D4.6 – Demonstration of automated synthesis procedure

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ABSTRACT

The purpose of this report is to provide a detailed demonstration of two modular hardware and software platforms for the automated synthesis. The first platform is located at ULIV and covers semi-automated inorganic synthesis of alumina coatings on Li-ion positive electrode powders. The second platform is dedicated to organic materials, specifically protective coatings for electrode materials and is currently installed at Fraunhofer ISC. The systems allow for the physical and software integration of heterogeneous single units comprising standard lab equipment like vessels, rotary evaporators and pumping units, providing maximum flexibility and is scalable. The designed systems are the physical part of the BIG-MAP fully autonomous platform capable of integrating computational modelling, materials synthesis and characterization. Therefore, a unified architecture was designed in cooperation with WP10 to allow for seamless machine-to-machine communication via intra- and internet.

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1 Introduction

Automatic systems for synthesizing organic molecules have been in use for decades. Already in 1965, Merrifield demonstrated the automated synthesis of peptides in a linear reactor array[1]. Combining process automation and state-of-the-art artificial intelligence (AI) techniques has propelled the synthesis of organic compounds[2]. The Cronin Group (University of Glasgow) developed a flow synthesis system including a chemical programming language called *Chemputer*, where synthesis steps are classified into four main activities and sequentially processed. [3]. Another example of an integrated synthesis was proposed by Chatterjee et al. with the concept of a radial synthesis of organic molecules[4]. Bédard et al. proposed a plug-and-play, reconfigurable, continuous-flow chemical synthesis system based on membrane technology where the different reaction modules are integrated as individual boards [5]. More recently, using the same modules as Bédard, an autonomous system has been proposed that uses a robot manipulator for exchanging modules around[6]. Furthermore, researchers at the University of Liverpool have demonstrated a dexterous, free-roaming robot that automated the search for improved photocatalysts for hydrogen production from water[7].

Due to the limitations in the reaction and purification chambers more complex polymers are hardly feasible, thus many of these concepts focus on the synthesis of molecules. Integrated systems working with syringes also have issues with clogging the reaction chamber and the transfer funnels[8], making it difficult to upscale these processes to larger batches in the liter-scale or beyond.

Utilizing standard lab equipment orchestrated by a human operator (semi-automated) or a one-arm robot (fully-automated) provides the capability of working on larger scales (i.e., up to 1000 ml), thus being able to produce large amounts of pre-polymers and polymers. A flexible system, which can include a robot arm manipulator to move the vessels around allows the integration of different types of lab equipment. This system is realized within WP4 by utilizing several modules that can be arranged to a dedicated platform to carry out the target synthesis process.

[1] R. B. Merrifield, “Automated Synthesis of Peptides: Solid-phase peptide synthesis, a simple and rapid synthetic method, has now been automated.,” Science, vol. 150, no. 3693, pp. 178–185, Oct. 1965, doi: 10.1126/science.150.3693.178.
[2] J. Li et al., “Synthesis of many different types of organic small molecules using one automated process,” Science, vol. 347, no. 6227, pp. 1221–1226, Mar. 2015, doi: 10.1126/science.aaa5414.
[3] S. Steiner et al., “Organic synthesis in a modular robotic system driven by a chemical programming language,” Science, vol. 363, no. 6423, p. eaav2211, Jan. 2019, doi: 10.1126/science.aav2211.
[4] S. Chatterjee, M. Guidi, P. H. Seeberger, and K. Gilmore, “Automated radial synthesis of organic molecules,” Nature, vol. 579, no. 7799, pp. 379–384, Mar. 2020, doi: 10.1038/s41586-020-2083-5.
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[7] B. Burger *et al.*, “A mobile robotic chemist”, *Nature*, vol. 583, pp. 237-241, 2020, doi: 10.1038/s41586-020-2442-2.
[8] Z. Wang, W. Zhao, G.-F. Hao, and B.-A. Song, “Automated synthesis: current platforms and further needs,” Drug Discov. Today, vol. 25, no. 11, pp. 2006–2011, Nov. 2020, doi: 10.1016/j.drudis.2020.09.009.

2 Inorganic platform

2.1 Protocol

The inorganic synthesis route for the formation of coatings on nickel-rich layered oxide materials for Li-ion positive electrodes utilises a "sol-gel" synthetic procedure. The procedure targets alumina, Al_2O_3, as the desired benchmarking coating material and has been demonstrated using $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (code NMC622). The process for the sol-gel synthesis of Al_2O_3 coatings within an individual reaction vial is described in five primary steps (Figure 1): solid powder dosing, liquid component dosing (including Al-precursor solutions), reaction heating/mixing, solvent evaporation/removal, and calcination.

The solid NMC622 powder (1 g) is dispensed into a glass vial (Figure 2). The bulk solvent (*e.g.,* anhydrous 2-propanol) is first deposited into the glass vials (volume 40 mL), followed by the chelating agent and then the solvent solution containing the aluminium precursor (*e.g.,* aluminium tri-*sec*-butoxide). The total liquid volume is fixed to 10 mL by adjusting the solvent volume. The resulting solid/liquid mixture is then heated with mixing for a given time before dry N_2 flows into the vial to promote evaporation of the bulk solvent. The reaction mixture is then calcined in a natural convection furnace (400-675 °C). Integrating these steps into the described partially automated procedure completed in batches of 11 samples per rack increases throughput to complete 22-44 samples per 6-7 h *versus* 6-7 h for 1 sample by a manual process. This increases the accessibility of the matrix of reaction variables/parameters that may be explored to optimize the coating conditions.

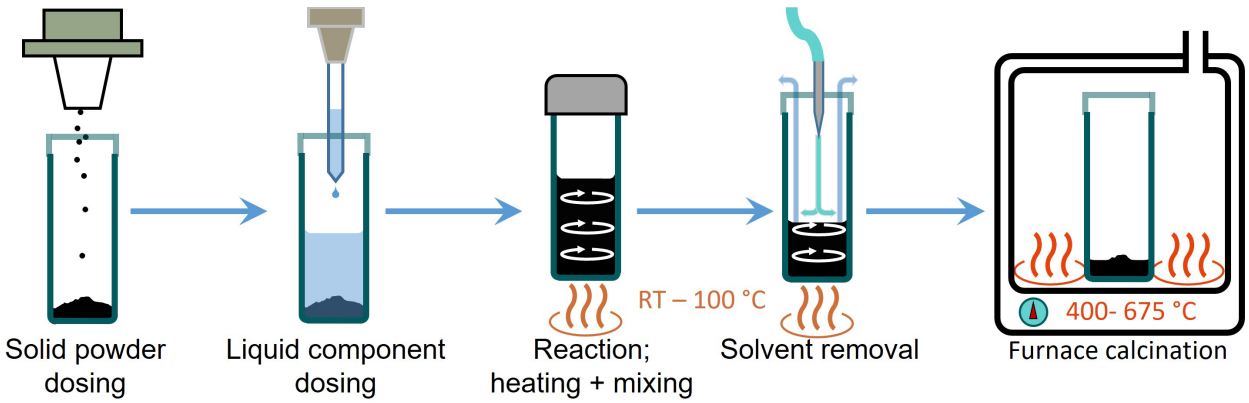


Figure 1. The semi-automated coating process of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (code NMC622) with alumina (Al_2O_3).

2.2 Hardware

2.2.1 Solid dosing

The dosing (weighing) of the solid NMC622 electrode powder is completed using an XPR204 automated balance (Mettler Toledo) with an automated sample changer carousel (Figure 2). The sample changer carousel can take up to 30 sample vials for a completely automated programmable run without additional user interference. The balance and carousel are set up inside a fumehood and connected to an instrument PC running the Mettler Toledo LabX software. The LabX software also provides templates for preparing and exporting data reports.

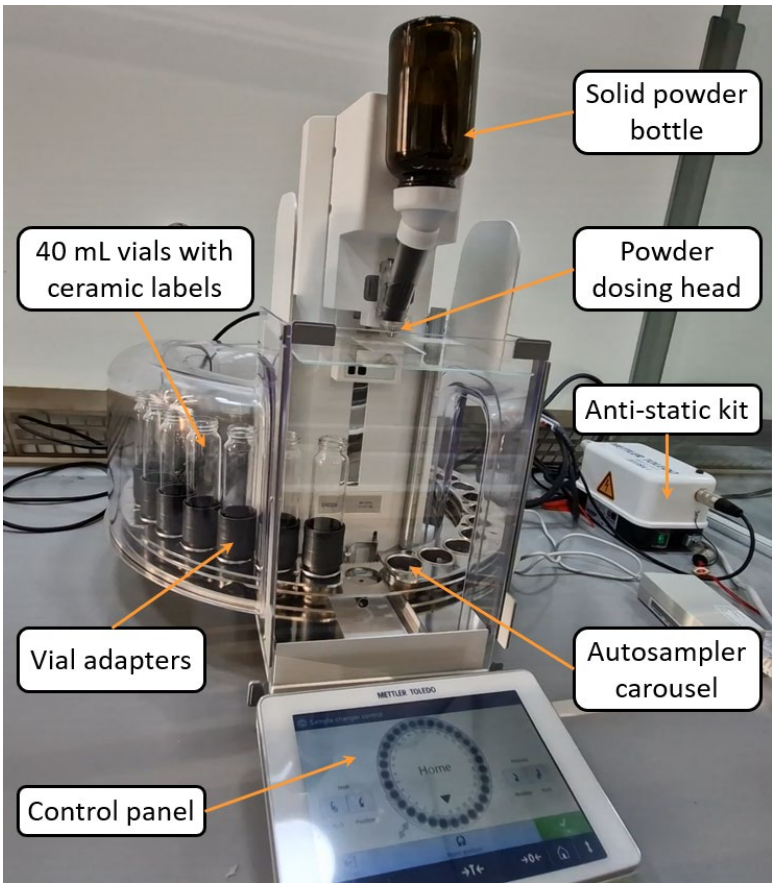


Figure 2. The XPR204 automated balance and sample carousel in place in the fumehood, with the NMC622 designated dosing head and bottle in place.

The balance operates for powders using dedicated powder dosing heads (*i.e.*, one powder/material per dosing head). Two dosing head types were demonstrated to be suitable for dosing NMC622, achieving better than 0.5 % tolerance at the 1 g target. The dosing heads are loaded with an RFID (radio frequency identification) chip containing coded with the material information/identifiers and the system contains internal feedback to "learn" the material dosing properties of the dosing head in order to improve the speed and reproducibility of the dosing procedure. The solid dosing step incorporates sensor feedback to improve performance and accuracy. A solid dosing run of 11 samples (i.e., 1 rack) is completed in approximately 10 minutes.

2.2.2 Liquid dosing

The liquid dosing step requires the addition of three liquid components, the aluminium precursor (i.e., aluminium tri-*sec*-butoxide), chelating agent (*i.e.*, ethyl acetoacetate) and bulk solvent (i.e., anhydrous 2-propanol or isopropanol, IPA). For the aluminium precursor, a dilute solution of aluminium tri-*sec*-butoxide (0.15 M) in anhydrous IPA with two equivalents of chelating agent is first prepared under the inert/dry conditions of an argon-filled glovebox (H_2O/O_2 <0.1 ppm). The viscous aluminium precursor is dissolved into a dilute solution to thin the liquid to facilitate dosing and the chelating agent is introduced to stop hydrolysis of the Al-precursor once exposed to moisture in the ambient atmosphere. The dosing of the three liquid components is completed using the same XPR204 automated balance, with the addition of a liquid dosing pump and three dedicated liquid dosing heads (Figure 3).

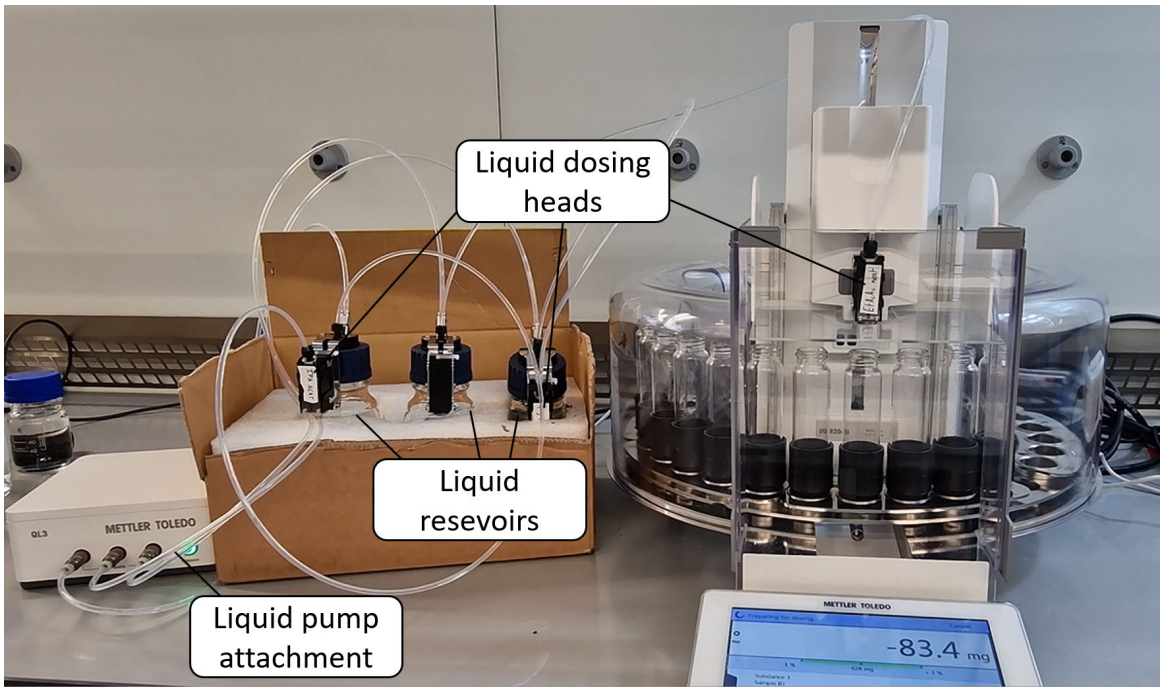


Figure 3. The XPR204 automated balance and sample carousel with the liquid dosing pump connected to the liquid reservoirs and dedicated liquid dosing heads.

The LabX software, controlling the XPR204 balance, allows for method/task design, import and implementation to complete all solid and liquid dosing steps within a single experiment. Sample series (i.e., a batch of samples) are inputted automatically using the software developed (discussed in section 2.3 and the sample IDs are created using a simple USB PoS barcode scanner (Datalogic, Model 1500I) to read the vial 2D array codes (Figure 3). Automated dosing for 11 samples (44 dosing steps per rack) is completed within 20 - 30 mins, requiring manual intervention to swap dosing heads in between component steps.

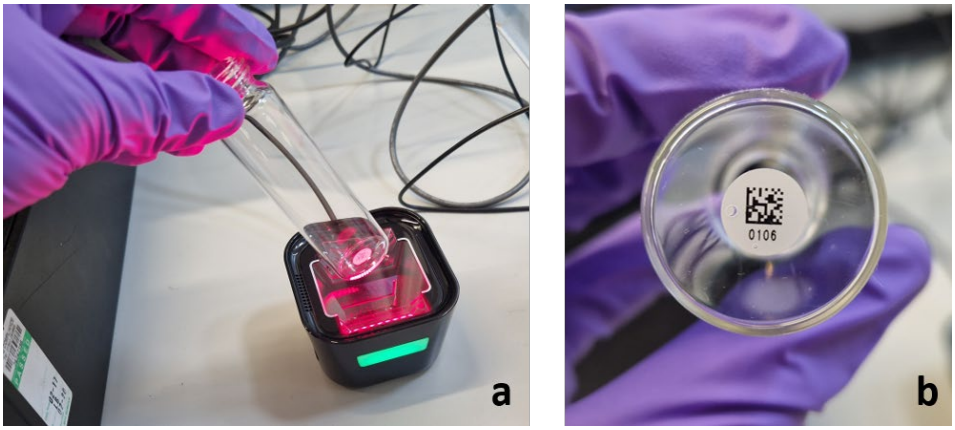


Figure 4. (a) USB PoS barcode reader attachment to the instrument PC running the LabX software and (b) the ceramic 2D array label, 10-digit code with human readable 4-digit code, on the base of the glass sample vial.

2.2.3 Reaction stage

Once all components are dosed into the glass vials, samples are loaded into custom-made reaction racks, constructed using brazed stainless-steel tubing to provide good thermal conductivity as well as stability at calcination temperatures. The sample racks containing 11 vials are transferred to the

RS9000 heater/shaker stage (Electrotherm) and screwed into position (Figure 6). The heater/shaker is interfaced with the instrument PC and software via an Arduino Uno microcontroller to operate, control, and feedback the conditions and parameters. The microcontroller is also interfaced with an external thermocouple (using a separate Arduino MKR-series board and MKR THERM shield) to provide additional parameter feedback, accounting for value discrepancy at the sample stage which can then be accounted for. The heater/shaker has a 2D orbital shaking motion to a maximum of 600 rpm and a maximum heating temperature of 150 °C. Both the temperature and rotation speed are gently ramped over fixed periods following protocols implemented by the user via the software.

Prior to the final calcination step, a flow of dry N_2 can be introduced directly into each vial to aid the evaporation of a given proportion of the bulk IPA solvent. A prototype mk.1 manifold was prepared using simple pneumatic push fittings to split the gas flow to the 11 vials. These were fitted using bulkhead fittings to a solid plastic board to carefully match vial positions and allow gas flow while sample shaking is ongoing.

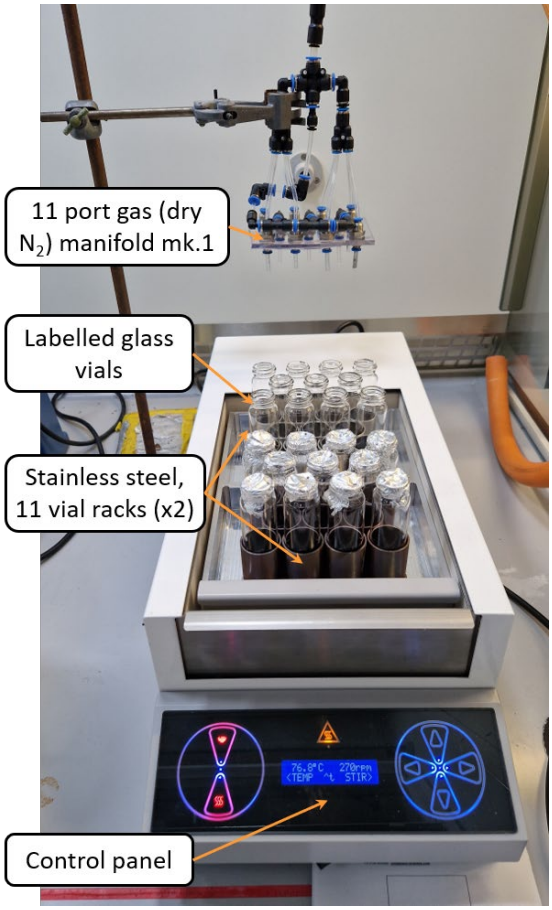


Figure 5. Heavy duty RS9000 heater/shaker (Electrotherm) reaction stage containing two racks of 11 samples each. The prototype gas inlet manifold, allowing the flow of dry N_2 into the reaction vials during shaking, is also pictured.

2.2.4 Calcination

Following the reaction stage, the sample racks are transferred to a natural convection box furnace inside a fumehood to complete the calcination step at high temperatures (Figure 7). The entire stainless-steel rack containing up to 11 samples is loaded into the furnace, and multiple sample racks can be calcined simultaneously. The furnace controller is interfaced *via* an ethernet comms port to control heating ramp/dwell times, for up to 675 °C maximum - determined by the thermal stability of the glass sample vials. At temperature >675 °C, major deformation of the glass vial is observed.

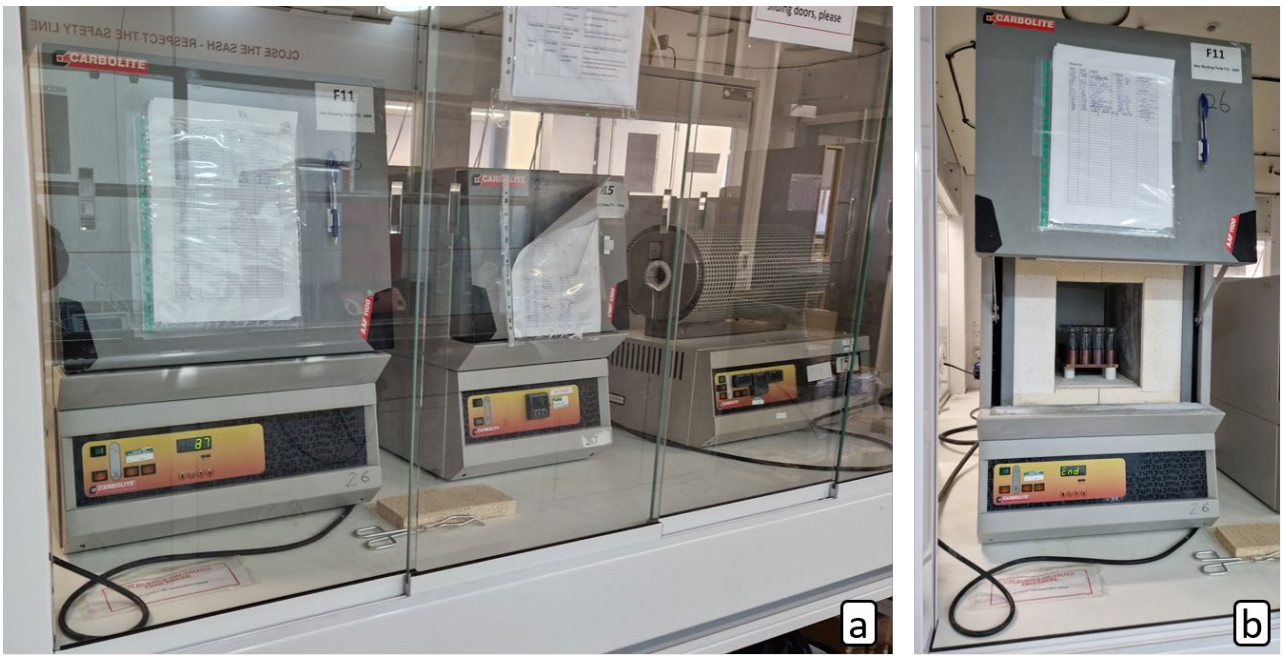


Figure 6. Natural convection box furnace placed inside a fumehood (a) in a dedicated furnace lab and (b) the pair of stainless-steel sample racks at the end of a completed calcination step.

2.3 Software

The software used for the automated inorganic synthesis process allowed for control of the solid and liquid dosing, as well as the reaction stage. At present, the software modules for these two steps are separate, but they are run on the same instrument PC in the same Python environment, so their direct integration in the future will be straightforward. Further software development will integrate the calcination of samples in the furnace into this control scheme in the same way as the two earlier steps. Automated experimental sequences will be enabled through the Modbus TCP protocol over the laboratory network, via the ethernet comms port on the furnace temperature controller using the Python module *pyModbusTCP*.

Future development is also intended to allow for interfacing with the 'fast intention agnostic learning server' (FINALES) developed as part of BIG-MAP. This will enable an external web-based user to fully define the parameters of a synthesis procedure, which then proceeds with minimal manual intervention. A lab-based experimenter only needs to carry out the sample transfer without defining or reporting any process variables. The relationship between the custom software modules and the software provided by manufacturers of the equipment is shown in Figure 7.

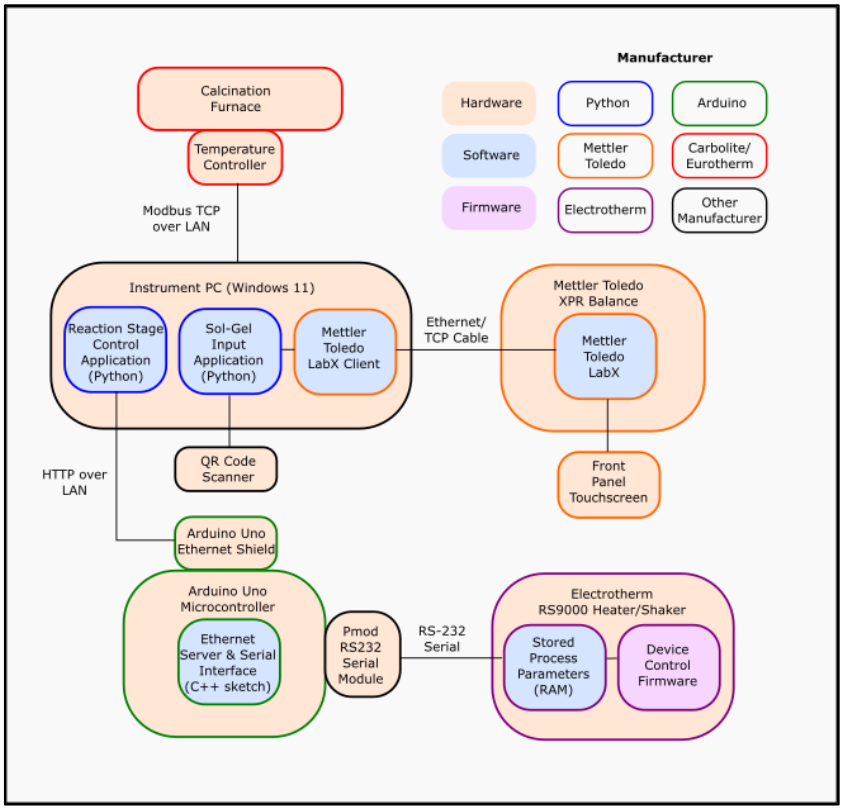


Figure 7. Network diagram for software used for the automated process, along with their corresponding hardware components.

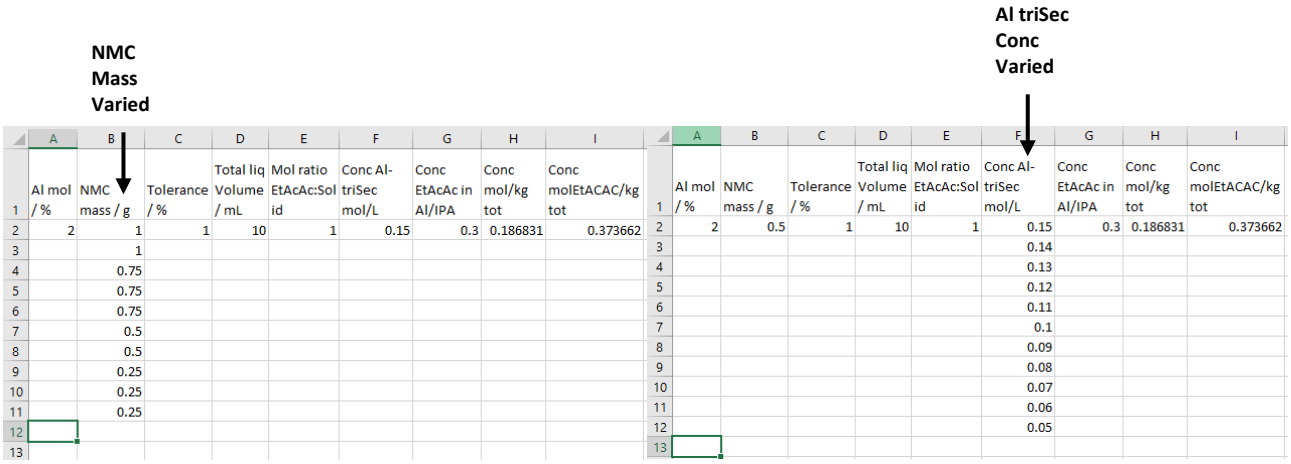
2.3.1 Sol-gel input application for solid and liquid dosing

A user may manually calculate target masses and tolerances and input these into the LabX software (Mettler Toledo) for every component and every sample, but this approach is time-consuming, especially for multi-component syntheses and large sample sets. The LabX software also includes the capability to define import templates to automatically import a file containing target masses and tolerances, so long as the file matches the expected format and is saved in the expected directory location. Once imported, the dosing process for the sample series can be started by a user from the XPR204 touchscreen without the need to manually create a sample series.

The function of the custom sol-gel input application is, therefore, to automatically calculate the target values for a sample series, then transfer these values to the relevant directory for automatic import, in the format expected by the LabX template. As there is then no need to manually populate a new sample series, this custom application saves the user a significant amount of time. It also allows for external users to easily define a set of process parameters without direct access to the LabX software.

This application is written in Python 3 and includes its own graphical user interface (GUI) accessible to a user running a Python interpreter. The application functions separately to the LabX software that controls the dosing system, as its output is a file containing target masses and tolerances. The application ensures that these values are packaged in a file of the necessary format, which is saved in the directory on the instrument PC defined for import by a template created in the LabX software.

The Python-based input script is publicly available on GitHub[9], with required modules and source files also included in the repository.



	A	B	C	D	E	F	G	H	I
1	Al mol / %	NMC mass / g	Tolerance / %	Total liq Volume / mL	Mol ratio EtAcAc:Sol id	Conc Al-triSec mol/L	Conc EtAcAc in Al/IPA	Conc mol/kg tot	Conc molEtACAC/kg tot
2	2	1	1	10	1	0.15	0.3	0.186831	0.373662
3		1							
4		0.75							
5		0.75							
6		0.75							
7		0.5							
8		0.5							
9		0.25							
10		0.25							
11		0.25							
12									
13									

	A	B	C	D	E	F	G	H	I
1	Al mol / %	NMC mass / g	Tolerance / %	Total liq Volume / mL	Mol ratio EtAcAc:Sol id	Conc Al-triSec mol/L	Conc EtAcAc in Al/IPA	Conc mol/kg tot	Conc molEtACAC/kg tot
2	2	0.5	1	10	1	0.15	0.3	0.186831	0.373662
3						0.14			
4						0.13			
5						0.12			
6						0.11			
7						0.1			
8						0.09			
9						0.08			
10						0.07			
11						0.06			
12						0.05			
13									

Figure 8. Examples of different forms of process input, with a set of fixed parameters and one varied parameter, as selected by the user. Any variation of this kind can be imported and used to calculate masses. The number of samples is also variable (up to 30).

The application allows a user to define a sample series based on a set of varied parameters, for example, the concentration of the Al sol-gel precursor relative to a solid mass. Examples of an input file with other parameters varied are shown in Figure 8. A comma-delimited file (.csv) containing the material information (e.g., density) is contained in the same directory as the script.
The process of generating a sample series for dosing is shown in Figure 9. From the varied and fixed values in the input file (Figure 8), the necessary solid and liquid masses are calculated and displayed in a user-editable table within the GUI. At this point, the experimenter may enter sample IDs, either manually or through the QR code scanner. At this stage, the experimenter loads the sample vials onto the matching numbered position on the sample changer carousel (see Figures 3 and 4). The IDs (which are also displayed in human-readable form on the vials) remain associated with the samples throughout the process.

Once the user has approved the calculated values, a .csv file, readable by the XPR204 balance LabX software, and containing the solid and liquid masses and tolerances, is generated and saved in the import directory. The file created must match the format defined in the import template, with the input application in its current form working with a specific import template developed for this study. However, there is scope to enable the script to replicate the format of any import template, as LabX allows templates to be exported in text form.

Once LabX is started and the file for import is created, the import template executes, and a new sample series is created, associated with the specific dosing method (see section 2.2). The experimenter can then start the dosing process by selecting the new sample series on the touchscreen of the XPR204 balance, after which dosing of the one solid and three liquid components proceeds as described in sections 2.2.1 and 2.2.2. Once the dosing has completed, the software generates a report file containing the target and real masses, as shown in section 2.4.

[9] https://github.com/BIG-MAP/wp4-solid-liquid-dosing-input

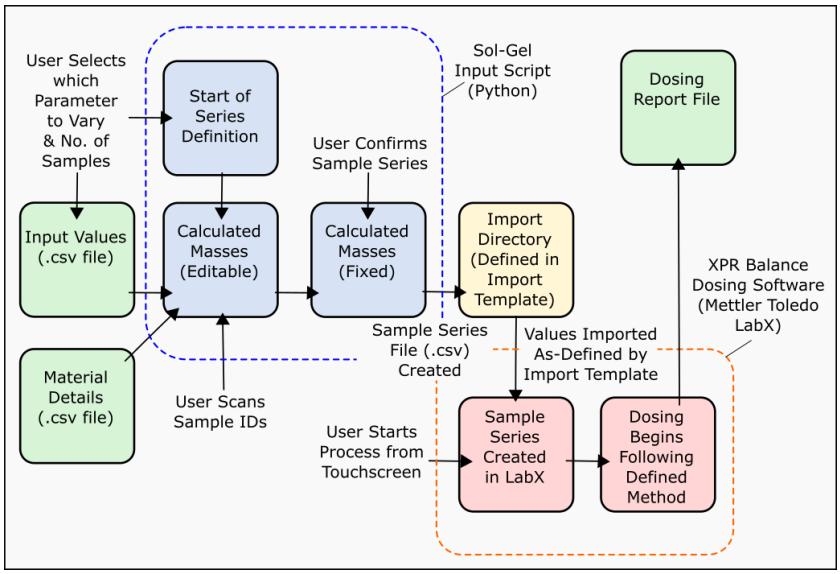


Figure 9. The flowchart shows the use of the input application to define a sample series for dosing and begin the dosing process. The input application runs on the instrument PC connected to the balance. The form of files used for 'Input Values' is shown in Figure 8.

2.3.3 Control software for heater/shaker

Remote control of the RS9000 heater/shaker stage is by way of the device's RS-232 serial port, with digital communications using frames of 4 bytes each for a read or write command. The Arduino Uno microcontroller is integrated with a Digilent Pmod RS232 Module and an Arduino Ethernet Shield 2 to allow for RS-232 interfacing and communications over the laboratory local area network (LAN), respectively. Figure 10 shows the wiring diagram for the serial interface. A null-modem adapter to the serial cable is used so the microcontroller acts as a data terminal equipment (DTE) device - the RS9000 heater/shaker always acts as a data communications equipment (DCE) device. The microcontroller communicates with the instrument PC over the laboratory LAN. Additionally, the main Arduino Uno microcontroller is interfaced with the Arduino MKR board (which operates an external thermocouple) using the I2C pins (SCL and SDA), also shown in Figure 10.

No proprietary software was available for remote control of the reaction stage, so custom scripts were created to enable this. This software includes an application written in Python 3, and is run on the instrument PC, as well as scripts loaded and run on the Arduino Uno & Arduino MKR microcontrollers, written in the Arduino integrated development environment, using the C++ language. The Arduino Uno functions as a serial interface and server accessible from the instrument PC via HTTP, with its loaded software (sketch) concerned primarily with transferring the 4-byte frames to the heater/shaker for read/write commands. The frames themselves are generated and interpreted by the Python application on the instrument PC, as discussed below. A secondary function of the Arduino Uno is to read external thermocouple temperature measurements from the Arduino MKR board and relay these to the instrument PC in the same format as the measured values from the heater/shaker. Both the Python-based control application and the scripts for the Arduino microcontrollers (Uno & MKR) are publicly available on GitHub[10]. HTTP communication between the instrument PC and the Uno is achieved using the Python 'requests' module.

[10] https://github.com/BIG-MAP/wp4-sol-gel-reaction-stage

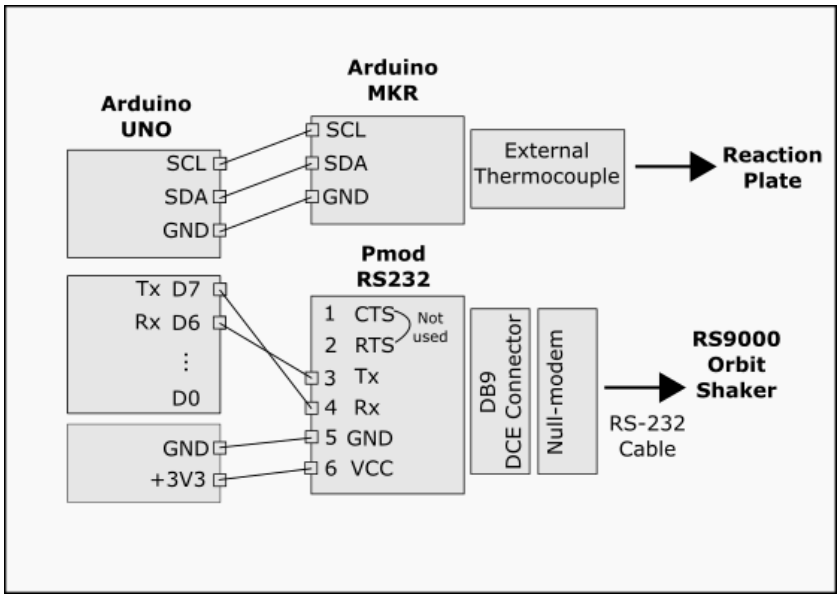


Figure 10. Wiring diagram for the Arduino Uno and peripherals: PmodRS232 module used to interface with the RS232 serial port on the RS9000 heater/shaker reaction stage; Arduino MKR for interfacing with external thermocouple.

Arduino microcontroller software

The principal microcontroller sketch configures the Arduino Uno to act as a server using the Arduino 'Ethernet' and 'EthernetClient' modules. RS-232 communications *via* the Pmod module make use of the 'SoftwareSerial' Arduino module. The transmission (Tx) and receiver (Rx) pins for the serial connection are configured as shown in the wiring diagram in Figure 10, but any pair of digital pins 2-7 on the Arduino Uno can be used for this purpose. Digital pins 11-14 are reserved for the ethernet shield in this case so they cannot be used. Upon receiving a frame via a request from the application on the instrument PC, the Uno microcontroller sends the frame to the heater/shaker over the software serial pins and receives the 'checksum' and data values, which it then sends to the instrument PC in the form of HTML.

Communications between the Uno and the MKR thermocouple board is via the Arduino 'Wire' software module, and the Uno is configured to read these values upon receiving a frame from the instrument PC containing the device address of the MKR (defined in both board's sketches), as opposed to the heater/shaker, otherwise treating the values the same way as in communications with the heater/shaker. The MKR itself also runs a simple custom sketch which, upon a request from the Uno, executes a measurement of the temperature from the external thermocouple (using the 'Arduino_MKRTHERM' module) and sends this value to the Uno.

Control software on workstation PC

The reaction stage control application, written in Python 3, allows for both the basic remote operation of the heater/shaker and the definition of a complete autonomous sequence. This enables finer control over the heater/shaker since, under manual operation, only a single setpoint and ramp are possible for the temperature and agitation speed, whereas the process definition allows for stepped setpoints without the need for manual intervention. This removes the need for an experimenter to supervise the entire process, manually adjusting setpoints to achieve a smooth

ramp, and so frees up significant time for the experimenter, while also enabling a more reproducible series of process steps. The script for the process control is publicly available on GitHub[11].

Serial communication with the RS9000 heater/shaker is via 4-byte frames, each addressed to a single RAM location, corresponding to the operational parameters (e.g., speed ramp). The Python-based control application is, therefore, responsible for translating user-defined values into the required bytes and sending the frames in the correct order. After receiving a frame, the RS9000 requires 7ms before the next frame, thus 10 ms was left between frames. Upon receiving data bytes from the heater/shaker via the microcontroller, the software then similarly translates these into real values.

During user operation of the software, the series of process steps can be imported from a .csv file (as well as, or instead of, inputting values manually), saving time and allowing for easy consistency across multiple batches. Once a process has been started, a process monitor window shows the real-time values (e.g., temperature, agitation speed) to be viewed by the user. These values are periodically logged by the software and, once the process has concluded (or stopped for any reason), automatically output in a file. Figure 12 in the next section shows an example of this process data report file.

2.4 Demonstration

The automated steps of solid/liquid dosing and reaction stage control provide feedback in the form of data and parameter reports. An example dataset for the automated solid and liquid dosing process is shown in Figure 11, wherein a selection of these samples was dosed at 0.5 g solid mass. The dataset shows the sample IDs, substance IDs, the target dosing amounts, tolerances, and the actual net dosed amount. Additionally, Figure 12 shows an example dataset output from the reaction stage control software, containing the logged operational parameters during the procedure.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	Sample index in scope	Sample ID1	Sample start time	Overall state	Net Substance 1 (NetSubstance1)	Unit of Net Substance 1 (NetSubstance1)	Net Substance 2 (NetSubstance2)	Unit of Net Substance 2 (NetSubstance2)	Substance 1	Target Substance 1 [mg]	Tolerance Substance 1 +/- %	Substance 2	Target Substance 2 [mg]	Tolerance Substance 2 +/- %	Subst
2	1	0000000187	05/10/2023 12:48	OK	502.0	mg	2641.2	mg	NMC622	500	1	IPA Neat	2641	1	EtAc/
3	2	0000000188	05/10/2023 12:49	OK	501.9	mg	2641.0	mg	NMC622	500	1	IPA Neat	2641	1	EtAc/
4	3	0000000189	05/10/2023 12:50	OK	501.2	mg	2641.3	mg	NMC622	500	1	IPA Neat	2641	1	EtAc/
5	4	0000000190	05/10/2023 12:51	OK	501.0	mg	2641.1	mg	NMC622	500	1	IPA Neat	2641	1	EtAc/
6	5	0000000191	05/10/2023 12:52	OK	501.3	mg	2641.1	mg	NMC622	500	1	IPA Neat	2641	1	EtAc/
7	6	0000000192	05/10/2023 12:53	OK	500.9	mg	2641.5	mg	NMC622	500	1	IPA Neat	2641	1	EtAc/
8	7	0000000193	05/10/2023 12:54	OK	1001.6	mg	5282.3	mg	NMC622	1000	1	IPA Neat	5282	1	EtAc/
9	8	0000000194	05/10/2023 12:55	OK	1002.2	mg	5282.2	mg	NMC622	1000	1	IPA Neat	5282	1	EtAc/
10	9	0000000195	05/10/2023 12:56	OK	1002.2	mg	5282.5	mg	NMC622	1000	1	IPA Neat	5282	1	EtAc/
11	10	0000000196	05/10/2023 12:57	OK	1002.6	mg	5282.3	mg	NMC622	1000	1	IPA Neat	5282	1	EtAc/
12	11	0000000197	05/10/2023 12:58	OK	1002.2	mg	5282.4	mg	NMC622	1000	1	IPA Neat	5282	1	EtAc/

Figure 11. Partial screenshot of a dataset containing solid and liquid dosing data and sample information from the XPR204 automated balance.

[11] https://github.com/BIG-MAP/wp4-sol-gel-reaction-stage

	A	B	C	D	E	F	G	H	I	J
1	Time (s)	Temp Setpoint (C)	Temp Measured (C)	Speed Setpoint (RPM)	Speed Measured (RPM)	Heater Power (%)	Stirrer Status (on/off)	Error Status	Process Status	
2	61.1	106	28.2	100	99	21	On	No Errors	RampHeat&Stirr	
3	123.3	106	32.8	100	99	25	On	No Errors	RampHeat&Stirr	
4	185.6	106	37.6	100	99	29	On	No Errors	RampHeat&Stirr	
5	247.9	106	41.6	100	99	32	On	No Errors	RampHeat&Stirr	
6	309.5	106	46.3	100	98	35	On	No Errors	RampHeat&Stirr	
7	371	106	48.4	200	109	37	On	No Errors	Speed step 2/19	
8	433.7	106	53.2	200	129	40	On	No Errors	Speed step 2/19	
9	496.4	106	59.5	200	151	42	On	No Errors	Speed step 2/19	
10	558.7	106	64.3	200	171	43	On	No Errors	Speed step 2/19	
11	621	106	68.1	200	191	44	On	No Errors	Speed step 2/19	

Figure 12. A partial screenshot of the report file dataset containing the operational parameters from the RS9000 heater/shaker stage, automatically logged during the synthesis of the coated NMC622 powder.

After completing the partially automated synthesis procedure, the resulting *coated* NMC622 powders were used to prepare an electrode cast. The electrochemical performance of the coated sample was compared with an unmodified NMC622 sample (Pristine - uncoated) and with a coated sample prepared manually. The manually coated sample was prepared using the same mol% target coating and the same furnace conditions, and the mixing was completed by a magnetic stirrer bar (removed before calcination) on a hotplate stirrer. Under the standard BIG-MAP cycling procedure (3 formation cycles at 0.1C, then cycled at 1C between 2.5 - 4.5 V *vs*. Li^+/Li in 1 M Li[PF_6] in ethylene carbonate/ethyl methyl carbonate [with 2 wt% vinylene carbonate]), the Li|NMC622 half-cells prepared using the coated electrodes provided more stable cycling compared to the uncoated sample. Importantly, the automated procedure was shown to produce a coated powder replicating the performance of that prepared using the manual coating procedure.

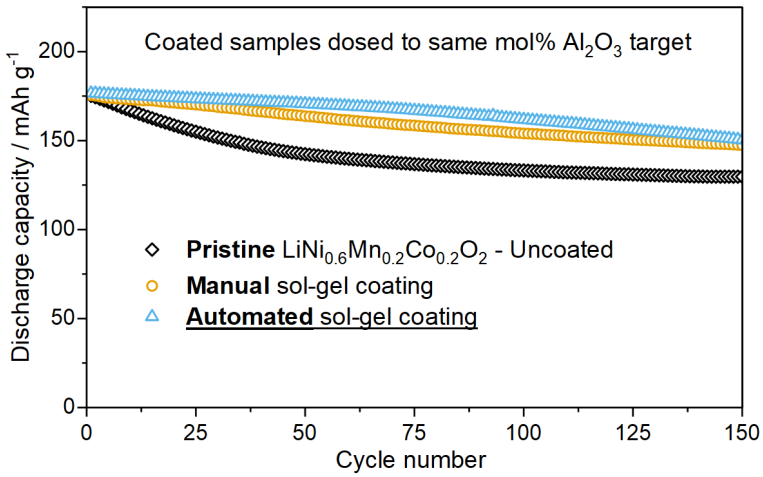


Figure 13. Electrochemical performance of Li|NMC622 half cells prepared using uncoated NMC622 material and the NMC622 with an Al_2O_3 coating prepared by the manual and automated procedures.

3 Organic coating platform

The organic coating platform is dedicated to protective coatings for electrode materials and is installed at Fraunhofer ISC.

3.1 Synthesis Process

The automated robot-assisted synthesis focuses on preparing inorganic-organic hybrid polymers for use as flexible and protective coatings for anode-active materials. The polymer must exhibit

chemical stability against the anode and electrolyte, as well as electrochemical stability at low voltages. The hybrid polymers originate from a sol-gel route, synthesizing a pre-polymer through hydrolysis/condensation, resulting in organically modified polysiloxanes.
Sol-gel synthesis offers a convenient setup and an eco-friendly process (moderate temperatures; T << 100 °C). Currently, the manual synthesis of the pre-polymer is sensitive to environmental changes like temperature and humidity, leading to variability. To overcome this, the manual steps should be automated for efficiency.
In the manual route, alkoxylated silanes are combined, dissolved in a solvent, and subjected to hydrolysis with added water. Adjusting the pH accelerates the condensation reaction, forming the three-dimensional inorganic backbone. NMR spectroscopy monitors the reaction, and after completion, the solvent is removed under reduced pressure.
For purification, the residue is dissolved in water, and impurities are removed through extraction with ethyl acetate. The pre-polymer remains in the aqueous phase. In a second extraction with dichloromethane, the pre-polymer is separated, and after solvent removal, it is dried under a vacuum to eliminate residual solvents and water.
With a honey-like viscosity, the resulting pre-polymer serves as an inorganic-organic hybrid polymer. Subsequent organic cross-linking/polymerization can occur through thermal or UV reaction steps. For anolyte/binder application, polymerization includes a lithium salt, while coating material application omits the addition of Li salt during polymerization.

3.2 Hardware

The robotic system (Figure 14) for organic synthesis has been constructed using a combination of hardware components from various manufacturers. The system allows for the physical and software integration of heterogeneous single units comprising standard lab equipment like vessels, rotary evaporators, and pumping units, providing maximum flexibility and scalability.

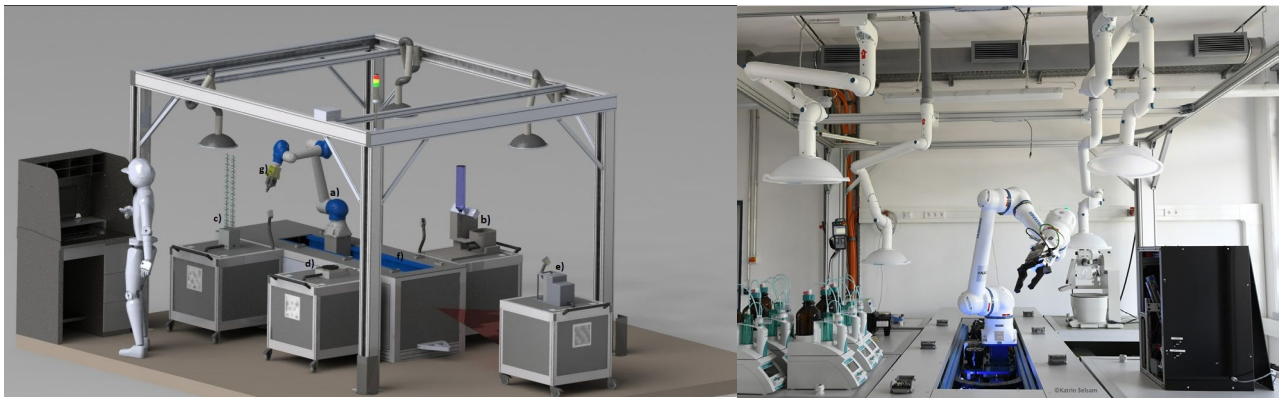


Figure 14. Left: Concept illustration of the Fraunhofer ISC setup. Robotic arm (a) installed on a linear axis (f) and equipped with a robotic gripper (g). Liquid-liquid extraction device (c). Magnetic stirrer with heating plate (d). Precision scale / dosing device (e). Rotary evaporator (b). Right: Assembled robot platform.

The MOTOMAN HC10DT is used as a central 6-axis robot. It is designed for collaborative operation with a payload of up to 10 kg, enabling human-robot interaction without a protective fence, due to power and force-limiting technology. Safety is enhanced by surrounding trolleys and a safety light grid. The HC10DT serves as the central manipulator for moving components during synthesis.

For precise glass vessel manipulation, the electric robot gripper Schunk EGL 90-PN is attached to the HC10DT, with a 42.5 mm stroke and 600 N gripping force. Recommended for workpieces up to 3 kg, it accommodates vessels used in the process with a maximum finger length of 165 mm. The parallel gripper's design ensures even force distribution, preventing damage to objects.

The specially configured fingers of the HC10DT robot with EGL 90-PN gripper securely grip sensitive glass vessels, such as those in the Büchi R-300 rotary evaporator, ensuring safe handling during synthesis. A 2-meter-long linear axis (TS-100D) aids the HC10DT robot in moving to trolleys, expanding the robot's manipulation range. This extended reach allows the robot to access different areas of trolleys from various positions, facilitating quick switches. The traversing axis is controlled similarly to the robot arm's axes and stepper motors.

The Büchi R-300 with vacuum pump and cooler is an innovative rotary evaporator system that offers maximum convenience and versatility for laboratory applications. The R-300 can reach temperatures of up to 220°C and offers a maximum capacity of 5 liters. Its receiver flask protection and central interface for controlling each component make it suitable for the synthesis application and allow it to connect easily to the control system.

3.2.1 The Liquid-liquid-extraction (LLE) module

The LLE installed in the system is composed of three main parts a funnel box, a pump and valve box and a tubing sensor between the funnel and the pump (Figure 15), all are controlled through serial communication using a USB-serial commander protocol (CmdMessenger) by an external computer (Raspberry Pi 3). The main functionality of the device is exposed using a HTTP API to the central PLC controller. The API can be found in the BIG-MAP GitHub-Repo[12]. The diagrams below (Figure 16) describe the liquid connections between the two boxes and the power and data connections between components. Liquids are loaded into the funnel from the vessels attached to the rotary pump, which eliminates the need to fill the funnel from the top. Draining of the different layers is also controlled by the pump and the rotary valve is used to divert the different liquids to different containers.

[12] https://github.com/BIG-MAP/wp4-LLE/tree/master/Detection/Software/API/FastAPI

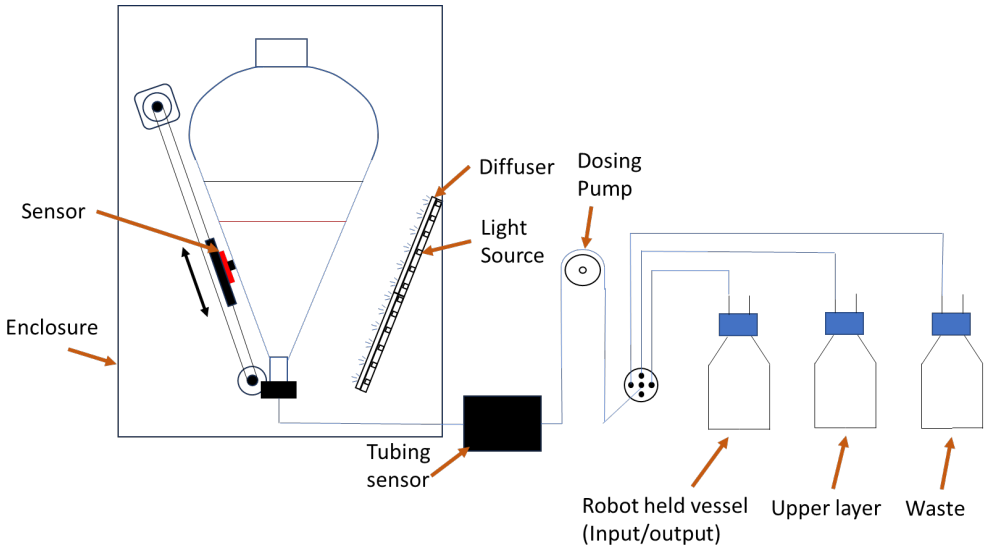


Figure 15. Flow diagram for LLE device. One input can be used as input output for the robot arm to load the device.

The funnel box contains a 3L funnel, an optical sensor (SparkFun Triad Spectroscopy Sensor – AS7265x) mounted, and a camera both on a belt and a light source. The 3L funnel is connected to the outside pump and valve box using a GL45 standard cap and PTFE tubing. A rail guide, located on the opposite side of the sensor belt, houses a controllable LED strip with 16 evenly spaced 470-700nm WS2812B LEDs. The LEDs illuminates the funnel for the sensor to be able to detect the interface. The main detection methodology uses the refraction and reflection of the liquid-liquid interfaces[13]. The controller for the light strip, the belt mechanism, and the sensor are also placed inside this box and are connected to the outside via a USB connector on the side of the box.

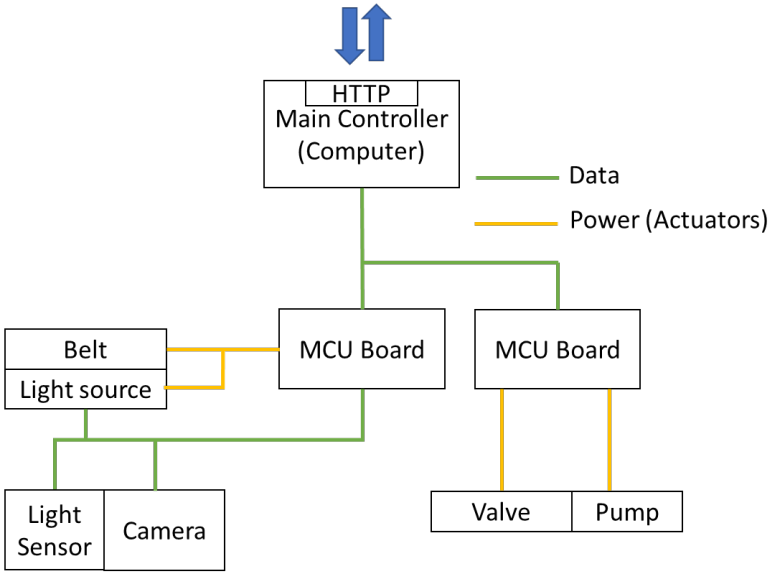


Figure 16. Connection and control diagram for LLE device.

[13] R. Moreno, A. Faina, and K. Stoy, "Near Infrared Sensor Setup for General Interface Detection in Automatic Liquid-Liquid Extraction Processes," IEEE Sens. J., vol. 22, no. 10, pp. 9857–9867, May 2022, doi: 10.1109/JSEN.2022.3164188.

Immediately outside the funnel box sits a sensor box housing another optical sensor attached to the PTFE tubing. This sensor follows the same principle of detection as the funnel but has the advantage of attaching to the line without any modifications to it. It is used as a redundant cutoff point for the interface when draining liquids.
The pump box houses an Spetec Precision Standard OEM pump with four pumping channels. Two of the channels are used to move the liquids from the funnel to external bottles and in the opposite direction. The box also houses a 4-position selection rotary valve from Biochem Fluidics (rv-en0-s4c-Pthb) that selects which bottle the funnel liquid will be moved to.

3.2.2 Dosing modules

To achieve precise dosing tailored to varying material quantities and chemical requirements, the 876 Dosimat Plus system was acquired. This Metrohm-designed liquid dosing unit is intended for manual titration and dosing, offering five operations: manual dosing, manual titration, titration dispensing, manual pipetting, and manual transfer. Suitable for both aqueous and non-aqueous liquids, it serves laboratory and production needs. The six units of the 876 Dosimat Plus facilitate dosing up to six specific liquids and can be mounted on a mobile trolley for convenience (see Figure 17 left). Equipped with accessories like a manual dosing syringe, dispense bottle, and titration beaker, it also offers optional items such as a stirring device and dispensing valves. The dosing trolley initiates the process by dosing initial components mixing them before transferring to the evaporator unit.

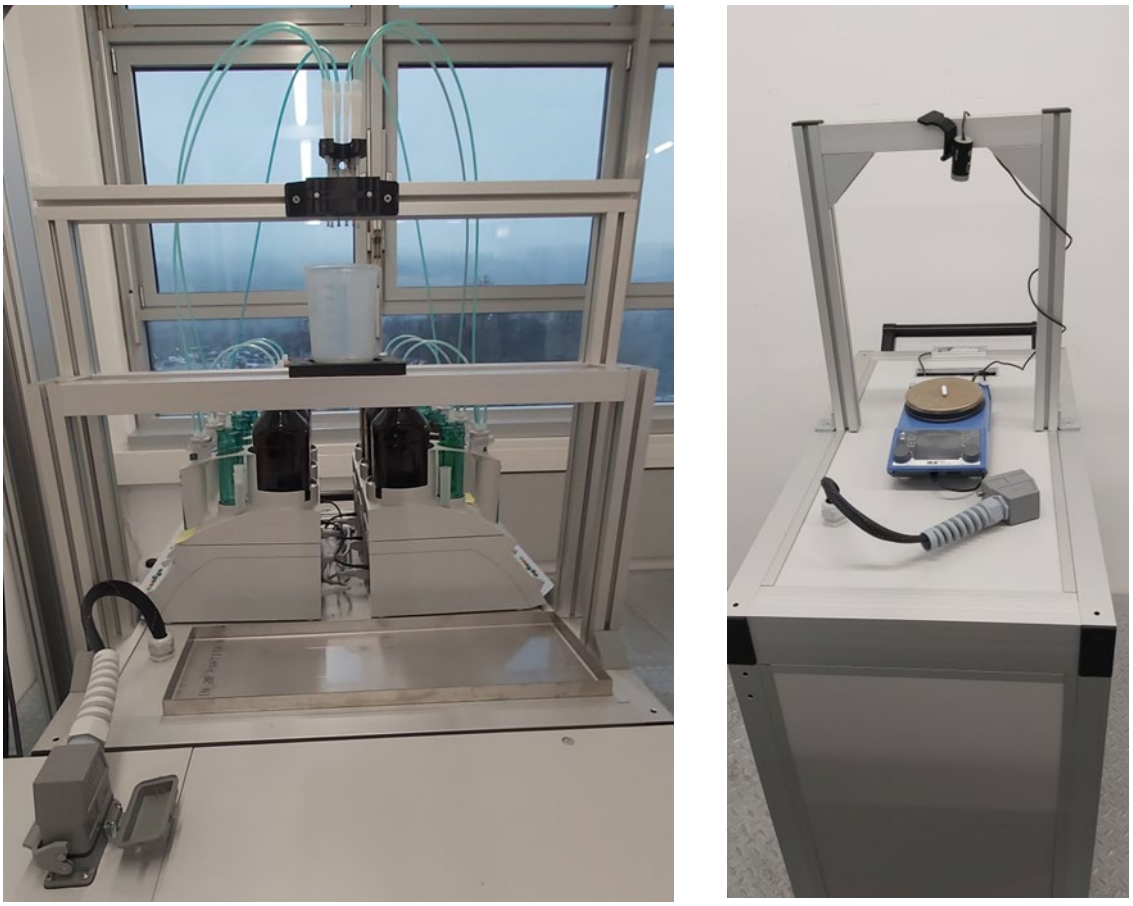


Figure 17. Dosing trolley (left) and scale and heat stirrer trolley (right)

3.2.3 Scale and heat stirrer trolley

In order to carry out syntheses for the production of organic electrode materials, a heating stirrer is indispensable. Many important steps begin with the mixing of the various materials. To do this, a beaker is placed on the stirrer with the help of the robot arm, and the temperature-controlled stirring process is started via the higher-level control system (see Figure 17 right). A camera mount bearing a webcam has been installed above the scale to monitor handled substances visually.

3.3 Software

One of the main goals of the software development was to ensure the modularity of the platform. Various software tasks such as low-level device communication, module orchestration, and planning of experimental campaigns are encapsulated from each other. Specific hardware needs must be dealt with on the device-communication level, whereas on the intra- and inter-laboratory level, harmonized communication and higher abstraction levels are desirable. For communication between modules, the HTTP and OPC-UA protocols have been favorized. The source code of all custom-made module-controllers is available on GitHub[14,15,16].

Due to the Covid-19 pandemic issues with postponed deliveries of key hardware components, the initially envisioned central PLC had to be dealt with. Software solutions (CODESYs soft-PLC on a RaspberryPi) were developed to resolve the dependence on single manufacturers.

For international collaboration between laboratories first tests demonstrate interfacing with a FINALES[17] broker.

3.3.1 System architecture

The overall system architecture is depicted in Figure 18. A central platform controller PC runs Python-based scripts that interface with module controllers over HTTP or OPC-UA. If devices offer OPC-UA or HTTP natively, those interfaces could be used out of the box. In the other cases, Raspberry Pi 3 single-board computers were used as module controllers to translate between protocols, increase the abstraction level and mitigate range and reliability issues.

[14] https://github.com/BIG-MAP/wp4-dosing-unit
[15] https://github.com/BIG-MAP/wp4-LLE
[16] https://github.com/BIG-MAP/wp4-stirrer-heater
[17] https://doi.org/10.1016/j.matt.2023.07.016

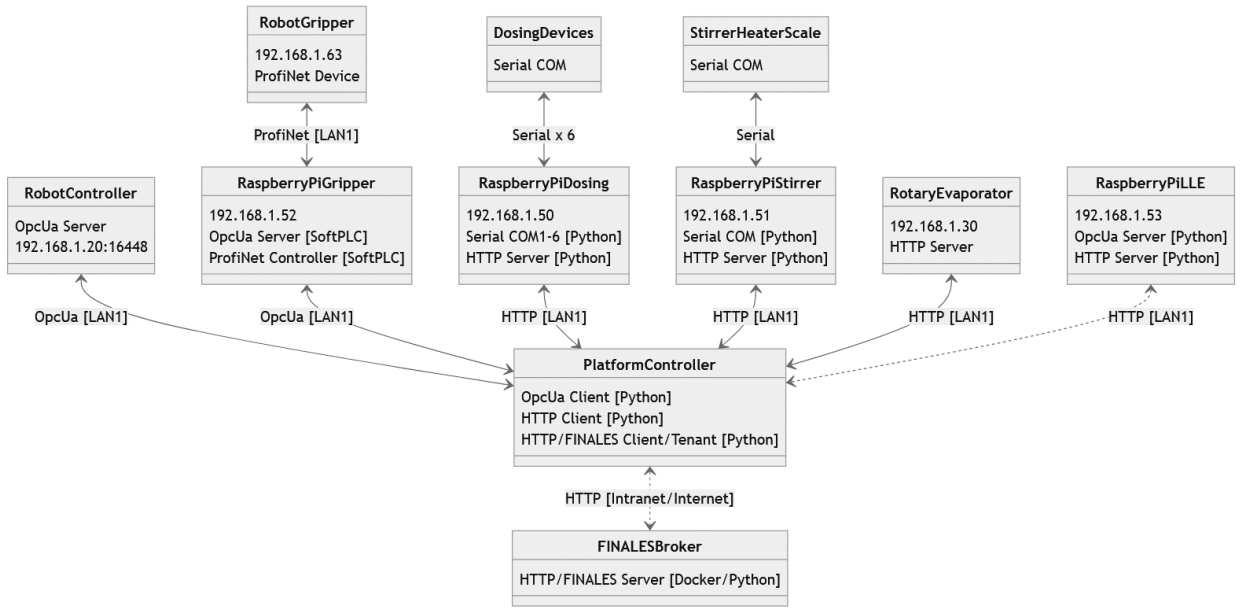


Figure 18. Communication architecture of the robotic platform at Fraunhofer ISC displays hard- and software components and communication protocols in between.

The following paragraphs contain detailed descriptions of the various modules.
The robot's gripper is controlled by PROFINET, a communication protocol and an open industrial Ethernet standard used for real-time communication in industrial automation systems. It is used to transfer data between programmable controllers, I/O devices and other components within an automation system and offers fast communication, short cycle times, and determinism, making it suitable for use in demanding automation applications. Due to a delivery delay for the central PLC, a Raspberry Pi computer with a CODESYS soft PLC was used to translate between PROFINET and OPCUA.

The Yaskawa YRC 1000 controller offers an OPC-UA server that can expose pre-programmed routines that can be defined via its manual control panel. This mode of operation turned out handy when teaching trajectories manually. Regarding future uses with computer vision and live-changes in trajectory planning, however, the current OPC-UA interface lacks parametrization capabilities for function calls.

The Büchi rotary evaporator offered a native HTTP server, which can be readily accessed via HTTP requests from the central platform controller.

The LLE main controller computer (PC or Raspberry Pi) receives commands from the platform controller via HTTP and manages serial communication with multiple microcontrollers within the LLE device.

The 876 Dosimat Plus can be controlled via RS-232 and requires RS-232/USB box. The RS-232/USB Box is connected to the USB interface of the Dosimat. A Raspberry Pi single-board computer has been used as a module controller and provides a custom-made HTTP interface.

The heat stirrer in this setup has an integrated scale, which allows for real-time monitoring of the reactant quantities being used in the reaction. This information is transmitted via USB and is handled by a Raspberry Pi single-board computer interfacing with the platform controller via HTTP. The measured in-line quantities can be used to adjust the reaction conditions based on the quantity of reactants being used. This not only ensures that the reaction conditions are optimal, but it also helps to maintain a consistent product quality and yield.

3.4 Demonstration

The following sections showcase technology demonstrations of single modules as well as the integrated platform. Due to pending safety measurements, no experiments involving harmful substances could be run on the full robotic platform yet. Single module tests and representative setups were chosen instead.

3.4.1 Liquid-liquid extraction

A full extraction involving all the extraction steps defined for the organic synthesis was performed inside a glovebox to demonstrate the functionality of the liquid-liquid extraction module. The extraction steps include three extractions that mix the water-polymer solution with ethyl acetate, followed by three that mix the resulting water-polymer solution obtained with dichloromethane.
Mixing the water-polymer solution with the solvents in each respective step was performed using a magnetic mixer and a round magnetic bit. The magnetic bit spins at up to 250 RPM to prevent overmixing and mixing air into the solutions. The mixed solution was attached to the rotary valve and pump box and pumped inside the funnel to allow it to settle.
Settling of the first steps involving ethyl acetate took a minimum of seven hours and up to 22 hours, depending on the observed conditions. To monitor the progress of the extraction, the mixture was scanned with the optical sensor and the camera every hour. 1200 ml of water-polymer solution was mixed with 300 ml of ethyl acetate in excess (400 ml in excess for the last step). To drain the solution

Figure 19. LLE module inside a glovebox during a draining step of ethyl acetate and water-polymer solution.

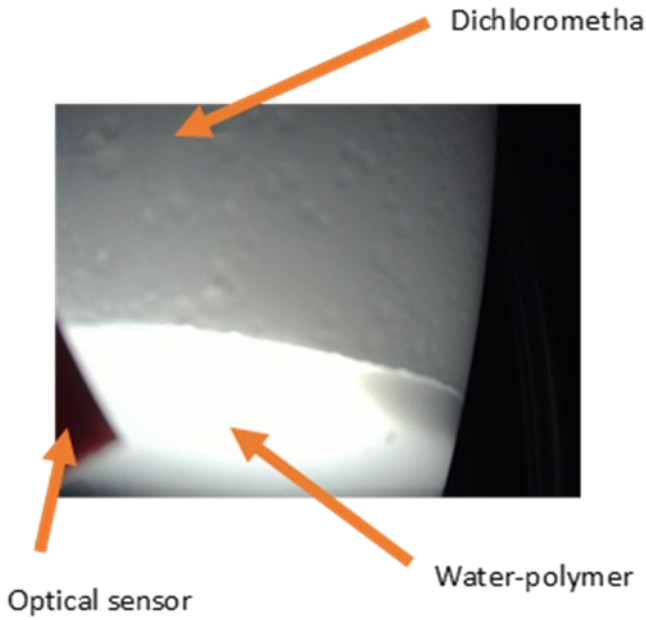


Figure 20. Image of the interface between the solvent dichloromethane (upper foamy layer) and the water-polymer solution (lower transparent layer) as the optical sensor camera crosses in front of it during a scan of the settling process.

The LLE proceeded to scan the mixture again and determine the position of the interface in the funnel. Using this information, the volume of the lower phase was calculated and drained to the output vessel (Figure 19). The tubing sensor was used as a redundant cutoff point. 9 ml of the upper phase was pumped in excess for the two first steps.
The same procedure was performed for the dichloromethane steps. Again, 1200 ml of water-polymer solution was mixed with 400 ml of dichloromethane in excess and pumped into the funnel. The mixture was scanned every 30 minutes (Figure 20) and left to settle for a minimum of two hours, with the last one staying overnight for 15 hours. Draining was also performed in a similar fashion to the ethyl acetate steps. To eliminate any trace of ethyl acetate from the system, the funnel was sprayed with demineralized water using a dedicated diaphragm pump. The pump is set up to be controlled directly from the central controller of the synthesis system in order to wash the LLE funnel when necessary.

3.4.2 Module interaction

The first integration of the full platform tests has proven successful, showcasing the platform's capabilities in fully autonomous optimization. For example, the platform has demonstrated its ability to optimize the recipe for mixing user-defined colors from differently colored liquids (see Figure 21), highlighting the practical application of the engineering concepts embedded in both the hardware and software. This paves the way for future integration of modules specifically designed for battery material optimization. A demonstration video can be found online[18]. The Python library ax [19] has been used to implement the optimization loop for Bayesian optimization.

[18] https://www.big-map.eu/key-findings/modular-robotic-synthesis-platform .
[19] https://github.com/facebook/Ax

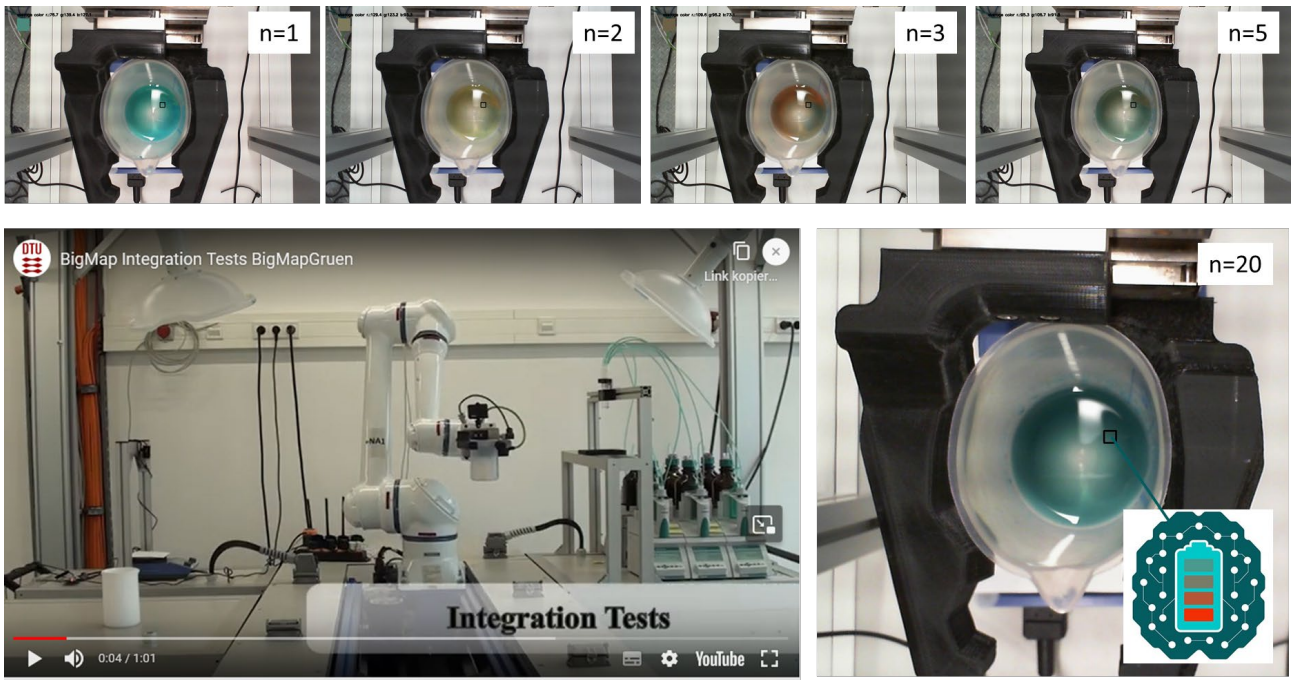


Figure 21. Demo video showcasing an automated optimization loop.

3.4.3 Integration into BIG-MAP

The robotic platform for organic synthesis is being developed as an autonomous system with a focus on security. The platform's network is not exposed directly to the internet or WP partners. However, the system is designed with possible future integrations in mind. The Broker component allows the extraction of data from all subsystems of the platform and sends it to a server in an external network that can be made accessible to other BIG-MAP partners using commonly used protocols, e.g., HTTP, TCP, OPC-UA, AMPQ, and others.

An interface to a FINALES server developed in WP10 has been demonstrated. The local platform is registered as a FINALES tenant by defining schemas of input or output types. The running FINALES tenant continuously polls for requests offered by the FINALES broker. These can be registered by remote scientists or optimization algorithms. This ensures modularity on a high level, separating the planning or parametrization and execution of workflows. Therefore, our platform can act as part of an international ecosystem for science collaboration.

3.5 Conclusion

Methods of accelerated research have been demonstrated successfully for two battery-related research fields. The work was conducted in a complex full-stack engineering field, spanning chemistry, hardware automation and software development. The involved partners can now start to migrate conventional lab workflows step-by-step to the platforms. They act thereby as seeds for a full-grown ecosystem by adding additional hardware modules in the future and connecting local platforms via software orchestration.