# Publishable Summary for 21GRD01 OpMetBat
# *Operando* metrology for energy storage materials

**Overview**

The development of new battery materials is key to improving the performance, lifetime, safety and cost of energy storage technologies such as Li-ion batteries for electric vehicles. However, innovation is hampered by the inability of industry to reliably characterise their structure and chemistry in an operating environment. This project will build a metrological framework supporting traceable *operando* characterisation of state-of-the-art battery materials under dynamic charge / discharge conditions. This includes advancement and validation of *ex-situ* methods, establishing new protocols, cells and a best practice guide for *operando* approaches and developing new instrumentation enabling hybrid, multiparameter measurement to inform new materials development.

**Need**

The European Green Deal targets net zero $CO_2$ emissions of greenhouse gases in Europe by 2050, specifying zero emissions from new cars by 2035. Electrification of the automotive industry is key to meeting these goals, but rapid advances in energy storage technologies such as lithium-ion batteries are required to realise this. Many new materials combinations for battery electrodes are emerging that can begin to address performance targets, but lifetime issues remain problematic. Hence, there is an urgent need for traceable analytical techniques to decipher structure-behaviour relationships and elucidate degradation and failure mechanisms to improve battery performance by design, rather than empirically.

Quantification of elemental composition, and determination of oxidation and chemical binding states, coordination and phase structure are crucial for an enhanced understanding of battery electrode degradation (Objective 1). Moreover, investigations must be conducted in real-time, allowing aging mechanisms to be linked to battery state of charge (SoC) and state of health (SoH). Currently, degradation studies are performed *post-mortem*, using *ex-situ* methods where the cell is disassembled, leading to chemical modification which can distort the result. To avoid that, *operando* methods, where electrode materials are characterised simultaneously during cell charge-discharge, are needed. Whilst some *operando* methods are available, they are not sufficiently reliable or quantitative to allow confident data interpretation (Objective 2). Moreover, there is a need for new hybrid *operando* methods, where multiple measurands are synchronously probed during electrochemical cycling, to establish causal links between materials properties and their impact on cell performance (Objectives 3 and 4). Such advanced measurements bring new challenges as they require special sample environments such as dedicated electrochemical cells with thin probing windows, while ensuring that the electrochemical behaviour remains unperturbed. Hence, there is a need for establishing a robust, validated metrological framework for *operando* metrology, that can be transferred to battery developers and demonstrated through industrial case studies.



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### Objectives

The project aims to develop *operando* techniques and hybrid (multi-modal) instrumentation, supported by quantitative and validated *ex-situ* analysis and electrochemical measurement methods, to enable beyond state-of-the-art materials characterisation for high-capacity energy storage technologies.

The specific objectives are:

1. To develop traceable chemical, physical and structural analysis methods for *ex-situ* characterisation of high-capacity energy storage materials (e.g Li-ion and Li-S) and components (e.g. Cobalt, Nickel, Manganese) with a focus on x-ray spectroscopic techniques. This includes the fabrication and qualification of at least 3 calibration samples and verification by interlaboratory studies (post-mortem). A relative uncertainty in elemental composition determined by XRS of below 10 % will be targeted.
2. To establish a Good Practice Guide for current and emerging in *operando* spectroscopy methods including X-ray and vibrational spectroscopy, validated by *ex-situ* analysis and round robin tests, in order to establish and, where possible improve, experimental repeatability and accuracy with respect to elemental and species analysis of battery materials. In addition, to develop measurement protocols to assess the influence of cell geometry, electrode configuration, and measurement parameters on observable phenomena, as well as to assess the extent and influence of vacuum ultra-violet (VUV) or X-ray radiation damage.
3. To develop novel dynamic electrochemical approaches combined with in *operando* spectroscopy and dimensional metrology for the correlative assessment of the relationships between material structure and cell performances.
4. Based on the results of Objectives 1-3, to develop novel in *operando* instrumentation and hybrid methodologies for multi-parameter spectro-electrochemical characterisation of materials and components for high-capacity energy storage (e.g. in Li-ion and Li-S battery systems). To investigate the causal relationship between electronic/molecular- and microstructure information and charge carrier dynamics as measured with electroanalytical methods, to gain information on the state of health and state of charge.
5. To facilitate – in cooperation with the EMPIR JRP 20NET01 Clean Energy – the take up of the data and measurement infrastructure developed in the project by the measurement supply chain (NMIs, DIs, calibration laboratories), standards developing organisations (e.g. ISO/TC 201) and key end users (materials suppliers and battery manufacturers). To promote technology transfer of the project outputs as lab-based alternatives to synchrotron radiation-based methods, towards industry and manufacturers.

### Progress beyond the state of the art and results

*Traceable ex-situ characterisation of high-capacity energy storage materials (objective 1):*
Despite a variety of existing approaches to *operando* characterisation of energy storage materials based on X-ray spectrometry, vibrational spectroscopy and X-ray diffraction, practices vary substantially across academia and industry. There is little agreement and consistency in terms of electrochemical cell geometry, materials handling methods and measurement protocols, leading to a lack of confidence in data comparison.

This project aims to make progress beyond state of the art by establishing a foundation for *traceable* and quantitative *operando* measurement built on *ex-situ* methods that are validated by adopting appropriate reference materials, calibration specimens or standardised procedures. Methods have been developed to characterise pristine NMC cathodes for Li-ion batteries using analytical techniques such as X-ray absorption spectroscopy (XANES, EXAFS and XRF), X-ray diffraction, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and secondary ion mass spectrometry (SIMS). XRF, XPS and SIMS measurements have provided information on the elemental composition (depth profile or at surface), and the measurement of fundamental parameters (e.g. absolute mass attenuation coefficients) with reduced uncertainties allows XRF measurements to be traceable to the international system of units (SI). XANES has enabled determination of the oxidation states of compounds and complements XES experiments with respect to revealing the entire electronic structure, while EXAFS measurements have given the interatomic distances to neighbouring atoms, in excellent agreement with the rather long-range order XRD studies. Moreover, the crystalline structure of the cathode material unveiled by XRD investigations by partners was used as an input to the theoretical calculations of its electronic structure. The new Li-S battery system developed within this consortium is now operational and has been studied by the same techniques as for the Li-ion with NMC662 cathode.

*Good practice guide for current operando spectroscopy and diffraction methods (objective 2):*
For the first time, this project will develop and disseminate a good practice guide in the application of *operando* X-ray and optical techniques such as Raman spectroscopy. This will be achieved by developing cells and protocols validated by physical modelling, performing parametric studies to optimise experimental conditions, and undertaking interlaboratory comparisons to establish the root of uncertainties to improve experimental repeatability.

Various *operando* cell designs for use with different spectroscopic techniques have been discussed among partners (NPL, HZB, PTB, Uliv, ELECTRO) and two of these designs have been taken forward to the manufacturing stage. Electrochemical tests on cells assembled using a Li-ion full cell arrangement (NMC622/graphite) indicate that these *operando* cells can reliably be charged/discharged well over 50 times over the course of several weeks. The electrochemical cycling performance of the *operando* cells has been measured using rate capability tests and performance has been shown to compare well against conventional coin cells, indicating that the presence of the spectroscopic window has minimal effect on the electrochemical characteristics of the cell. Modelling has also been performed to show that small modifications to the internal geometry of the cell has limited effect on the electrochemical environment within the cell.

Measurement procedures have been established for using *operando* cells to characterise battery materials using Raman spectroscopy, XRS and XRD. This includes measurements to establish thresholds for sample damage caused by the laser or X-ray beam used in these techniques. In addition to analysis of the benchmark Li-ion chemistry, *operando* XRS measurements using calibrated instrumentation have been performed on the latest Li-S materials produced by UNIROMA1, which have revealed some interesting insights into the reversibility of the Li-S chemistry.

*Novel dynamic electrochemical analysis approaches for combination with operando spectroscopy and dimensional metrology (objective 3):*
HZB, NPL, UNIROMA1, PTB, ELECTRO, ULiv and WWU has made significant progress in developing and refining a battery impedance simulator. This instrument is crucial for accurately analyzing spectroscopy data as it accounts for correcting time drift as part of our innovative approach to dynamic electrochemical spectroscopy. The focus has been on developing a device that not only fulfils the technical specifications but is also user-friendly, taking into account feedback from all partners to improve usability and performance.

Notable progress includes HZB's leading role in developing the simulator, ensuring that it adheres to the detailed specifications and incorporates collective insights for excellent operation. Initial evaluations comparing the simulator's measurements with calibrated resistors have emphasized our commitment to traceability and precision. These careful tests and optimization measures underline our commitment to further developing this important device. The collaboration with NPL was crucial as they assisted in developing the simulator, particularly with the voltage/resistance measurement uncertainties and drift correction algorithms. Their contribution was decisive in the evaluation of the application of the simulator on coin cells. Similarly, UNIROMA1's involvement in the impedance discussions and PTB's expertise in accurate measurements contributed significantly to our project's scientific integrity and technical depth. The collaborative nature of the project was also demonstrated by ULiv's proactive steps in procuring additional test equipment and ELECTRO's role in combining technical fabrication and electrochemical acumen. HZB took the lead in documenting the design and implementation strategies, culminating in a comprehensive report for EURAMET. This report symbolizes the participants joint achievements and sets the course for further progress.

The project also focussed on refining the measurement script for electrochemical impedance spectroscopy (EIS). This endeavour aimed to improve the accuracy of battery performance analysis by addressing operational subtleties to ensure the script's compatibility and effectiveness with different devices. The development of this script, in conjunction with the generation and analysis of synthetic EIS data, represents a significant leap forward in the ability to simulate and correct operational drift accurately. In parallel, the projects study of Li-ion batteries is progressing through combined operational EIS and XRS techniques, with PTB improving its equipment for integrated measurements and partners such as ULiv and UNIROMA1 securing important beam time for operational XAS. This collective effort will deepen the understanding of Li-ion battery technologies and demonstrate our commitment to pioneering advances in battery analysis through innovative spectroscopic methods.

*Novel operando instrumentation and hybrid methodologies for multi-parameter characterisation (objective 4):* Finally, the new knowledge generated throughout the project will be built upon to develop novel *operando* instrumentation and methodologies that further extend the state of the art by: (i) improving sensitivity compared to current approaches by developing new *operando* cell windows; (ii) allowing advanced X-ray methods normally confined to synchrotrons to be transferred to laboratory-based instrumentation; and (iii) enabling simultaneous, *hybrid*, multiparameter measurement to allow causal links between materials property changes to be established, and their links to cell performance loss to be identified unequivocally.

Regarding the further development of new cell design and window materials for traceable *operando*, multimodal or hybrid analytical and dimensional measurements several activities have been undertaken: HZB has successfully designed and provided multimodal *operando* analysis cells to its own labs, UNIROMA1, NPL, PTB, and ULiv. Furthermore, HZB already proposed an improved cell design based on the valuable suggestions received from all partners. The improved cells, already up-taken and manufactured by EMPA, feature a larger solid angle of acceptance allowing for X-ray and Raman experiments. OG, HZB and INRIM have successfully produced and delivered novel *operando*-cell window materials. These have been characterised using XRS by PTB, Raman by INRIM and AFM by CMI. JSI and TUB have further improved the ab-initio simulation tool for XES spectra. TUB conducted sensitivity calculations for laboratory and synchrotron XES equipment, which can be applied to any dispersive spectrometer with known detection angle and incident photon flux. JSI provided DFT calculations of Mn valence-to-core XES spectra. A quantitative investigation of the formation of soluble polysulfides in Li-S batteries with C/S composite electrodes (UNIROMA1) was carried out through an *operando* study spanning several synchrotron beamtimes (PTB).

The new framework for *operando* metrology is to be demonstrated by means of several industrial case studies, in which the tools developed shall be combined to deconvolute some of the most challenging degradation mechanisms. Such degradation is currently observed by battery developers and that can often not be resolved by current *ex-situ* characterisation techniques. For this reason, the Fiat Research Center S.C.p.A. (CRF) affiliate of the large automotive manufacturer Stellantis will carry out industrial impact case studies that will demonstrate how *operando* and *hybrid* characterisation techniques can overcome these issues. From an industrial perspective, regarding both R&D and quality management, the intended demonstration of transferability from large-scale facilities into the laboratory is highly desirable. One of the case studies led by CRF has been introduced to the Stakeholder Committee to provoke interest and seek specific challenges of relevance. The CRF study is focused on the comprehension of degradation mechanisms of commercial Li-ion cells for automotive applications; a disassembly laboratory protocol was setup to collect cathode, anode and electrolyte materials. Then these materials will undergo extensive chemical, physical and structural characterisation by *ex-situ* techniques, to compare results with newly developed metrology.

A new industrial collaborator has expressed interest in assessing electrolyte additives with respect to SEI modifications in NMC batteries under operation conditions which will be included in another case study. For all the industrial case studies intended, the traceable *operando* methods already applied to the novel Li-S systems may be extended to commercial battery chemistries without the need for any substantial changes.

**Outcomes and impact**

The following dissemination activities have been undertaken so far:

- 4 open-access peer reviewed publications and 3 dataset published in Zenodo repository
- Organizing dedicated session at international conferences (IWES 2024 and EMRS ALTECH)
- 8 training course/workshop/seminar for external (PTB, INRiM, UNG and UniRoma1)
- partners provided inputs to 10 standardisation committees
- 8 members of Stakeholder Committee from across industry and academia
- 22 presentations to international conferences / workshops / congresses

The first one of the four peer-reviewed papers one is a review concerning the selective infiltration of metals into nanostructured polymers. This process is generating interest in the development of optically-transparent window decorated with plasmonically-active nanostructures for *operando* surface enhanced Raman spectroscopy. The second paper focuses on determining the x-ray scattering coefficients for nickel being crucial for accurate X-ray analysis. The third paper underlines that the accurate X-ray fluorescence analysis relies on good knowledge of the excitation source's spectral distribution. The study demonstrates the feasibility of a reference-free XRF method using polychromatic X-rays. The fourth paper is about the realization of nano-structured reference samples based on self-assembling block copolymer. Here a hybrid metrology strategy offers comprehensive material characterization and insights into nanoscale properties and functionalities.

*Outcomes for industrial and other user communities*
Through various dissemination activities, the protocols and best practice guidance established for the implementation of *operando* X-ray spectroscopy, Raman spectroscopy and X-ray diffraction for energy storage materials characterisation will be adopted by battery manufacturers (e.g. VW, Tesla, CATL) and user communities in Europe (e.g. European Battery Alliance, Battery European Partnership Association, Battery 2030+). The uptake of the good practice guide by battery and materials developers will add value to their materials characterisation. The EIS measurement protocol will be an ideal tool to access valuable information about processes in operating industrial cells, at low cost. In the first 18 months different operando experiments and related ex-situ experiments on various battery materials were conducted in view of analytical discrimination and sensitivity capabilities. The BIG-MAP project showed interest to co-work on the standardisation of battery materials and procedures. A UK SME battery developer joined the stakeholder committee.

*Outcomes for the metrology and scientific communities*
The good practice guide developed will benefit the scientific community by improving reliability, reproducibility, and fidelity of *operando* measurements. By encouraging the uptake of a common set of measurement protocols, the comparability of data across the literature will be greatly improved, allowing more conclusive links between materials chemistry/structure and behaviour. The consortium develops cells for *operando* and *hybrid* (multimodal) spectroscopy. The project will pioneer *operando* metrology for battery research at several European synchrotron radiation facilities and the transfer into laboratories to support industry and researchers.

*Outcomes for relevant standards*
The NMI participants are involved in key international organisations (ISO, BIPM, EURAMET). The most relevant standards committee is ISO TC201 with subcommittees on Raman and x-ray spectroscopies. The consortium will engage with VAMAS on the topics of Raman spectroscopy (TWA 42) and surface chemical analysis (TWA 2). INRIM provided a general presentation the consortium activities at the VAMAS Steering Committee in 2023. NPL attended two BIPM CCQM EAWG meetings in 2023 and presented the OpMetBat project. PTB introduced the project at the ISO TC201 SC10 meeting in 2023. A new sub-group within ISO TC201 (SG2) has been initiated on the topic of metrology for energy materials. SG2 compiled expert inputs in the fields of batteries, photovoltaics and other renewable energy sources and held its first technical meeting in 2023, chaired by PTB. Regarding OpMetBat discussions were held within the Battery European Partnership Association (BEPA) regarding standardisation that is crucial for advancing battery technology and metrology.

*Longer-term economic, social and environmental impacts*
The transition to hybrid electric vehicles is essential to reduce human impact on air pollution, global warming, and their effects on public health. Improved confidence in measurement is key to the development of next generation energy storage materials with sufficient performance and lifetime for automotive applications, and therefore underpins this energy transition. The methodologies under development, validation or application in OpMetBat were compiled for the strategic research agenda of the JNP on 'clean energy' that became an European Metrology Network (EMN) on 'clean energy' by February 2024.

**List of publications**

1) Irdi Murataj, Eleonora Cara, Nicoletta Baglieri, Candido Fabrizio Pirri, Natascia De Leo, Federico Ferrarese Lupi, *"Liquid Phase Infiltration of Block Copolymers"* Polymers, *14*, 20, 4317 (2022).
https://doi.org/10.3390/polym14204317

2) André Wählisch, Malte Wansleben, Jan Weser, Christian Stadelhoff, Ina Holfelder, Yves Kayser, Burkhard Beckhoff "*Experimental determination of differential scattering coefficients for nickel by means of linearly polarized x-ray radiation*" Metrologia 60, 3 035001, (2023). https://doi.org/10.1088/1681-7575/acca87

3) André Wählisch, Malte Wansleben, Rainer Unterumsberger, Yves Kayser, Burkhard Beckhof "*Reference-free X-ray fluorescence analysis using well-known polychromatic synchrotron radiation*" J. Anal. At. Spectrom. 38, 1865-1873 (2023). https://doi.org/10.1039/D3JA00109A

4) Angelo Angelini, Eleonora Cara, Samuele Porro, Burkhard Beckhoff, Yves Kayser, Philipp Hönicke, Richard Ciesielski, Christian Gollwitzer, Victor Soltwisch, Francesc Perez-Murano, Marta Fernandez-Regulez, Stefano Carignano, Luca Boarino, Micaela Castellino, Federico Ferrarese Lupi "*Hybrid Metrology for Nanostructured Optical Metasurfaces*" ACS Appl. Mater. Interfaces 15, 50, 57992–58002 (2023). https://doi.org/10.1021/acsami.3c13923

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

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| Project start date and duration: | 01.09.2022, 36 months | |
| Coordinator: Burkhard Beckhoff, PTB Tel: +49 30 34817170 E-mail: Burkhard.Beckhoff@ptb.de<br>Project website address: https://opmetbat.inrim.it/ | | |
| Internal Beneficiaries:<br>1. PTB, Germany<br>2. CEA, France<br>3. CMI, Czechia<br>4. INRIM, Italy | External Beneficiaries:<br>5. CRF, Italy<br>6. HZB, Germany<br>7. JSI, Slovenia<br>8. MEU, Türkiye<br>9. TUB, Germany<br>10. UNG, Slovenia<br>11. UNIROMA1, Italy<br>12. WWU, Germany | Unfunded Beneficiaries:<br>13. OG, Germany |
| Associated Partners:<br>14. ELECTRO, United Kingdom,<br>15. Empa, Switzerland,<br>16. JM, United Kingdom,<br>17. NPL, United Kingdom,<br>18. Uliv, United Kingdom | | |
| RMG1: INRIM, Italy (Employing organisation); PTB, Germany (Guestworking organisation) | | |

*JM ceased participation on 01 November 2022