Experimental report

28/07/2025

Proposal: 1-04-251 **Council:** 4/2023

Title: Investigating the artificial interphase of lithiophilic nanoparticles(Au/Zn) during galvanostatic lithium plating by operando SANS

Research area: Chemistry

This proposal is a new proposal

Main proposer: Gilles WITTMANN

Experimental team: Lucas KREUZER
Gilles WITTMANN

Local contacts: Nina-Juliane STEINKE

Samples: Zn Decorated Ti
Au decorated Ti
ZrS2O8
[(ZrSO8)xH2O] (C24H51N)(0.1-0.7M) (C10D22)

Instrument	Requested days	Allocated days	From	To
D33	3	3	05/09/2023	08/09/2023

Abstract:

Anode free batteries are designed to significantly decreases the weight of a cell.They necessitate immaculate reversibility of the charge and discharge process, as no further lithium other than the amount loaded into the cathode is available. Homogeneous plating and stripping of lithium onto a current collector is not readily achieved when plating on e.g. on copper. Lithiophilic metals like Au and Zn can be used to engineer the surface of a current collector, for example through the application of a thin sputtered film (50 nm), with which the lithium forms metallic interphases and hence drastically changes the plating environment. This can be explored further through the electrodeposition of said metals, which can be generated with different size and number density and therefore provide a variety of plating substrate configuration. With this proposal we suggest the investigation of such decorated current collectors with SANS, in order to correlate the electrochemical parameters of the system to the nanoparticle morphology. We believe that neutrons are ideally suited for this experiment, as their weak interaction energy will not negatively impact the ongoing sensitive reactions.

ILL Experimental Report Amendment: 1-04-251 @D33

- Period: 5/9/23-8/9/23
- Team: Gilles Moehl, Lucas Kreuzer
- Local Contact: Nina-Juliane Steinke
- Aim of the experiment: Observing the lithiation (and delithiation) of electrodeposited Au/Zn nanoparticles operando with SANS on D33.
- SANS cell assembly: All cells were assembled in a glovebox under Argon atmosphere. Cell parts and battery materials were dried (110°C) prior to the experiment or arrived at ILL sealed in pouch bags for direct introduction into the glovebox. Battery stacks consisted of the following components: Ti foil (25 um), Lithium foil, 2 layers of Celgard separator soaked with LP30 electrolyte, 1 Au nanoparticle coated Ti foil (25 um),Ti foil (25 um)

cell	sample	comments
1	Au NPP100	
2	AuNPP100	
3	AuNPP100	no Li
4	AuNPC200	no sep, PTFE spacer
6	Li vs Al	
8	AuNPP200	No Al spacer inside, cell housing ground to 0.2 mm
9	AuNPP200	cell housing ground to 0.2 mm

Full analysis

The most promising experiments of this run where cells 2 and 9, which both had decent electrochemistry. The results of those and also of cells 3 and 6 for reference are summarised and analysed in the following part. During the experiment, it was very clear that the changes in the scattering data would only be very small. On the one hand, the cell background played a major part in that, on the other hand, the severely underestimated sample volume added to that too. These are assumptions that we made from the experiments themselves. However, we managed to find interesting differences in the measurements made under these non-ideal conditions, which could motivate further – optimised-measurements. Figure 1 shows a double panel plot of radial integrations of the 2D detector images, relative to the first measurement of the run in the top panel, as well as the corresponding electrochemical data of current and potential over time in the bottom one, for cell 2. The plots shows hence the change of intensity profiles in time with respect to the initial scattering profile. This initial profile shows essentially the scattering of the unlithiated Au particles and all of the other cell parts. The cell was first "discharged" to 0V in order to reach full lithiation of the Au particles, then set to rest for some time and then delithiated to 0.5V in order to drain the Au particles from all of the lithium again. This process was repeated twice. The scattering data does not really reflect any of the key moments of the electrochemistry – there is no alternating behaviour to be seen. However, even to the naked eye it is visible that over the whole experiment, the low q intensity increases, while the high q intensity decreases. We are aware that the changes are minor and that this observation is very crude, but it is a starting point. From there, we decided to integrate q regions both in low and high regimes of the detector over time, in order to see whether the impression can be confirmed. Figure 2 shows the first and last radial integration of the cell 2 measurements on the left, as well as a high (q(¿0.26) and low (q¡0.02) segmental integrations. The latter confirm the mentioned trend, that is also visible in the raw radial profiles of start and end on the left. The same procedure was applied to cells 3 (Fig. 3), 6 (Fig. 4) and 9 (Fig. 5).

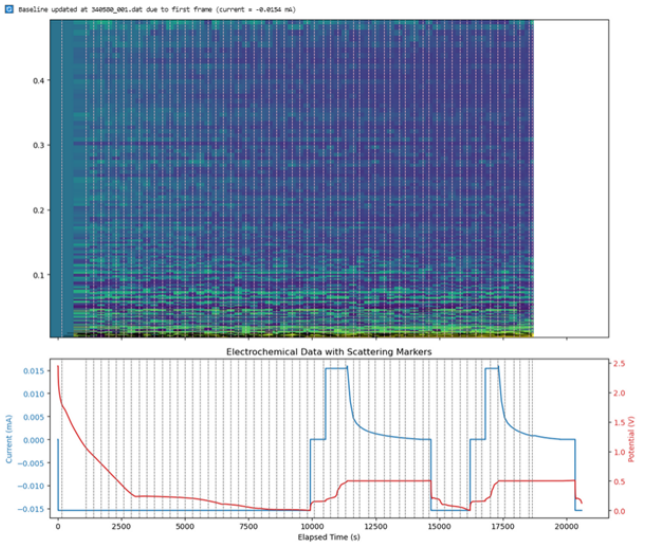

Figure 1: (Top) Delta of the radial intensity profiles vs time. (Bottom) Current and potential vs time measured during the SANS experiment on the operando SANS cell (cell 2).

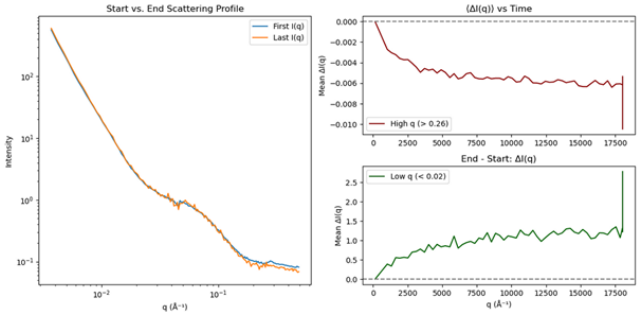

Figure 2: Cell 2 – start vs end radial scattering profiles (left), high and low q integrations vs experiment time (right).

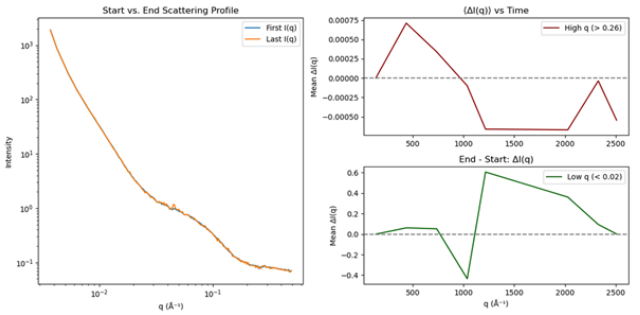

Figure 3: Cell 3 – start vs end radial scattering profiles (left), high and low q integrations vs experiment time (right).

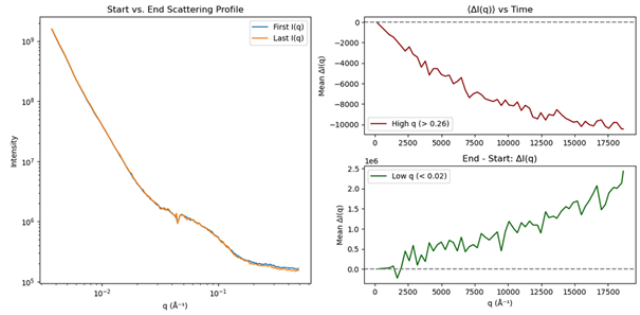

Figure 4: Cell 6 – start vs end radial scattering profiles (left), high and low q integrations vs experiment time (right).

To meet the typical requirements of SANS data analysis in the community, a power law model was used to fit the data (SasView). This excludes of course the broad shoulder around 0.05 Å-1 present in the data for cell 2,3 and 6, but this signal clearly stems from the cell housing, as it was no longer present after milling the cell walls thinner. Figure 6 shows that while the power law exponent seems to be correlated with the general scaling, the background continuously decreases over the course of the experiment. The same can be seen for cell 9 (Fig. 8), which was done with the "removed background cell" and hence does not even show the aforementioned peak anymore. Cell 6 on the other hand (Fig. 7), does practically not move at all, which shows that even lithium plating into Al does not lead to this kind of signal.

The wildest interpretation of these results seems to be the increase in feature size of the Au-Li alloy, with a complete loss of the smallest structure. This could correspond to the pulverisation of Au when lithiated as reported previously in the literature (ACS Energy Lett. 2021, 6, 5, 1749–1756). It would be very beneficial to repeat the experiment with a massive Au foil instead of the nanoparticles, for comparison.

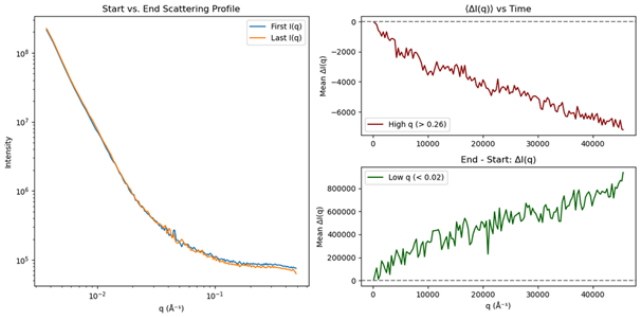

Figure 5: Cell 9 – start vs end radial scattering profiles (left), high and low q integrations vs experiment time (right).

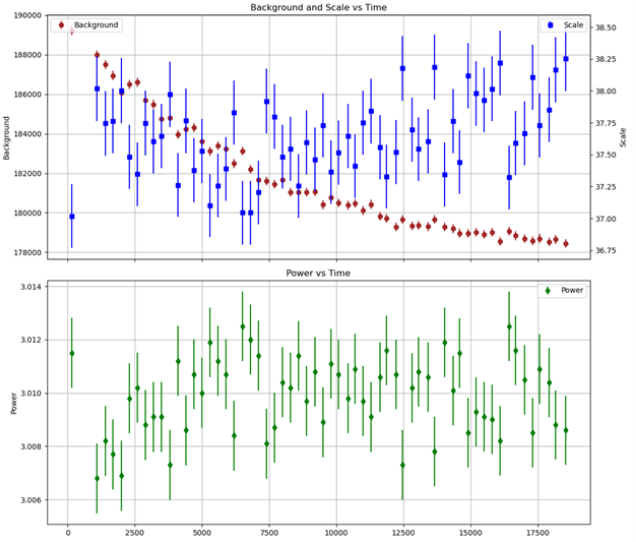

Figure 6: Cell 2 – fit parameters vs time, model: power law.

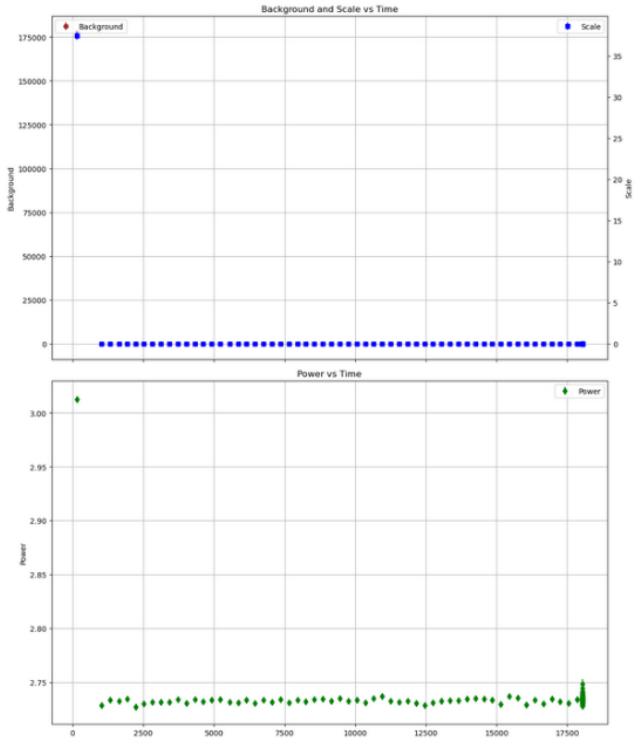

Figure 7: Cell 6 – fit parameters vs time, model: power law.

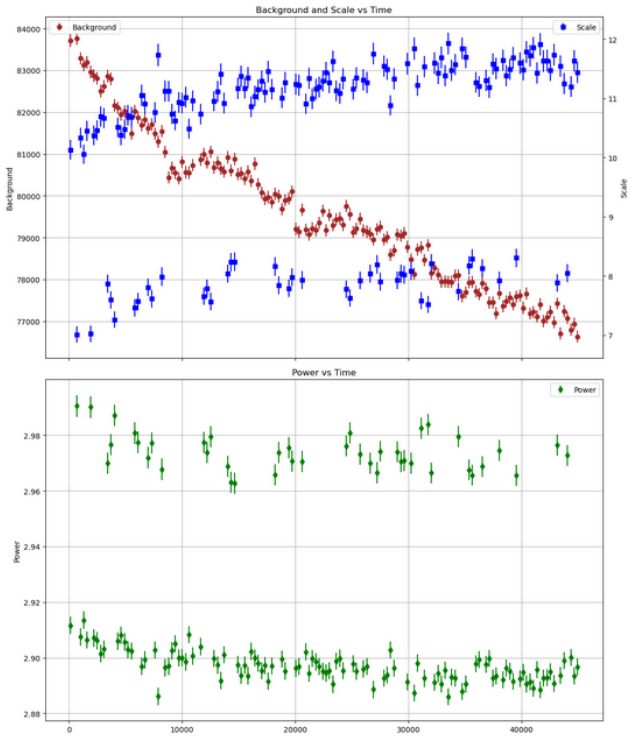

Figure 8: Cell 9 – fit parameters vs time, model: power law.