Battery Interface Genome - Materials Acceleration Platform

D4.1 – Specification (flow chart) of hardware and software architecture

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ABSTRACT

One of the overarching goals of BIG-MAP is to accelerate material discovery through digital integration. A core element of this is to make automation of specific processes available to the wider consortium and in time the community.

In BIG-MAP we have identified four key processes which are suitable for automation and digital integration. These include synthesis of organic and inorganic coatings, formulations and characterization of electrolytes, and sputtering of thin films. For synthesis of organic coatings, we aim to develop a modular system with functional groups placed on moveable carriages placed around a robotic manipulator allowing for rapid reconfiguration and setup of specific processes. For inorganic coatings BIG-MAP can take advantage of an existing system consisting of an automated powder and liquid dispensing system (Quantos), a formulation engine using a XYZ module, and a mobile dispensing unit. For formulation and characterization of electrolytes an existing system will also form the starting point. This system is custom-made and consists of a formulation system, a bridging component, and a cell assembly and a characterization system. For sputtering of thin films, a magnetron sputtering apparatus is detailed.

These systems have heterogeneous laboratory information management systems (LIMS). The goal of this project is to integrate the systems across the consortium with a standardized software architecture. To this end we propose an architecture based on the Open Platform Communications Unified Architecture (UPC UA) ensuring simplicity, extensibility, and security by using a widely used standard. The consortium plans to interface the existing systems though this general architecture.

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1. Introduction

The overarching aim of BIG-MAP is to develop a material discovery platform that accelerates the discovery of new battery technologies and materials by digitally integrating the entire development chain from theoretical research to in-cell testing. An important subtask of this effort is to develop and tie the laboratory infrastructure of BIG-MAP together digitally in such a way that it can be accessed remotely and deliver results to other elements of the development chain.

The purpose of this document is to document the current and to be developed lab hardware infrastructure in BIG-MAP as a basis for understanding how best to design a network architecture including communication standards and protocols that best allows us to integrate across labs. This challenge is significant because of the high heterogeneity of the systems in BIG-MAP and their different applications and hence an understanding of these system is paramount for designing a suitable network architecture. The title of this deliverable is "Specification (flow chart) of hardware and software architecture" indicating that it should contain a general overview of the to be designed hardware and software architecture. However, we feel that this would not give significant value and therefore have dedicated significant effort to describe the machinery, the processes to be automated, and existing software systems as well.

In Section 2 we outline the planned robotic system for synthesis of organic coating materials, in Section 3 we provide an overview of the existing robotic system for synthesis of inorganic coating materials. For the analysis needs of the project we describe in Section 4 the existing high-throughput infrastructure for formulation and characterization of electrolytes. Finally, in Section 5 we describe the concept of the machinery for combinatorial sputtering of thin films. These sections provide an overview of the existing and planned infrastructure. In Section 6 we describe the considerations and plans for network architecture that in time will allow the above-mentioned systems to be integrated and accessed remotely.

2. Modular synthesis robotics for the synthesis of organic coating materials

2.1 Purpose of the machinery and system concept

The aim of the FISC development within WP4 is to develop a robotic platform that allows the synthesis of optimised organic molecules and materials. The formulations for these processes are being developed in WP10. Since the exact recipes are not yet known at the start of the project and may also change in the future, the aim is to design the system as flexibly as possible.
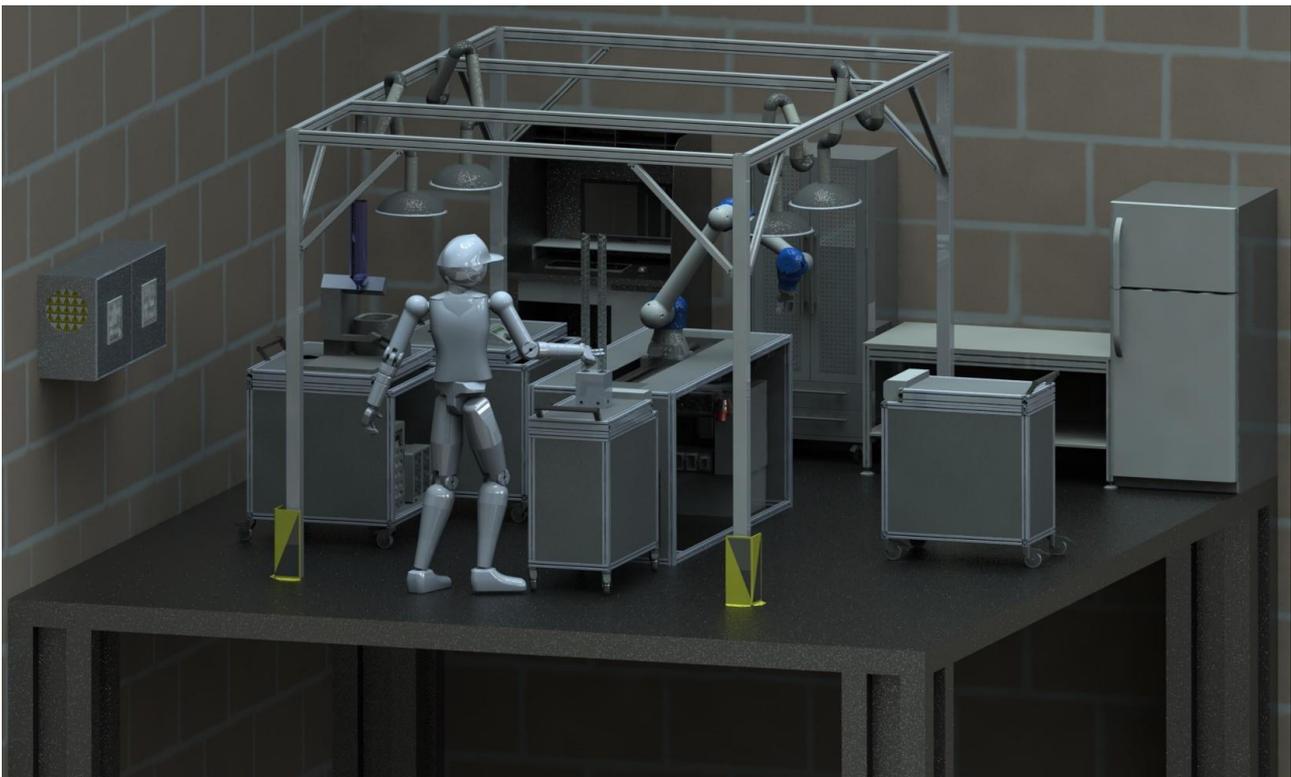
Figure 1: Concept illustration of Fraunhofer ISC setup

Figure 1 shows an illustration of the concept study. A robot arm (Yaskawa HC10DT) is located in the centre of the plant. Its range is further increased by mounting it on a linear unit. Functional groups on movable carriages can be connected to the sides of this main construction, thus adapting the range of functions for the desired processes. These functional units can be, for example, a rotary evaporator, dosing stations but also liquid extraction units and other generic and self-developed laboratory equipment. Various hoods allow individual use and thus effectively protect against the release of gases into the environment.

The manufacturing process for the production of polymers of the ORMOCER® family serves as a basis for the development of the individual components. This makes it possible to define the necessary hardware and software requirements and to validate the system after it has been set up. Within the system boundaries, the influencing factors described in 2.3 can be alternated for each individual step. This leads to a very high number of combinations of the process parameters and thus to the possibility of optimisation. After successful automation, autonomous processing can be directly implemented using the in parallel developed communication standard in WP4. In the future, this system will be an important building block for generating an efficient closed-loop materials discovery process.

2.2 Material classes to be synthesized

The basis of BIG-MAP's activities towards an AI-orchestrated autonomous materials synthesis platform are generation 3 lithium-ion battery cells (LIB) with enhanced energy density. One way to achieve a high specific energy of LIB cells is the employment of cathode active materials with high Ni contents such as NMC ($Ni_xMn_yCo_zO_2$ with xyz: 811 or higher) or pure $LiNiO_2$ (LNO) and by replacing

graphite by silicon or Si@C composites as anode active materials. However, the enhancement of energy density comes along with major drawbacks e.g.

- **Cathode**: NMC(811) and LNO are characterised by voltages beyond 4 V, and are prone to degradation of a carbonate based liquid electrolyte due to a limited electrolyte stability window. Even more, layered lithium metal oxides such as NMC(811), the higher content in nickel also results in early capacity fading and a low temperature off-set of thermal run-away.

- **Anode**: Silicon offers a theoretical capacity of 3579 mAh/g which is almost 10 times higher compared to graphite (327 mAh/g). However, this capacity is characterized by a large volume change of up to 300% during lithiation resulting in material stress generating new electrochemically active surfaces for SEI formation (loss in lithium inventory) and thus limiting its cyclability.

There are different approaches to overcome these obstacles:

1. Prevention of electrolyte degradation by coating the cathode active material with either (hybrid) organic or inorganic moieties
2. Coating of anode active material by (hybrid) organic moieties accommodating volume changes inhibiting further SEI formation
3. Developing new electrolyte systems with non-corrosive additives and novel lithium salts.

In BIG-MAP two different organic classes of materials are chosen for coating of active material.

1. Protective organic coatings for cathode active material (e.g. PEDOT)

Nickel rich (NMC) cathode materials, despite their attractive merits of high energy density and low cost, suffer severe performance degradation originating from multiple odious events including layered to spinel/rock-salt phase transition, associated lattice oxygen release and the cathode-electrolyte side reactions. The structure instability induced strained is released through the formation of inter/intragranular cracks. Surface coating is one effective method practiced mitigating these issues, but limited improvements are achieved. An ideal coating requires conformal thin layer covered onto primary and secondary particles prohibiting irreversible side reactions at the cathode surface. In addition to a physical barrier supressing attacks from the electrolyte, HF moisture *etc.*, the coating material must also provide efficient electronic/ionic pathways to improve the reversible capacity and rate capability. Conductive polymer coatings are a viable approach to improve the charge transfer process at the Ni-rich cathode surfaces compared to the electrically insulating inorganic materials such as oxides, phosphates and fluorides. Among the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) stands out due to its high electrical conductivity and excellent electrochemical cycling stability. Hence, several approaches have been employed to coat PEDOT over NMC cathodes, of which energy-intensive chemical vapor deposition techniques are found best. However, to augment the battery performance, it is equally important to improve the ionic conductivity, which is often significantly lower in conjugated polymers. PEDOT also has limited ionic conductivity. In-situ or ex-situ polymerization of EDOT or derivatives with tailored Li-ion conducting moieties like PEO can enhance the ionic conductivity as well as solution processability of the coatings. Improving the solution processability favors development of facile wet chemical methods of NMC coatings in non-aqueous solvents. In-situ polymerized PEDOT in presence of NMC

should facilitate uniform coverage. In another approach copolymers or even blends of PEDOT with single Li-ion conductive blocks such as poly acrylic acid (PAA) can be used to achieve balanced electronic and ionic conductivities favorable for smooth Li ion migration through the coating. Grafting or mixing PEDOT or derivatives with conductive carbons such as graphene, CNTS etc. can also be tailored to develop superior dual conductive coatings for sensitive Ni-rich cathodes.

2. **Flexible and protective organic coating for Si and Si@C anode materials based on Ormocer®**
In order to use silicon and/or Si@C composites with high loading of SiO_x, the mechanical properties namely the volume change during lithiation requires a polymer coating which accommodates the volume changes during cycling. In addition, this polymer must also be

- chemically stable against anode material (e.g. silicon) and the electrolyte system
- electrochemically stable at these low voltages for preventing electrolyte degradation.

Specific hybrid inorganic-organic polymers of the ORMOCER® family can be tailored in order to fulfil the above specified requirements for their application as anolyte and/or anode protective coating. These hybrid polymers are synthesized via a sol-gel route forming a network of organically modified polysiloxanes representing the liquid polymer precursor. The subsequent organic cross-linking / polymerization can be induced either by a thermal or UV reaction step. While the inorganic framework provides mechanical and thermal stability, the organic components such as ethylene oxide chains accounts for ionic conductivity of the hybrid polymer.

2.3   Process flow chart

In order to automate a complex process such as the synthesis of organic polymers of the ORMOCER® family, the first step is to translate the Standard Operating Procedure (SOP) into a flow chart. This allows system requirements to be defined and clearly discussed across disciplines and departments.
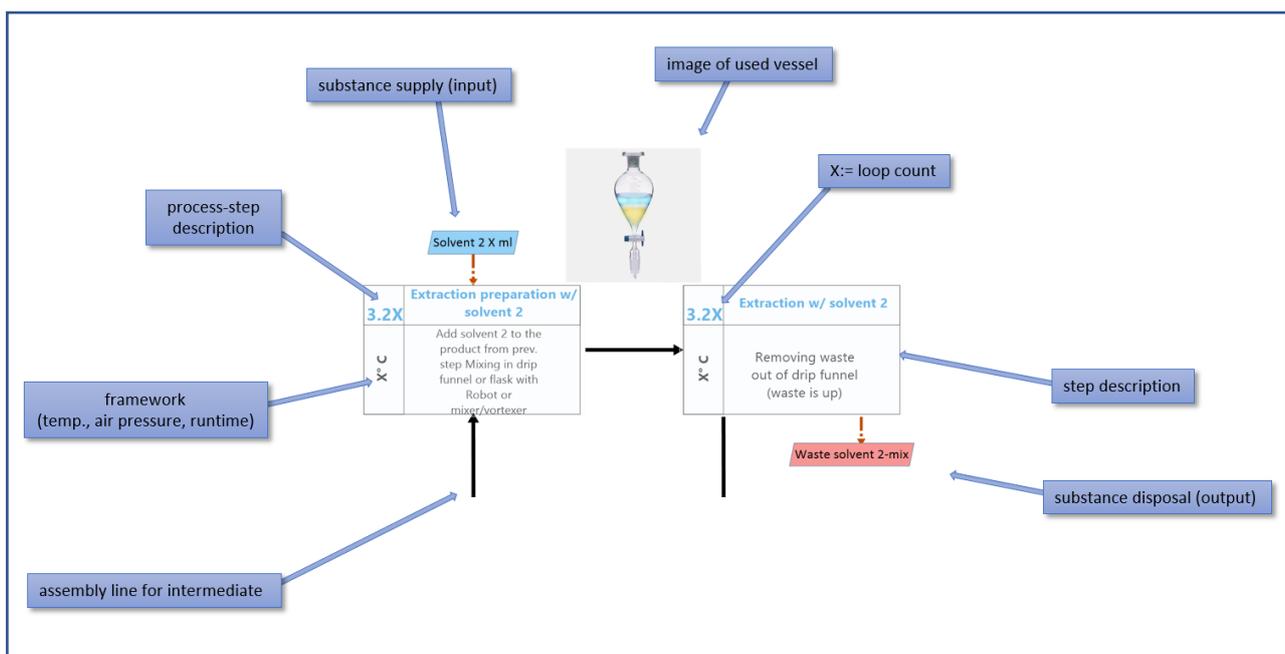

Figure 2: Excerpt of the complete flow chart of the synthesis process

Figure 2 shows an excerpt of the complete flow chart (found in the Appendix). To explain the entire process chain, two related process steps are explained in detail. The individual process step is displayed as a box with a variety of parameters. Each step is clearly defined by its consecutive number and title. The parameters of the framework conditions are also defined for each step. The blue and red parallelograms indicate the substances to be added or removed. The reaction vessel to be used can be clearly identified by schematic representation. Subsequently the different processes are connected black arrows which are indicating the flow direction of the intermediate products. Also, there are several logic operators placed in the whole flow chart.

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2.4 Hardware involved

List of hardware including brief description of relevant parameters

Hardware	Description
Rotary evaporator	preparing and processing of the substances (time, temperature, speed, atmospheric pressure)
Magnetic stirrer	mix up substances (temp., speed/rpm, time)
Dosing unit incl. scale	precise dosing of substances (volume, weight, time, type of substance)
Recirculating chiller	provides the temp. in rotary evap. (temp.)
Vacuum pump	provides right atmosphere (quality of the vacuum, atm. pressure)
Robotic arm	carries the gripper (position in the room)
Robotic gripper	manipulates and interact w/ periphery (concrete position of fingers)
Robotic control & programming pendant	programs & contributes to the movement of robot/gripper (bit records, OPC-UA)
Engine for linear unit	linear shifting of the robotic arm (position in the room)
Hazardous substance extraction & suction	ensures a safe working environment (risky process steps → aspirate atmosphere)
High vacuum valves	shut-off valve for air vent
Centrifugal fan	suction effect for ventilation
Fan starter	equipped with PTCrelay, Monitoring relay for temperature monitoring of motor windings
Programmable Logic Controller	saves and initiates process sequences, coordinate peripheries, (signal data sets, network interface, TIA, OPC-UA)

Human-interface device	HID implemented in human-machine-interface HMI, connects machines with physical input hardware (signal data sets, network interface, HTML)
Storage & fridge	for goods stored at room temperature & in a cooled environment
Workstation	special computer designed for technical and scientific applications (monitoring, control, security centre, and interface for data access)
Liquid-liquid extractor	adapted mixer and settler for automatic solvent extraction of compounds (mixing time, mixing speed/rpm, settling time, clearness)
Peristaltic pump	moves liquid inside liquid liquid extractor (speed/rpm)
Switching valve	routes liquids inside liquid liquid extractor (position)

2.5 Description of the low-level software layer

The internal software structure will be built around a central Programmable Logic Controller PLC. This will be used to define permissible interactions of the individual peripherals with each other, as well as process sequences. Together with other peripheral systems such as the robot, the rotary evaporator and sensors, the PLC is connected via a superordinate network. The communication standard here will be OPC-UA. This enables all devices to communicate independently on a common standard and to process all data centrally in a semantic database. Here, a digital twin of the entire system is created which is mirrored on the decentralized database. In addition to the process values, a description of the data can also be provided through the use of OPC-UA. Process definitions and orders from partners can then also be transmitted via the central server. In order to operate the system directly, an HTML-based human-machine interface is also being developed. This also means that since the system builds on OPC-UA natively it can without modification be used as a basis for communicating with other machinery in BIG-MAP as the OPC-UA standard is also the basis here.

3. Automated synthesis of inorganic coatings on particles

3.1 Purpose of the machinery and system concept

Automated synthesis of inorganic coatings on Li-ion positive electrode powders will enable bespoke particle coatings that enable greater high voltage stability and performance lifetime. Robotic data handling protocols to be initiated within WP4 will allow variation of key process variables including precursor concentration, reaction time, temperature and atmosphere.

A partially automated process will be benchmarked at partner University of Liverpool (ULIV) using the atmospherically stable mixed transition metal oxide layered rock salt power: $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (code NMC622) and coating with alumina (Al_2O_3). Robotic mixers will dispense precursors into vials and gently heated and agitated (up to 80 ^{o}C) for sol-gel coating. The Al_2O_3 coating will act as a physical protection layer by masking positive electrode powder surface functional groups and acting as a hydrogen fluoride (HF) scavenger. It has been shown that the Al_2O_3 layer can lead to the generation of lithium difluorophosphate ($LiPO_2F_2$) within the cell and is acknowledged electrolyte additive that improves the cycling stability and lifetime of a variety of lithium-ion chemistries[1].

Electrochemical testing of coated materials will take place at ULIV and FISC for robust coin cell cycling datasets. BIG-MAP ink formulation and coating protocol to be followed. Once benchmarking has taken place (comparison with coatings made via traditional lab route by partner Kemijski Institut (NIC)) then $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (code NMC811) will be coated with Al_2O_3 under nitrogen.

The benefits of the approach are that it provides a systematic opportunity to fine tune coating synthesis (concentration of coating solution, mixing time, heating etc), and allows us to generate a matrix of synthesis conditions and to develop methods for multilayer coatings. The work will provide the foundation for moving towards autonomous process as the initial work will set out the boundary conditions which the process can operate. Limitations of present set-up is the that the final step of high temperature calcination step is not currently automated.

3.2 Material classes to be synthesized

As described above NMC622 will be initially coated with Al_2O_3 to test and optimise the automation system. NMC811 will then be coated with Al_2O_3 initially using test protocol developed for NMC622. Finally, a multi coating layer protocol with second coating material will be selected to demonstrate versatility of approach in generated multifunctional coatings.

Table 1. Materials to involved in automated synthesis of inorganic coatings on particles during BIG-MAP project (ULIV)

Materials	Supplier	Coating
$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$	UMI	Al_2O_3
$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$	UMI	Al_2O_3
$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$	UMI	Al_2O_3 + 2nd coating material (to be determined)

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[1] Hall et al. ACS Appl. Mater. Interfaces 2019, 11, 14095–14100

Process flow chart

Figure 3 shows the advanced process flow chart of base line synthesis of Al_2O_3 coated NMC622. Material dispensing, mixing and decanting process can be automated with the final calcination step remaining a manual process.
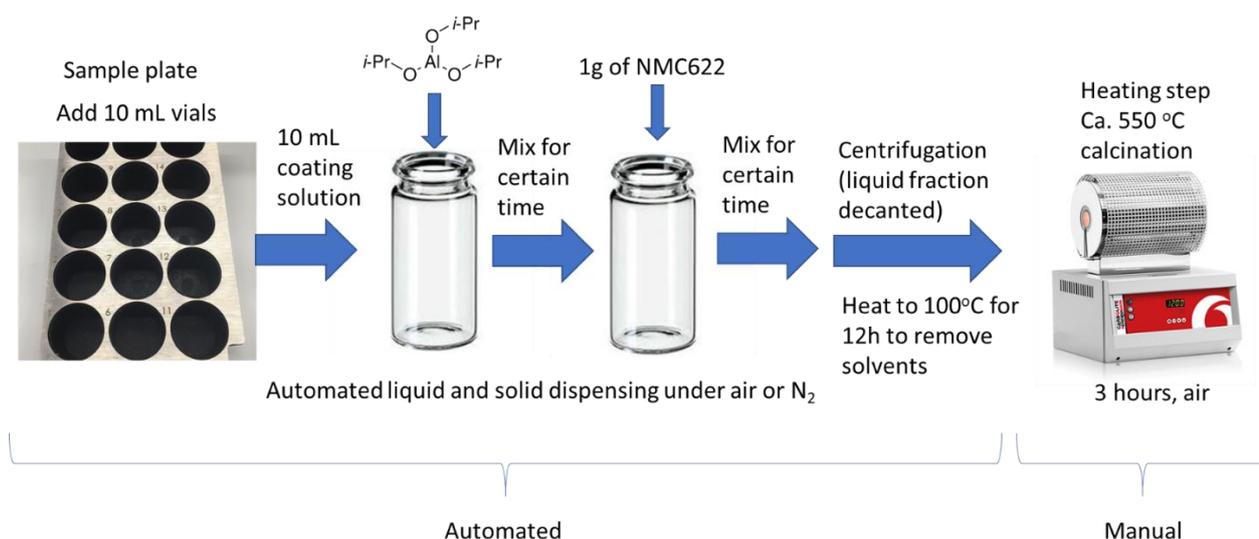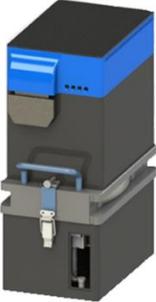

Figure 3. Automated coating process of LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (code NMC622) with alumina (Al$_2$O$_3$).

Typical synthesis is as follows: 0.005 g aluminium tri-isopropoxide to be completely dissolved in 10 mL ethanol at room temperature. The active positive electrode powder (0.995 g) to be gradually added into the solution. Then, the solution containing the active material is constantly stirred at 80 °C accompanied by a slow evaporation of solvent. Coated powders to be fired at 550 °C in air for 3h. The following parameters will be modified during coating procedure: mass ratio of aluminium tri-isopropoxide to positive electrode powder to be varied from 0.5:99.5 to 5:95. Length of stirring time and firing temperature (400-550 °C)

The following characterisation of the coated powders will be undertaken, electrochemical cell testing, electrochemical impedance spectroscopy, Raman spectroscopy, energy Dispersive X-Ray Analysis (EDX), and powder x-ray diffraction (PXRD). As part of the BIG-MAP project an automated analytical technique will be proposed for material screening.

3.3 Hardware involved

Table 2 lists the main automation hardware to be utilised within the automated coating process of lithium-ion positive electrode material powers.

Equipment	Description
Bench top Quantos	Bench top Meller Toledo Quantos enables dispensing powders of different quantities into vials with a manual intervention step for heating and shaking. Process is partially automated, but allows an easy proof of concept for new processes. https://www.mt.com/gb/en/home/products/Laboratory_Weighing_Solutions/Automated_Sample_Preparation/Autosampler.html
Formulation Engine using the XYZ module:	The XYZ module is a gantry robot: enables a partially automated process with dispensing (using an integrated Meller Toledo Quantos balance) shaking, ultrasonication and heating (maximum 100 ˚C) into 10 mL gas chromatography–mass spectrometry (GCMS) vials under atmosphere or dry nitrogen. A dosing and shaking step, as well as solvent decanting, can be used before removal for a further final heating step within a furnace
Mobile Dispensing Units (MDUs)	MDUs provide raw materials to the processing modules in the Formulation Engine. They are capable of dispensing; Powders, Low/high viscosity, liquids, Slurries.

Table 2. Hardware involved in automated coatings with description of relevant parameters (ULIV)

3.4 Description of the low-level software layer

At ULIV, the Materials Innovation Factory (MIF), where the robotic platforms are located, has a scientific data management system called FL:EX, this a bespoke data repository developed by Liverpool's industry partner Unilever which we have licenced a version of, the software can be accessed by University and third party users as we have built in 'silos' to separate data . A illustrative slide is shown in Figure 4.

Effectively the software is an oracle database with a html front end and run from University of Liverpool servers and can be accessed via an internet browser using university credentials, the majority of the MIF equipment has been linked to this database via the FL:EX API (application Programming Interface) often using a piece of linking software to scoop up data, pull down data from the database. This link software has been necessary as the variety of equipment we have is broad and from many different suppliers so we have integration partners to help here (CSols & Peak Analysis and Automation). FL:EX can be thought really as two pieces of linked software each with its own API:

FL or Formulations: Can effectively be thought of as containing information on recipes and raw ingredients, i.e., where raw material inventory information (batch, lots, supplier, grade, owner, storage, amount, hazards etc) and Formulation information (Materials, amounts, order of addition, process steps, conditions) are stored in a structured way.

EX or Experiment: linking of the materials or formulation to a measurement or experimental matrix, e.g., you could link data from a measurement to given formulation/reaction in a structured manner.

The FL:EX API supports content negotiation and can return data in JSON & XML format and the plan is that ULIV will use this API to interface FLEX with OPC UA.
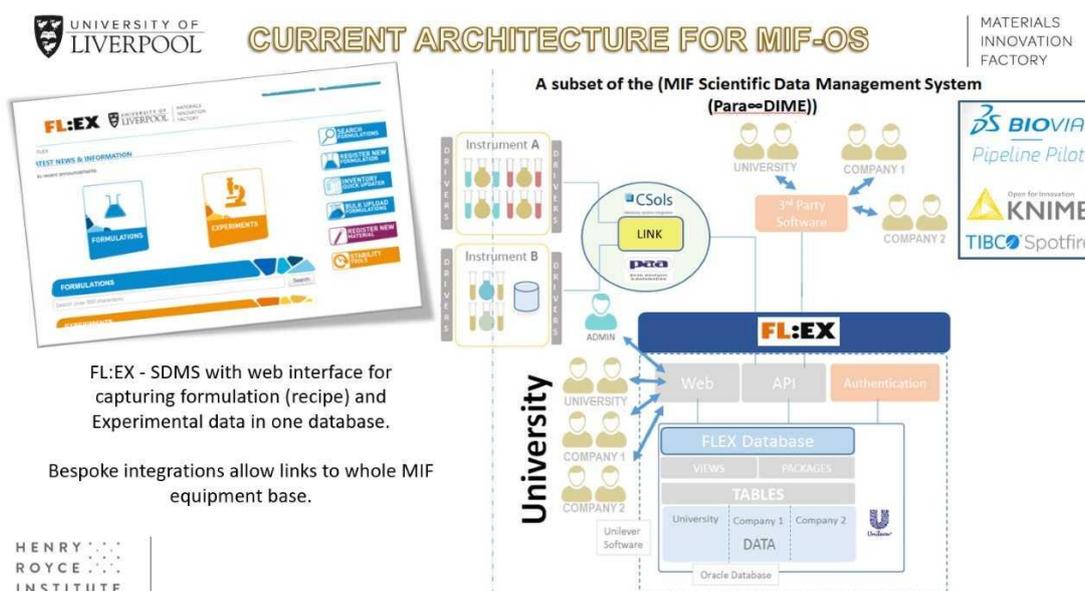

Figure 4. Present software for robotic/automated systems at ULIV.

4. High-throughput formulation and characterization of electrolytes

4.1 Purpose of the machinery and system concept

High throughput screening (HTS) systems represent a highly valuable tool for accelerating the search towards identifying advanced and optimized electrolyte formulation for given cell chemistry candidates, electrolyte|electrode interfaces, overall cell performance, safety and cost. The developed and well-established HTS experimentation setup comprises of fast and systematic, fully automated formulation of up to 96 different liquid electrolytes per working day (wide variety of electrolyte components including conducting salts, solvents/co-solvents and (multi)-functional additives), cell assembly of up to 96 cells either in two (coin cell) or three (EL-CELL®) electrode setup (Figure 5), as well as preselected physicochemical (determination of conductivity, viscosity and transference number) and electrochemical measurements (EIS, LSV, CV, galvanostatic cycling experiments) on a electrolyte and cell level, serving as a filtration effect towards identifying affordable, electrochemically and thermally outperforming hit/lead electrolyte candidates for a targeted application in a given cell chemistry (Figure 6). The entire value chain, governed by the laboratory information management system (LIMS), enables prediction of vital electrolyte properties and establishment of structure-property-performance relationships, and enables preselection, rating/ranging, prediction/decision and recommendation in respect to new combinations of electrolyte formulations, either in terms of concentrations or even different components in order to optimize relevant physicochemical and electrochemical properties governing the overall cell performance and safety.
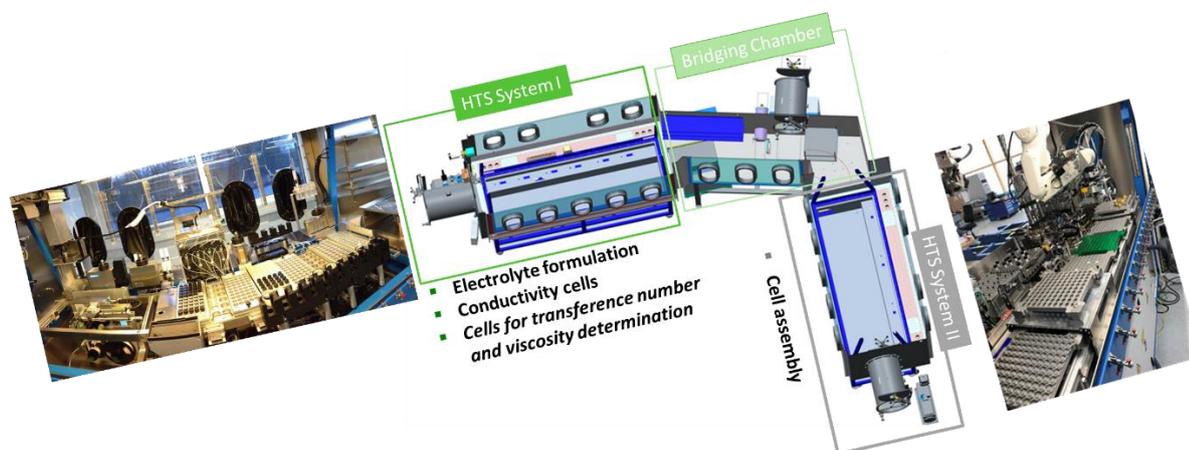
Figure 5. Fully automated high throughput screening system for electrolyte formulation and cell assembly with a complex, however, user friendly configuration and correlation to Laboratory Information Management System (LIMS)
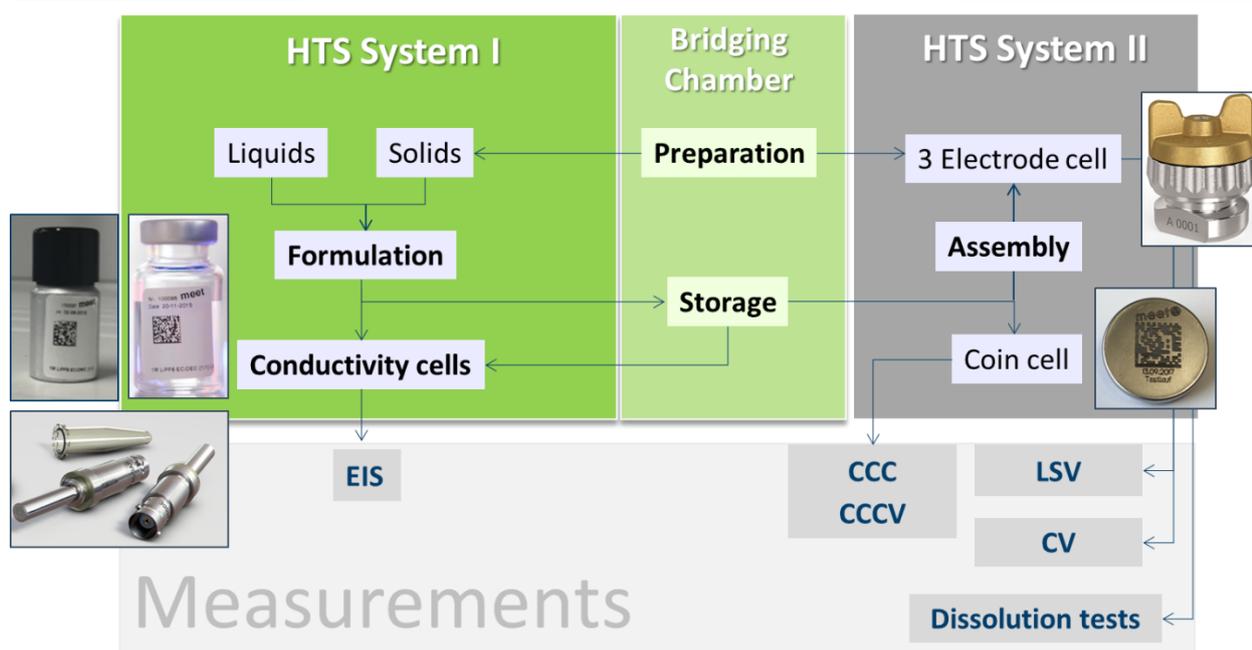
Figure 6. High throughput screening sequence and first round of automated filtration measurements

4.2   Description of combinatorial formulation approach

The HTS experimentation facility is used in the research and development of advanced liquid electrolyte formulations for high performing lithium-based battery cells with enhanced safety by following a high throughput formulation-characterization-performance-elucidation-optimization evaluation chain. The facility uses a unique high throughput approach from strategy to analysis (Figure 7) for the discovery of novel and optimization of existing liquid electrolyte formulations for diverse cell chemistries and targeted applications. The HTS experimentation approach in general, is based on a filtration effect based on the previously established set of requirements: starting with a certain number of formulations for a given cell chemistry, the goal is to identify lead/hit candidates for a targeted application, based on a first round of preselected, automated tests/experiments. All the formulations that fulfilled the given requirements will be characterized further, whereas the ones that did not, will be discarded. Thereafter, the second round of experiments/tests will be conducted, and the same procedure repeated, reducing the number of formulations. Obtained results are used to design the next round of experiments. Within the entire value chain and each formulation to analysis loop narrowed, the most promising formulations under a spectrum of different variations regarding the presence and amount of selected electrolyte components, known for their key and decisive role in respect to the overall performance and safety of a battery cell will be identified and further optimized.
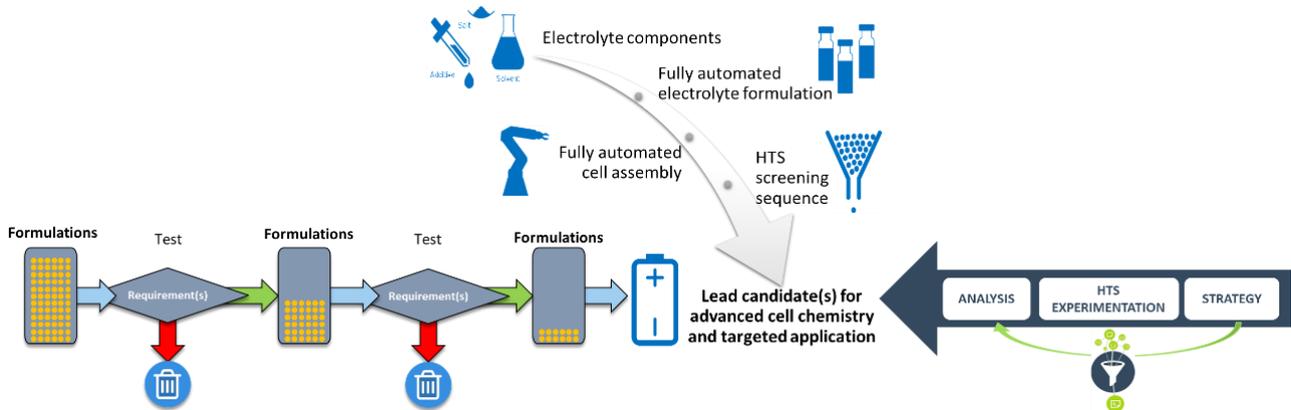
Figure 7. Entire value chain towards identifying lead candidates for targeted application

4.3 Process flow chart

Developed and well-established high throughput electrolyte formulation, cell assembly and selected electrochemical methods workflows are automated throughout the entire value chain process. The electrolyte formulation workflow, depicted in Figure 8, comprises of an automated formulation platform in which a wide variety of electrolyte components, namely conducting salts, solvents/co-solvents and functional additives are being combined in respect to presence and amount.
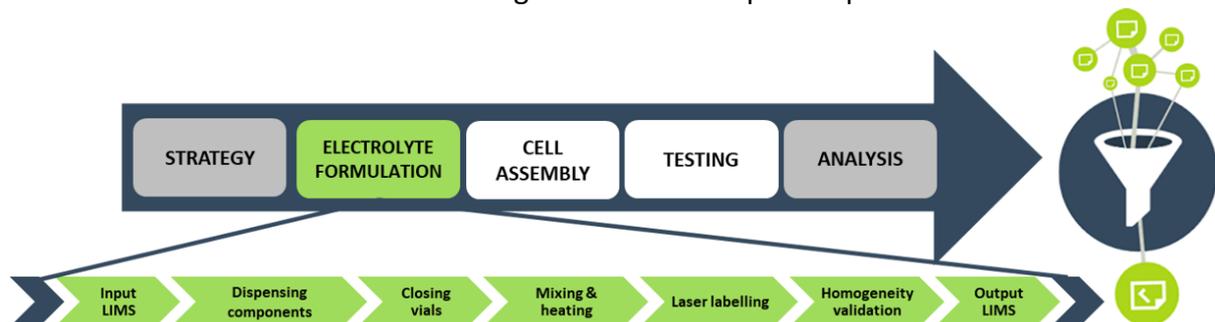

Figure 8. Flow chart of fully automated electrolyte formulation

In Figure 9, the fully automated assembly workflow for two electrode coin cells is displayed. The assembly workflow for the three electrode cells follows a very similar automated process.
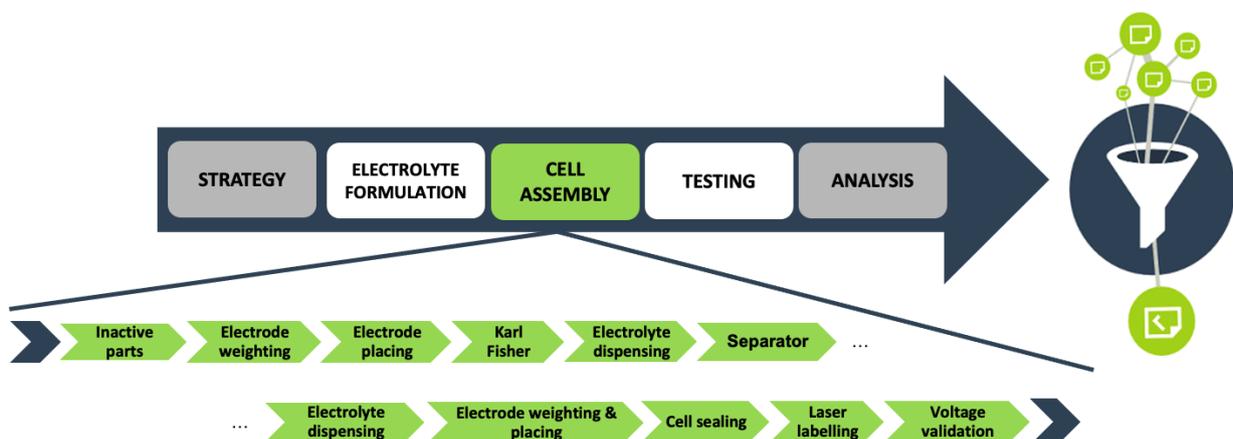

Figure 9. Flow chart of fully automated coin cell assembly

A first round of selected physicochemical and electrochemical methods, namely determination of electrolyte conductivity, viscosity and transference number, LSV/CV and galvanostatic cycling measurements under various conditions and parameter variation, serving as a first filtration towards identification of promising electrolyte formulation candidates follow the general workflow shown in Figure 10.
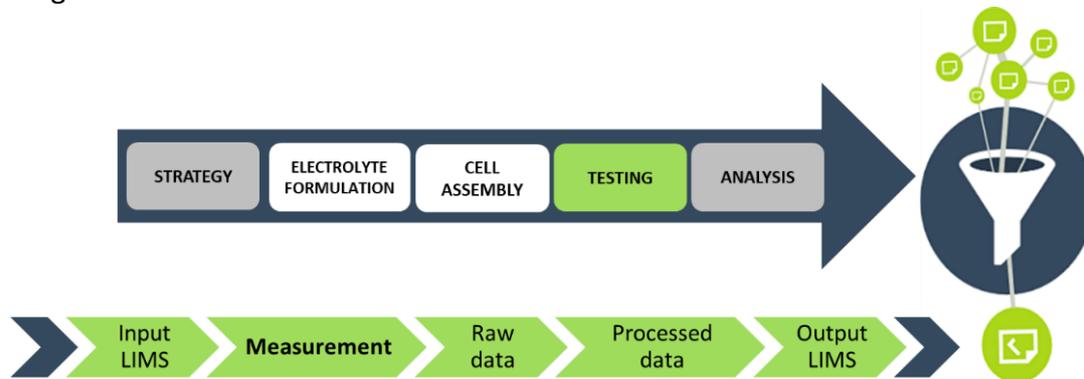

Figure 10. Flow chart – first round of automated measurements serving as a filtration effect: EIS, LSV/CV and CCC/CCCV

4.4   Hardware involved

HTS facility hardware includes following main parts of vital importance for the overall operation:

- **HTS system I** for fully automated formulation of diverse nonaqueous aprotic electrolytes (96 formulations per working day), automated filling of conductivity cells with electrolyte as well as cells for viscosity and transference number determination *(work in progress)* positioned in the glovebox under nitrogen atmosphere
- **Bridging chamber** fused for preparation and storage purposes, positioned in the glovebox under nitrogen atmosphere
- **HTS system II** for fully automated cell assembly in two and three electrode setup (96 cells per working day) positioned in the glovebox under nitrogen atmosphere
- **Modular potentiostat/galvanostat** (Autolab, **Max. ± 400 mA | ± 10 V** *(Optional +/- 10 A)*) with multiplexer (12 x 8 channels) and a corresponding climate chamber for EIS measurements, conductivity, *viscosity and transference number (under development)* determination
- **Battery test system** (Arbin, voltage range: (-10) to 10V, current range: 100mA/1mA/10µA) for galvanostatic cycling experiments in coin cells (96 channels) with a corresponding climate chamber
- **Battery test system** (Scienlab, voltage range: -2 to 8 V, output current: up to ± 5 A measuring ranges: ± 150 µA, ± 5 mA, ± 150 mA, ± 5 A, automatic range switching) for galvanostatic cycling experiments and LSV/CV measurements in three electrode cell setup (96 channels) with a corresponding climate chamber.

4.5 Description of the low-level software layer

Each module of the HTS facility is operated independently by a customized instance of the **L**aboratory **I**nformation **M**anagement **S**ystem (LIMS) developed by the Quality Systems International (QSI) GmbH. As the system's central entity, it also serves as a material and data archive that ensures data provenance and enables backtracking of experiments. Materials data include specific identifiers (Supplier, Batch Number, Purity etc.) whereas experimental data consists of test protocols and relevant experimental parameters (e.g. temperature). Besides saving the raw experimental data, the system is capable of processing the raw results and bundling them with relevant metadata (e. g. details on the used electrolyte) into a machine-readable output format in order to provide users with all available information on a given experiment.

In addition to manual user input, the LIMS is capable of interaction with users or third-party devices by means of .XML files through which materials data as well as experiment related requests can be provided. The overall interaction between the LIMS and HTS hardware modules is displayed in Figure 11.

The well established and custom designed laboratory information management system (LIMS) is flexible by nature and the output data can be adapted to requirements and specifications within the BIG MAP consortium through an adequate interface generated on a basis of know-how and expertise of partners in charge.
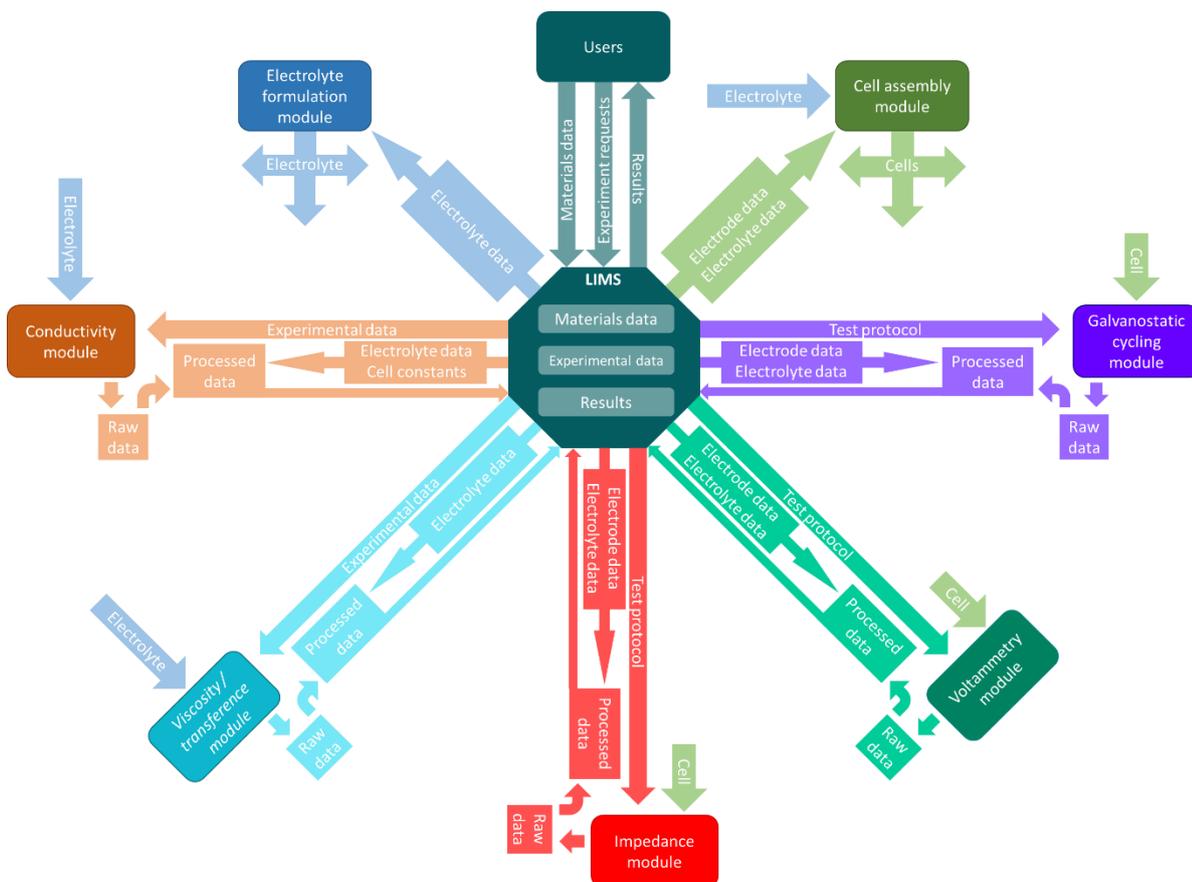

Figure 11. Schematic overview of the overall LIMS - HTS hardware interaction workflow

5. Combinatorial sputtering of thin films

5.1 Purpose of the machinery and system concept

A magnetron sputtering apparatus will be used to prepare model materials under the form of thin films that will be deposited on chosen substrates. In order to evaluate the influence of the composition and the thickness of coating materials on Ni-rich layered oxide (NMC, LNO) cathode materials, the approach will consist in preparing thin film electrodes in a homogeneous way at the surface of an electronically conductive substrate (Pt-coated glass or passivated Si wafers), then in depositing coatings at the surface of this electrode in a combinatorial way by using three different sources (targets), to be finally able to assess the electrochemical behaviour of the coated electrode and the impact of the protective film.

The principle of sputtering is quite simple (see Figure 12). In a vacuum chamber, a target (or cathode) is bombarded by energetic ions generated in a glow discharge plasma situated in front of the target and accelerated in the electric field generated between the target (cathode) and the substrate (anode). This process causes the removal or sputtering of target atoms, which may then condense on a substrate as a thin film. Conversely, the ion bombardment generates secondary electrons that are emitted from the target surface and play an important role in maintaining the plasma. In order to improve the ionization efficiency, the deposition rates and to limit heating of the substrate, a magnetron is positioned below the target in such a way that the magnetic field constraints the motion of secondary electrons in the vicinity of the target and generates a denser plasma in this region.
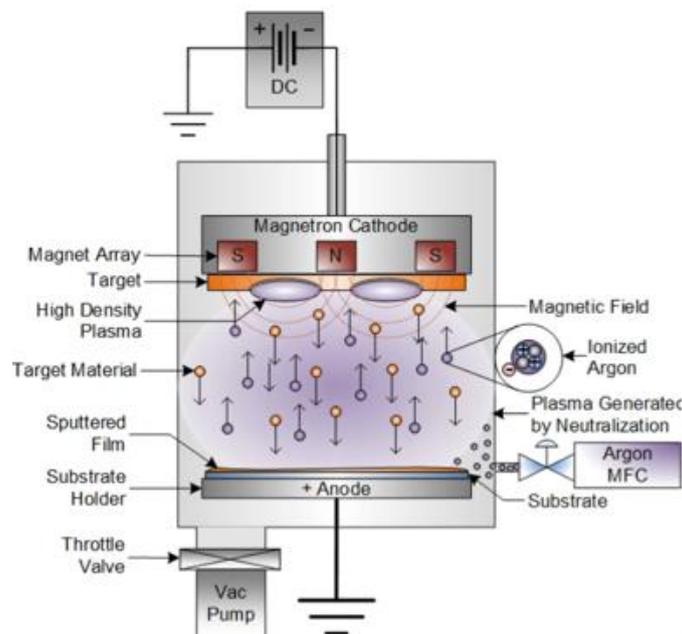

Figure 32: Principle of magnetron sputtering

The apparatus is composed of four main parts: the vacuum system, the sputtering system (target, substrate); the power supply and working gas supply (Ar and/or reactive gas). The sputtering process is then mainly conditioned by the nature of the working gas types, the gas flow rate, the gas pressure, the supplied sputtering power, substrate bias potential, the target-to-substrate distance and the target orientation. Depending on the electronic conductivity of the target and the targeted film properties, sputtering may be carried out either in DC, pulsed DC, HiPIMS or RF modes. Deposition is directional, hence is mainly adapted to planar/low aspect ratio substrates.

The apparatus, Figure 13, in which both conventional (homogeneous) and combinatorial depositions will be carried out is equipped with 4 deposition positions (two 2''cathodes, one 4'' cathode and a group of three orientable 2'' cathodes), and a turntable supporting 4 substrate holders (polarizable, one of these with additional heating and rotating capabilities) for 4'' wafers. Each target holder can be supplied either in DC or RF mode. The vacuum chamber is connected to an argon-filled glovebox, so that the substrates, the films and the targets are always handled in a controlled atmosphere. The loading of the substrates is manual. 4 substrates can be positioned in the apparatus at a time. The deposition process on each substrate is programmable: different deposition/etching sequences above each position, and their succession can be defined, and duplicated on the 4 substrates.
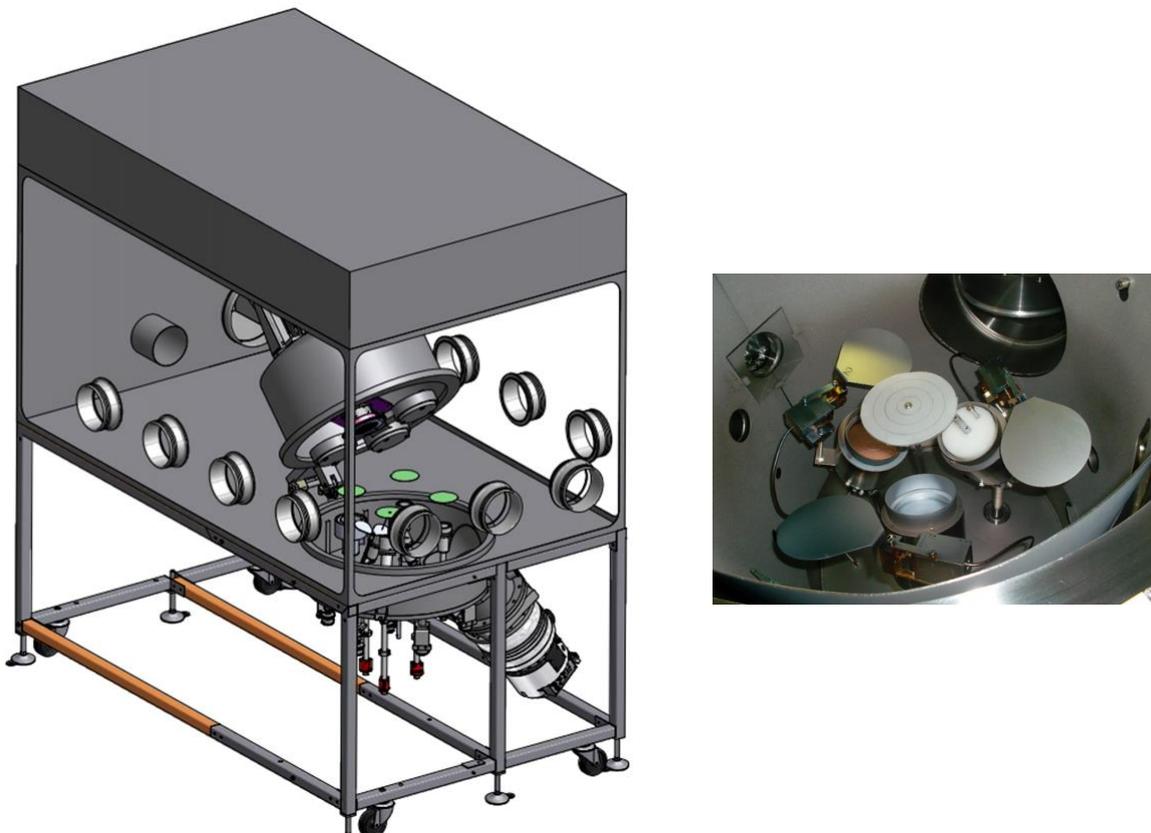
Figure 13: Possible design of the future magnetron sputtering apparatus connected to a glove box (expected 10/2021). View of a group of 3 targets in confocal geometry, similar to the one that will be used to generate the combinatorial films

The 4'' cathode will be preferentially used for the deposition of NMC films, since it will provide a better film homogeneity (composition, thickness) on large substrates such as 4'' wafers. The target that will be used at first will have the same composition as the targeted one in the films i.e. $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_x$ or $LiNiO_x$. Since the sputtering yield of each element depends on the nature of the element, the chemical bonding in the target material and the sputtering conditions, the latter will have to be optimized in order to achieve to maintain the right stoichiometry in the film. As a last resort, it will be possibly necessary to change the composition of the target in order to meet this goal. The resulting thin films will be amorphous and will require post-annealing in air or oxygen in order to generate the layered structure. Consequently, only the substrates that can sustain a thermal treatment (500-700°C) under oxidative conditions will be used: Pt foils, Pt-coated passivated Si or glass wafers. Note that the preferred orientation (00l) will have to be avoided since the latter is detrimental to the lithium diffusion in the film. The target in term of film thickness is about 1 μm. The elemental composition will be checked by ICP, then possibly by other methods (WDS, EDX,…), the phase purity and crystal structure will be determined by (GI)XRD and Raman spectroscopy, the thickness, deposition rate, weight and density will be measured using a stylus profilometer and a microbalance.

Combinatorial coatings will be prepared using the group of 3 cathodes placed at an in-plane angle of 120° relative to each other. Films will be generated on the top of the model thin film electrodes by combining components originating from these 3 sources at the same time. Compositions will be assessed at first in the Li_2O-(P_2O_5, B_2O_3, SiO_2) system, but additional components can be envisaged (Li_2SO_4, LiF,…). These coatings will be amorphous (glassy materials), and their composition as well as their thickness will depend on their position on the substrate. Given the insulating character of the target materials, the RF-mode sputtering mode will be used. The target for the coating thickness on the electrode films is 5-100 nm. The deposition rate and thickness distribution will be determined by stylus profilometry either on thin film obtained by sputtering single targets or the combination of three. The thin film composition distribution will be roughly estimated from a mixing rule (thickness and/or weight). Indeed, since the film will be composed here mainly of light elements, it will be difficult to obtain a precise (quantitative) composition mapping. A feasibility study using XPS analyses will be conducted in this aim.

5.2   Description of combinatorial sputtering approach

Different approaches have been proposed for the preparation of material libraries by sputter deposition, i.e. the deposition of thin films which composition vary according the position on the substrate.

A first approach consists in the sequential deposition of components using a set of shadow masks[2]: layers of individual components is deposited (or not) on the top of the previous one depending on the presence of an aperture (or not) in the mask; this requires changing the mask/pattern before every deposition step; then mixing of the components and the homogenisation of the multilayer film is achieved by thermal treatment (or possibly achieved *in situ* by using a heating substrate holder). Such an approach is compatible with the present apparatus (sequential deposition using 3

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[2] J. S. Cooper et al. *Rev. Sci. Instrum*. **2005** 76, 062221 – DOI : 10.1063/1.1921552

distinct positions) but is not really applicable here due to the presence of the NMC electrode film above the combinatorial coating.

A second approach[3] consists also in a sequential deposition of individual components, but in this case an intimate mixing of the components is achieved by depositing very thin layers of individual components (1 atom layer ≤) at each step: the substrate is fixed to a turntable that is rotating at relatively high frequency, so that the residence time of the substrate in front of each target is very short; since it is not possible to change a shadow mask between each deposition step, a shadow mask with a particular design is now fixed above each target, and the substrate is forced to tilt when passing in front of each position; thanks to the geometry of the aperture in the shadow mask a linear evolution of the amount of a given component according to a direction at the surface of the substrate is obtained that allows to control the mixing ratio of the components and there location on the substrate; this requires particular hardware design and has a low efficiency in term of deposition rate (compatible with metal elements, but not really with oxides).

The third option that will be used here, will be to generate compositional gradients (Figure 14) for the protective coatings by co-sputtering[4,5]. Three components originating from the 3 individual targets positioned in-plane at 120° relative to each other will be sputtered at same time. The way they mix on the surface of the substrate will mainly depend on the relative power applied to each sputtering gun, the target-to-substrate distance, the angle of each sputtering gun with respect to the substrate normal. As a consequence of the multi-parameter influence of the distribution of the composition and deposition rate on the substrate, this approach does not allow to precisely monitor *a priori* the composition and the thickness simultaneously on all locations of the substrate. Nevertheless, the compositional range and thickness gradient of the films deposited on the substrate can be adjusted by carrying out at first 'calibration' experiments using each gun separately in order to get a thickness mapping (stylus profilometry) and a mean composition (ICP) for a given set of sputtering parameters (the power applied, the tilt angle and deposition time in particular). Then different samples (substrates) will be treated (coated) using chosen sputtering parameters in order to cover large or reduced compositional ranges, and different thicknesses for a fixed compositional range. The target in terms of appropriate coating thickness should be about 5-20 nm, but thicker films will be required to carry out different calibrations.

XPS will be assessed to get accurate composition/structure mapping of these amorphous films on the 4'' substrates. Electron probe micro-analyzer (EPMA) could also help to cross-check some elemental analyses.

At the first stage of material development, the substrates will be either plain $Si/SiO_2/Si_3N_4$ wafers (4'') or $Si/SiO_2/Si_3N_4$ wafers with additional patterned thin film electrodes (Figure 15) to allow ionic and electronic conductivity measurements on the films. Depositions will be duplicated on $LiNiO_2$ and $LiNi_{0.8}Mn_{0.2}Co_{0.2}O_2$ thin films prepared either on sets of 8/12 mm discs of Pt foils placed on a 4'' holder (button cells) or on patterned $Si/SiO_2/Si_3N_4//Pt$ wafers (4'') for further electrochemical characterization. Some set-ups for the characterization of patterned wafers are provided in Figure for example.

[3] V. Chevrier et al., *Meas. Sci. Technol.* **2006**, 17, 1399–1404

[4] M. Otani et al., *Jpn. J. Appl. Phys.* **2009**, 48, 05EB02 – DOI : 10.1143/JJAP.48.05EB02

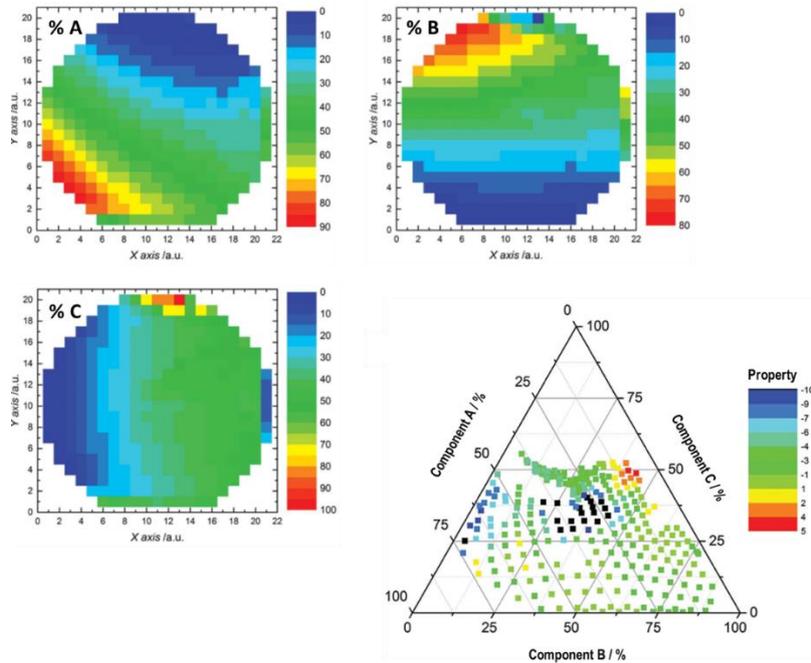[5] K. S. Chang, *Appl. Phys. Lett.* **2006** 89, 142108 – DOI: 10.1063/1.2357011

Figure 14: Surface distribution of sputtered components in a thin film prepared by co-sputtering (combinatorial) of three targets (2'' diameter) on a silicon wafer (100 mm diameter). Representation of the prepared compositions in a ternary diagram with the corresponding magnitude of a particular property. (Adapted from M. Wambar et al.6)
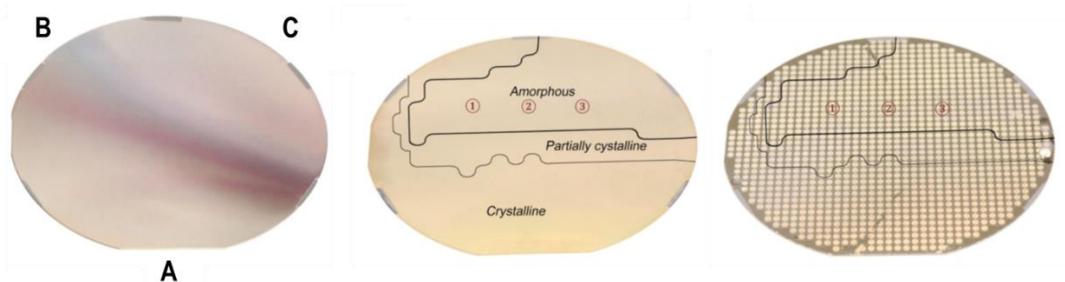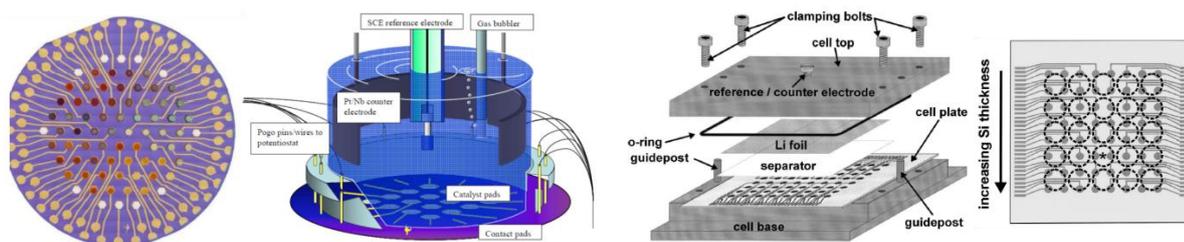

Figure 15: Example of a material library (gold alloys) generated by co-sputtering of 3 targets (120°) deposited on plain and patterned wafers (Adapted from J. Liu et al.7)

[6] M. Wambar et al., *Adv. Electron. Mater.* **2016**, 2, 1500208 - DOI: 10.1002/aelm.201500208

[7] J. Liu et al., *Gold Bull.* **2015**, 48, 111-118 - DOI 10.1007/s13404-015-0167-z

Figure 16: Set-ups designed to carry out the electrochemical characterization of materials libraries: Pt-Mn-Co catalyzers for the ORR and OER reactions prepared by sequential deposition using a series of shadow mask[8], Si-based anode materials for Li-ion batteries prepared high-frequency sequential deposition[9]

5.3   Hardware involved

Hardware involved is the magnetron sputtering apparatus connected to an Ar-filled glove box described above. The connection to the glove box allows the loading/unloading of the sputtering targets, the substrate and the films samples in/out the chamber without any air exposure. These operations are and will remain manual. Only the deposition sequences and their succession are programmable thanks to a proprietary controller. Note that 4'' target will have to be purchased, but that 2'' targets can be possibly made in-house.

5.4   Description of the low-level software layer

As the machine is under development by an external manufacturer, the software aspects are unknown at this stage. However, we will seek to understand if it is possible to interface the machine into the BIG-MAP network architecture based on OPC-UA.

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[8] J. G. Gauth et al., *ACS Comb. Sci.* **2015**, 17, 355–364 - DOI: 10.1021/acscombsci.5b00030

[9] M. D. Fleischauer et al., *J. Electrochem. Soc.* **2003**, 150, A1465-A1469 -

6. Software Architecture

In the previous sections we outlined the expected processes to be automated, the machinery to achieve it and the existing software infrastructure (if available). It is evident that there is quite a high degree of heterogeneity in terms of software infrastructure already in place and. Still, we aim to converge on a common network architecture and application programming interface (API) that allows interoperability of these machines and also integration with data streams to and from other work packages of BIG-MAP. In our initial work we have considered the following aspects important for the envisioned network architecture – simplicity, extensibility, security, and standardization.

The need to be simple comes from the fact that architecture needs to be used by a diverse community and hence the simpler, the easier it is to interface and the more likely we will succeed. A diverse community also means that the architecture needs to be adapted to many processes that are still to be specified, thus the network architecture must be extensible to these and new processes as the project progresses. Some of the information involved in BIG-MAP is sensitive and it is important to maintain a high level of security when interchanging data through the network. Furthermore, the point is to allow partners to operate equipment remotely, which again, requires a safe coupling to prevent accidents. Finally, it would be useful to build on an established standard which some hardware already is prepared for, thus saving development time.

We have in the first phase compared the potential of different existing communication protocols including the Robot Operating System (ROS)[10], the Standardization in Lab Automation (SiLA)[11] protocol standard, FastAPI[12], and the Open Platform Communications – Unified Architecture (OPC-UA)[13] protocol standard as a basis for interoperability of robotic hardware in BIG-MAP (see Table 3). The comparison criteria are related to the four aspects mentioned before:

- **Communication (Standardization)**: The underlying communication mechanisms that are currently supported by the protocol.
- **Patterns (Simplicity/Standardization)**: The communication patterns that are currently supported by the protocol. Pub/Sub: Publisher-subscriber
- **Authentication (Security):** The type of authentication supported by the protocol. PKI: Public Key Infrastructure.
- **Encryption (Security):** Whether the protocol supports encryption by default.
- **Semantic data (Simplicity):** Whether the protocol supports annotating data with its meaning to be correctly and automatically interpreted and used by other agents.
- **Open-source implementation available (Extensibility):** Whether there is one or more open-source implementations of the protocol available for use and development.
- **Product or organization standard certification (Extensibility):** Whether there is a consortium or organization that certifies products conforming to the protocol standard.
- **Restful (Simplicity/Extensibility):** Whether the protocol definition supports the REST[14] paradigm or part of it.

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[10] https://www.ros.org/
[11] https://sila-standard.com/
[12] https://fastapi.tiangolo.com/
[13] https://opcfoundation.org/
[14] R. T., Fielding, *Arch. Sty. and the Des. of Net-bas. Soft. Arch.* **2000** Doct. Diss. Univ. of California

- **Serialization (Simplicity/Standardization):** The type of data serialization/encoding supported by the protocol.
- **Used in industry (Standardization):** Whether the protocol is already used in industrial settings and how much (based on the number of industry related organizations in each consortium).
- **Partner familiarity (Simplicity/Standardization):** Whether a partner in WP4 already has familiarity with the protocol.

|	OPC-UA	SiLA 2	ROS	Fast API
Communication	TCP, UDP[15]	TCP	TCP, UDP[14]	TCP
Patterns	Request-response, Pub/Sub	Request-response	Request-response, Pub/Sub	Request-response
Authentication	User, PKI[14]	User	Mac[14]	User, PKI
Encryption	Yes	Yes	No	Yes
Semantic Data	Yes	Yes	No	No
Open-Source implementation available	Yes	Yes	Yes	Yes
Product or organization standard certification	Yes	Yes	No	No
Restful	No – can be added	Yes - gRPC	No – can be added	Yes
Serialization	UA-Binary, XML	Protocol buffers	ROS Messages	JSON
Used in industry	Yes - High	Yes - Low	Yes - High	No
Partner Familiarity	Yes	No	No	Yes

Table 3. Comparison of communication protocols

While some protocols provide some of the aspects sought, OPC-UA represents the best choice as it constitutes an emerging industrial standard with built in security features, it also includes a simple way of annotating data with its meaning, for it to be correctly interpreted and used by other agents when adding new processes to the system and provides an open-source implementation to use and develop. In contrast to conventional industrial buses, OPC UA also does not require any specific hardware and merely presupposes an ordinary network controller. Only an optional real-time implementation requires a Time Sensitive Network (TSN).

Even though OPC UA provides all the necessary functions for the local shop floor, there is no cloud implementation per se to connect machines and production lines across different institutions. For this function, which is essential for the project, a separate network architecture must therefore be designed and implemented.

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[15] S. Profanter et al. *Int. Conf on Ind. Tech*. **2019**, 955-962 – DOI : 10.1109/ICIT.2019.8755050

The simplest solution to share data with external institutions is to open the ports of the associated servers in the firewall for incoming connections (see Fig. 17). However, this poses a significant security risk, as it is very costly to intercept all unauthorized access behind the open firewall.
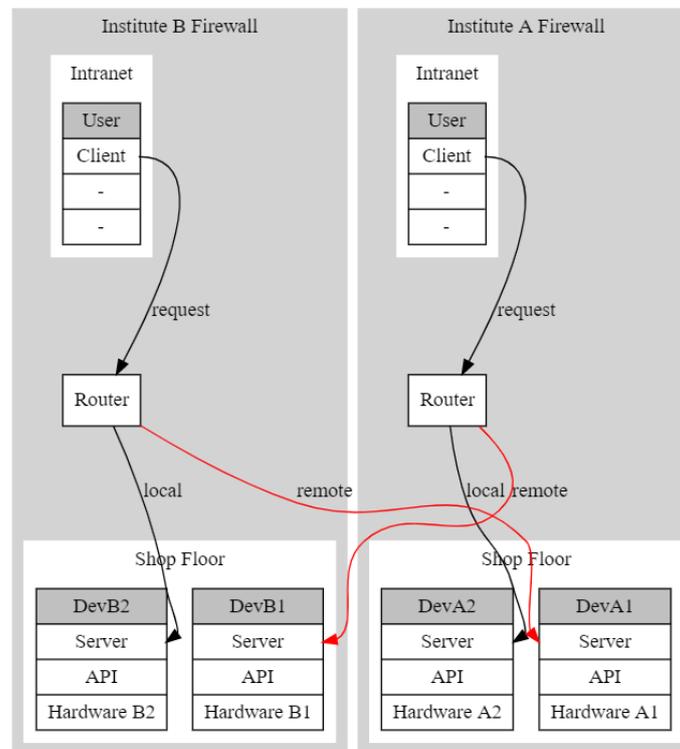
Fig. 17: Data exchange via exposed servers requires open ports for incoming connections (red) in the institutional firewalls

It is therefore better if the institutions connect to a shared, public server where only the relevant data is stored (see Fig. 18). While security is served by this, there is an additional effort for developers, since external data is accessed via a different protocol (e.g. SQL, Websockets, etc.) than internal device data (e.g. OPC UA, ROS, etc.).
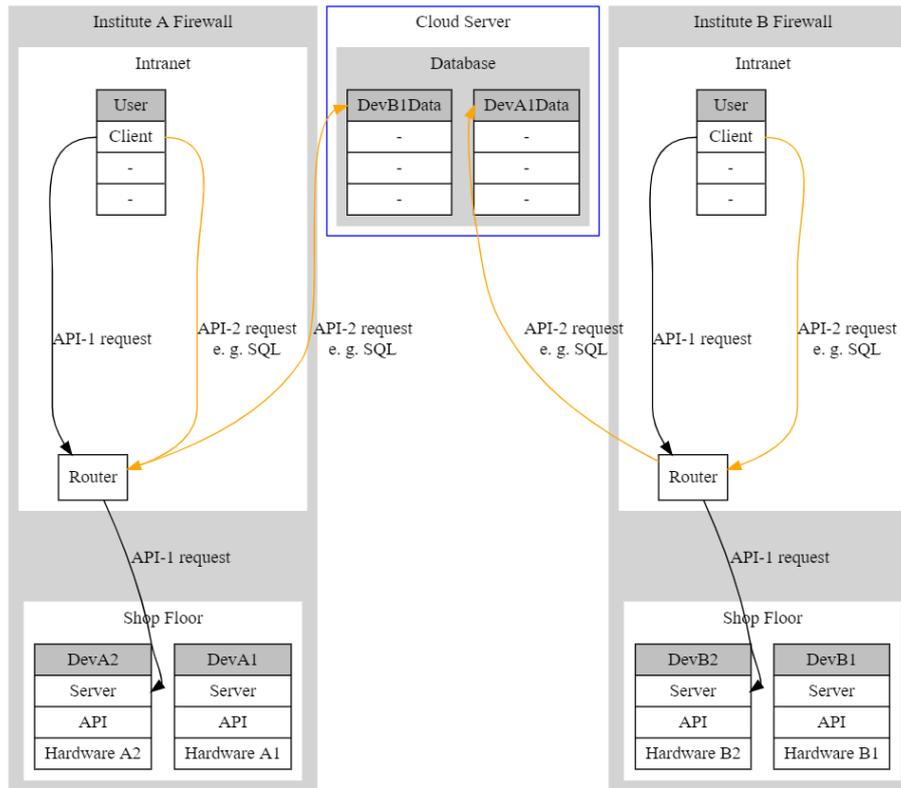
Fig. 18: Man-in-the-middle architecture with a central public cloud server. Relevant data is stored on the cloud server and is accessible by other institutes. Institutional firewall have only secure outgoing connections (orange), but developers have to implement different APIs depending on accessing internal or external device data.

To compensate this disadvantage as well, virtual OPC UA devices can be made available on a public server of the respective other institution, as demonstrated in this example code[16] (see Fig. 19). These virtual devices behave exactly like the physical devices, except that no physical hardware is present. Instead, incoming and outgoing data is synchronized between the virtual and the physical device via internal authorized mirrors. If OPC UA is, as recommended, also used on the shop floor, users / developers don't have to switch protocols to access both local and remote devices.

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[16] https://github.com/BIG-MAP/Public-OPC-UA-Mirror-Demo
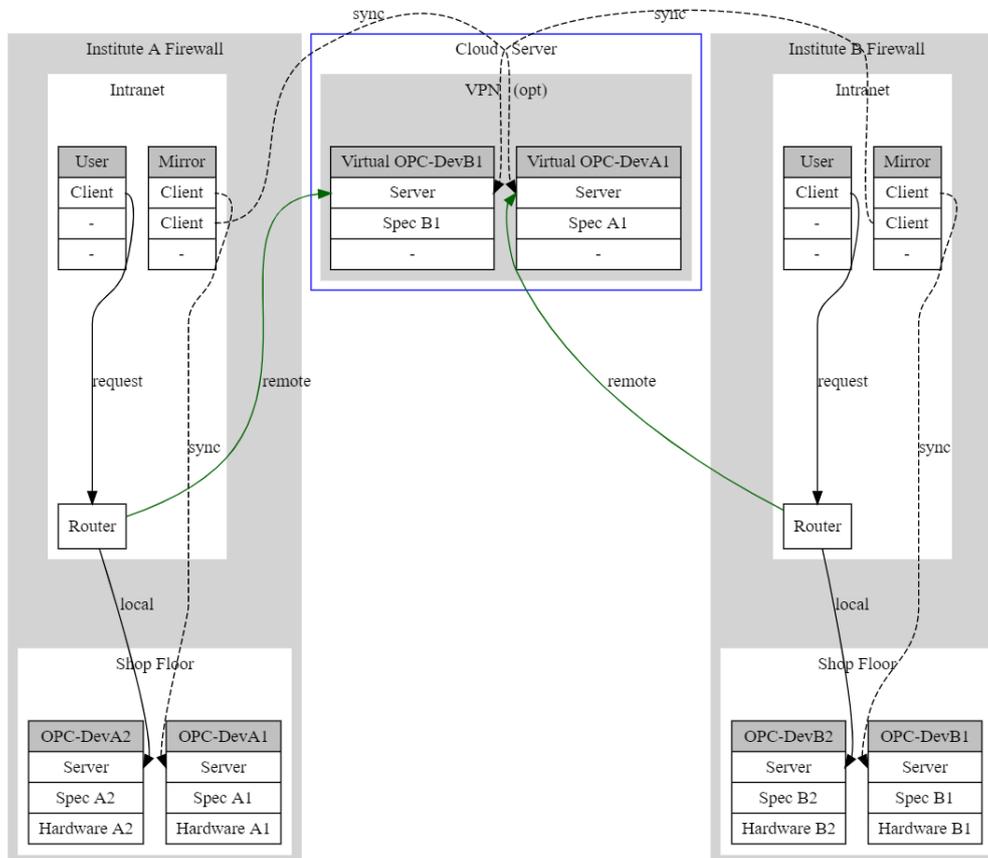
Fig. 19: Architecture with virtual OPC UA devices on a public cloud server. Synchronization is realized via dual-client mirrors which allows a fine grain and central access control. If OPC UA is, as recommended, also used on the shop floor, users / developers don't have to switch protocols to access both local and remote devices (green).

Since this architecture is both secure and uniform with respect to the protocol used (OPC UA), it is preferred for this project. For implementation, the consortium partners have to create an OPC UA specification of their devices once (e.g. with an OPC UA modeler[17] [18]). This specification can then be used to (automatically) create the server of both the physical and the virtual device. The mirrors can use both a predefined server specification and the auto-discovery feature of the OPC UA standard to synchronize relevant data.

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[17] https://www.unified-automation.com/products/development-tools/uamodeler.html
[18] https://github.com/FreeOpcUa/opcua-modeler

7. Outlook

This deliverable presented the processes to be automated, the hardware infrastructure and the software currently available or under development in the BIG-MAP consortium. It also argued for an OPC-UA based network architecture to serve as the interface across machines and between institutions. The work ahead of the consortium is to implement interfaces that allow the existing software to interface with an OPC-UA cloud layer in order to provide a uniform accessible interface across the consortium as a whole.

Appendix

Flow-chart for synthesis of organic polymers of the ORMOCER® family (see Section 2.3).