D6.4 – Advance direct SEI investigations for chemistry-neutral lithium-based batteries by integrated high-throughput electrochemistry with ex-situ high-throughput spectroscopy

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ABSTRACT

Underlying the platform aspect of BIG-MAP is lab automation of instruments that can investigate interfacial properties following electrochemical and chemical processes. It is, however, not enough to simply characterize a series of interfaces from cells; there needs to be innovative ways of synthesizing interfaces and interphases in great numbers. To this end, we have developed two setups within BIG-MAP, specifically for battery research, that can generate and characterize interphases for battery research. One is the scanning droplet cell as part of the millimeter scale high-throughput battery research system (MISCHBARES), and another is the high-throughput spectrometer (HITS) that combines large area scanning probes for Raman and FTIR spectroscopy. In the following, we will briefly describe the setup of the systems, their automation, and data management and show some selected results. The detailed results for MISCHBARES and HITS are currently being submitted for publication.

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1. Introduction

High-throughput experimentation for investigations of interphase phenomena necessitates ways to synthesize and characterize interfaces and interphases at great speed and reproducibility. Herein we will briefly introduce the unique design of the millimeter scale high-throughput battery research system (MISCHBARES), its automation, the data management, its interaction with the high-throughput spectrometer, and some preliminary results.

1.1 Scanning droplet electrochemistry

The basic idea behind scanning droplet cell electrochemistry is that a miniaturized electrochemical cell is built by moving a measurement probe that houses a counter and reference electrode across a substrate, as shown in Figure 1. This allows for a variety of compositions on the working electrode, variations of the electrolyte, or variations of the electrochemical protocol. Typically one only varies just one, but the method does, in principle, impose no restrictions on the user. Different designs of scanning droplet cells roughly fall into two major categories: flow and no-flow cells. As in batteries, as investigated in BIG-MAP, there is no continuous flow of electrolyte; we chose to utilize a no-flow SDC design. For a three-electrode configuration, there is, however, the challenge that one needs to design and find stable reference electrodes. In the following, we will briefly describe the measurement procedure and demonstrate the method on some selected battery materials.

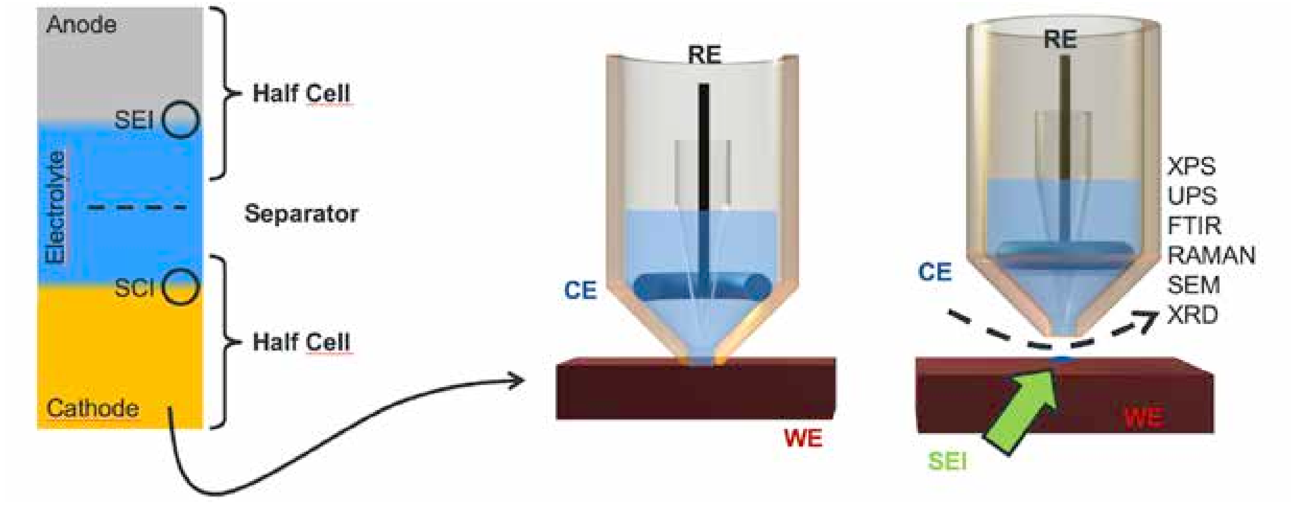


Figure 1. The general idea of splitting the full cell of a battery into two half cells to be investigated in a scanning droplet cell. This concept is relatively established in catalysis research but not in the field of batteries, i.e., there are only a handful of battery-related SDC papers. Here a half cell refers to a three-electrode cell with a reference electrode made out of Li-Au, which has been empirically found to be stable for a few days of operation.

The general process of a scanning droplet cell experiment is that the cell column is flushed several times with electrolyte, and the measurement probe containing the reference and counter electrode is moved above the subsequent measurement position. The probe is then lowered, and the experiments are started after some initial wetting period has passed. After finishing the experiment, the probe head is lifted under a slight negative pressure to avoid squirting the electrolyte over the substrate. The remaining SEI on the material's surface can be investigated using a series of techniques, as shown in Figure 2. The experiment is then repeated over and over at different substrate positions. The automation of this experiment is performed using HELAO as described in some of the other deliverables in WP 6, 9, and 10.

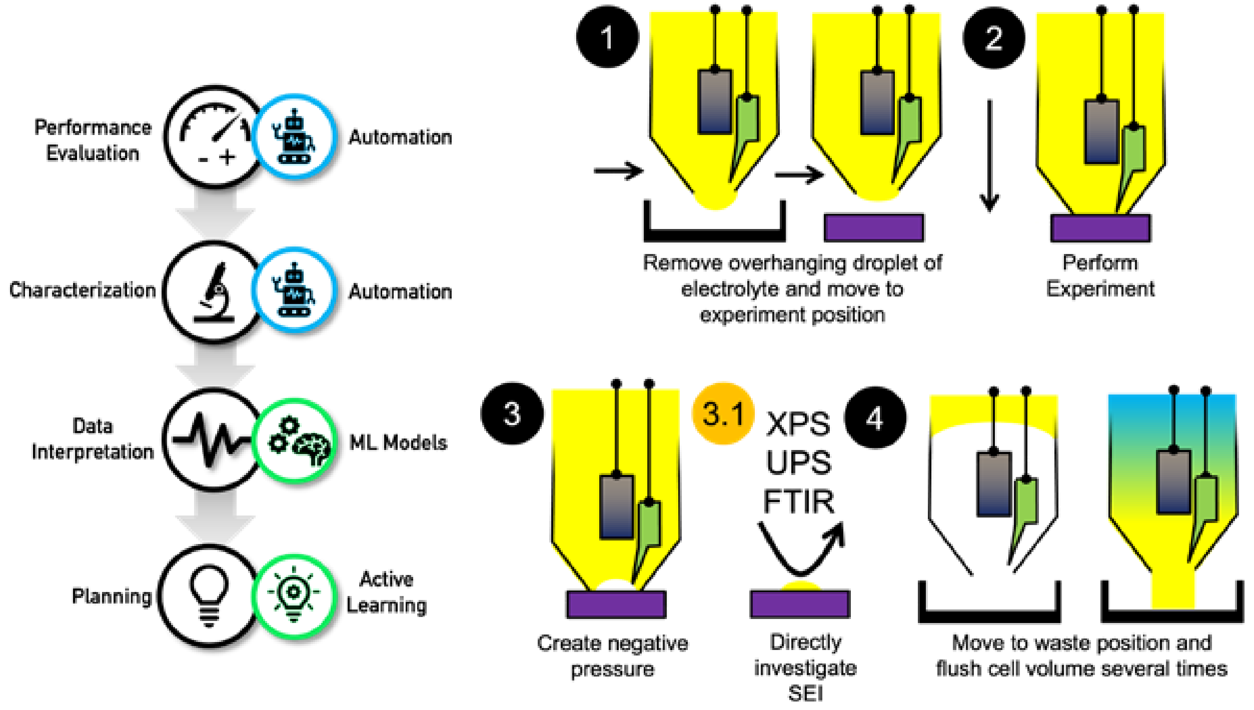


Figure 2. The general procedure of a scanning droplet cell experiment in battery research to investigate synthesized SEIs. The automation side of this setup is performed using HELAO.

To correlate experiments performed using the SDC, integration with other characterization techniques such as FTIR, Raman and XPS must be integrated. We have developed a universal sample holder that can fit square or round substrates. Foil substrates can be mounted using a plate adapter. The universal sample holder can be mounted into any device as part of PLACES/R (the platform for accelerated electrochemical energy storage located at HIU/KIT and published in https://doi.org/10.1016/j.coelec.2022.101053) by either snapping, falling or being screwed securely into place. Another design aspect of these holders is that they can be mounted with standard 4” wafer carriers such that positions from scanning electron microscopy and X-ray fluorescence can be easily translated to generate true composition-structure-interface-protocol-function relationships.

Figure 3. Universal sample holders to transfer samples between electrochemical testing, structural characterization, and composition.

With stable reference electrodes and the lab automation in place, there is one issue: for the investigation of anode materials, i.e., when the SEI on the anode is sought after, there needs to be some form of a Li- or Na-reservoir. As the glovebox atmosphere in which these robotic systems are housed is comprised of dry nitrogen, the counter electrode cannot be made from metallic Na or Li as these would quickly form passivating layers. Instead, we use a spatially distributed charge and discharge trick to investigate the SEI on anode materials. The basic working principle developed for BIG-MAP to enable SEI investigations on carbon anode materials is first to discharge the NMC foil, move the probe over to the anode and discharge the now charged counter electrode onto the anode. With this, no extra Li- or Na-reservoir is needed, and the reactive material is kept in the metallic form at a minimum. Generally, Pt is used as a counter electrode due to its excellent stability in most solvents. If a too high discharge rate is applied, there is an increased risk of forming dendrites upon plating onto the counter electrode. Example pictures of the overall setup are shown in Figure 4, and the split anode-cathode design is shown in Figure 5.

Since NMC can be much faster discharged than carbon could be charged, we apply a 10C rate equivalent to NMC to discharge the Li onto the counter electrode, as shown in Figure 6, and different charge (formation) curves are shown in Figures 7-8. These charge curves were stopped at different times to relate to a different state of charge. Due to some nonuniformity of the droplet upon touchdown, the effective current density changed and thus the resulting state of charge after some time. We, therefore, use the end potential as a measure of the state of charge.

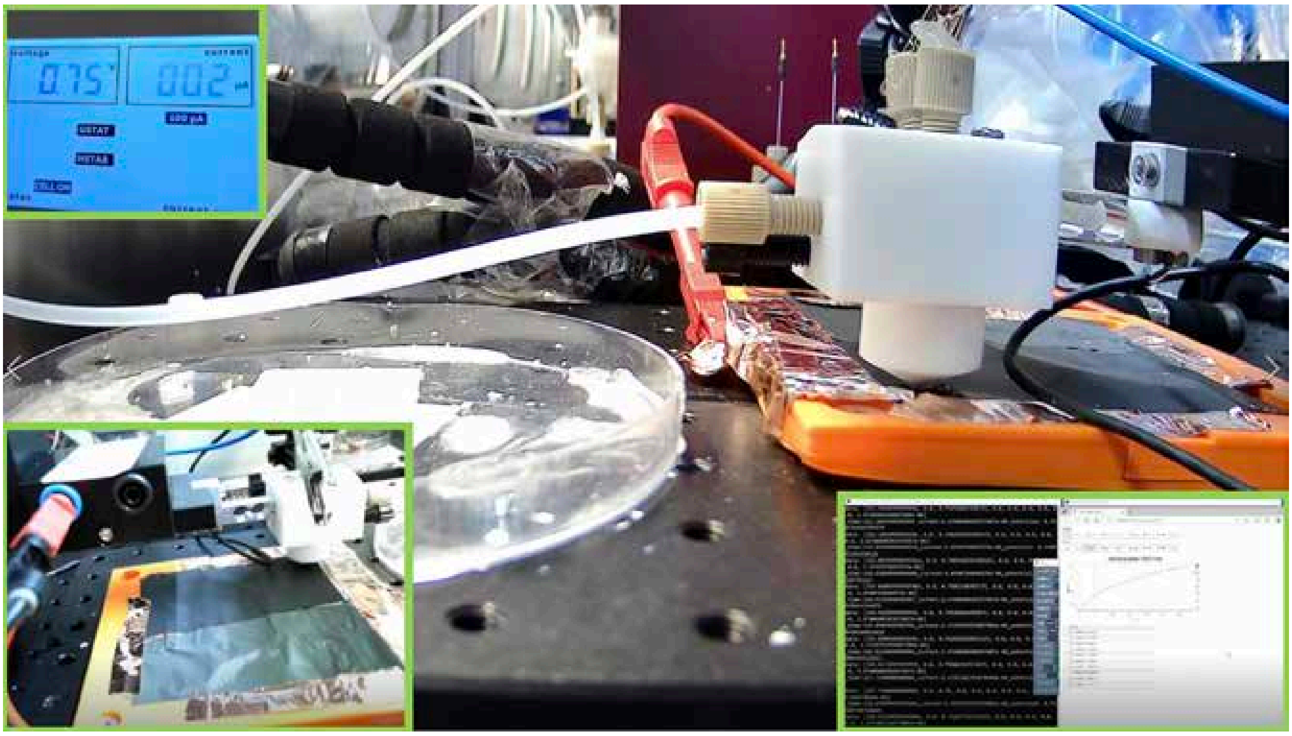


Figure 4. Screenshot of the SDC command computer showing a live video of the potentiostat applying 2 µA at a potential of 0.75 V vs. the Au/Li reference. The bottom left shows a small picture of the anode and cathode split. The big picture in the background shows a closeup of the measurement probe head. The bottom right inset shows the HEALO orchestrator and live data view.

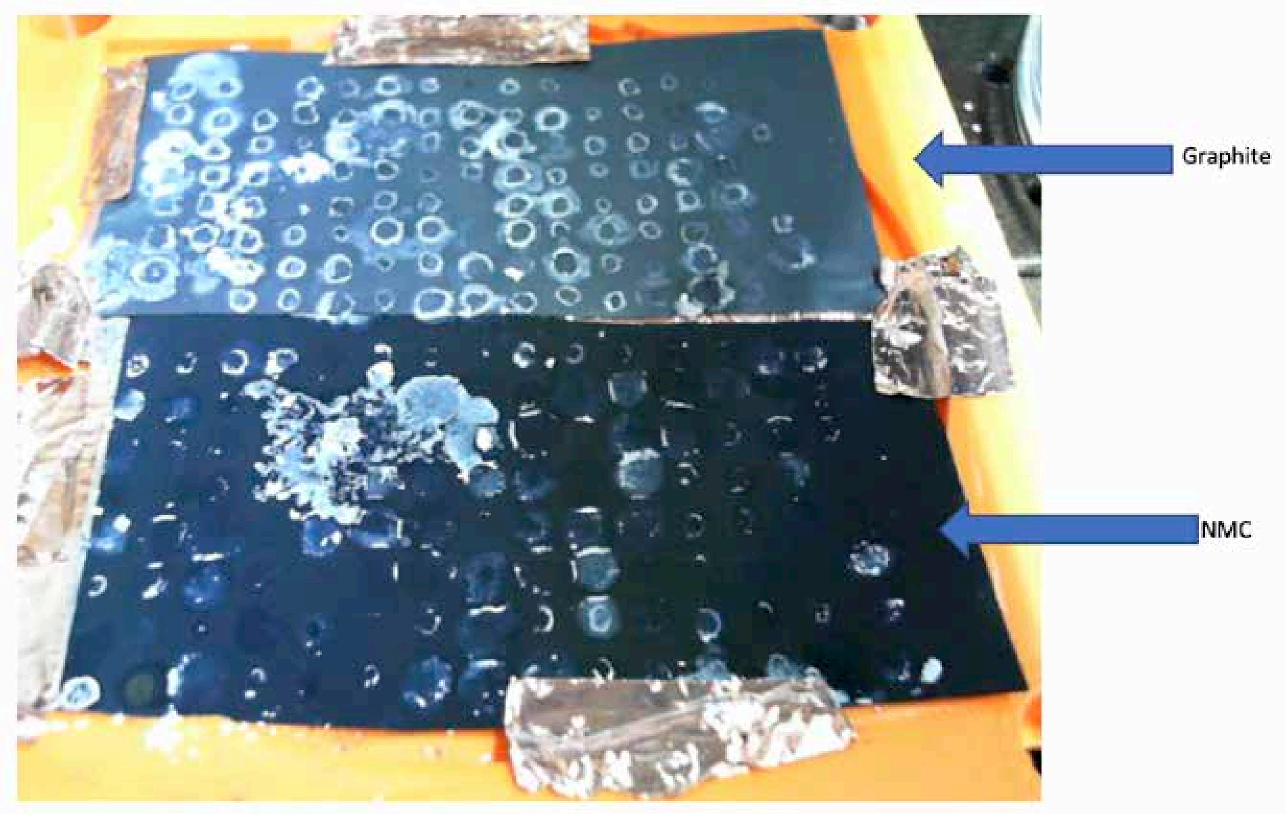


Figure 5. Detailed view of both the anode and cathode after finishing over 80 experiments in them. The remaining salt crust is washed away using PC.

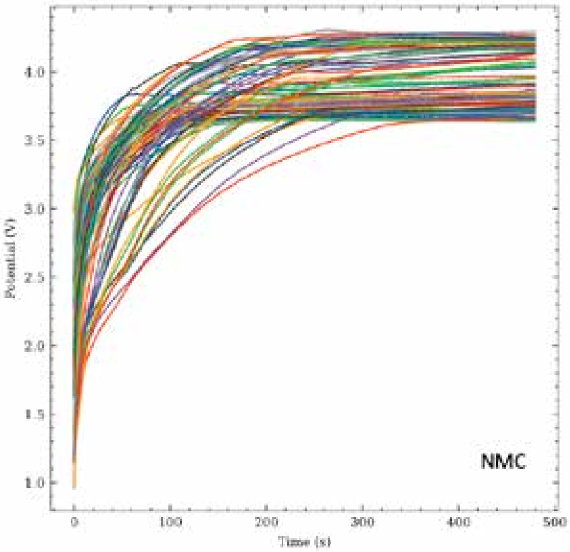


Figure 6. Voltage profiles of NMC in an SDC performed at over 80 positions. Potential is vs. Li/Au in a three-electrode configuration

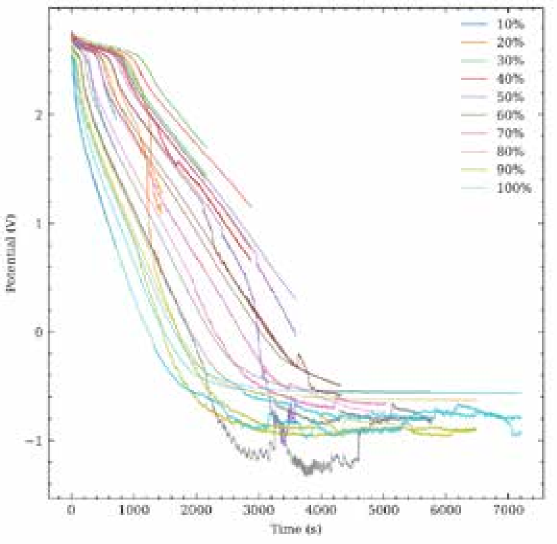


Figure 7. Voltage profiles of graphite in an SDC were performed at over 80 positions. Potential is vs. Li/Au in a three-electrode configuration at a C/2 equivalent rate. The experiment was stopped after different times that would correspond to another nominal state of charge at C/20.

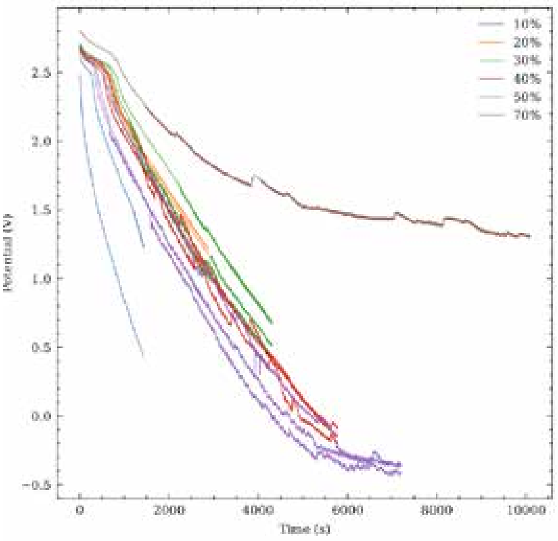


Figure 8. Voltage profiles of graphite in an SDC were performed at over 80 positions. Potential is vs. Li/Au in a three-electrode configuration at a C/4 equivalent rate. The experiment was stopped after different times that would correspond to another nominal state of charge at C/20.

There is still some considerable variability between experiments, which is why experiments were designed for the SDC to eliminate the influence of electrode inhomogeneity and exhibit a more uniform wetting behavior. To this end, thin film electrodes were sputtered using reactive magnetron sputtering. The outlook is to do this in a combinatorial way, i.e., variation of the elements across a substrate. To gauge repeatability, we have deposited pure Au onto Si to assess SDC drop repeatability. An example picture of a thin film Au wafer after an SDC series of experiments is shown in Figure 9.

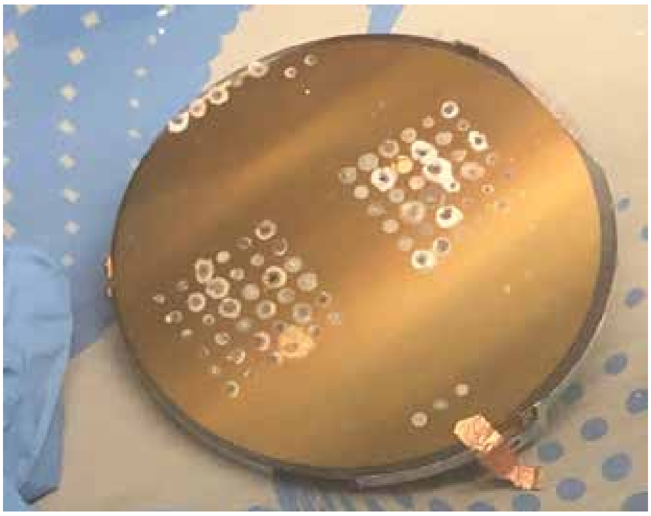


Figure 9. Au wafer post-SDC experiments to test repeatability

The optical microscopy image in Figure 10 shows an emblematic example of an SDC experiment post-cleaning. It is visible here that the PTFE seal of the tip performed well but that once the tip wears (exemplified by the small kink at the bottom right), the droplet will leak out, creating a larger contact area leading to noisy capacity data. Ways to overcome this are currently being investigated using shadow masks.

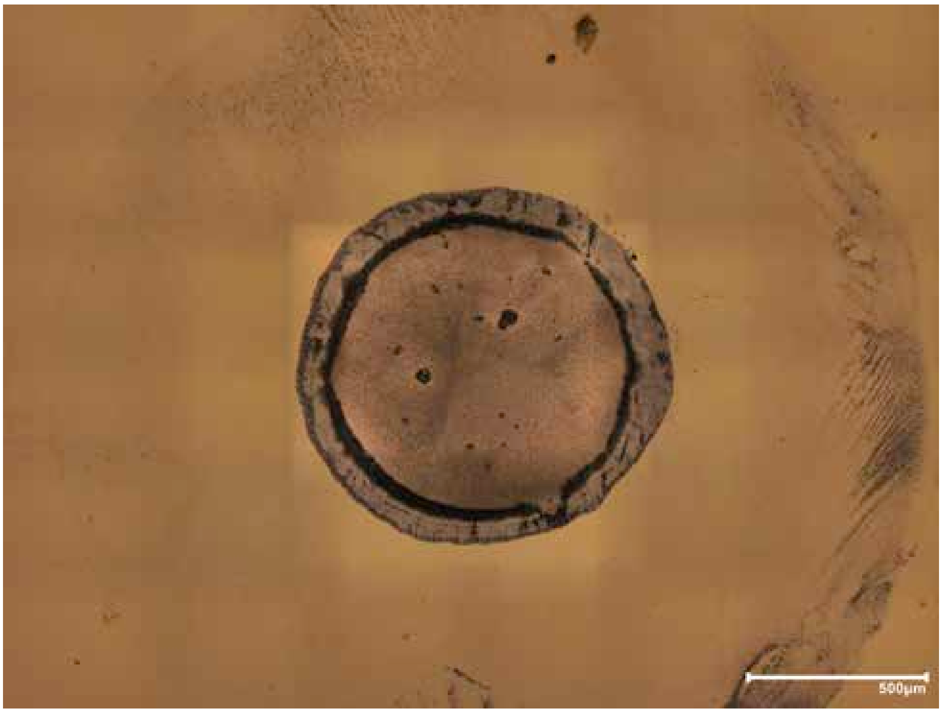


Figure 10. Emblematic microscopy image of a clean SDC experiment

Subsequent to an SDC experiment, their electrochemical performance can be correlated to structural data obtained from Raman and FTIR spectroscopy.

1.2 High-throughput spectrometer

To assess and fingerprint different formed SEIs, we have developed the high-throughput spectrometer (HITS). Figure 11 shows the detail and grant view of the system in the large volume glovebox. The HITS consists of two measurement probes (one for FTIR and one for Raman) that are mounted on z-stages with an x-y table underneath that allows us to map wafers of up to 8” squares. This instrument's software is HELAO, allowing us to correlate electrochemistry with spectroscopy very easily.

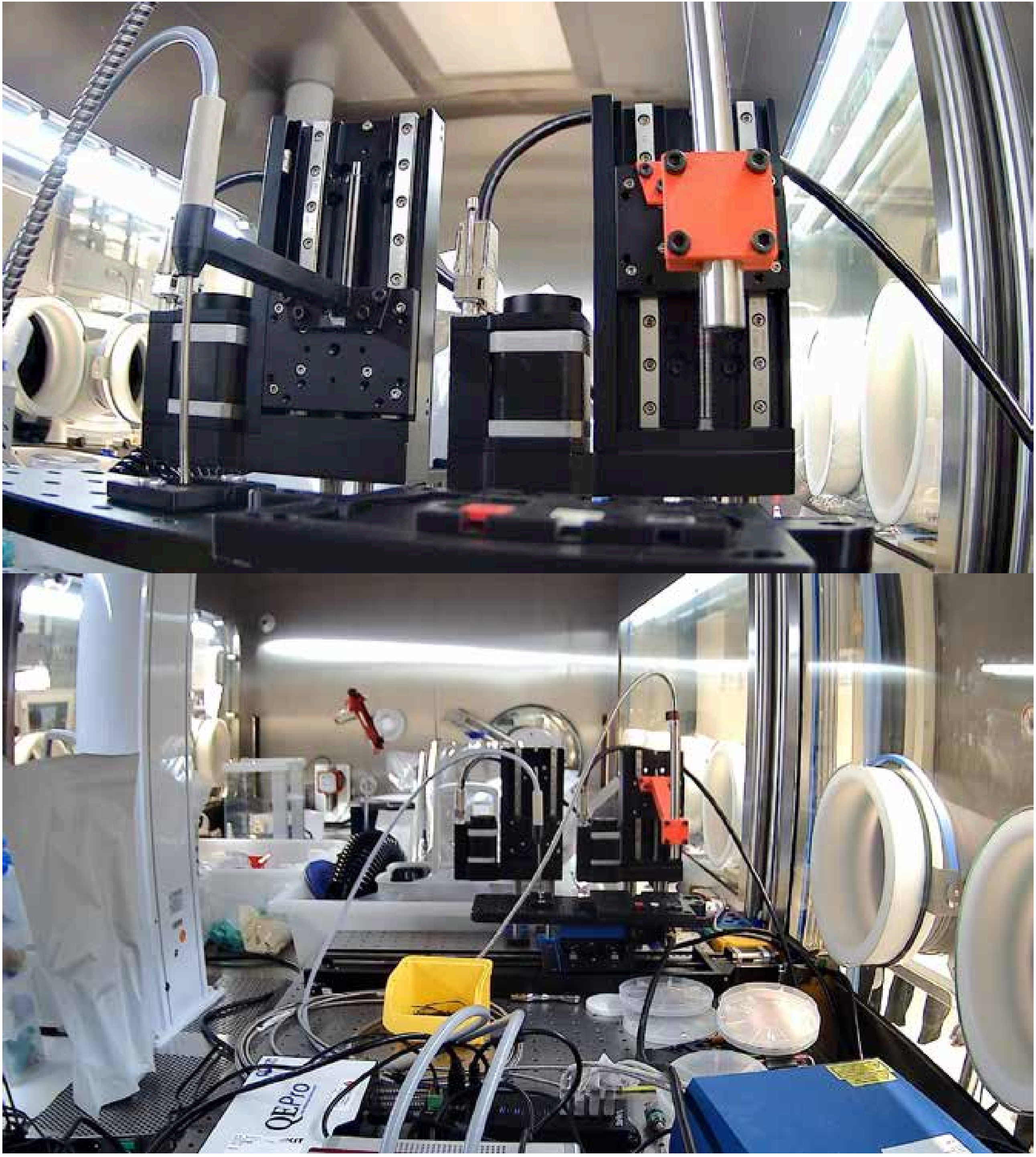


Figure 10. Detailed and grand view of the HITS in the large volume glovebox. The top image shows the FTIR probe on the left and the Raman probe on the right. A recent upgrade added a green laser Raman to the setup allowing us to probe an extensive range of the optical vibration spectrum.

As there is no other system like HITS that can scan large areas of substrates in a glovebox using full automation control, we build a polymer library to assess the system's fidelity. Some select results are shown in Figure 11, highlighting that between 1000-2000 cm^{-1}, we observe no noticeable difference to a state-of-the-art Lumos II FTIR microscope from Bruker, but that above 2000 cm^{-1}, the attenuation of the fiber optic probes becomes dominant. The same analyses exist for Raman spectra but with an even better agreement between our home-build and commercially available setup.

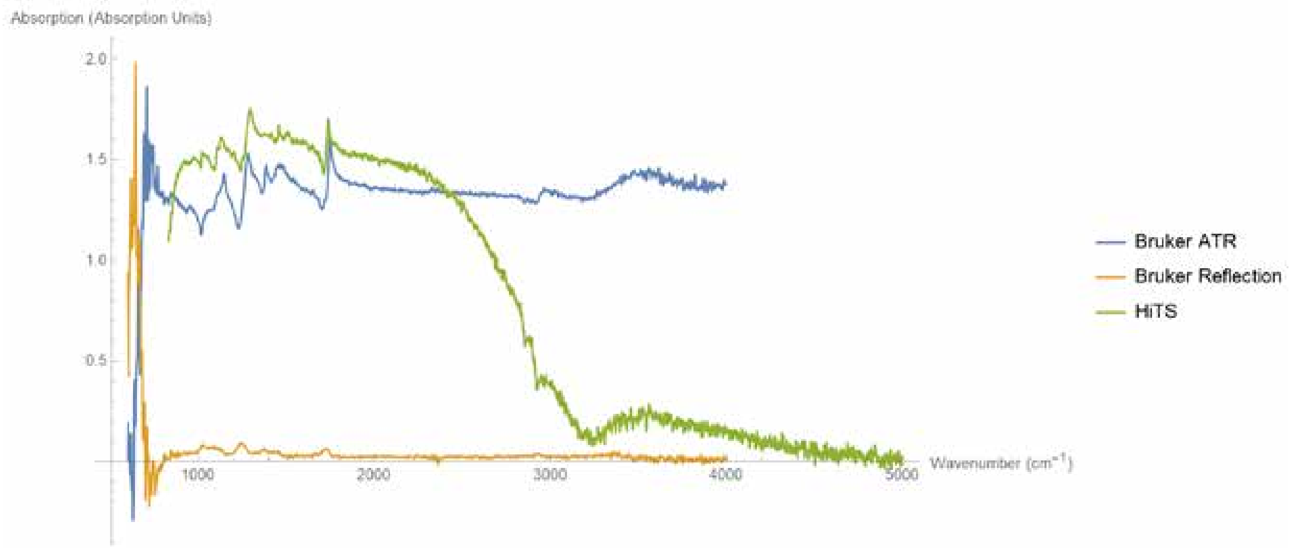


Figure 11. Example FTIR spectra from a polymer library.

Using the Raman spectrometer, we can investigate solid-state materials on the surface of our substrates, as shown in Figure 12. Here we can also see leaky and clean SDC experiments through a corona that forms around the center of measurement areas.

Consequently, we can also probe molecular species formed in the SEI through false color mapping using the FTIR spectrometer. In Figure 13, an example on the Au wafer similar to the one shown in Figure 9 is shown together with the decomposed spectra.

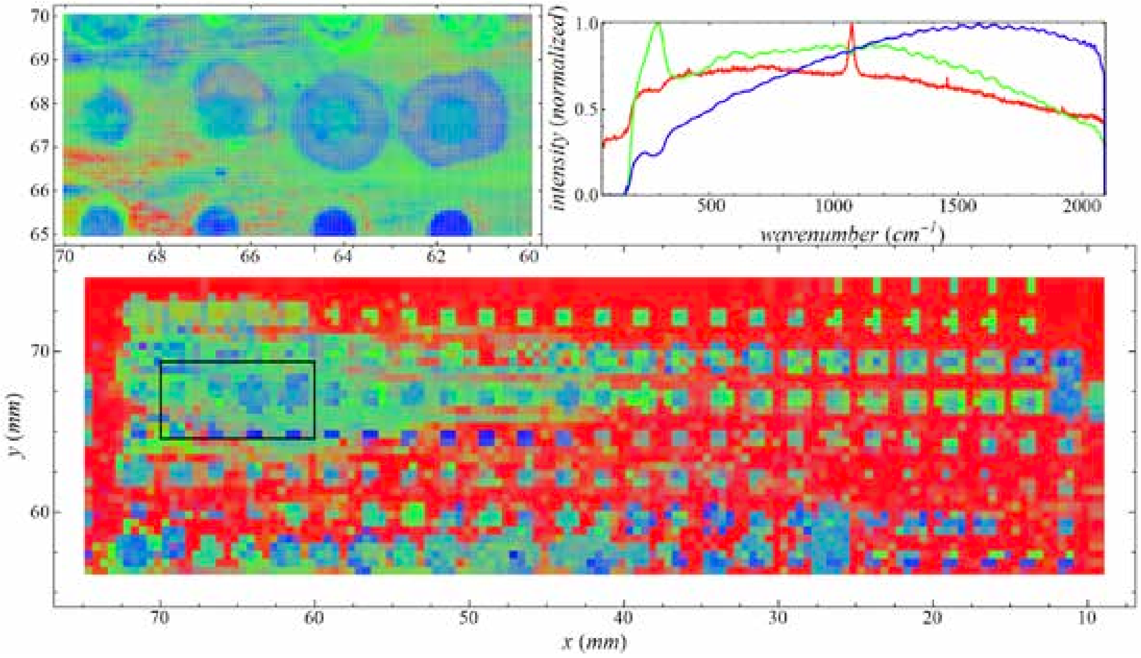


Figure 12. Example measurements with a high-resolution false color Raman mapping in the top left, decomposed spectra on the top right, and a large area scan on the bottom span several dozens of SDC experiments.

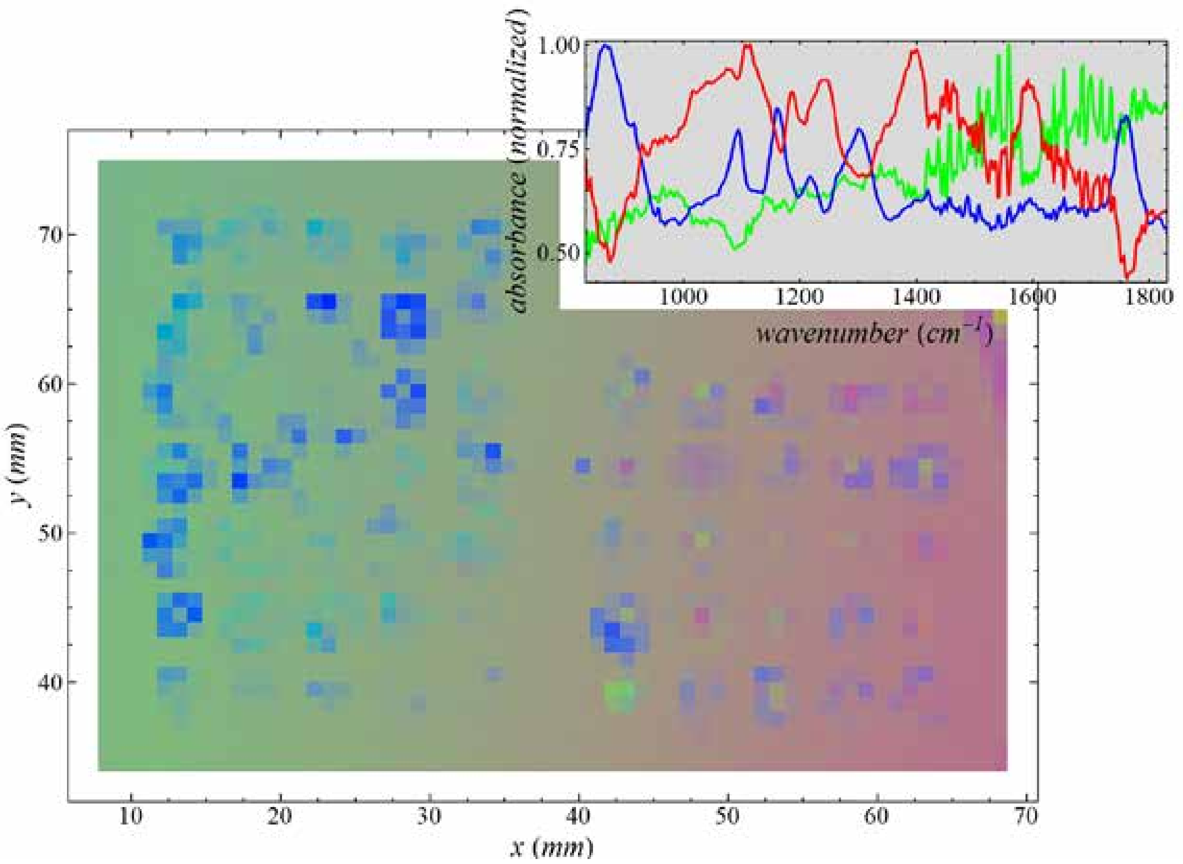
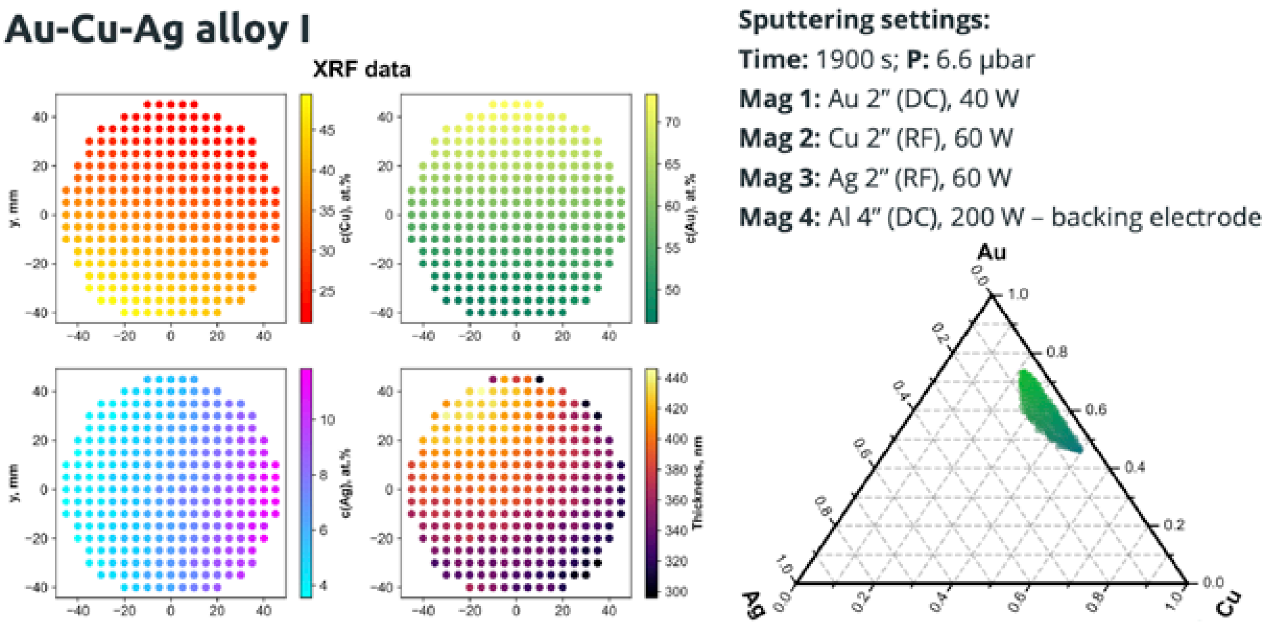


Figure 13. Coarse view of an Au wafer with 50 SDC experiments that are rapidly analyzed using the FTIR of HITS to detect molecular species.

1.3 Outlook

With the unique high-throughput electrochemistry tools and spectroscopy methods demonstrated and deployed in BIG-MAP as part of this deliverable, we are currently gathering large datasets for SEI and CEI evolution to decouple chemical and electrochemical corrosion phenomena.
Using combinatorial sputtering techniques, we are also investigating the LiF formation on the model system anode Au-Cu-Ag. To this end, the first materials libraries were manufactured, as shown in Figure 14, and DFT simulations were started together with WP2 and WP3.



Au-Cu-Ag alloy I

Sputtering settings:
Time: 1900 s; **P:** 6.6 µbar
Mag 1: Au 2" (DC), 40 W
Mag 2: Cu 2" (RF), 60 W
Mag 3: Ag 2" (RF), 60 W
Mag 4: Al 4" (DC), 200 W – backing electrode

Figure 14. Summary of composition measurements of Au-Ag-Cu as a model electrode to investigate LiF formation on different compositions with materials exhibiting other working functions, which are believed to be the main correlator to predict LiF formation on metals.

We also programmed a NAP-XPS and SIMS for in-depth, high-throughput analyses. For SIMS, we have created an extensive database for LiF and other SEI component detection, as shown in Figure 15. The goal is to make large arrays of SEIs, characterize them using Raman, FTIR, and XPS, and take selected samples to the SIMS.
Investigations of new electrolytes from WUT (LiTDI, LiPDI, LiHDI) are underway.

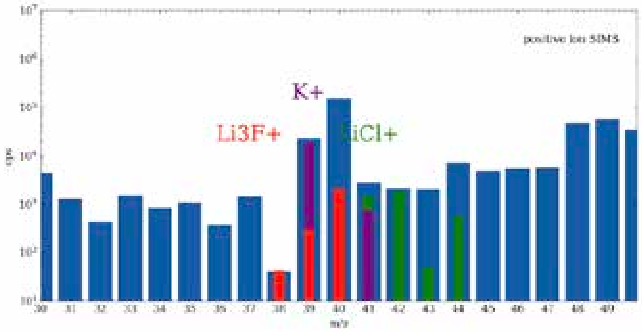


Figure 15. Positive ion SIMS of an SEI

1.4 Summary

In summary, we have developed instruments and protocols to investigate large numbers of SEIs and advanced their characterization by developing integrated workflows that characterize function, composition, structure, and interface composition using XRF, Raman, FTIR, XPS, and SIMS. All setups for this except the commercial ones operate using the BIG-MAP developed HELAO framework and follow the data management guidelines. The development of universal sample holders and a spatially split half-cell design to investigate anode materials in a high-throughput design are innovations in this field.