



BIG-MAP



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ABSTRACT

The design of a robotic system to increase the autonomy of an inorganic synthesis procedure is described. Specifically, the design and workflow have focused on developing an autonomous and high-throughput method to coat battery active powders with an inorganic layer (such as alumina). Since the start of the BIG-MAP project, the workflow has progressed from a fully manual process (*i.e.*, no automation) towards partial automation utilising automated solid and liquid dispensing units. This progress imparts significant time savings and high-throughput capability, as well the removal of significant sources of human error within the synthesis process. Connectivity and integration of the high throughput coating produced into BIG-MAP will be achieved via implementation of Open Platform Communications Unified Architecture and high-throughput work within WP6

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1. Introduction

The coating of nickel-rich layered oxide materials for Li-ion positive electrodes (e.g., $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ [code NMC811] and LiNiO_2) with thin metal oxide layers have been demonstrated as a viable strategy to improve cycling stabilities in lithium-ion cells. Therein, a thin coating may impede or prevent some degradation processes linked to particle cracking and transition metal dissolution and provide a physical protection layer to attack from HF (formed by electrolyte decomposition). Moreover, a well-controlled coating could feasibly lower the reactivity of NMC811 and LiNiO_2 particles with CO_2 and moisture in the ambient atmosphere (leading to unwanted surface Li_2CO_3 and LiOH) and, in turn, improve the manufacturability of resulting coated powders for the preparation of electrode castings and full-cells.

Alumina, Al_2O_3 , is the primary example of an inorganic coating for nickel-rich positive electrodes. A sufficiently thin Al_2O_3 coating can enhance the high-voltage cycling stability of layered oxide cathode materials without passivating the interface and preventing electrochemistry. The stabilisation is attributed to the inhibition of electrolyte decomposition and HF attack of the particle surfaces. Furthermore, a spontaneous reaction between the conventional LiPF_6 electrolyte salt and Al_2O_3 results in the *in situ* generation of LiPO_2F_2 , an established electrolyte additive that can improve the cell lifetimes in various Li-ion chemistries (D. S. Hall et al. *ACS Appl. Mater. Interfaces* 2019, **11**, 14095–14100). Other inorganic materials used to form particle coatings have included LiNbO_3 (J. L. White et al., *J. Phys. Chem. C*, 2020, **124**, 16508-16514.), Li_2ZrO_3 , LiAlF_4 (J. Xie et al., *ACS Nano*, 2017, **11**, 7019-7027.).

The development of an automated process for the coating of cathode powders is targeting the utilization of Al_2O_3 as a benchmark coating material. An established sol-gel synthetic procedure is being used to prepare the Al_2O_3 coatings, wherein automation and control of a wide array of reaction parameters and variables are possible, including reactant type, reactant concentration, co-solvents, reaction time/temperature, atmosphere, and calcination temperature. To begin, a partially automated process is being developed based on the fabrication of Al_2O_3 coatings firstly on the atmospherically stable layered oxide powder $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (code NMC622). The variables will initially be explored over wide ranges to establish suitable boundary conditions and limitations of the process and the resulting coatings. For example, one expected boundary is to be found at large weight% of Al_2O_3 used in the synthesis wherein an overly thick and, therefore, passivating coating blocks normal interfacial processes of the electrode powders. Once the process is fully implemented, the automated coating procedure will be conducted under a dry nitrogen atmosphere to complete coatings on the more air/moisture-sensitive NMC811 powders. Furthermore, the methodology will be applied to a second coating material to explore the demonstration of multi-layer coating protocols on these powder materials.

1.1 Why automate the synthesis of battery coatings?

The coating of battery materials with an inorganic coating layer *via* a sol-gel synthetic route involves a variety of tuneable reaction conditions and precursors that may ultimately alter the minute characteristics of resulting films and the quality of resulting powders. Automation, enhancing speed and accuracy control of slight differences in these controlled variables, creates the opportunity to explore wider matrices of reaction parameters rapidly and, subsequently, more readily optimise coatings for enhanced or improved properties (namely relating to electrochemical performance). A



fully automated process would enable continuous 24 h operation as required without the requirement for standard rest breaks. Subsequently, by combining this output with careful information feedback from important characterisation methods (utilising machine learning methodologies), the automated process could realistically identify optimised parameter ranges and more readily identify the limitations of the synthetic procedure.

1.1.1 Automated vs. manual synthesis of inorganic coatings

The manual synthesis of coatings primarily benefits from greater adaptability within the method to adjust for new (or challenging) precursors/reactants/materials, reaction vessels, atmospheric requirements, etc. For example, the accuracy (or even the possibility) of solid dosing by automated machines has been affected by the particular qualities (particle size, static, etc.) of the powder being weighed. Additionally, should a novel precursor require completely anhydrous, inert conditions, a dedicated researcher could straightforwardly adapt the procedure to include containment methods (*i.e.*, Schlenk line apparatus or glovebox environments).

The automation of an established sol-gel synthetic route (with degrees of control at the various preparative, reaction, and post-processing steps) dramatically enhances the accessible matrix of controllable variables that may be realistically explored in a finite time period. Furthermore, providing for reliable input commands within the experiment design, errors, and variance in measurement and different reaction conditions should be minimised across many samples (especially where total differences are minimal) and consistent (*i.e.*, no human error once initialised) within the tolerance of the machines used. Such a degree of control and repeatability, with the enhanced throughput that automation allows, creates an opportunity to fine-tune reaction parameters. Coupled with relevant performance knowledge from electrochemical and surface characterisation of the coated powders, this should facilitate the optimisation of the procedure to fabricate uniform and stable coatings that promote improved stability and more stable long-term cycling.

1.1.2. Existing state-of-the-art automated solutions

There are some existing solutions available for automated processing of materials that offer some of the comparative features required for this synthetic procedure, but none designed in full based on the required specifications for a sol-gel coating (of battery powders). Module systems developed by LABMAN (UK), such as the Inert Processing Module, utilise robotic systems able to dispense an array of liquids and solids into different vials (*i.e.*, reaction vessels used here) under controlled atmospheres and provide mixing steps at elevated temperatures. Chemspeed Technologies (Switzerland) offers modular systems with similar capabilities in addition to an array of reactor modules for small-scale multi-step synthesis methods, including mixing, heating, refluxing, evaporating steps.

2. Process design

The process for the sol-gel synthesis of Al_2O_3 coatings in an individual reaction vial (not including transfer steps) can be described by 5 main steps: solid powder dosing, liquid component dosing (including Al-precursor solutions), reaction heating/mixing, solvent evaporation, and calcination (Figure 1). In more detail, the preparation is as follows. The solid NMC622 powder (1 g) is dispensed into a glass vial. The bulk solvent (*e.g.*, 2-propanol) is first deposited into glass vials, followed by the chelating agent and then the solvent solution containing the aluminium precursor (*e.g.*, aluminium tri-sec-butoxide or aluminium isopropoxide). The total liquid volume is an adjustable factor but will initially be fixed at 10 mL, and the molar/weight ratio of Al to cathode powder can be varied (*e.g.*, 0.1:99.9 to 10:90). The resulting mixture of components is then heated and mixed for a period of time before a flow of dry N_2 is introduced directly into the reaction vials to aid evaporation of the solvent during completion of this step. The vials are then transferred directly to a box furnace (natural convection) customised to hold multiple racks of multiple vials per run to be fired at temperatures from 400–675 °C for a fixed time. The glass vials, to be provided with ceramic-based QR code labels, have been stability tested for the calcination step up to 650–675 °C. Above these temperatures, major deformation of the vial was observed after cooling.

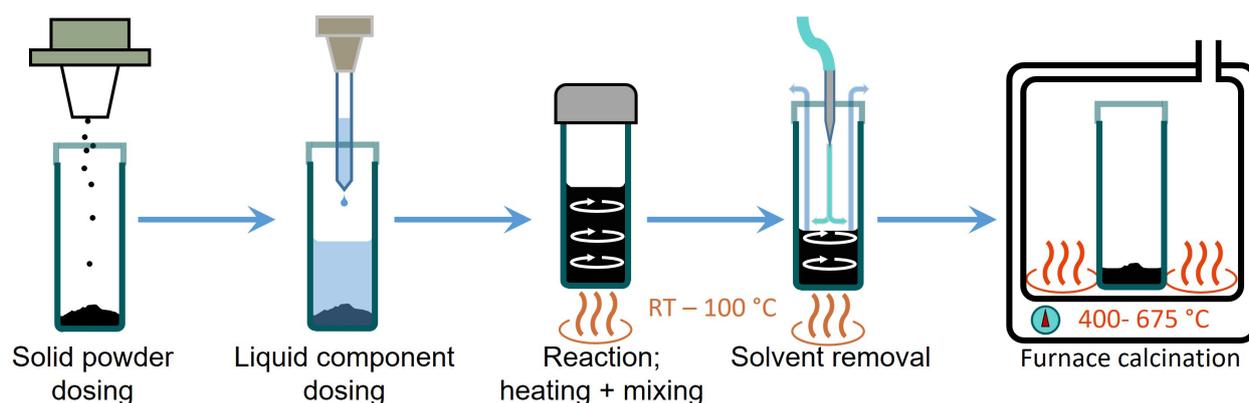


Figure 1. The semi-automated coating process of $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (code NMC622) with alumina (Al_2O_3).

At present, the process relies on discrete units, individually capable of delivering an increased level of automation and high-throughput capability for each step. As such, manual input for transferring reaction vessels (or blocks of reaction vessels) between the sequential steps is required, and it is a logical longer-term goal to automate these steps (*i.e.*, introducing robot arms for transferring and (de)capping vessels).

The operation and design of experiments will be implemented through a single, centralised, and unified file linked with reaction vessel identifiers (QR codes) and integrated with operations to generate instructional input files for the various individual modules. Therein, a user selects the target outputs for an experimental run (powder quantity, target coating wt%, reaction conditions) from which input files are generated and sent remotely to each discrete module within the procedure. Conversely, where data is generated from the various steps of the procedure (namely mass accuracy of solid dosing in accordance with prescribed acceptable tolerance), output files generated therein will feedback data to the centralised, unified experimental file.



The main tuneable variables that will be explored include the Al-precursor coating concentrations (affecting final coating thicknesses), reaction times, reaction temperatures, solvent evaporation rate, calcination temperature. Secondary variables that may be considered include the Al-precursor, solvent type/volume, chelating agent type/amount.

Table 1. A simplified breakdown of 5 primary sol-gel synthesis steps, with individual quantities/ranges per reaction vial.

Reaction step	Material/method	Scale + unit	Exp. accuracy	Time frame /h
Solid powder dosing	NMC622, NMC811	1 g	1%	0.1 – 0.2
Liquid dosing	Solvent (2-propanol, or other alcohol)	1-10 mL	1%	0.4 - 0.6
	Al-precursor solution	0.1-10 mL	1%	
	Chelating agent	1 mL	1%	
Reaction heating/mixing	Shaker or sonication	20-120 °C, 1-4 h		1 - 3
Solvent evaporation	Dry N ₂ flow into vials during heating/shaking to aid evaporation	80-120 °C		0.25 - 2
Calcination	Box furnace	400-675 °C, 2-5 h		2 - 5

2.1 Hardware

Equipment	Description
 <p>Benchtop Mettler Toledo Quantos</p>	<p>Benchtop Mettler Toledo Quantos automated balance enables dosing of powders of different quantities into vials with a manual intervention step for heating and shaking. The process is partially automated but allows an easy proof of concept for new processes.</p> <p>Purpose bought dosing head for fine battery powders acquired.</p> <p>https://www.mt.com/gb/en/home/products/Laboratory_Weighing_Solutions/Automated_Sample_Preparation/Autosampler.html</p>
Eppendorf EpMotion	<p>Eppendorf EpMotion is an automated liquid dispensing system that can combine and mix a series of liquid components into multiple racks of multiple reaction vials. A mixing station is included within the system but not designed for the level of solvent evaporation (<i>ca.</i> 110 mL per rack) required in this workflow.</p>



	https://online-shop.eppendorf.co.uk/UK-en/Automated-Pipetting-44509/Liquid-Handling-Workstations-44510/epMotion5075I-PF-68891.html
Reaction stage	To be defined.
Purge gas manifold	In-house designed gas feed to supply uniform flow of dry N ₂ gas directly and simultaneously into 11 vials per rack to aid bulk solvent evaporation. Coupled with heated reaction stage to promote enhanced evaporation (of <i>ca.</i> 10 mL per vial).
Box furnace	Natural convection box furnace, custom-modified with multiple internal shelves to carry multiple racks (of 11x reaction vials) per heating run

2.1.1 Hardware capabilities

The Quantos automated balance is coupled with a carousel autosampler, enabling the automated weighing of powders sequentially up to 30 vials per run. The readability and accuracy of the weighed powders should exceed the required target tolerance (i.e., 1 % in 1 g) depending on the careful pairing of the correct dosing head with the target solid powder. Therein, the Quantos system interacts with dedicated dosing heads for each material being used (in part to mitigate contamination issues but also to pair the dosing head type/capability with the physical properties of the target solid powder). The system relies on an internal feedback loop based on the output mass and tolerance levels to automate the optimisation of solid dosing for each head. Thus, with the automated optimisations built-in to the system, the accuracy of material dosing for a given material (within the lifetime of a dosing head) should improve with each successive dosing step.

The Quantos balance dosing heads are designed to deliver different types of powders of varying quantities with different physical properties (including particle size, static). Following coordination with Mettler Toledo staff, we have acquired dedicated dosing heads designed for powders similar to those used in this project.

The EpMotion liquid handling system utilises a robotic arm combined with dispensing tools of different working volumes combined with Eppendorf pipette tips. Correct pairing of suitable dispensing tools (i.e., pipetting heads) with the target working volumes being deposited should



enable accuracies better than 1% (for deposition volumes of 500-1000 μL). The established software allows the design of a series of liquid dosing runs from standard or specialised sample reservoirs into multiple racks of vials, feasibly allowing for the run of 7/8 racks of 11 vials each in a single automated set-up.

The combination of utilising the Quantos and EpMotion has allowed significant progress in automating the synthesis procedure. The conventional lab synthesis was undertaken in Liverpool previously relied on purely manual steps without any automation. The progress achieved thus far by utilising discrete automated steps for higher throughput has enabled the completion of many more synthesis reactions per run. It is the intention to link this setup to high-throughput work within WP6, where there is significant overlap, namely WP6.5 (High-throughput experimentation of inorganic protective coatings).

2.1.2. Hardware limitations

The automated dosing of a fixed mass (1 g) of solid powders used in the project (*i.e.*, NMC622, NMC811) can be completed in a series of reaction vials using the Quantos automated balance. However, one limitation with the target hardware is the lack of pairing with other robotic hardware for loading, capping, and decapping the reaction vials before and after completion of this step. Likewise, due to the current separate nature of the separate hardware being used currently without communication (physical or informational), loading the vials to the racks on the EpMotion system (11 vials per rack) and transferring the racks between the EpMotion, heating, and furnace systems will currently rely on manual intervention making this process partially automated overall.

One present limitation that requires future consideration is all the various steps of this workflow currently operate under ambient atmosphere and cannot be readily placed under inert conditions. This is a critical consideration for the air/moisture-sensitive LiNiO_2 and $\text{LiN}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ powders and is also important for moisture-sensitive reagents (inc. Al-tri-sec-butoxide). Anhydrous solvents may be used at each stage to reduce moisture contamination (that may result in unwanted hydrolysis reactions of Al precursors). The evaporation of bulk solvent must also be considered during deposition steps since, if this is sufficiently rapid, the final solution concentrations would be affected.

An additional limitation of the current process design (briefly outlined earlier) is the manual nature of the intermediate steps within the process, namely loading vials, transferring vial racks between modules, and initiating procedural steps. The automation of these intermediate transfer steps could foreseeably be achieved by the adaptation of established robotic arm technology. However, it is not the purpose to implement this within BIG-MAP as it will require further hardware.



2.2 Process flowchart

The workflow design for the partially automated synthetic procedure is presented in Figure 2, broken down into the 5 main steps described earlier in addition to the experimental design input and feedback loop.

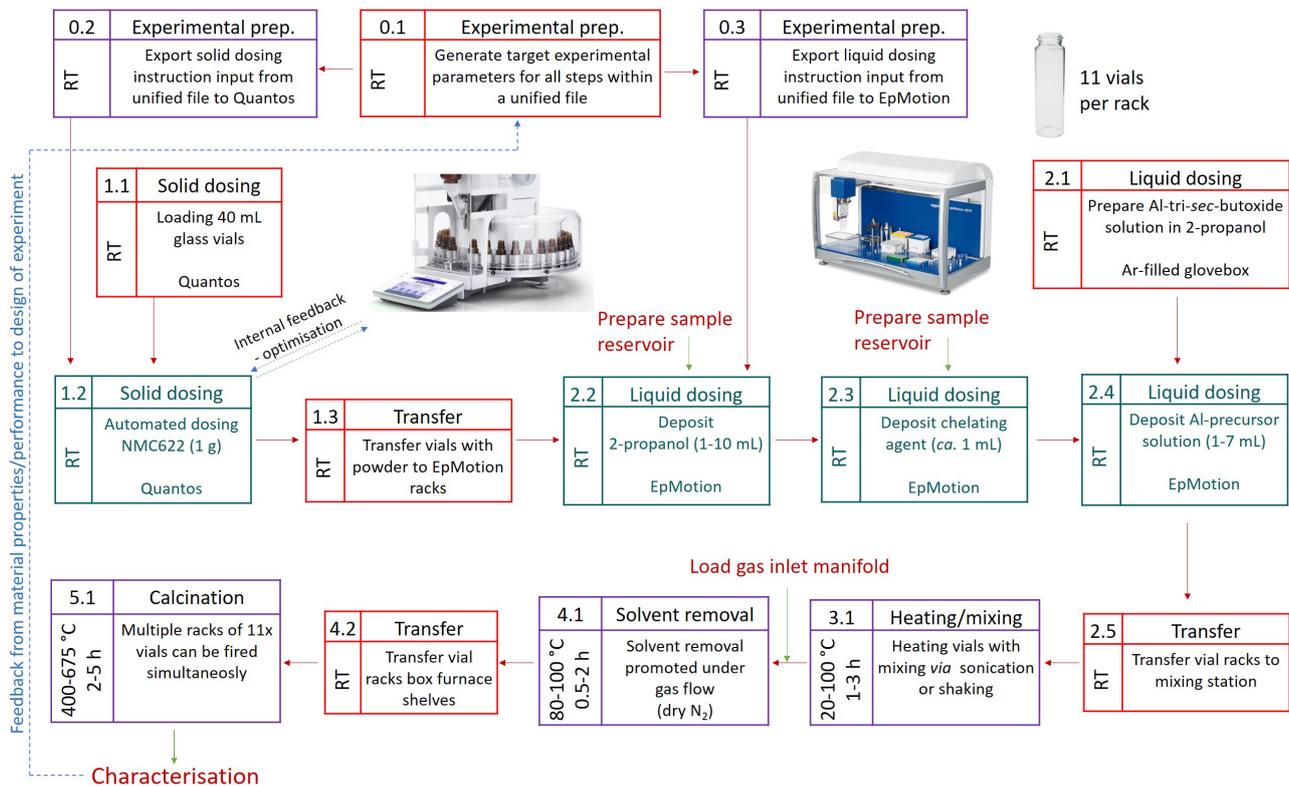


Figure 2. Process workflow for the partially automated synthesis procedure of Al₂O₃ coatings on 1 g of LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622) powder using aluminium tri-sec-butoxide as a precursor. The steps are colour coded by steps that are manual (red), automated (green), or partially automated (or manually initiated on multiple reaction vessels, purple).

Within the synthetic procedure, two primary feedback processes for optimisation are illustrated. Firstly, as described above (2.1.1.), the solid dosing hardware includes an internal feedback loop (partial loop optimisation) towards optimising the accuracy of the automated weighing procedure. Therein, the module should improve solid dosing capabilities and accuracies with continued use of the solid dosing head (within the finite lifetime of the dosing head for a specific material).

Secondly, full loop optimisation of the process (and ultimately of the target materials) will arise from a feedback loop from the characterisation of the coated materials (electrochemical, spectroscopic, and physical characterisation) to the design of experimental parameters/inputs.



3. Software design

The discreet operating modules rely on dedicated software programs (Table 2) for operation. The systems are operated by networked PCs and should therefore be connected to receive instructions (experimental design/input) from the centralised operator.

Table 2. Software used to control the automated systems.

Reaction step	Hardware	Established software control	Internet remote connection/control
Solid dosing	Quantos	LabX (Mettler Toledo)	Possible
Liquid dosing	EpMotion	epMotion	Possible

A unified and centralised experimental file with the capability to generate input (trigger) files for the individual for process modules is to be designed and implemented. Table 3 shows an approximation of the user interface of the file, allowing for input of specified target parameters by the user. Input files for the steps (notably for solid and liquid dosing) can then be automatically generated within the required input file format and sent remotely to the required software (Lab X for Quantos and epMotion for EpMotion) for the module or operating instrument PC.

Table 3. The example proposed unified file for the experimental design of synthesis procedure

Vial code	Material	Quantos solid dosing			epMotion liquid dosing			Reaction		Calcination	
	Cathode powder	Solid target / g	Solid result / g	Within tolerance (1%)	Wt% Al-precursor	Chelating agent / μL	Solvent (IPA) / μL	Reaction temp / $^{\circ}\text{C}$	Reaction time / min	Calcination temp / $^{\circ}\text{C}$	Calcination time / h
	NMC622	1 g	**	**	2	*	*				

Example user information and required input columns presented; formulae and calculations deriving parameters from user target inputs not shown.

* Automatic input based on other variables for standard procedure

** output information as feedback from communication with Quantos system

Designated vials to be ordered with ceramic-based QR-coded labels; glass stability as well as the material and positioning of the QR code label have been tested as stable up to 650-675 $^{\circ}\text{C}$. Software (TBD) to be used to read codes and store associated experimental data specific per vial and rack.

4. Integration robotic system for inorganic synthesis into BIG-MAP

It is a target to implement the integration of the coating system into BIG-MAP through the proposed OPC-UA (Open Platform Communications Unified Architecture) infrastructure. The separate hardware of the coating system will be interfaced through this general architecture. In collaboration with WP4 partners, ongoing work will initially target the development of an HTTP API protocol for the remote communication and execution of the discreet hardware modules via networked instrument PCs. With the implementation of a unified experimental file described above, compiled and executed remotely, a user will feed automation run information to connected devices and



ideally trigger experimental runs and receive data feedback. By achieving interconnectivity between the presently separate hardware modules to interface with dedicated software and read/output data, the complete synthetic procedure in lieu of automated transfer steps may become remotely executable. Beyond this point, expert help from partners developing the OCP-UA for BIG-MAP will be required to interface the system with this infrastructure to enable partners to design, execute and receive data from experimental runs.

5. Conclusions

- A partially automated coating process has been designed and set up to vary the chemistry, thicknesses, and post-processing treatments of inorganic coatings on Li-ion positive electrode powders.
- 11 coatings can be “carefully” prepared per rack (with several racks per run feasible).
- A single run on 11 coatings can be completed in an approximate time frame of *ca.* 4-10 h (10 mins solid dosing, 25-35 mins liquid dosing, 1-3 h reaction time, 15 mins-2 h bulk solvent removal, 2-5 h calcination). The primary time-saving benefit arises from the automation of the weighing/deposition steps.
 - With a comparable consideration for sample weight accuracy, the solid dosing would realistically take 1-2 h manually. Likewise, manually completing the liquid deposition consisting of *ca.* 100-140 depositions of varying volumes would reasonably take 1-2 h. This means a minimum run for 11 vials increases to 6 h.
 - It is important to note that the degree of human error per measurement/dosing step would be larger and is reasonably expected to increase significantly for many repetitive tasks. The error of automated processes should be minimised relatively and consistent across the entire dosing run.
- The workflow also allows for multiple racks to be prepared and completed per individual experiment run, limited by like-for-like conditions for multiple racks during only the calcination stage.
- The designed workflow is chemistry agnostic and is set up to be transferable methods to provide controlled inorganic coatings on other types of “micron-sized” powders.
- A unified user experimental file will be designed and implemented to allow for centralised generation and sending of trigger/input files for the dedicated discreet automated modules.
- From the initial stage of the project, wherein the synthesis procedure could only be completed entirely manually, the coupling of discreet modules (with various adaptations for this procedure) has increased the level of automation and throughput capability of this procedure.
- Outlook: moving from a partially automated to a fully automated process with full interconnectivity between hardware steps will be challenging to realise because of the integration of the hardware and software of different equipment. However, a design and process framework will be explored in order to optimally design a fully integrated system.