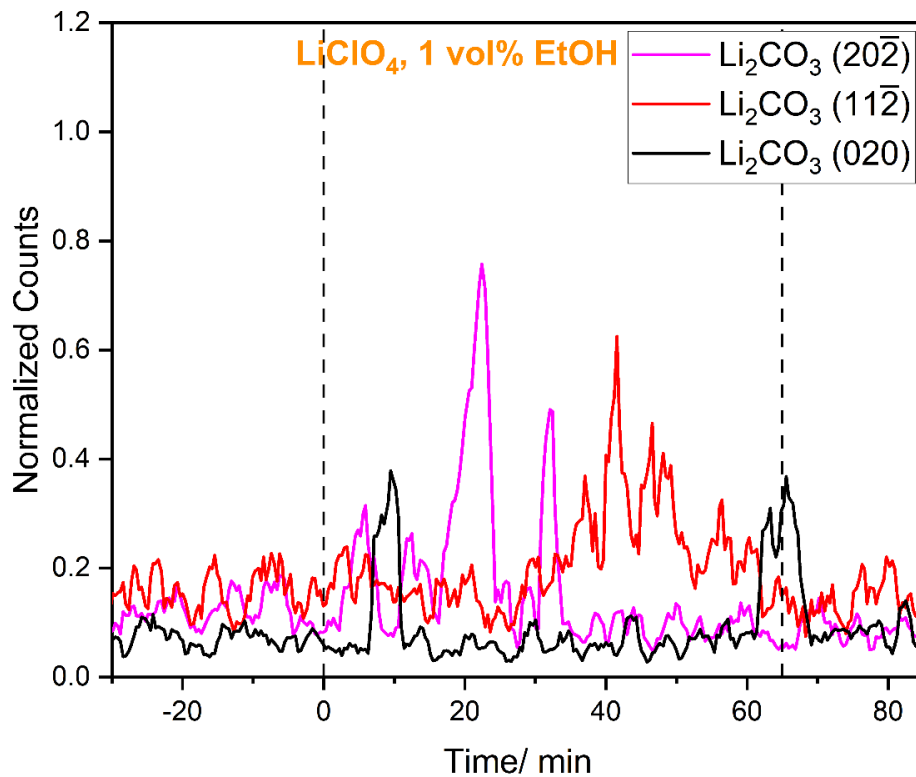


Figure S88: Time development of peak intensities corresponding to the $(20\bar{2})$, $(11\bar{2})$ and (020) reflections of Li_2CO_3 when using LiClO_4 with 1 vol% EtOH in the electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

12 Substrate Changes

12.1 LiBF₄, no EtOH

12.1.1 Experiment 1

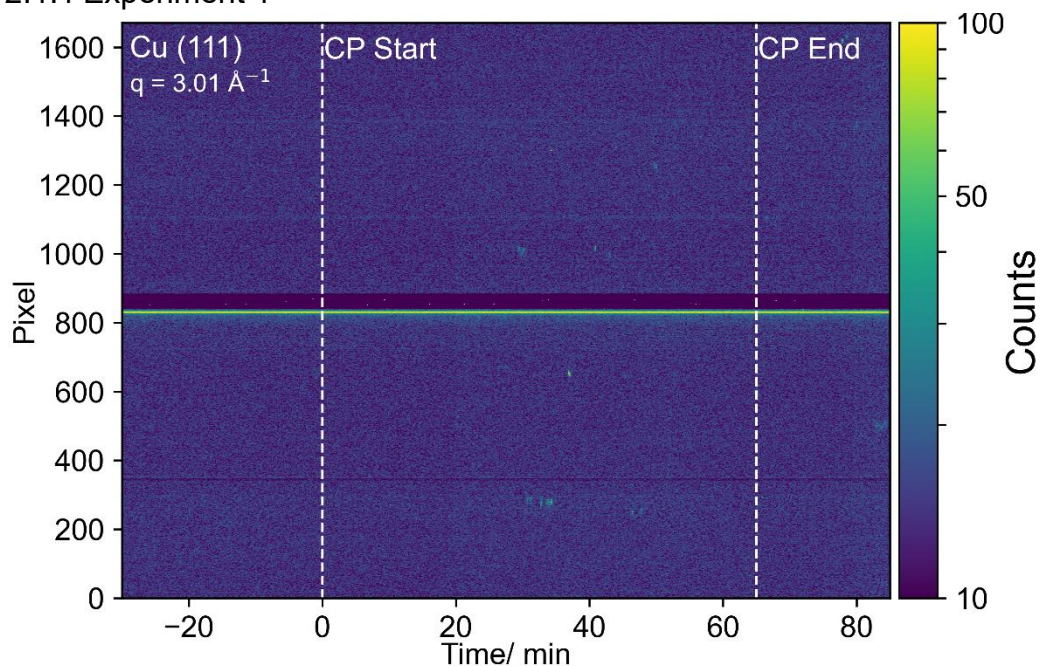


Figure S89: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 0 vol% EtOH was used as electrolyte.

12.1.2 Experiment 2

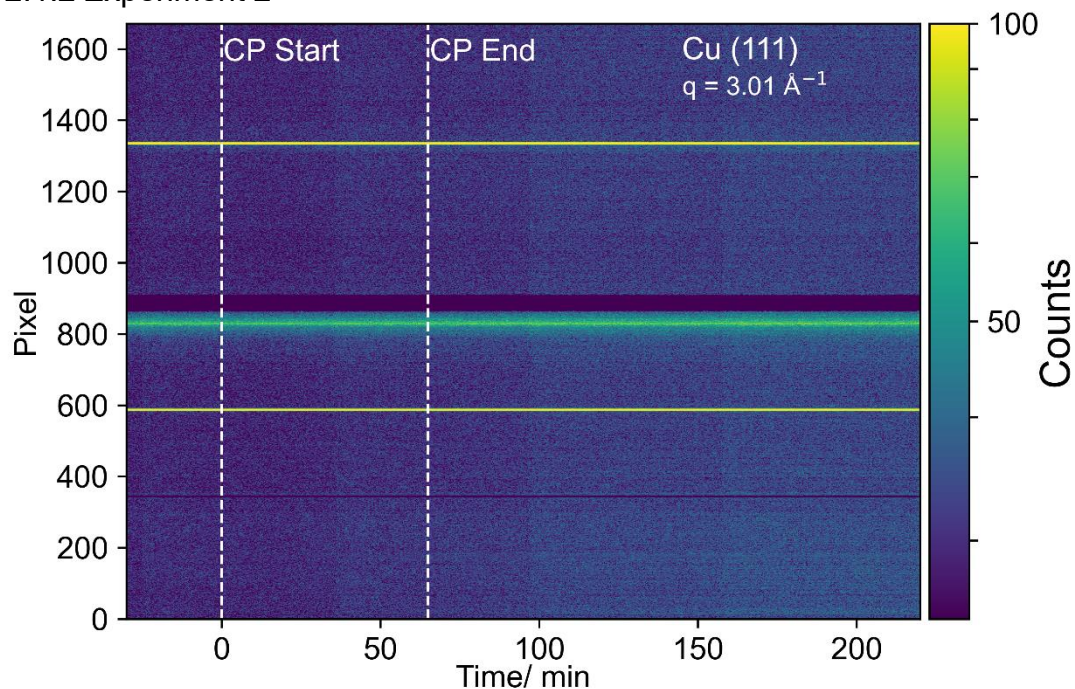


Figure S90: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 0 vol% EtOH was used as electrolyte.

12.2 LiBF₄, 1vol% EtOH

12.2.1 Experiment 1

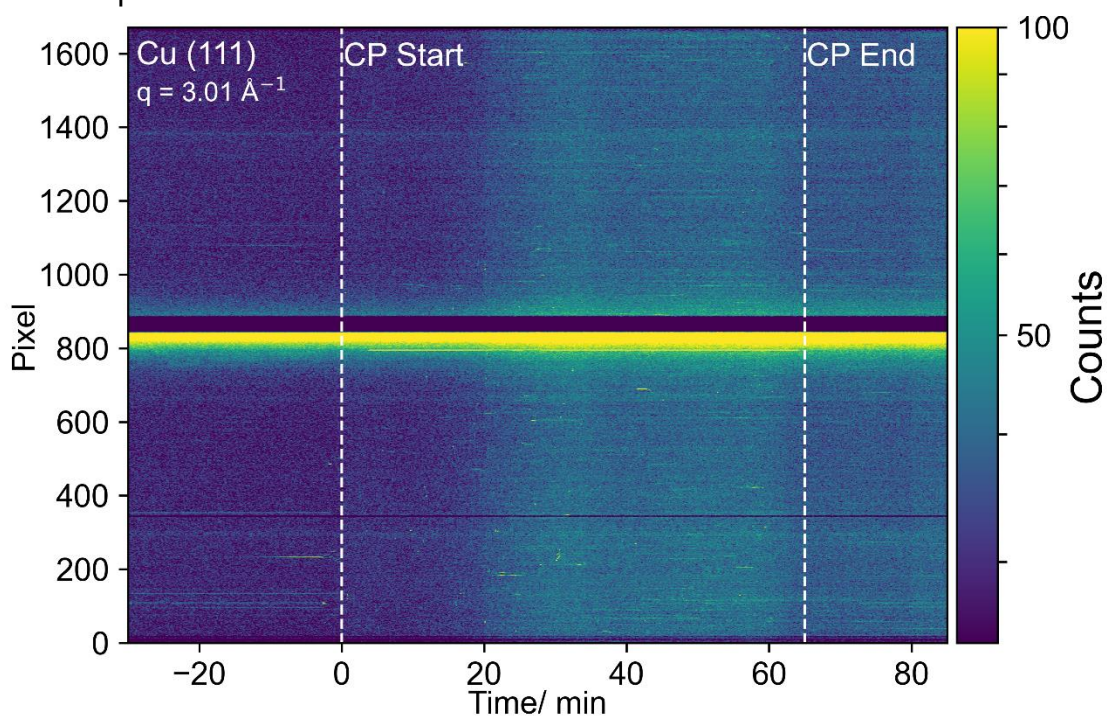


Figure S91: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 1 vol% EtOH was used as electrolyte.

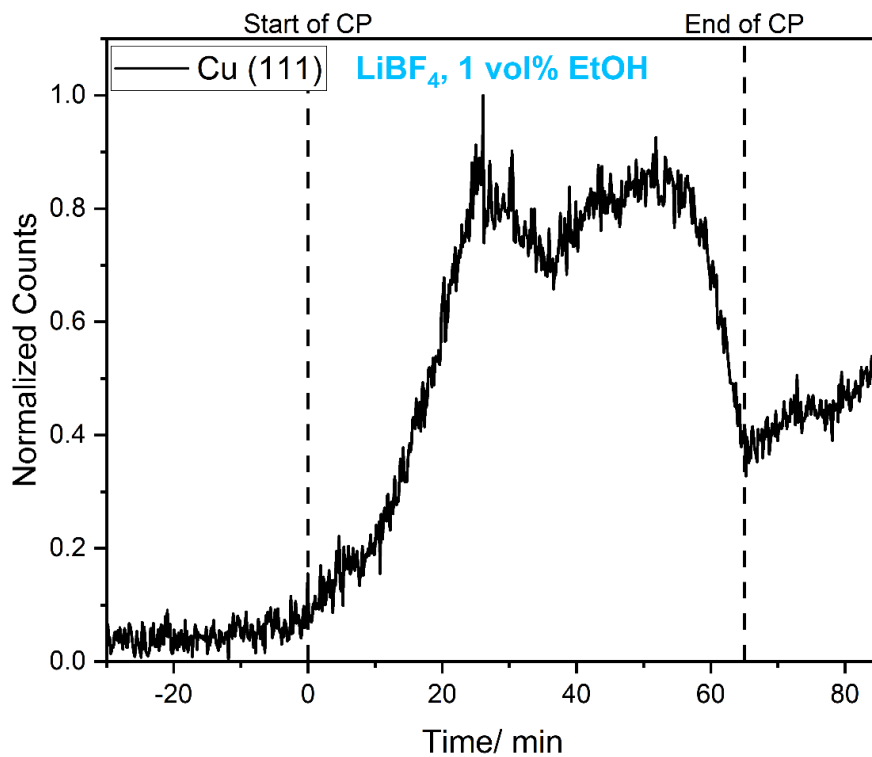


Figure S92: Time development of peak intensities corresponding to the Cu (111) reflection when using LiBF₄ with 1 vol% EtOH in the electrolyte.

12.3 LiClO₄, no EtOH

12.3.1 Experiment 1

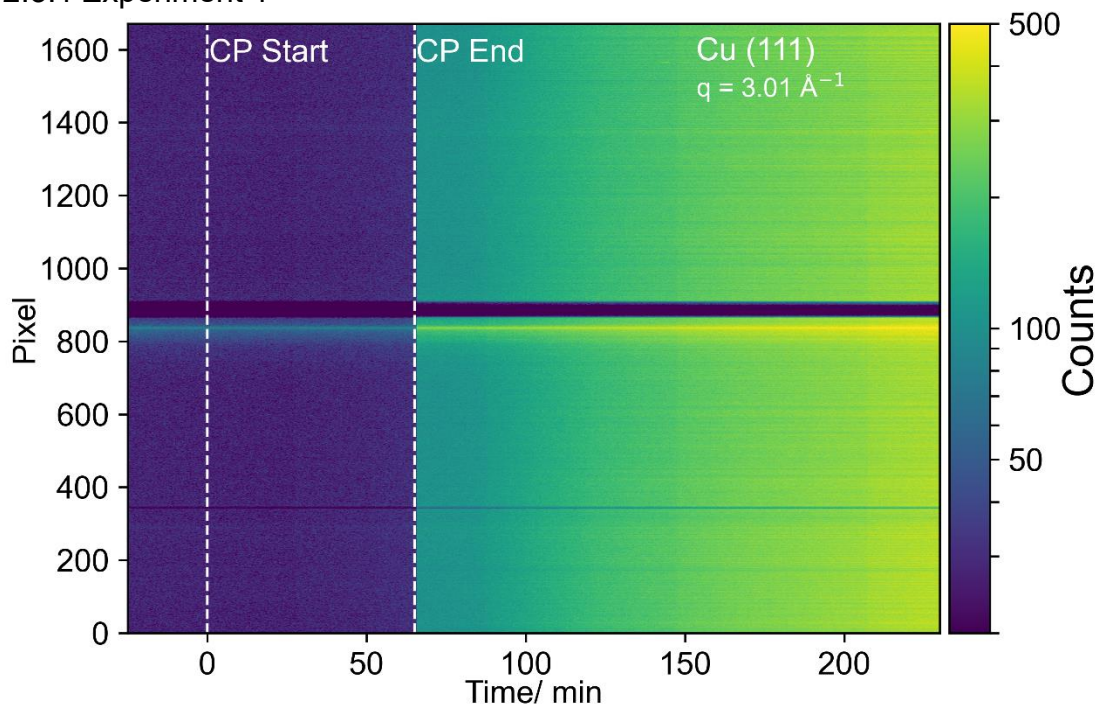


Figure S93: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO₄ in THF with 0 vol% EtOH was used as electrolyte. The abrupt increase in intensity after the CP is due to a change in beam attenuation.

12.3.2 Experiment 2

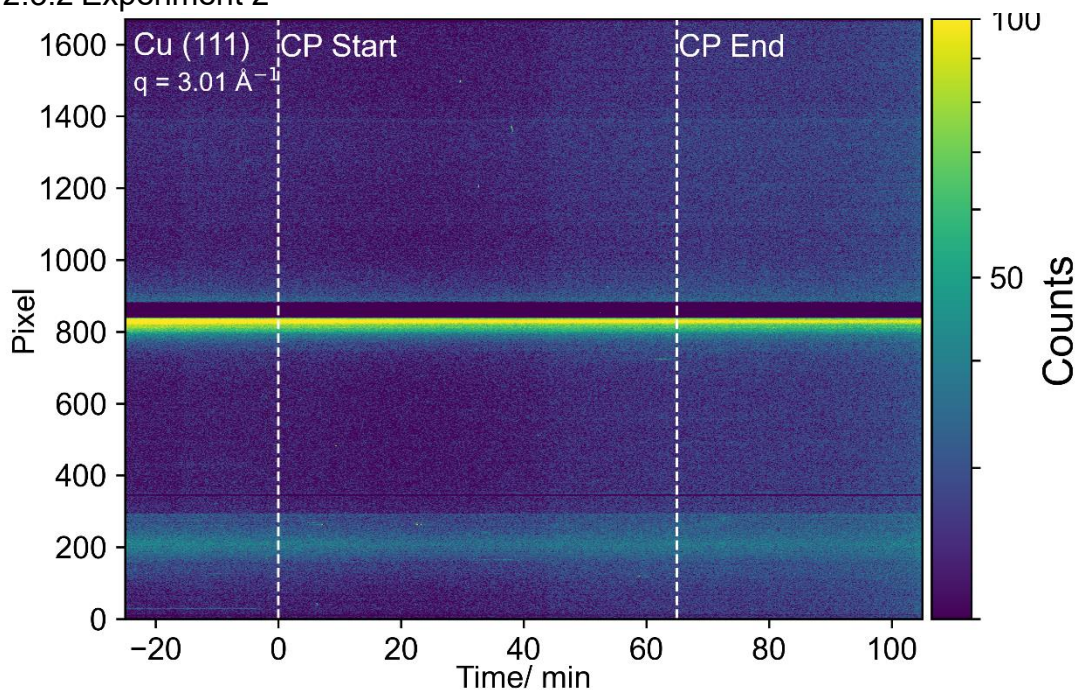


Figure S94: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO₄ in THF with 0 vol% EtOH was used as electrolyte.

12.4 LiClO₄, 1vol% EtOH

12.4.1 Experiment 1

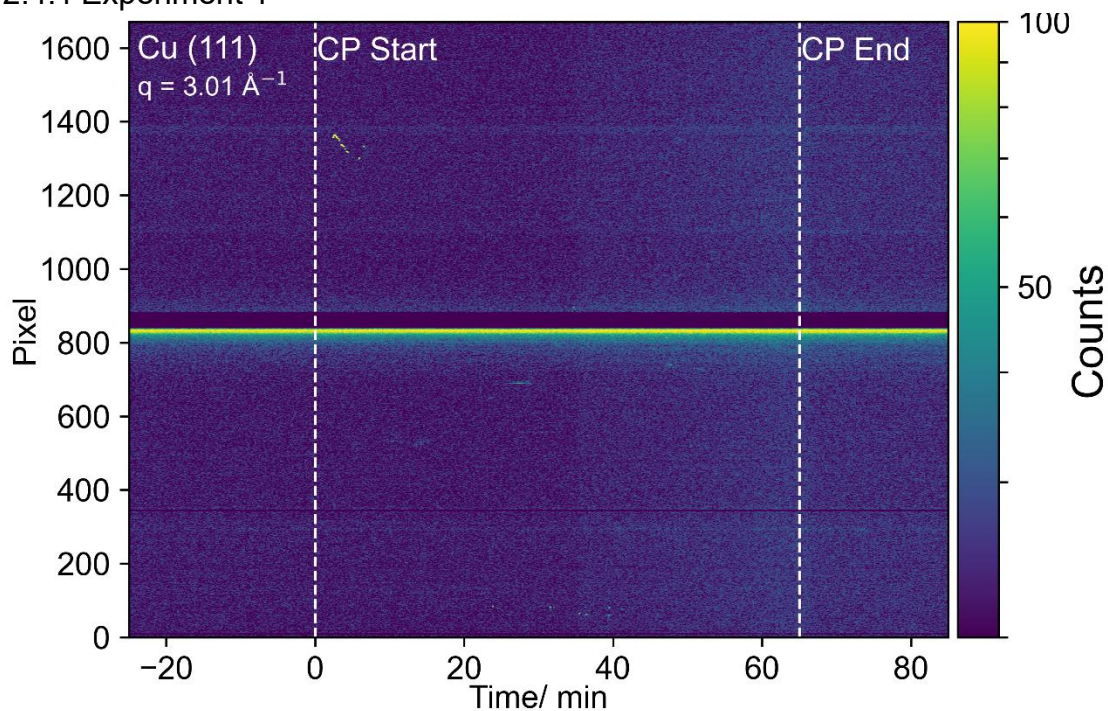


Figure S95: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiClO₄ in THF with 1 vol% EtOH was used as electrolyte.

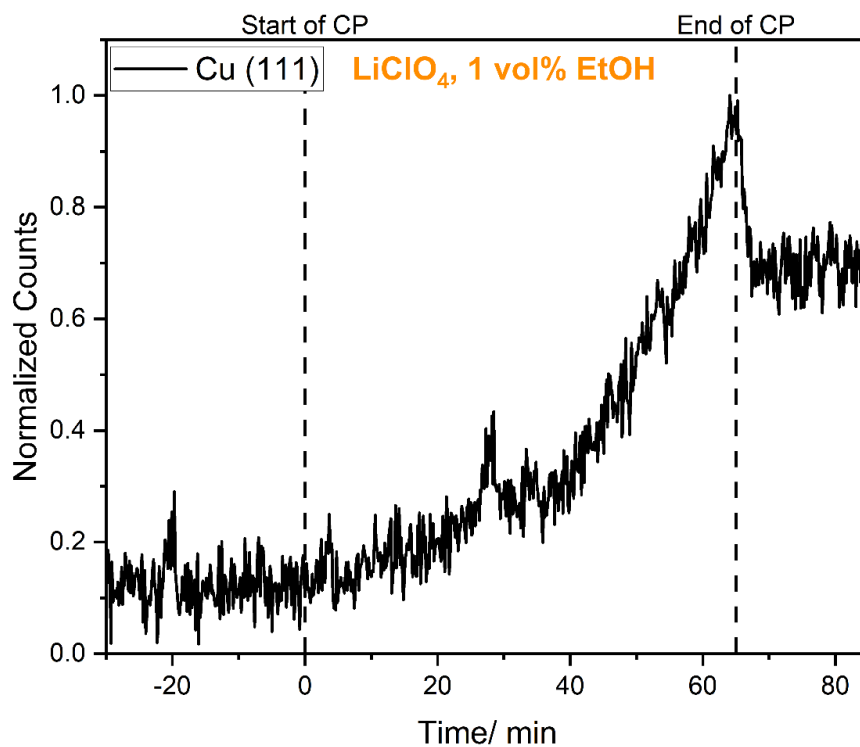


Figure S96: Time development of peak intensities corresponding to the Cu (111) reflection when using LiClO₄ with 1 vol% EtOH in the electrolyte.

12.4.2 Experiment 2

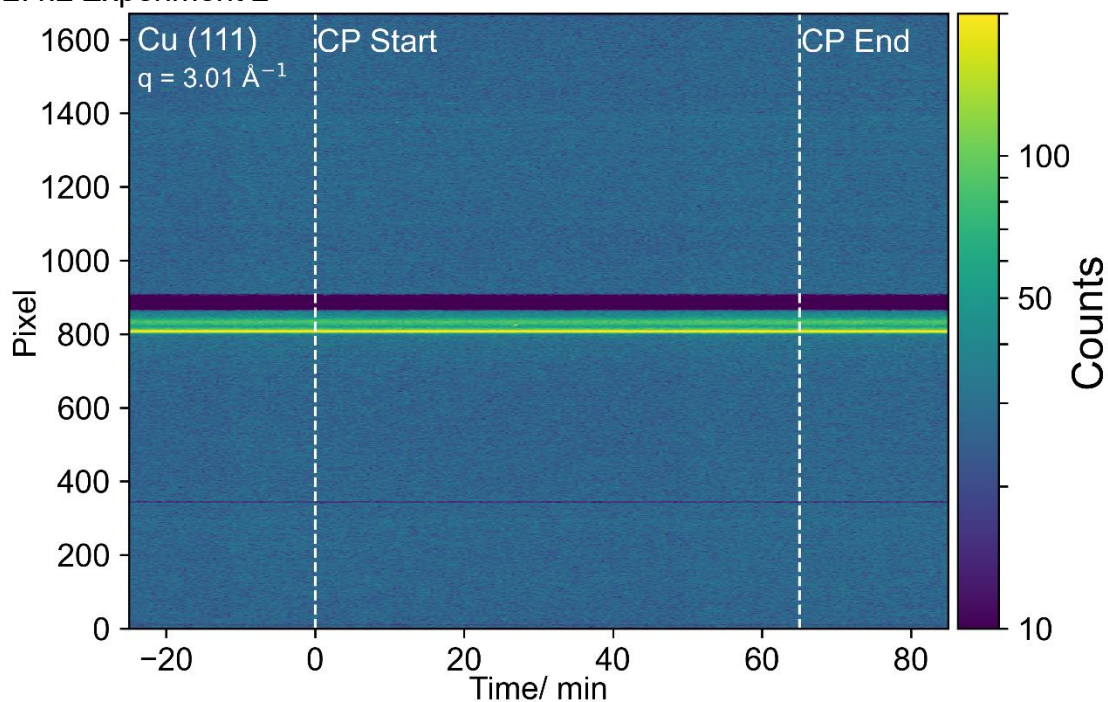


Figure S97: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 1)

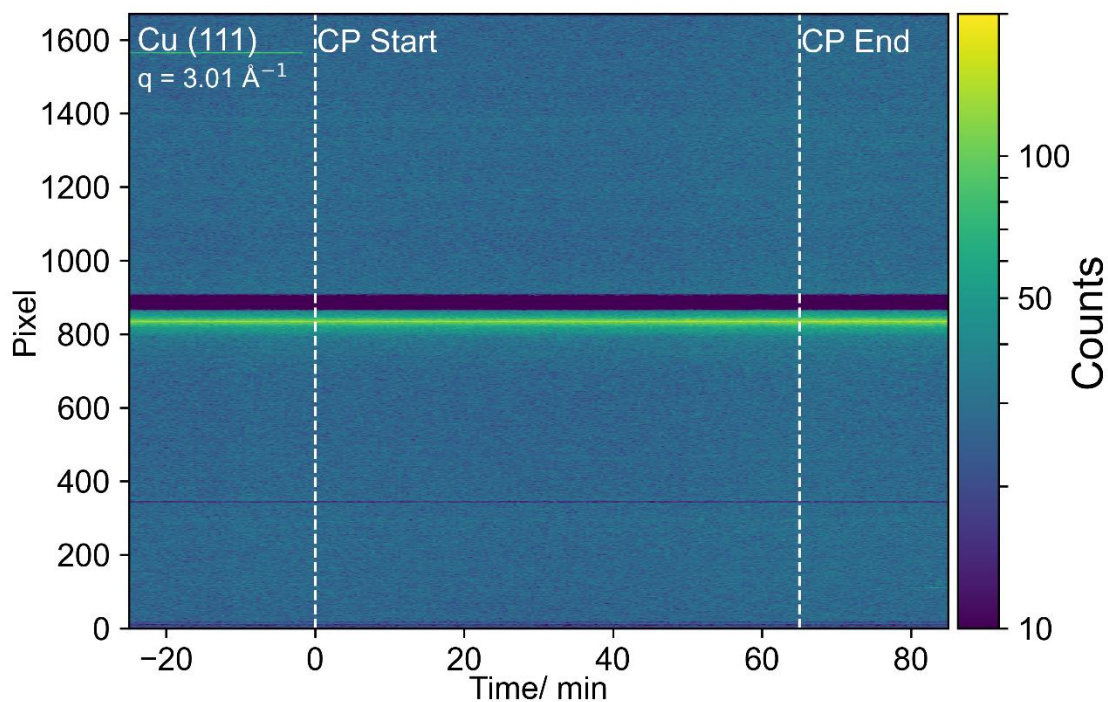


Figure S98: All pixels corresponding to the Cu (111) reflection ($q = 3.01 \text{ \AA}^{-1}$) for all measurement frames. GI-WAXS was measured every 5-10 s on a Cu (111) single crystal working electrode. The counter electrode was a Pt-mesh and an LFP electrode was used as reference. A solution of 1 M LiBF₄ in THF with 1 vol% EtOH was used as electrolyte. During this experiment GI-WAXS was measured alternating on two different spots on the working electrode. (Spot 2)

13 References

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