EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

ESRF

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

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Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- ➢ 1st March Proposal Round - **5th March**
- ➢ 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Investigation of the solid electrolyte interphase (SEI) layer in the electrochemical Li-mediated ammonia synthesis	**Experiment number**: MA-5447
Beamline: ID 31	**Date of experiment**: from: 26 Oct. 22 to: 01 Nov. 22	**Date of report**:
Shifts: 18	**Local contact(s):** Valentin Vinci, Jakub Drnec	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The solid electrolyte interphase (SEI), formed as a consequence of Li plating during the Lithium mediated ammonia synthesis (LiMeAS) is often invoked to explain observed changes in stability and faradaic efficiency[1,2]. Nevertheless, the exact function and composition of the SEI remained largely unexplored as most studies rely on ex-situ techniques[1,3,4]. The work described in this report, represents the first and currently only in-operando study of the LiMeAS using the state of the art electrolyte salt LiBF$_4$. The previous standard electrolyte composition was also studied with a 5 s time resolution compared to at best 3 min in previous in situ studies[5,6].

In this study the deposits on a Cu(111) single crystal working electrode was investigated using grazing incidence wide angle x-ray scattering, during chronopotentiometry (CP) at $-$ 2 mA cm^{-2}. Figure 1A shows the time development of the Li (110) reflection, when different electrolyte compositions were used. Whithout ethanol (EtOH) in the electrolyte the intensity increased continuously while a current was applied and decreased only slowly afterwards, independent of the electrolyte salt used. This is in accordance with the current understandingof LiMeAS that EtOH is needed to protonate intermediate Li-N-species to form ammonia. As faradaic efficiencies were below 5% when using the synchrotron cell due to the low nitrogen availability, the main reaction occuring was likely the competing reaction to form H$_2$ ($2\,Li + 2\,H^+ \rightarrow H_2$). Therefore the addition of EtOH in the electrolyte should hinder Li plating. Indeed, as shown in Figure 1A when LiClO$_4$ was used as electrolyte salt, the Li(110) reflection was only observed temporarily while current was applied, indicating fast reactions of the plated Li. Contrary, when LiBF$_4$ was used the Li(110) signal initially increased continously until a decrease was observed. The difference in the Li plating behaviour clearly indicates a significant difference in the formed SEI. The initial increase in Li(110) intensity shows that the SEI formed by LiBF$_4$ limits proton transport to the plated Li as otherwise Li would react and dissolve. To understand the difference between the SEI layers formed from different electrolytes, other species have to be considered.

When using LiClO$_4$ the only crystalline species detected is Li$_2$CO$_3$, which is only observed when also EtOH is present, potentially indicating that EtOH is decomposed. More likely however, Li$_2$CO$_3$ is formed from decomposition products of the organic solvent, that only form with EtOH[7].

When $LiBF_4$ was used, LiF was already detected in the first measurements, indicating thermal decomposition of the electrolyte salt. As shown in Figure 1B and 1C the intensity of peaks associated with LiF continued to increase before the CP, caused by beam induced decomposition of $LiBF_4$[8]. However, when a current was applied the intensity of LiF peaks increased steeply in all electrolytes with $LiBF_4$. Throughout the experiment, when more Li was deposited, less LiF could be detected. With EtOH, later an increase in LiF peak intensities was observed, when less Li could be detected. This opposing behaviour indicates that Li was plated below a layer of LiF so that when enough Li had been deposited this LiF layer had been lifted out of the x-ray beam. As shown in Figure 1C, after 26 min, a steep decrease in Li peak intensities was observed when EtOH was used. At the same time multiple new peaks appeared which have been attributed to LiH, LiEtO, $LiNH_2$ and Li_3N. This could indicate the formation of a crack in the SEI, suddenly exposing Li to the electrolyte, leading to the formation of multiple reaction products. The formation of LiH further shows the proton limiting properties of the SEI formed with $LiBF_4$ as in the presence of protons LiH would react to form H_2 ($LiH + H^+ \rightarrow Li^+ + H_2$). Furthermore, the presence of Li_3N and $LiNH_2$ would for the first time confirm the propsed mechanism of LiMeAS in which Li and N_2 react to form Li_3N which is then protonated, forming NH_3. However, the assignment of these intermediate species is not entirely certain, due to the low intensities of the corresponding peaks.
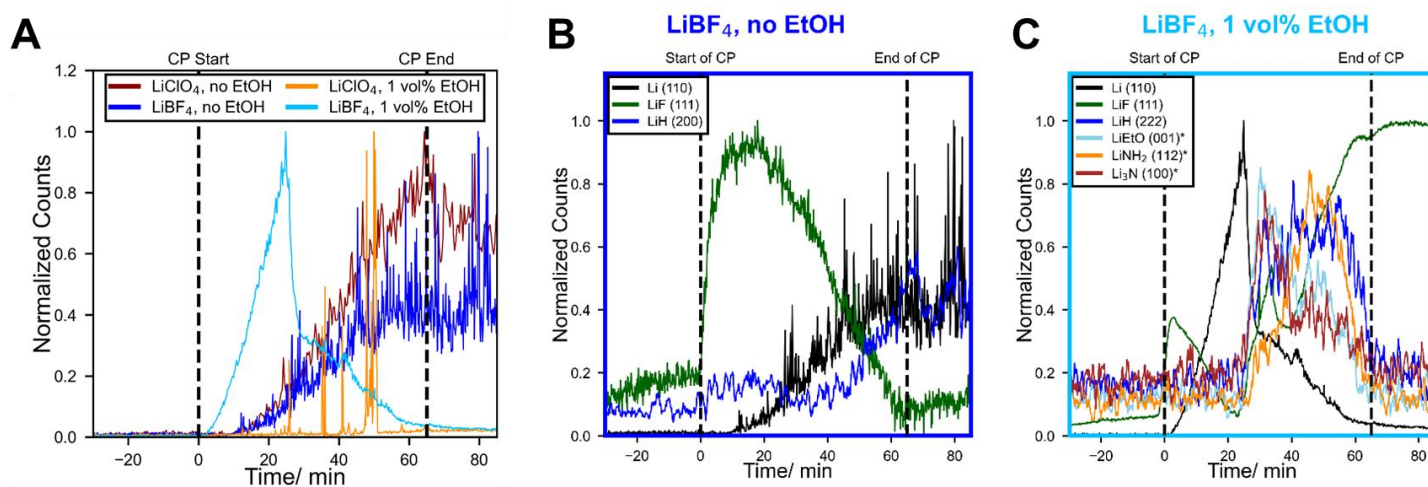

Figure 1: A: Time development of the Li(110) peak when using different electrolyte compositions. B: Time development of peaks corresponding to different species detected when using 1M $LiBF_4$ in THF as electrolyte. C: Time development of peaks corresponding to different species detected when using 1M $LiBF_4$ and 1 vol% EtOH in THF as electrolyte. Species that could not be identified definitely are marked with *[9].*

References

1. Li, S. *et al.* Electrosynthesis of ammonia with high selectivity and high rates via engineering of the solid-electrolyte interphase. *Joule* **6**, 2083–2101 (2022).

2. Li, K. *et al.* Enhancement of lithium-mediated ammonia synthesis by addition of oxygen. *Science* **374**, 1593–1597 (2021).

3. Steinberg, K. *et al.* Imaging of nitrogen fixation at lithium solid electrolyte interphases via cryo-electron microscopy. *Nat Energy* **8**, 138–148 (2022).

4. Fu, X. *et al.* Continuous-flow electrosynthesis of ammonia by nitrogen reduction and hydrogen oxidation. *Science* **379**, 707–712 (2023).

5. Blair, S. J. *et al.* Lithium-Mediated Electrochemical Nitrogen Reduction: Tracking Electrode–Electrolyte Interfaces via Time-Resolved Neutron Reflectometry. *ACS Energy Letters* **7**, 1939–1946 (2022).

6. Blair, S. J. *et al.* Combined, time-resolved, *in situ* neutron reflectometry and X-ray diffraction analysis of dynamic SEI formation during electrochemical N $_2$ reduction. *Energy Environ. Sci.* 10.1039.D2EE03694K (2023) doi:10.1039/D2EE03694K.

7. Valbæk Mygind, J. B. *et al.* Is Ethanol Essential for the Lithium-Mediated Nitrogen Reduction Reaction?, *manuscript accepted.*

8. Steinrück, H. G. *et al.* Interfacial Speciation Determines Interfacial Chemistry: X-ray-Induced Lithium Fluoride Formation from Water-in-salt Electrolytes on Solid Surfaces. *Angewandte Chemie - International Edition* **59**, 23180–23187 (2020).

9. Deissler, N. H. *et al.* In operando Investigations of the Solid Electrolyte Interphase in the Lithium Mediated Ammonia Synthesis, *manuscript in preparation.*