

Report on CERIC's Expert group on batteries

Benedetto Bozzini, Antonella Iadecola, Lorenzo Stievano
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Authors: Antonella Iadecola (CNRS), Benedetto Bozzini (Politecnico di Milano), and Lorenzo Stievano (Institut Charles Gerhardt Montpellier)

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About the report: The report is a part of the efforts of CERIC-ERIC, a distributed research infrastructure in the field of materials characterisation and modification, to produce its Research and Infrastructure Roadmap. General Assembly has in 2019 approved a pilot action on Batteries, in order to identify the bottlenecks and needs for upgrades of CERIC-ERIC in this domain. To this end, an expert group consisting of Antonella Iadecola, Lorenzo Stievano and Benedetto Bozzini was contracted and the group submitted their report May 18th 2020. The activity is supported by the project ACCELERATE, co-funded by the European Union Framework Programme for Research and Innovation Horizon 2020 under grant agreement 731112 and coordinated by CERIC.

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1. Introduction

1.1. Battery research and importance/relevance.

1.1.1. Role of batteries (energy management, inclusion of energy storage in the energy mix and different applications, etc.)

One of the primary challenges of our century concerns the rapidly increasing energy demand associated with the population growth and industrial development. The increase of the average temperature and the extreme climate change over the last 20 years are clearly indicating that a paradigm shift from fossil fuels as the primary power supply towards greener and more sustainable resources is mandatory in order to prevent and invert these threatening trends. Nevertheless, the major drawback of the targeted renewable energy sources, i.e., solar, wind, geothermal, and tidal power, resides in their intermittent nature, thus requiring appropriate intermediate stationary energy storage devices to be implemented at the large scale. Placed after industries, transportation represents the second source of air pollution, which strongly impacts on the global health. [1] Among the different technologies proposed to replace the thermal engines, electric vehicles are becoming more and more popular thanks to the boosted research looking for safer and more powerful rechargeable batteries. Indeed, thanks to their rechargeable power, high energy secondary batteries represent the most promising strategy for an oil-free future, whereat lithium-ion batteries (LIB) take a sublime position.

Among the most studied families of batteries, LIB are widely recognized as one of the biggest milestones in the development of electrochemical energy storage since Alessandro Volta presented the first voltaic pile in 1800. Originally conceptualized to feed small portable electronic devices, they spread quickly, due to their superior storage capacity, long cycle life and high charging currents, to become essential for modern high technology society.[2] Furthermore, LIB do not show a memory effect, feature low self discharge and can operate in a wide temperature range of typically -20° to 60° C, which contribute to their superior role. As a universal recognition of their current and future key role, the 2019 Nobel prize in chemistry was awarded to John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino, who are pioneers in LIB.

All electrochemical cells, including LIB, have a mutual assembly, which comprises two electrodes: the positive and the negative one, an electrolyte and other ancillary constructional components. In Figure 1, the typical setup of a LIB is schemed. During discharge, the negative electrode material hosting the intercalated Li^+ ions (in this example lithiated graphite, LiC_6), is oxidized and the lithium ions migrate through the ion conducting electrolyte to be inserted in the positive electrode material (in this case partially delithiated lithium cobalt oxide, $\text{Li}_{1-x}\text{CoO}_2$). In order to make batteries usable for electric work, the electrons are conducted through an external circuit. While recharging, electric current is forced in the opposite direction and electrical energy is hence converted to chemical throughout the reformation of the charged products.

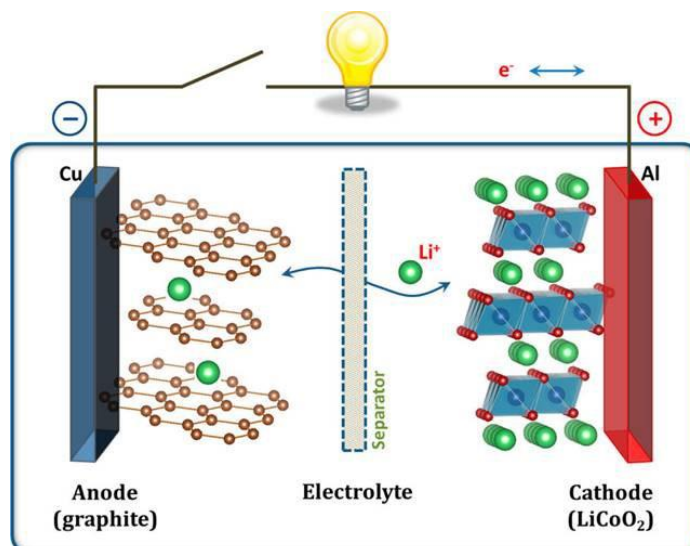


Figure 1: Schematic representation of a LiCoO₂/graphite LIB.

In contrast to other battery technologies, many different materials can be used to host Li⁺, both at the anode and at the cathode. Cathode materials can be categorized mainly in three types, namely layered lithium metal oxides (e.g., LiCoO₂), transition metal phosphates (e.g., LiFePO₄) or spinels (e.g., LiMn₂O₄), even though many other alternative materials have been studied. In the case of anode materials, many systems, also working with different electrochemical mechanisms (e.g., alloying and conversion) have been proposed. [3] However, from such a wide spectrum of potential redox reactions, only few meet the high demands to reach the state of commercial application.

The amount of electrical energy per mass (or volume) that a battery can deliver is a function of the cell voltage and capacity, which are strongly dependent on the chemistry of the electrode materials. Playing with the cathode material, a viable route to increase its capacity is i) to activate multiple redox reactions or ii) to increase number of available ions, always preserving the structural stability. On the anode side, carbon is the most common negative material for its low cost and high abundance, even if it shows lower capacity compared to silicon (which lithiates via an alloying reaction) [4] or metallic lithium. In particular, the voltage window stability of the electrolyte represents a limiting factor for high voltage cell. Looking into the future, while long life span, high energy, sustainability and cost represent important parameters to take into account in the search for new materials. Safety remains a non-negotiable one. One of the issues that plays a key role in the performance of LIB is represented by the anode/electrolyte interphase, usually named the "Solid Electrolyte Interphase" (SEI). [5] It determines the safety, power capability, lower-temperature performance, Coulombic efficiency and cycle life, and is usually formed by the irreversible decomposition of the electrolyte components at the anode surface, which results in the formation of a surface passivation layer. The latter is always formed in any electrolyte system, usually prior to lithium intercalation, causing an irreversible current consumption (first cycle irreversible capacity), and its characteristics greatly affect the electrode behavior with time: a stable SEI results in long cycle life and enhanced safety. To this regard, an important step toward further enhancement of specific energy while increasing notably the level of safety is represented by all-solid-state batteries with a polymeric, ceramic or hybrid electrolyte and a lithium metal anode, where these interfaces can be in principle controlled from the conception of the battery. [6]

The rush towards safer, cheaper and more sustainable batteries, together with a growing uncertainty

about the long-term availability and possible price volatility of lithium,[7] has also triggered in the last years the search for alternative systems, also centered on the "rocking-chair" mechanism of LIB, but using other more abundant and widespread alkali or alkaline-earth metal such as sodium, potassium, magnesium or calcium, or other abundant metals such as zinc and aluminum.[8] While the cost of such Li-free system is going to be more favourable, their energy density is still lower compared to that of LIB, implying their application for residential storage than for power portable electronics. The research for some of these systems is already quite advanced (as in the case of sodium-based batteries, already commercialised), but in other cases a long-term research activity is forecast since their reversible operation, which is essential for long-term cyclability, is not yet fully guaranteed and a full comprehension of the battery operation is necessary.

1.1.2. Challenges in the studies of batteries

1.1.2.1. Past and actual studies, from crystallochemistry to performance

Since the discovery of the insertion of lithium in solids by Wittingham, and the development of research on intercalation materials, many characterisation techniques have been used to study the mechanism of the electrochemical reaction of lithium with solids allowing the development of the so-called "rocking-chair battery".[9] Since most of the solids proposed as electrode materials are crystalline (TiS₂, LiCoO₂, LiMn₂O₄, LiFePO₄, Graphite, etc.), the observed changes in the diffraction patterns can be used to retain information on the original structure, on how that structure evolves and the types of reaction mechanisms, and how the atomic distribution change. Of course, complementary information can be obtained by implementing both neutron and X-ray diffraction (XRD), since only the first one allows detecting the lithium ions in the structure. The high penetrating properties of X-rays and neutrons also allowed, more recently, the development of in situ cells enabling the study of the electrochemical reaction in operando conditions, i.e., during the cycling of the cell. [10, 11] To these techniques, many other have added along the last decades, especially with the discovery of other materials working through different reaction mechanisms such as alloying and conversion reactions, which proceed via the formation of mostly amorphous complex phases [12, 13, 14, 15].

This development has enabled a more and more sophisticated, space and time resolved investigation of the structure-property relationships of electrode materials, providing information on the tuning of the battery performance by chemically altering the makeup of the electrode material or the electrochemical conditions of battery use, and thus stimulating a steady progress in battery performance [16, 17, 18, 19, 20, 21, 22, 23].

While these studies – strongly related to the development of electrode materials – were the largest part of the published studies of batteries, in the last year the attention has been shifted towards the improvement of the lifetime and of the sustainability of battery systems. This approach, which concerns the detection of the aging and failure mechanisms, is intrinsically more complex, since it implies the consideration of the battery as a whole, multicomponent chemical reactors that can differently evolve through their lifetime depending on their specific design, environment, and operation conditions. Such studies have to rely on the development and on the implementation of improved experimental and modeling characterization tools coupled to the fundamental knowledge gained through the previously mentioned materials research. These developments are more and more crucial as batteries are implemented in stationary energy storage systems and electric transportation, for which durability is a

critical issue and also has a direct impact in application costs. [24, 25]

1.1.2.2. Different types of batteries and specific issues

As mentioned above, the development of non-aqueous LIB systems has stimulated a large deal of research of new electrode materials, but at the same time also the exploration of alternative rocking-chair battery systems. Such new so-called "post-LIB", either based on different cathodes (Li-sulfur, Li-O₂) batteries, cations (Na⁺, K⁺, Mg²⁺, Zn²⁺, Al³⁺, etc.) or electrolytes (Li-polymer, all-solid-state, etc.) have all brought along a large number of new issues, some of them specific to a given system. For instance, the development of Li-sulfur batteries has shown the difficulty of mastering the formation of polysulfide species which are soluble in the electrolyte and that diffuse in the whole battery, giving rise to a "shuttle" mechanism that reduces the efficiency and the lifetime of such batteries [26, 27, 28]. Among the latest development, one of the most important ones is that of all-solid-state batteries. For such systems, the crucial points are the ionic conductivity of the solid-state electrolyte, and the mastering of the interfaces formed among electrodes and solid electrolytes. In fact, while they represent a vital component of the battery since from their behaviour depends the long term performance of the cell, they are mostly buried inside the battery, small in dimension, are heterogeneous in composition and morphology, and are usually dynamic, which makes their study and understanding extremely complicated.

1.1.2.3. Towards space and time resolved systems (interfaces)

The improvement in performance of LIB, as well as the improved understanding of post-LIB systems resides in the availability of cutting-edge techniques requiring innovative cell design for both ex situ and in situ /operando study of both structure and reactivity of the battery components, and especially of the interfaces. The development of new space-resolved characterisation tools (and the improvement of the existing ones, especially in the time scale), and often the coupling of several of them are essential to better understand, and thus to improve their performance.

The development of such systems goes along with the production of increasingly large amounts of data, which will call for improved calculation tools to be fully exploited. Moreover, a complete synergy between theoretical calculations and experimental results for interpretation and prediction of the analytical data is mandatory to deepen their understanding.

1.2. Ongoing and future projects on batteries (including Battery 2030+, etc.)

In October 2017, the European Commission launched the 'European Battery Alliance' cooperation platform with key industrial stakeholders, interested Member States and the European Investment Bank. The immediate challenge to create a competitive and sustainable battery manufacturing industry in Europe is immense, and Europe has to move fast in this global race. With the Strategic Action Plan, the European Commission aimed to put Europe on a firm path towards leadership in a key industry for the future, supporting jobs and growth in a circular economy, whilst ensuring clean mobility and an improved environment and quality of life for EU citizens.

1.2.1. BATTERY2030+

BATTERY 2030+ is a large-scale cross-sectoral European research initiative bringing together the most important stakeholders in the field of battery R&D. The initiative is working on concrete actions to support the European Green Deal with a long-term vision of cutting-edge research reaching far beyond 2030. The consortium consists of 17 partners, leaders in their fields, from 9 European countries. The initiative is coordinated by Uppsala University. The BATTERY 2030+ aims are:

- To invent ultra-high performance batteries that are safe, affordable, and sustainable, with a long lifetime.
- To provide new tools and breakthrough technologies to the European battery industry throughout the value chain.
- To enable long-term European leadership in both existing markets (e.g., transport and stationary storage) and future emerging sectors (e.g., robotics, aerospace, medical devices, and Internet of things).

The keystone of BATTERY 2030+ is a chemistry-neutral approach: the main goal is to create a generic toolbox for transforming the way we develop and design batteries than developing a specific battery chemistry. Thanks to this chemistry-neutral approach, BATTERY 2030+ will have an impact not only on current lithium-based battery chemistries, but also on post-lithium batteries, including redox flow batteries, all solid-state batteries (AASB) and on still unknown future battery chemistries. In order to invent the sustainable batteries of the future, the efforts will be focused on three overarching themes encompassing six research areas:

1. Accelerated discovery of battery interfaces and materials to secure new sustainable materials with high energy and/or power performance and high stability towards unwanted degradation reactions. Special attention must be paid to the complex reactions taking place at the many material interfaces within batteries.
2. Integration of smart functionalities to enhance the lifetime and safety of batteries, along with the development of sensors probing chemical and electrochemical reactions directly at the battery cell level, and the use of self-healing functionalities to restore lost functionality within an operational battery cell.
3. Cross-cutting areas such as manufacturability and recyclability need to be addressed early in the discovery process. Manufacturability is addressed from the perspective of the fourth industrial revolution. Digitalisation tools will be developed utilising the power of modelling and of AI to deliver solutions to replace classical trial and error approaches for manufacturing. New recycling concepts, such as reconditioning active materials and electrodes, are central in this respect.

1.2.2. Batteries Europe

Batteries Europe is the European Technology & Innovation Platform (ETIP) on batteries, created to

provide the community with a forum to spearhead Research and Innovation (R&I) actions. Its main goal is to accelerate the establishment of a globally competitive European battery industry, driving the implementation of battery-related research and innovation actions of the Strategic Energy Technology (SET) Plan and the Strategic Transport Research and Innovation Agenda. Batteries Europe will be a “one-stop shop” for the battery R&I ecosystem, supporting the development of a competitive and sustainable battery value chain in Europe. The thematic working groups are made of experts representing the battery-related industry, the research and the associations, dealing with the following topics:

- WG 1: New and Emerging Technologies
- WG 2: Raw Materials and Recycling
- WG 3: Advanced Materials
- WG 4: Cell Design & Manufacturing
- WG 5: Application and Integration – Mobile
- WG 6: Application and Integration – Stationary

1.2.3. DESTINY

The MSCA COFUND DP project DESTINY will contribute substantially to the launching of BATTERY2030+ at the education level through its advanced DP training adhering to key research areas of the Battery2030+ long-term roadmap, including the development of a materials acceleration platform (MAP) and the establishment of the battery interface genome (BIG), combined as BIG-MAP. DESTINY will also contribute to short-to-medium term roadmaps identified by Batteries Europe so as to bring know-how and new emerging technologies for the future, for both industrial and academic professionals. DESTINY is coordinated by the French CNRS that will create a paradigm change in battery research, in line with the new European context. The 5-year project will train 50 PhDs on:

1. Reinvent battery materials discovery and engineering;
2. Develop smart batteries and functionalities;
3. Implement new technologies in industry.

The DESTINY consortium is made of 40 partners from 12 European countries, including Universities, Research Centers, Large Scale Facilities and 8 Companies. All candidates will be trained at the very forefront of battery research to enable them to accelerate and exploit novel technologies from a solid basis of knowledge and skills. Interdisciplinary competences and skills will be favoured through the complementarity within DESTINY. In addition, DESTINY includes a broad set of trainings in transferable skills: personal effectiveness, research governance and entrepreneurship.

2. State of the art of the techniques available in CERIC

2.1. Austria

Director: Heinz Amenitsch – heinz.amenitsch@elettra.eu

The Austrian partners contribute to the offer of CERIC-ERIC via several services located at the Institute of Inorganic Chemistry of the Technical University of Graz, as well as at synchrotron Elettra.

2.1.1. Light scattering experiments (TU Graz)

Responsible: Angela Chemelli – angela.chemelli@tugraz.at

Description of the facility:

The light scattering equipments are hosted at the Institute of Inorganic Chemistry of TU-Graz. Two types of equipment are available:

- Static Light Scattering (SLS): The flat cell light scattering instrument consists of a GLG5360 Helium-Neon Laser and an array of 160 photodiodes for simultaneously detecting light scattering curves of suspensions from 1° to 60°.
- Dynamic Light Scattering (DLS): Three different DLS instruments are available:
 - DLS - 532 nm: The DLS equipment consists of a laser diode (wavelength = 532 nm, power = 5 W) and a goniometer with single-mode fiber detection optics.
 - DLS - 632.8 nm: The DLS equipment consists of a Helium-Neon-Laser (wavelength = 632.8 nm, power = 25 mW) and a goniometer with few-mode fibre detection optics.
 - Multispeckle DLS: The Multispeckle DLS consists of a GLG5360 Helium-Neon Laser (wavelength = 632.8 nm, power = 10 mW) and a goniometer with single-mode fiber detection optics.

Actual state of the art of battery studies:

Only the DLS instruments were used in the past for the determination of the particle size distribution of a suspension of Li₄ Ti₅ O₁₂ to be used as electrode materials for LIB [29].

So far, no CERIC-ERIC user has used this light scattering equipment for battery research.

Possible adaptation of the facility to battery studies:

At TU-Graz, an extensive research activity exists in the field of batteries, but the main part of is not carried out at the Institute of Inorganic Chemistry. Nevertheless, several glove-boxes (N₂ and Ar) are available in the vicinity, as well as some potentiostats.

Interest of the facility in battery studies and perspectives:

No specific interest in this field of research was underlined, but the facility is open to host studies on new research themes.

2.1.2. Deep X-ray Lithography (DRXL) Beamline (Elettra Trieste)

Responsible: Benedetta Marmiroli – benedetta.marmiroli@elettra.eu

Description of the facility:

Deep X-Ray Lithography (DXRL) is a manufacturing process by which a material, which changes its dissolution rate in a liquid solvent (developer) under high-energy irradiation, is exposed through an X-ray mask to synchrotron radiation. The pattern of the mask is transferred to the material. This is possible by the availability of synchrotron radiation characterized by high resolution, high intensity and extreme parallelism. Microstructures have been obtained with high spatial resolution (200 nm for a wall thickness of 100 μm), high aspect ratios (up to 40), great structural heights (up to 3 mm) and parallel edges.

Coupled with electrodeposition, casting, hot embossing, molding, or microelectro-erosion (the so called LIGA process), it allows using a wide range of materials: plastics, metals and alloys, ceramics. Furthermore, due to the great variety of shapes that can be obtained, it becomes a very flexible tool for fabricating micro-devices.

The beamline performs an irradiation of samples with controlled X-ray doses, allowing therefore material science studies and the fabrication of microdevices made of new materials, such as silica and titania. It has the possibility of fabricating micromolds or microelectrodes for the production of small batches of microdevices, makes LIGA process suitable for industrial applications.

Actual state of the art of battery studies:

Actually, the service is not involved in battery research. Part of the activity is dedicated to the irradiation of novel materials to obtain improved functionalities in desired areas, but it is a more general research, and it is not specifically focused on battery applications.

Some previous CERIC users were concerned by energy applications, but only concerning materials for fuel cells, for catalysis and for solar cells.

Some work in this field might be carried out at DXRL beamline (and connected instruments) in two ways:

- Design and fabrication of miniaturized devices,
- Development of new materials with improved performance upon controlled irradiation.

Possible adaptation of the facility to battery studies:

The list of instruments available at the beamline is not updated on the website. Nevertheless, since the service is mainly dedicated to the modification of materials, some recent additions concerned:

- An Oxygen plasma system to clean and activate surfaces,
- A UV lithography station
- A Keithley 2420 sourcemeter for metal electrodeposition.

There is in any case a very tight connection with the SAXS beamline at Elettra, with mutual sharing of the available ancillary instruments.

Interest of the facility in battery studies and perspectives:

The service manager is very interested in opening the service to battery research.

2.1.3. Laboratory Small Angle X-ray Scattering (Laboratory-SAXS) facility (TU Graz)

Responsible: Manfred Kriechbaum – manfred.kriechbaum@tugraz.at

Description of the facility:

The Laboratory-SAXS facility consist of a sealed tube X-ray generator (DebyeFlex3000) with three opening ports and shutters where three independent SAXS cameras (A. Paar, Graz, Austria) are attached, one of which can also be used for grazing incidence (GISAXS) studies. Several sample holders for liquid and solid samples are available, with thermostated sample holder stages. Several measurement modes are available:

- SAXS mode: (1D or 2D detector) with an angular range from 0° to 8° (corresponding to d-values from 100 to 1 nm).
- SWAXS mode: (SAXS: 1D or 2D, WAXS: 1D) with an additional WAXS range from 17.5° to 35° (corresponding to d-values from 0.5 to 0.25 nm).
- Continuous SWAXS mode: with an image plate the entire angular range from 0° to 40° is covered.

Actual state of the art of battery studies:

Some research on the electrochemical energy storage properties of carbon-based materials for Li-O₂ batteries implying the laboratory-SAXS facility has been recently conducted in the same institute in collaboration with C. Prehal (post-doc in the group of H. Amenitsch) using a homemade in situ cell. [30] No CERIC-ERIC user has accessed the facility for battery applications.

Possible adaptation of the facility to battery studies:

Actual appropriateness of the techniques: the available SAXS facility consists of high-quality state-of-the-art equipments, which are in particular optimized for the homemade sample cell set-up described above. Some modification/upgrades might be needed if the design and/or the concept of the sample cell are different. A discussion with the users prior to experiment is necessary in this case.

Actual appropriateness of the sample environment: glove boxes are already available at the chemical lab of the institute for sample preparation and possible cell assembly. They could be accessible for sample preparation to the CERIC users if their use is required in advance. However, no in situ cell is currently available for the users for battery studies.

Interest of the facility in battery studies and perspectives:

The laboratory is definitely very interested in hosting more studies in the field of batteries. This kind of technique is probably more adapted than synchrotron SAXS (vide infra) to classical battery studies because very rapid time scales are not necessary for such measurements.

2.1.4. Synchrotron Small Angle X-ray Scattering (Synchrotron-SAXS) beamline (Elettra Trieste)

Responsible: Heinz Amenitsch – heinz.amenitsch@elettra.eu

Description of the facility:

The SAXS beamline at Elettra allows time-resolved studies on fast structural transitions in the sub-millisecond time region in solutions and partly ordered systems with a SAXS-resolution of 1 to 140 nm in real-space, as well as GISAXS measurements to study the structure of thin films and the self-assembly processes on surfaces.

Of the intense radiation of the wiggler photon source, shared and used simultaneously with a Macromolecular Crystallography beamline, the SAXS Beamline uses 3 discrete energies (5.4, 8 and 16 keV, corresponding to 0.077, 0.154 and 0.23 nm, respectively). The beamline optics consists of a flat, asymmetric-cut double crystal monochromator and a double focusing toroidal mirror. An additional wide-angle X-ray scattering (WAXS) detector is also available to monitor simultaneously diffraction patterns.

The sample stage is set on an optical table for allowing a versatile optimisation of the measurement conditions and the introduction of the users' own specialised sample equipment.

Actual state of the art of battery studies:

The beamline has already some experience in battery studies, having set collaborations with several research teams, namely with the group of S. Freunberger (Institute of Science and Technology Austria) in the fields of Li-O₂ batteries [30], and with O. Paris (Montanuniversität Leoben) in the field of supercapacitors [31, 32, 33, 34, 35]. Both groups had access to the beamline through CERIC-ERIC. In particular, the contribution of a C. Prehal, formerly a post-doc of Freunberger group, was essential, since he helped developing new data evaluation tools and brought in the know-how for the in situ battery cell design from his previous research activity on supercapacitors.

Additional collaborations in the field of energy materials and electrochemistry have concerned fuel cells, with several publications and the recent development of a new in situ half-cell for GISAXS measurements.

Possible adaptation of the facility to battery studies:

Actual appropriateness of the techniques: While SAXS is a well known standard method for the study of the structure of various objects in the spatial range from 1 to 1000 nm, and has already proven to be a very interesting tool for the study of batteries, the time scale offered by the SAXS beamline is even too

short for the study of batteries: synchrotron radiation might be an overshoot for such experiments with a duration of several hours, which can also be performed at the laboratory scale.

Actual appropriateness of the sample environment: the sample environment at SAXS beamline is already well adapted to the study of batteries, since several tools are already available for the users, such as an argon-filled glove-box, a potentiostat, a new electrochemical GISAXS cell. There are also plans to commercialise the in situ cell developed together with the Freunberger group.

Interest of the facility in battery studies and perspectives:

The group is already well introduced in the study of energy materials, with strong collaborations with well-established Austrian groups in the fields of batteries and supercapacitors

2.2. Croatia

Director: Milko Jakšić – milko.jaksic@irb.hr

The Croatian partner of CERIC is the “Laboratory for ion-beam interactions” (LIBI), which is part of the Division of Experimental Physics of the Ruđer Bošković Institute (RBI), based in Zagreb. The head of LIBI is Milko Jakšić (milko.jaksic@irb.hr). Specific information for this survey regarding RBI has been obtained by interacting with Dr. Jakšić, who acted on behalf of the whole Institution and of each beamline, in particular.

2.2.1. Generalities on LIBI

The LIBI group runs two electrostatic tandem accelerators (6 MV HV EN Tandem Van de Graaff and 1 MV HVE Tandetron) feeding 9 beamlines, out of which 5 are CERIC’s partners (see below for details).

Description of the accelerators

The 6.0 MV EN Tandem Van de Graaff accelerator features: (i) a multicathode sputtering ion source for all ions except helium (ii) RF gas source with Rb charge exchange that is mainly used for acceleration of He isotopes. The accelerator actually operates in the range 0.5 ÷ 4 MV.

Heavy ions, such as Au, I and Cl are typically used for ERDA (see below for some details on the analytical methods), W, Cu and Fe ions are employed for fusion related experiments while Si, O and C are exploited in detector damage studies. Light ions Li, ⁴He and ³He are used mainly for analytical applications (RBS and NRA), while protons serve mostly for PIXE analysis and serve as a probe for charge transport properties investigations, using ion-beam induced charge technique.

The 1.0 MV Tandetron accelerator operates with two ion sources: (i) a duoplasmatron with Na charge exchange, used for ³He and ⁴He beams; (ii) a sputtering source for all other ions (mainly: H, Li, C, O, Si, Cl, Cu). Terminal voltages currently in use span the range 0.1 ÷ 1.0 MV.

Key activities of LIBI

LIBI research is focused on the study of interactions of ion-beams with matter for analytical and material modification purposes. Specifically, LIBI studies concern the development of methods, on the one hand to characterize and modify properties of materials, in particular nanostructured ones, and, on the other hand, for testing high-energy physics radiation detectors by ion microbeams. The main fields of application are: biomedicine, environment and cultural heritage. More specifically, ongoing projects involve the following topics:

- Photovoltaics;
- Diamond radiation detectors (2 students);
- Development of SIMS using MeV ions (2 students);
- Irradiation of fusion materials (1 student) and
- Development of RBS for silicon electronics (1 student).

In addition, the LIBI postdocs are involved in the following subjects:

- High resolution X-ray spectroscopy for chemical speciation;
- SIMS of organic materials and
- Luminescence as ion-beam based analysis method.

Actual state of the art of battery studies

The only experience of LIBI in the field of batteries is co-authorship in one publication, dating back to 2000, in which the Li and F distributions were measured in a gel electrolyte for LIB. [36]

Possible adaptation of the facility to battery studies

The available sample environments of the beamlines can host battery material samples and even cells brought by the users, which can be reasonably easily customized for the sample stages. Since September 2020 (see next section), a PhD student will start to design and construct appropriate setups for tests at the LIBI facilities.

Interest of the facility in prospective battery studies

All methods that are documented in the battery literature (PIXE, RBS, NRA, PIGE, ERD, for details, see below, in correspondence of each beamline / method) are available at LIBI. Since September 2020 LIBI will host a PhD student, funded by the Government, but dedicated to CERIC-related activities, who will be involved partly in development and applications of ion-beam techniques to battery characterisation. An additional position for a postdoc will most probably be available soon.

2.2.2. Description of the beamlines and methods

RBS/PIXE: Particle-Induced X-ray Emission and Rutherford Backscattering

➤ Method and analytical capabilities

PIXE spectroscopy is a technique used for the determination of the elemental composition. Its analytic

specificity is related to the emission of characteristic X-rays, resulting from the interaction of charged particles of energies in the low-MeV energy range with the material. Generally, concentrations of elements ranging from Na to U can be detected with limits of ca. 1 ppm.

Highly energetic ions can also interact with atomic nuclei through elastic collisions, thus the detection of backscattered ions (typically protons, He and Li ions) can be used to determine the concentration and depth profile of elements in the near-surface region of the sample exposed to the ion-beam. This analytical approach, denominated RBS, is based on the detection of backscattered ions at angles close to 180°. RBS is particularly sensitive to light element concentrations and is thus complementary to PIXE, which is more responsive to heavier elements.

➤ **Instrumentation**

The RBS/PIXE beamline is equipped with two PIXE detectors: an SDD detector for the analysis of light elements (Na and above) and an Si(Li) detector with a Mylar filter, optimized for heavy elements (K, Ca and above). The analysis chamber has an integrated sample changer, which can take up to 16 samples (sizes between 10 and 25 mm). The samples are typically exposed to a 2 MeV proton beam of circular shape (3, 5 or 8 mm) with beam currents in the range 1 ÷ 10 pA.

Nuclear microprobe

➤ **Method and analytical capabilities**

Nuclear microprobe is a device that uses a system of quadrupole lenses (depending on the application it could be doublet, triplet or quintuplet) to focus an ion-beam to the micrometer size. This beamline enables applications of almost all available IBA techniques: PIXE, PIGE, RBS, ERDA, Nuclear Reaction Analysis (NRA), IBIC and Scanning Transmission Ion Microscopy (STIM). Below, we report very briefly some information regarding the types of available analysis methods (for information regarding PIXE and RBS, see previous section and for ERDA see the following section):

- *Nuclear Reaction Analysis (NRA) and Particle-Induced Gamma Ray Emission (PIGE)*. Fast ions, upon approaching the nucleus of a target atom, can overcome the repulsive Coulomb force and penetrate into the nucleus. If a nuclear reaction occurs, it can result in the emission of particles and/or γ rays. Detection of particles (usually done by a Si particle detector) – is the basis of NRA, while detection of γ rays (typically by a large-volume Ge detector) is employed for PIGE. Both techniques can run in conjunction with PIXE and RBS and are mostly used to quantify concentrations of low Z elements such as: Li, Be, B, C, N, O, F, Na, Mg and Al.
- *Scanning Transmission Ion Microscopy (STIM)* is based on the measurement of the energy of transmitted ions at some particular sample position and yields information on structure and density variations within the analysed object. By using different ion species at selected energies, a wide range of sample thicknesses can be studied.
- *Ion-Beam Induced Charge (IBIC)*. If ions are stopped in a semiconductor, the charge pairs formed

in it, drift in an electric field that can be either built in the sample (e.g. a pn junction) or applied externally. This process induces a measurable charge signal. By correlating ion position (using nuclear microprobe system) with charge signal, images of charge-collection properties can be obtained. In addition to IBIC imaging, this technique is suitable for quantifying the electronic transport parameters of the charge carriers. By injecting different ion species with different energies, IBIC can also probe electronic transport at different depths.

➤ **Instrumentation**

The ion-beam is scanned over the sample surface (up to $1 \times 1 \text{ mm}^2$). The available beams are protons ($0.4 \div 8 \text{ MeV}$) and most of other heavier ions up to a ME/q^2 ratio of 15 MeV . Typical currents used for most of the ion-beam analysis (IBA) techniques, such as PIXE, RBS, NRA and ion-luminescence are between 1 and 1000 pA, while for the low current techniques (STIM and IBIC) currents are reduced to the fA range. The beam spot size depends on the ion species being focused, their energy and current. For the most favourable conditions the beam spot size can be as low as 250 nm.

All the above techniques can be used for imaging (e.g. elemental distributions), or to perform quantitative analysis at some particular point or in a specific region.

Time-of-flight Elastic Recoil Detection Analysis (ToF-ERDA)

➤ **Method and analytical capabilities**

ToF-ERDA is a spectroscopic technique for the measurement of elemental concentrations and their depth profiles in unknown samples down to $\sim 500 \text{ nm}$. ERDA is used to obtain elemental concentration depth-profiles in thin films. Similarly to RBS, ERDA exploits elastic nuclear interaction between the ions of the beam and the atoms of the sample – depending on the kinetics of the ions, the cross section area and the loss of energy of the ions in the matter – to obtain quantitative elemental analysis. Additionally, ERDA provides information about the depth-profile of the sample for a wide range of elements (from hydrogen to rare-earth elements) with similar sensitivity and depth resolution. Concentrations of 0.1 at % can be detected routinely. In comparison to conventional ERDA, with an ion-stopping foil, in ToF-ERDA all elements (including hydrogen isotopes) are separated and analysed in a single measurement.

➤ **Instrumentation**

The ToF-ERDA setup is based on the use of beams of heavy ion (such as Cl, I, Au) with energies of up to 40 MeV, to recoil atomic nuclei from the target surface layers in the forwards direction. Energy and time of flight of the recoiled nuclei are measured in coincidence, enabling separation of all elements by energy and mass. Time/energy spectra are converted to depth profiles. Because of the high stopping power of heavy ions, depth resolutions down to the 5 nm range can be achieved for C, N and O.

Samples are exposed to the beam at a grazing angle of 20° and therefore only samples with a surface roughness below 10 nm can be reliably analysed. Sample size is limited to $10 \times 10 \text{ mm}^2$. Up to 4 samples can be simultaneously loaded into the analysis chamber, in which the working vacuum is $\sim 10\text{--}8 \text{ mbar}$.

The system is equipped with two detectors. For energy, a gas ionisation detector is used, while the time-of-flight detector consists of two timing gates separated by ca. 0.5 m. LiF-coated foils are used for the detection of the passing ions. Electrons emitted from the ion-foil interaction are multiplied by a microchannel-plate detector.

Ion-irradiation beamlines

Two more beamlines can be accessed through CERIC, which are devoted to irradiation experiments:

- *DiFu* (Dual ion-beam end station for fusion materials research)
- *Dual Microprobe*

Both instruments are designed for dual-beam irradiation of general sample types, using wide range of ion-beams. These are primarily material modification beamlines, and they lie out of the scope of applications for battery analytics.

With *DiFu* all ion-beams that can be produced by any of the two RBI accelerators can be directed into the irradiation chamber. *Dual Microprobe* is still under construction and it is planned to offer microbeam-focusing capabilities for both of the ion-beams.

2.2.3. Applications of ion-beam methods in battery studies

Ion-beam analyses can be employed in battery studies as a non-destructive method to map lithium distribution with micrometric lateral and depth-profiling capability down to several tens of nm. In addition, these techniques are appropriate for in situ / in operando measurements. Information about lithium distribution is of interest for battery technology, because it gives quantitative access to diffusion processes that control several aspects of battery performance, such as: capacity, cyclability and charging rate. Moreover, lithium-mapping capabilities allow the monitoring of the activity of single particles with respect to intercalation-deintercalation processes.

Below, we report a representative selection of the literature dealing with battery studies performed with ion-beam techniques.

Elastic Recoil Detection (ERD)

ERD, in combination with RBS, has been used to measure Li⁺ and H⁺ distribution at both the anodic and cathodic electrode-electrolyte interfaces of LIB with ceramic electrolyte.

In-plane analyses of Li distribution, carried out with He²⁺ and O⁴⁺ probe-beams, are reported in [37] (*ex situ*) and [38] (*ex situ*), while [39] describes *in situ* depth profiling obtained with an O⁴⁺ beam. Electrode Li⁺ concentration gradients were associated with the formation of interfacial ion-transfer resistance. [37, 38] also faced instrumental development and beam-damage issues and [37] assessed Co segregation in a LiCoO₂ cathode.

Rutherford Backscattering Spectrometry (RBS)

Ex situ RBS was used – in combination with NRA, and employing 4 He⁺ or H⁺ beams – to characterize Li intercalation in a series of cathode materials. Several studies were carried out:

- Quantification of composition and homogeneity in LiNiVO_4 [40].
- Measurement of the Li, Mn and O concentrations resulting from the chemical delithiation of LiMn_2O_4 [42].
- Study of the distribution of Li, Fe and Mn in Mn-doped LiFePO_4 cathode materials extracted from batteries at different DODs: in this research, RBS was combined with PIGE and PIXE and allowed the authors to correlate Li clustering with SEI formation [42].

Also some works concerning the *in situ* application of RBS were reported recently:

- μ -RBS (H^+ beam) was used, in combination with μ -PIGE to obtain elemental maps of an LIB with liquid electrolyte at different DODs [43].
- RBS (O^4 beam), combined with ERD, was employed for the investigation of lithium distribution at the electrode-electrolyte interface in all-solid state LIB [39].

μ -PIGE/PIXE

Ex situ μ -PIGE/PIXE with H^+ beam, has been used to investigate the Li distribution in different battery components.

- In-plane and cross-sectional imaging of Li distribution with micrometric resolution in a $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode as a function of charging conditions was recently reported; jointly, also the distribution of active cathodic (Co, Ni, Al) and binder (F, O) materials was measured. Li heterogeneity was correlated with the charging rate [44].
- As described above in the section on RBS, the Li distribution could be measured in Mn-doped LiFePO_4 cathodes together with that of Fe and Mn, at different DODs [45].
- In a similar study, combined with NRA, elemental mapping of cathode materials (Li, Fe / Li, Ni for LiFePO_4 and $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) previously subjected to electrochemical treatments was performed [46].

Elemental mapping and profiling based on *in situ* PIGE/PIXE (H^+ beam), were recently reported:

- PIGE and PIXE were exploited to obtain Li and Fe profiles at various DODs and times (tens of min) for a LiFePO_4 in a cell with liquid electrolyte [47].
- μ -PIGE, combined with μ -RBS, was employed to record Li and F maps at the electrode-electrolyte interface of a cell with liquid electrolyte [43].

Nuclear Reaction Analysis (NRA)

A few papers have been published, in which *ex situ* NRA (p, α) was used for the measurement of Li distribution of cathode material.

- The Li content resulting from intercalation of Li^+ into LiNiVO_4 (electrochemical treatment), MoO_3 (electrochemical treatment) and LiMn_2O_4 (chemical treatment) was measured in different works, combined with RBS (see above) [40, 41, 42].
- The Li depth profile of LiFePO_4 , resulting from electrochemical treatment, was measured by combining NRA, μ -PIGE and μ -PIXE [46].

2.3. Czech Republic

Director: Matolin Vladimír – matolin@mbox.troja.mff.cuni.cz

Czech Republic participates to CERIC-ERIC with several instruments located at the Charles University (Prague) and the MS beamline at Elettra synchrotron (Italy).

2.3.1. High Resolution Field Emission Scanning Electron Microscope (FESEM) (Charles University, Prague)

Responsible: Iva Matolínová – imatol@mbox.troja.mff.cuni.cz

Description of the facility:

The FESEM laboratory is located in the Department of Surface and Plasma Science at Charles University. The FESEM uses a high brightness Schottky emitter as the electron source allowing to tune the acceleration voltage from 200 V to 30 kV, or 100 V to 30 kV with beam deceleration (BD). Compared to a conventional SEM, it produces clearer, less electrostatically distorted images, with spatial resolution down to 1 nm.

The Tescan Mira3 instrument is designed for high vacuum (HV) operation and is also rigged with detectors allowing electron back-scattering spectroscopy (EBS) and energy dispersion X-ray spectroscopy (EDX) for chemical element mapping of surfaces with sub-micron resolution.

Actual state of the art of battery studies:

No proposal has been submitted by the CERIC-ERIC users for battery research.

Possible adaptation of the facility to battery studies:

FESEM can be easily applied to the investigation of ex situ electrodes to retrieve information on the morphology and the chemical distribution within sub-micron particles.

Due to the UHV environment, ex situ electrodes are suitable sample to study.

Interest of the facility in battery studies and perspectives:

The facility has not shown a particular interest in expanding its users community to batteries field.

2.3.2. X-Ray and Ultra-Violet Photoelectron Diffraction (XPD/UPD) (Charles University, Prague)

Responsible: Kateřina Veltruská – veltrusk@mbox.troja.mff.cuni.cz

Description of the facility:

XPD is a crystallographic technique combining information on morphology, electronic structure and chemical composition of the material. This technique provides a direct structure determination tool and is best suited for applications on periodic surfaces, such as oriented single crystal surfaces, ordered adsorbate layers on crystalline substrates, or thin epitaxial films. Due to its high sensitivity to the surface structural details on the local scale, an XPD analysis can also be performed on systems lacking long-range periodicity, e.g., small atomic surface complexes and supported nanoclusters.

The suitable samples must be electrically conducting, ultra-high vacuum compatible (stable, low vapor pressure), and with negligible roughness. For this purpose, an in-situ sample preparation is mandatory: the electron beam stimulated evaporation sources are in place in the experimental chamber and reactive sputtering is in the preparation one; then, Argon ion surface cleaning and sample heating in the UHV, up to approximately 1000 C, will prepare the surface of the sample.

Two kinds of radiation sources are available to produce X-rays (Mg or Al Ka) or UV (He I, II lamp) photons, corresponding to higher and smaller penetration depth respectively.

Actual state of the art of battery studies:

No proposal has been submitted by the CERIC-ERIC users for battery research.

Due to the negligible roughness of the sample required by XPD, the battery materials presenting a moderate roughness in the best case (for example thin films for micro-battery) are not fitting the sample requirements.

Possible adaptation of the facility to battery studies

Only epitaxially grown thin films can be investigated with this technique, which is a limiting factor for battery study.

2.3.3. Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS) (Charles University, Prague)

Responsible: Břetislav Šmíd – smidb@email.cz; Mykhailo Vorokhta – vorokhta@gmail.com

Description of the facility:

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique, which measures the elemental composition, empirical formula, chemical state, and electronic state of the top approximately 10 nm of a material. XPS spectra are obtained by irradiating the material with a beam of X-rays while simultaneously measuring the number of electrons emitted by the material in dependence on their kinetic energy. Running the X-ray source and the electron analyzer requires high vacuum ($P \approx -8$ mbar) conditions in the analysis chamber and, therefore, conventional XPS is possible only under UHV conditions.

Near-ambient-pressure XPS (NAP-XPS) is an XPS system capable of operating at pressures of a few tens of millibars, allowing to study chemical interactions on the atomic level for vapor–solid interfaces. NAP-XPS also allows one to investigate electronic and structural properties of small organics., making it difficult to conduct investigations of surfaces under real-world conditions (i.e. in the presence of gases and possibly liquids). The NAP-XPS facility works in strong cooperation with the Material Science

beamline.

An electrochemical cell equipped with Pt wire as counter electrode and AgCl as reference is available to the user community. The main purpose of the cell is to avoid air exposure during electrochemical measurements and XPS measurements on post-mortem electrodes. Indeed, the electrode and the electrolyte are in contact only upon voltage bias, then the electrode is removed, dried, evacuated and transferred to analysis chamber. An additional buffer chamber serves as the transition chamber for sample transfer between the electrochemical cell and the (UHV) transfer chamber through an inert atmosphere (Ar).

A "real" in situ electrochemical cell has been developed by the Erlangen-Nurnberg University and used in the NAP-XPS station, allowing to study the electrode-electrolyte interface under working conditions. However, it is not available to the user community.

A SP50 Biologic potentiostat is already available.

Actual state of the art of battery studies:

No proposal has been submitted by the CERIC-ERIC users for battery research. Among the energy studies, they are mostly focused on fuel cells, solar cells and gas sensing, rather than batteries [48][49].

Possible adaptation of the facility to battery studies

XPS study on ex situ electrodes needs a transfer chamber from the glove-box to the load-lock of the instrument, in order to prevent the samples from air exposure.

Interest of the facility in battery studies and perspectives

The development of in situ electrochemical cell is suitable for electrode-electrolyte interface studies. Hard X-ray photoelectron spectroscopy (HAXPES) will enhance the contribution of the sub-surface, thanks to the increased penetration depth of the incoming photons and the photoelectron inelastic mean free path. This technique is therefore beneficial for the NAP experiments by improving the signal to noise ratio of the collected photoelectrons.

2.3.4. Material Science Beamline – MSB (Elettra, Trieste)

Responsible: Nataliya Tsud - tsud@mbox.troja.mff.cuni.cz, Tomas Skala – tomas.skala@elettra.eu

Description of the facility:

The MSB is a versatile beamline suitable for experiments in materials science, surface physics, catalysts and organic molecules on various surfaces, built in cooperation between the Institute of Physics of the Czech Academy of Sciences and Sincrotrone Trieste. The tunability of the photon energy over a wide range (22 – 1000 eV), with mainly linearly polarized light from a bending magnet source, offers classical UPS and XPS with high energy resolution and tunable excitation energy for the best photoionization cross sections. The beamline also allows resonant photoemission (RESPES) and near edge X-ray absorption fine structure (NEXAFS) spectroscopies in TEY mode. Sample rotation about two axes allows angle-resolved photoemission studies.

Some equipment currently used for electrocatalysis and sensors are available on the beamline and shared with the NAP-XPS laboratory in Prague.

In particular, the electrochemical cell available to the user community has been developed in cooperation with the NAP-XPS laboratory (vedi supra).

Actual state of the art of battery studies:

No proposal has been submitted by the CERIC-ERIC users for battery research. Among the energy studies, they are mostly focused on fuel cells, solar cells and gas sensing, rather than batteries [48][49].

Possible adaptation of the facility to battery studies

As for the NAP-XPS facility, the measurements of ex situ electrodes needs a transfer chamber from the glove-box to the load-lock of the instrument.

Interest of the facility in battery studies and perspectives

While the MS beamline has been widely exploited for energy-related studies, there is no re- search activity in battery.

2.4. Hungary

The Hungarian partner of CERIC is the Budapest Neutron Center (BNC). The neutron beamlines are fed by a 10 MW VVR-type reactor (i.e., light-water cooled and moderated), currently operating on 20% enriched U, operated by the Centre for Energy Research of the Eötvös Loránd Research Network. The reactor is of the tank type with the core surrounded by a beryllium reflector, with a maximum thermal flux of ca. $2.1 \cdot 10^{14}$ n/(cm²·s). The reactor cycle is ca. 4 effective days, followed by a weekend break, with an average operation time of 160 days/year. The key expertise developed at the BNC beamlines (see details below) is centred on: (i) neutron scattering investigations; (ii) neutron-based element analysis and (iii) imaging. The Director of Institute, Tamás Belgya (tamas.belgya@energia.mta.hu), is also the coordinator of research on renewable energy and the CERIC delegate of BNC.

2.4.1. Neutron Reflectometer with Polarized Beam Option (GINA)

Responsible: Dániel G. Merkel – merkel.daniel@energia.mta.hu

Senior responsible (external consultant): László Bottyán – bottyan.laszlo@energia.mta.hu

Brief introduction to the technique and its application to battery studies

Neutron reflectometry investigates elemental/isotopic surface and depth profiles. Battery studies include: structure and kinetics at / close to interfaces, variation of composition in depth, formation and evolution of interfacial phases, evolution of solid-liquid electrolyte interfaces, study of electrochemical reaction mechanisms [50, 51, 52, 53].

Description of the Instrument

The GINA neutron reflectometer (NR) is a constant-energy angle-dispersive, vertical-sample instrument. Reflectivity ranges over five orders of magnitude have been measured in magnetic and non-magnetic sample environments. A focusing graphite monochromator provides unpolarized and polarized neutron beams with wavelength optimized at 4.67 Å. The incident intensity is monitored by a beam intensity monitor. Beam position is defined by four slits, yielding a relative Q-resolution of 10÷2 % for the available Q-range of 0.005÷0.25 Å⁻¹. Higher harmonics are filtered by a Be block, allowing a transmissions of 41 % and 87 % without and with liquid nitrogen cooling, respectively. The polarized neutron beam is produced by using a magnetized supermirror (transmission and reflection options) and an adiabatic radio-frequency spin flipper. The beam scattered by the sample can be spin-analysed by an identical system of spin flipper and magnetic supermirror spin analyser, with polarized specular beam option. Neutrons are finally detected by a two-dimensional position-sensitive detector, consisting of a gas-filled (³He and CF₄) delay-line type multi-wire proportional chamber, encased in boron-containing shielding for background suppression.

The standard sample environment components include: permanent-magnet sample stage for large samples, cryostat (20÷300 K range, operating in vacuo), electromagnet (up to 0.55 T, compatible with cryostat), water cooled Helmholtz coils (up to 35 mT) and thermostated solid/liquid cell with temperature control (± 0.1 K). For room-temperature reflectivity measurements, the sample is held in position by vacuum. The incident angle on the sample surface is set by a goniometer. A flight tube is also available to minimize neutron scattering by air.

Key activities of Instrument

Research interests at GINA focus mainly on structure and properties of metallic multilayers and other heterostructures, including magnetic ones. To this aim, the GINA group operates, among other smaller instruments: (i) a molecular beam epitaxy (MBE), 13 atom sources in two e-guns and 5 effusion Knudsen cells, UHV laboratory (substrate sizes up to 2") specialized in isotope-specific depositions (⁵⁷Fe and ⁶²Ni), and (ii) a Mössbauer laboratory. Moreover, the GINA group has established collaborations with the Institute of Solid State Physics and Optics of the Wigner Centre, and with the Institute of Technical Physics and Materials Science of the Energy Research Centre, based in the KFKI (Central Research Institute for Physics) campus. More recently, soft matter research has been introduced – chiefly on biological membranes and self-assembly of nanoparticles in solutions – also driven by CERIC users.

Actual state of the art of battery studies

Contacts were established a few years ago with dr. E. Hüger's group (TU Clausthal, Dept. H. Schmidt), active in use on NR in battery-related research (see, e.g., [54, 55]), but no joint activities were finalized. No skills in electrochemistry or batteries are available within the Instrument group.

Possible adaptation of the facility to battery studies

Neutron reflectometry in general, and GINA in particular, are suitable for battery-related studies, with pros and cons, listed below.

➤ **Advantages:**

1. High sensitivity of NR to light elements (e.g. Li, O, H);
2. Strong isotope contrast / contrast matching possible (e.g. ${}^6\text{Li}$, ${}^7\text{Li}$, D_2O , H_2O);
3. Matching depth resolution to typical functional battery features (e.g. SEI);
4. Extended literature of NR is available (incl. in operando studies);
5. Well-established data-evaluation techniques are available including locally developed codes;
6. Electrochemical cells have been described for NR to perform in operando studies;
7. Auxiliary facilities, especially MBE and sputtering, can prove useful in preparing model layer structures (e.g. contact / current collector);
8. A number of methods / instruments / experts are available on the KFKI campus in the partner institutes.

➤ **Disadvantages:**

1. The Budapest neutron source is not particularly bright, therefore small (below 1 cm²) samples, off-specular scattering and fast processes would be difficult to study. Experience with battery work (including in operando) at the V6 reflectometer of the recently shut down BER II reactor in Berlin, of the same power as BNC, can offer practical guidelines for experiments at GINA;
2. GINA is a horizontal scattering plane (vertical sample) reflectometer: external user devices have to accommodate to this geometry;
3. GINA is a fix-lambda (no TOF) reflectometer, therefore not suitable for time slicing (the full reflectogram should be recorded to characterize a particular state of the sample).

Interest of the facility in prospective battery studies

The Staff is open to do projects in this field.

A preliminary cell design for GINA is available. The estimated fabrication cost is ca. EUR 10,000.

2.4.2. Material Test Diffractometer (MTEST)

Responsible: László Temleitner (till July 31st, 2020) – temleitner.laszlo@wigner.hu

Brief introduction to the technique and its application to battery studies

Neutron diffraction studies in Neutron Powder Diffraction (NPD) and Neutron Total Scattering modes can be employed for battery studies.

NPD can yield the following type of battery-relevant information: crystalline structure analyses of anodes, cathodes and solidstate electrolytes; phase composition; metastable phases developing during charge/discharge; microstress; crystalline structure distortion; lattice defects; atomic ordering, Li⁺ diffusion/migration paths [56, 57, 58].

Neutron total scattering (including both Bragg and diffuse scattering) allows joint investigation of long- and short-range structures (local ordering due to differences in cationic radii and valence state of cathode components) [59, 60, 61].

Description of the Instrument

The MTEST diffractometer implements the methods of NPD and total scattering analysis with thermal neutrons. The arrangement allows recording the total scattering powder diffraction pattern from 4.5 to 142.6° degrees in 2θ . The instrument is optimized to provide low/medium resolution (FWHM about $0.5 \div 0.6^\circ$), with a relatively low background for appropriate acquisition times (ca. 1 h for a good scatterer, such as liquid CCl_4 ; ca. 6 h for typical amorphous and crystalline samples; ca. 1 day for materials containing sizable amounts of hydrogen). The neutron flux at the sample table is $2 \cdot 10^6$ neutrons/($\text{cm}^2 \text{ s}$) at a wavelength of 0.133 nm. The standard size of the beam is 10 mm (width) \div 40 mm (height) and can be adjusted by slits. The instrument is equipped with a monochromator changer which uses 3 crystals: Ge(111), Cu(111) and Cu (220), allowing to tailor the beam for the required Q-range and resolution even during data collection. The flux of the thermal neutron beam is optimized at 1.44 Å (Cu(111) monochromator), which corresponds to a Q range of $0.4 \div 8.5 \text{ \AA}^{-1}$. With a Cu(220) monochromator, a wavelength of 0.88 Å is available, allowing to extend the Q-range up to 13.5 \AA^{-1} , at the cost of an intensity reduction of 15% could be achieved at 1.44 Å. Usual sample sizes are 1.2 cm^3 : smaller objects would require longer measurement times. A low-efficiency fission chamber monitor and a position-sensitive detector system serve for data collection. Samples for room temperature measurements can be mounted in standard O-ring sealed vanadium cans (6 and 8 mm in diameter). Additional sample environments include:

1. A low-background vanadium vacuum furnace (RT-1000°C)
2. An aluminium-shielded cryostat (77K-RT). Spinning the samples is possible at room temperature.

Key activities of Instrument

The M(aterial) TEST neutron diffractometer is a general-purpose neutron powder diffractometer. It covers the range of medium-resolution powder, liquid and amorphous total diffraction (Bragg and diffuse scattering) measurements.

Actual state of the art of battery studies

The MTEST staff has been involved in the ex situ study of raw battery materials by total scattering diffraction, and in the corresponding data modelling [62, 63, 64]. Moreover, a few beamtimes have been devoted to similar studies, with the Instrument Responsible as the main proposer. The Instrument Responsible also contributed as one of the proponents (main proposer: University of Bologna, Italy) in 2 PhD projects from the field of battery submitted to CERIC.

Possible adaptation of the facility to battery studies

In order to develop state-of-the-art in situ work, new detectors would be needed for shorter acquisition times. MTEST would welcome users that are available to develop sample environments for batteries to test them in this line. Dedicated funding would be appropriate after a demonstration test.

Interest of the facility in prospective battery studies

The Instrument Responsible expresses notable interest in the field.

2.4.3. Neutron Activation Analysis (NAA)

Responsible: Gméling Katalin – gmeling.katalin@energia.mta.hu

Brief introduction to the technique and its application to battery studies

Neutron Activation Analysis (NAA) has been employed for battery studies to gain the following types of information:

- Li⁺ diffusion/concentration depth profiling [65, 66] and in-plane mapping [67];
- Reaction rates: Li plating/stripping, Li⁺ intercalation/deintercalation. [65]

Description of the Instrument

NAA is a method for quantitative composition analysis of chemical elements, based on the conversion of stable nuclei of the sample to radioactive nuclei by nuclear reactions, followed by the quantification of the reaction products via their gamma radiation. NAA exhibits negligible matrix effects, excellent selectivity and high sensitivity. Even small amounts (few tens of milligrams) of, ideally, solid samples can be measured. Typically, the detection limit can reach down to less than 0.01 µg of a given element.

Samples for NAA are irradiated with neutrons in the core of the reactor: two dedicated channels are available for short- and long-time irradiation. The gamma-rays emitted from the sample are counted in one of the three available low-background gamma-spectroscopic counting chambers, equipped with high-purity Ge detectors and digital gamma spectrometers.

Key activities of Instrument

NAA is dedicated to irradiation experiments for elemental analysis, as well as homogeneity and ageing tests. One of the recently introduced key activities is the compositional analysis of solar panel construction materials.

Actual state of the art of battery studies

No previous experience in battery-related work.

Possible adaptation of the facility to battery

Modification of the analysis chambers might introduce some degree of lateral resolution that would yield valuable information for battery-work (see references above).

Interest of the facility in prospective battery studies

The Instrument Responsible did not show special interest in pursuing battery-related work.

2.4.4. Prompt Gamma Activation Analysis (PGGA)

Responsible: László Szentmiklósi – szentmiklosi.laszlo@energia.mta.hu

The Instrument Responsible is also Head of the Nuclear Analysis and Radiography Department that also involves the RAD Instrument (see below).

Brief introduction to the technique and its application to battery studies

PGAA is used for non-destructive elemental analysis of samples by detection of neutron-capture prompt gamma rays. Regarding battery studies, this approach has been employed for the precise determination of the proton content in pristine and chemically delithiated Ni-based oxides [68] and in as-fabricated Co-containing cathode materials [69]. Moreover, PGAA has been used to correlate long-term Mn dissolution and capacity retention in LFP/graphite and LFMP/graphite cells [70].

Description of the Instrument

Neutrons are brought from the cold-neutron source of the reactor to the experimental positions by a curved neutron guide, minimizing background from the core. The thermal-equivalent neutron flux at the PGAA sample positions is $9.6 \cdot 10^7 \text{ cm}^{-2} \text{ s}^{-1}$. The beam can be collimated to a maximum cross-section of $2 \times 2 \text{ cm}^2$. The intensity of the incoming neutrons is continuously monitored. A pulsed beam can also be used, with modulation of the order of milliseconds, by using a revolving chopper blade, while longer on-off periods can be achieved with a fast beam shutter. The experimental area is a $3 \times 6.5 \text{ m}^2$ space. A series of size collimators can tailor the beam.

The sample chamber can be evacuated or filled up with gases to decrease beam-induced background. The targets are mounted on thin Al frames by Teflon strings. An automated samplechanger with a capacity of 16 samples is also available. The detector system consists of an n-type high-purity Ge main detector with closed-end coaxial geometry, and a BGO Compton-suppressor surrounded by a 10 cm thick lead shielding. The sample-to-detector distance is adjustable, but it is typically 230 mm. By removing the front detector shielding, the Ge main detector can be placed as close as 12 cm to the target. The BGO annulus and catchers around the Ge detect a high fraction of the scattered gamma photons.

Key activities of Instrument

In addition to general-purpose analytical work, in part dedicated to catalysis, the topic on which the Instrument Staff is concentrating at the moment is the recycling and recovery of valuable/harmful/toxic materials from end-of-life products.

Actual state of the art of battery studies

The Instrument Staff members do not have any hands-on experience with batteries, although they believe research in the field would fit perfectly their scientific mission. Some preliminary work has been done on fuel cells, but a related internal CERIC CENTRE project was not funded. More in general, the Head of the Nuclear Analysis and Radiography Department informs that there are only a few in-house experts in electrochemistry at KFKI, and ca. 10 more in the country overall: the domestic contact network is thus limited.

Possible adaptation of the facility to battery

Development of a dedicated sample stage.

Interest of the facility in prospective battery studies

The Instrument Staff is open to initiatives and collaborations that can be completed with the knowledge and the hardware they have. Internally, a PhD research program has just been launched on the recycling of electronic waste that could provide some support for battery work.

In particular, the Instrument Responsible suggests that radioactive tracing as a method to follow the mobility of certain battery elements, could be rather straightforwardly implemented at PGAA.

2.4.5. Neutron Diffractometer with a Position Sensitive Detector system (PSD)

Responsible: Margit Fábán – fabian.margit@energia.mta.hu

Brief introduction to the technique and its application to battery studies

See corresponding Section for MTEST.

Description of the Instrument

PSD is a 2-axis diffractometer equipped with a linear position-sensitive detector system. The detector assembly is mounted on the diffractometer arm and it spans a scattering angle range of 25° at a given detector position. The entire diffraction spectrum can be measured in five steps. The detector system is based on three³ He-filled linear position-sensitive Reuter-Stokes detectors, placed above each other within the scattering plane. A high temperature in-situ cell (RT÷350° C) is available.

Key activities of Instrument

Research activity is currently centred on the structural investigation of different types of glasses: borosilicate, boromolybdate, chalcogenide and bioactive glasses for osteointegration.

Actual state of the art of battery studies

PSD is currently running a project, focusing on temperature-dependent structural properties of solid state Li- and Na- based oxide electrolytes, in the range RT÷150° C.

Possible adaptation of the facility to battery

Manpower would be the most critical issue to develop battery work with the existing facility. The present configuration of the Instrument is suitable for both *ex situ* and *in situ* battery work, but not for *in operando* experiments.

Interest of the facility in prospective battery studies

The PSD staff expresses interest in new collaborations in the battery field.

2.4.6. RAD – Static / Dynamic thermal-neutron and X-ray imaging station

Responsible: Zoltán Kis – kis.zoltan@energia.mta.hu

For items not explicitly addressed below, please refer to the subsection regarding the PGAA Instrument.

Brief introduction to the technique and its application to battery studies

Neutron imaging, tomography in particular, is gaining momentum for battery studies, owing to the penetrating power and sensitivity to Li. Neutron radiography, tomography [71] and Bragg-edge imaging [72] have been used to monitor Li⁺ transport and spatial distribution, evolution of Li⁺ concentration, distribution of Li⁺-containing electrolyte and gas-evolution phenomena. Moreover, n-tomography allows one to work with full-scale batteries in their casing used for normal commercial operation. [73]

Description of the Instrument

RAD is a combined thermal neutron / X-ray radiography / tomography instrument, fed by an in-pile, Cd-covered pinhole-type collimator for neutrons. At the same instrument, also fast neutron radiography and tomography have been recently demonstrated [74]. The facility offers two measurement positions along the neutron beam path with a beam diameter of ~200 mm, used for dynamic (DNR) and for static (SNR) imaging. Options are provided to use beam filters made of boron-containing rubber and lead bricks, resulting in a significant modification of the beam energy distribution, giving a fast/thermal neutron flux ratio of 77 instead of 0.6. The RAD facility is also equipped with an X ray tube (5÷300 keV), allowing dual-mode imaging. Two motorized sample stages are available, for small and large samples (up to 250 kg). A sapphire-crystal based filter is under installation to suppress fast neutrons. The detectors for 2D and 3D imaging are scintillation screens. Those for neutron radiography exhibit a space resolution in the range 70÷250 µm. Intensifying screens for X-ray radiography allows a resolution of 100÷200 µm. An option is available to apply larger or smaller Fields Of View (FOV: 41×34 mm², 110×93 mm²) with lower and higher spatial resolution, respectively. Static radiography and tomography are carried out with a large-area sCMOS camera. Different optical arrangements are available with interchangeable fixed focal-length lenses, coupled to a digital camera, giving different FOVs.

Dynamic radiography is performed by means of a fast low-light level TV camera, enabling real-time imaging. The zoom optics coupled to the camera provides a variable field of view. The two cameras can be used interchangeably in a light-tight camera box equipped with a rail system, providing appropriate optical path lengths. Typical exposure times for static imaging are in the range 1 ÷ 35 s per image, tomography is generally performed with 600 ÷ 1000 projections per tomogram. The image acquisition rate for dynamic radiography is 25 frames per second.

A photo-luminescent imaging plate (IP) technique is also available for high-resolution X-ray and neutron radiation detection with the transfer method, using In and Dy foils.

For the manipulation, reconstruction and visualization of the 3D neutron and X-ray datasets, Fiji-ImageJ, Octopus 8.9 and VG Studio 2.1 software packages are used.

Key activities of Instrument

The research based at this Instrument is mainly focused on: archaeometry (archaeometallurgy); materials science (nuclear fuel elements) and metallurgy (e.g., control of aeronautical castings).

Actual state of the art of battery studies

The RAD Instrument has never addressed battery research, but an indirectly related topic has been the object of a recent publication: a chemical Li oxidation reactor was recently studied in situ by fast-neutron tomography. [75]

2.4.7. Small Angle Neutron Scattering instrument – “Yellow Submarine” (SANS-YS)

Responsibles: László Almásy – almasy.laslo@energia.mta.hu, Len Adèl - len.adel@energia.mta.hu

Brief introduction to the technique and its application to battery studies

Small-angle neutron scattering (SANS) investigates structure at length-scales in the range nm÷µm. This approach has been used in battery studies for the following purposes: to assess materials nanostructure; to follow microstructure evolution and formation of interfacial phases (e.g., SEI); to characterize porosities and heterogeneity in cathodes; to analyse morphology and phase separation in polymeric electrolytes and to investigate ion solvation [76, 77, 78, 79].

Description of the Instrument

The SANS diffractometer covers the Q-range $0.003 \div 0.7 \text{ \AA}^{-1}$, allowing to probe structures at length scales $5 \div 1500 \text{ \AA}$. The instrument is installed on a curved neutron guide, made of supermirrors. The beam is monochromatized by a multidisc type velocity selector, allowing to separate wavelengths between 3 and 12 Å (cold neutrons). The width $\Delta\lambda/\lambda$ of the transmitted wavelength distribution can be varied between 12 and 30 % by changing the tilt angle between the selector axis and the direction of the neutron beam. The scattered neutrons are detected by a 64×64 pixels (1 cm × 1 cm pixel size) 2D position-sensitive detector, filled with BF₃ gas.

Sample temperatures can be controlled from an external bath between 10 and 90°C. A liquid nitrogen cryostat and a closed cycle refrigerator are available for experiments in the range $10 \div 300 \text{ K}$. A 1.6 T electromagnet with pole distance of 25 mm can also be mounted on the sample table. Automatic sample changers of different types are available for the different sample environments.

Key activities of Instrument

The Instrument is employed for a wide range of applications: studies of defects and precipitates in materials; alloy segregation; surfactant and colloid solutions; ferromagnetics; magnetic correlations; polymers; proteins and biological membranes.

Actual state of the art of battery studies

Two beamtimes have been granted in the recent past, in which pristine and aged electrodes have been analysed ex situ. No publications seem to have appeared, based on these measurements.

Possible adaptation of the facility to battery

Currently, an in situ cell for the SANS Instrument is not available, but it could be built with limited investment of manpower and funding.

Interest of the facility in prospective battery studies

Even if at the moment there are no researchers working at SANS on these topics, the Instrument Scientists manifest their interest and availability to develop this kind of activity and declare their availability to set up collaborations with users interested in the technique.

2.4.8. Thermal Neutron Three-Axis Spectrometer and Neutron Holographic Instrument (TAST/HOLO)

Responsible: Alex Szakál – szakal.alex@energia.mta.hu

Brief introduction to the technique and its application to battery studies

Quasi-elastic and inelastic neutron scattering can be used in battery research to measure local structural and vibrational dynamics, probing mobility as a function of spatial scale. Li⁺ conductivity in polymeric and ceramic electrolytes as well as in amorphous anodic materials, have been correlated with lattice dynamics. Dynamic information can be extracted on space- and time-scales 0.1 ÷ 100 nm and 10⁻⁹ ÷ 10⁻¹² s [80, 81, 82].

Description of the Instrument

TAST is a thermal neutron three-axis spectrometer, operating in the momentum-transfer range 1.5 ÷ 10 Å and energy-transfer range 1 ÷ 60 meV, with a resolution of ~ 1.0 meV. Independent control of the momentum (Q) and of the energy transfer (E) is possible, at variance with Time-Of-Flight spectrometers in which Q and E are related by the instrumental configuration. This spectrometer can also be used in a multi-purpose regime, such as: high-resolution diffractometry and inelastic scattering.

The monochromatic beam is provided by a horizontally and vertically focusing Cu[002] monochromator of 90mm height and 150mm width. In order to suppress the intensity of fast neutrons, a 15 cm long sapphire single crystal is inserted in the primary shutter. A Ge analyser can be optionally used for higher order filtering in the incident monochromatic beam. The beam divergence is determined by a thin film Soller-type Mylar collimators, coated with Gd₂O₃.

The detector is a high-efficiency (90 % at 1 Å) ³He single counter of 1" diameter. A two-dimensional position-sensitive detector is also available for medium-resolution operation. For energy analysis, a horizontally focusing pyrolytic graphite crystal assembly is used.

The spectrometer can be equipped by an Eulerian Cradle, or a tilt table that can hold various sample environments up to a mass of 100 kg. The TAST instrument can also be used for atomic-resolution neutron holography in neutron- or gamma-ray detection modes. For this purpose, it employs a BGO gamma detector, equipped with a special shielding to filter the gamma background, capable of detecting the low-intensity holographic signal.

Key activities of Instrument

TAST is mainly employed for the study of phonon and magnon dispersion in single crystals, and to

measure the phonon density of states for a wide range of hydrogen-containing materials.

Actual state of the art of battery studies

The Instrument Scientists report not having any experience in the field.

Possible adaptation of the facility to battery

A special sample environment would be needed, that the Instrument Scientists would be happy to develop in collaboration with electrochemistry groups.

Interest of the facility in prospective battery studies

The Instrument Responsible manifests his interest, but notifies that the group is seriously short in manpower.

2.4.9. Time-of-flight neutron diffractometer (TOF-ND)

Responsible: György Káli – kali.gyorgy@energia.mta.hu

Brief introduction to the technique and its application to battery studies

See the contents of the same Section of the TAST/HOLO Instrument.

Description of the Instrument

TOF-ND is a general-purpose high-resolution time-of-flight powder diffractometer. It covers the d-spacing range $0.5 \div 2.5 \text{ \AA}$ (Q-range $2.5 \div 12.5 \text{ \AA}^{-1}$) with variable bandwidth and resolution ($\Delta d = 0.0015 \div 0.15 \text{ \AA}$). The instrument operates on a thermal neutron beam, with fast neutrons filtered off by a single crystal silicon block. The monochromator system is chopper-based, with a double chopper, designed for a maximum speed of 12,000 rpm. In the high-resolution mode, 10 \mu s neutron pulses and a 25 m flight path allow an accuracy of $1.5 \cdot 10^{-3} \text{ \AA}$ on polycrystalline materials. To minimize the opening time and to optimize pulse separation, the neutron beam is reduced from 25 to 10 mm by using a 4.5 m upstream compressor neutron guide section and an identical decompressor guide downstream at the position of the pulse choppers. Longer pulses of variable duration can be obtained in the range $20 \div 200 \text{ \mu s}$. In the low-resolution mode, liquid diffraction can be performed with a good neutron intensity up to a scattering vector of 12.5 \AA^{-1} .

The detection system is based on a large-surface back-scattering bank of ^3He tubes. The data acquisition protocol has been specially designed to allow time-dependent in-situ experiments.

Key activities of Instrument

TOF-ND is typically employed for: structure determination and refinement; peak profile analysis; phase and texture analysis of crystalline materials and diffraction in liquids.

Actual state of the art of battery studies

A single, unsuccessful experiment has been attempted: no details have been provided.

Possible adaptation of the facility to battery

The Instrument scientists have no special comments to this point.

Interest of the facility in prospective battery studies

The Instrument Responsible would be interested in continuing the attempted experiments in the field of batteries.

2.5. Italy

Director: Marco Marazzi <marco.marazzi@elettra.eu>

Italy participates to CERIC-ERIC with several beamlines located at Elettra, a third generation synchrotron radiation facility located at Trieste. Its storage ring operates at 2.0 and 2.4 GeV, with emitted photons in the energy range from a few to several tens of KeV with spectral brightness of up to 10^{19} photons/s/mm²/mrad²/0.1% bw. A general upgrade of Elettra is planned in a few years.

2.5.1. Surface Physics Laboratory

Responsible: Alessandro Baraldi – alessandro.baraldi@elettra.eu

Description of the facility:

The laboratory is built in cooperation between the Elettra synchrotron and the University of Trieste. It hosts research groups having experience in the fabrication and characterization techniques for colloidal nanostructures and nanostructured materials that can be extended to modern approaches to electrochemical storage research.

A glove-box, a potentiostat and an electrochemical cell are available at the University of Trieste.

Actual state of the art of battery studies:

At present, the Surface Lab is not involved in the CERIC-ERIC consortium.

Possible adaptation of the facility to battery studies

Due the cross character of the Surface Laboratory and their expertise in the sample preparation in UHV environment, this laboratory should be involved in the consortium.

2.5.2. Band Dispersion and Electron-Phonon coupling (BaDElPh) beamline

Responsible: Luca Petaccia – luca.petaccia@elettra.eu

Description of the facility:

The BaDElPh beamline provides photons in the energy range 4.6-40 eV with high flux, high resolving

power, and horizontal-vertical linear polarization. The beamline serves an end station to perform primarily high-resolution angle-resolved photoemission spectroscopy (ARPES) experiments in the low photon energy regime. Due to the low photon energy, the surface preparation and the crystallinity of the sample are crucial.

Research takes place in fields related to condensed matter and surface physics, materials and nano science.

Actual state of the art of battery studies:

The beamline is not involved in battery research.

Due to the extreme low photon energy, and therefore to the high surface sensitivity, ex situ electrodes are not suitable candidate for surface studies on the BaDEIPh beamline.

2.5.3. ESCAMicroscopy beamline

Responsible: Luca Gregoratti – luca.gregoratti@elettra.eu

Brief introduction to the technique and its application to battery studies

The ESCAMicroscopy beamline hosts a Scanning photoelectron microscope (SPEM), combining chemically surface sensitivity with high spatial resolution. The spot size can be defined down to 120 nm and energy sensitivity is within 180 meV. The high-flux third-generation X-ray source feeding the line, enables micro-characterization on a spatial scale comparable to that of the processes and the phases occurring at morphochemically complex surfaces, enabling: space-dependent quantitative and qualitative chemical characterisation of complex materials. Typical experiments include chemical and electrochemical reactions; mass-transport processes, leading to lateral changes in the composition; morphology and electronic properties of materials. A special cell has been recently developed for Near Ambient Pressure SPEM. ESCAMicroscopy has been extensively employed for battery-related work as well as for other studies of interest for electrochemical energetics (see dedicated Section below).

Description of the Instrument

The SuperESCA and ESCAMicroscopy beamlines share a high-brilliance linear planar undulator, which produces horizontally polarised light. By adjusting the undulator gap, the photon energy can be varied in the ranges $90 \div 1500$ or $130 \div 1800$ eV when the Elettra storage ring works at 2.0 or 2.4 GeV, respectively. The possibility of tapering the undulator gap allows a controlled enlargement of the harmonic spectrum at particular energies.

In order to achieve space-resolution, the SPEM of ESCAMicroscopy uses a small focused probe, obtained with zone plate focusing optics, to illuminate the surface to be analysed.

The SPEM can operate in two modes: imaging and spectroscopy. In the former, the sample surface is mapped by scanning the sample across to the focused photon beam and collecting photoelectrons with a selected kinetic energy. The latter is photoelectron spectroscopy, obtained by analysing the photoelectrons emitted from a microspot.

The endstation consists of three UHV chambers:

1. The analysis chamber, hosting the SPEM;
2. A fast entry-lock connected to the small preparation chamber, where 5 sample holders can be kept in vacuo;
3. A preparation chamber with facilities for specimen preparation / characterization, based on the following tools: LEED, AES, PEEM, a sputter gun, plasma source, a gas inlet system, an evaporation source, a mass spectrometer and facilities for indirect and direct sample heating.

The sample holder can be fitted with a heating stage and with electrical connections and can be enclosed in a high-pressure cell for near-ambient pressure work (see previous Section).

Key activities of Instrument

The research fields in which ESCAmicroscopy is active are: (i) surface physics and chemistry and (ii) materials science and nanotechnology, including: micro and nanostructures; electrochemistry; nanocomposites and catalysis. This instrument is ideal for monitoring *in situ* dynamic processes, such as mobility of metal on a surface as a function of temperature and/or electrical/electrochemical bias.

Actual state of the art of battery studies

ESCAmicroscopy is actively employed by workers in different fields of electrochemistry, including battery studies. As far as batteries are concerned, SPEM work has concentrated on LIB [83, 84, 85] and zinc-air [86, 87] systems. Electrochemical work encompasses: high-temperature solid-oxide fuel cells,[88, 89] polymer-electrolyte fuel cells,[90] alkaline fuel cells, [91] electrodeposition, [92] electrocatalysis,[93] and corrosion. [94]

Possible adaptation of the facility to battery

ESCAmicroscopy staff is highly interested in improving and engineering the electrochemical cell approach based on an e-transparent graphene window that has been pioneered at this beamline [95] and to develop an improved version of the Nafion-based wet cell, dedicated to the recently developed NAP stage. [96]

Interest of the facility in prospective battery studies

The beamline is already actively involved in battery studies and is willing to continue and expand them.

2.5.4. GasPhase (GAPH) beamline

Responsible: Kevin C. Prince – kevin.prince@elettra.eu

Description of the facility:

The GAPH beamline was born as a joint venture between the Istituto Nazionale di Fisica della Materia (INFN), the Consiglio Nazionale delle Ricerche (CNR) and the Sincrotrone Trieste scpA (ST), and at present it is operated by a Research Team (ST+CNR). It offers a multi-technique approach for investigation of electronic properties of free atoms, molecules and clusters in the photon energy range

13-900 eV. Differently from most other beamlines at ELETTRA, there is not a permanent end station at GasPhase. A complete list of all the equipments is accessible online at the website of the beamline.

Three additional endstation have been developed within specific collaboration projects proposed by expert Users' groups Long Term Proposals. They are not owned by the GAPH beamline; but they are presently available also to users, after preliminary agreement with the owner and the beamline research team.

The research activity is focused on spectroscopy and dynamics of basic processes like inner-shell and multiple excitations and ionisation, as well as for characterising key processes relevant to several areas of science and technology (for example atmospheric chemistry, material science and biomedical sciences).

Molecules adsorbed on surfaces are usually studied and the obtained results are used as references for further experiments on the Material Science beamline.

Actual state of the art of battery studies:

At present, no proposals have been received for battery studies.

Possible adaptation of the facility to battery studies

Study of the electrolytes, with a special focus on the role of additives on the electrochemical properties.

Interest of the facility in battery studies and perspectives

The synergy between the GAPH and MBS beamline could be beneficial for battery studies.

2.5.5. IUVS Inelastic UltraViolet Scattering and IUVS-offline

Contact for battery-related activities (n.b.: this is not a formally defined task, all contacts can be found on the beamline webpage): Barbara Rossi – barbara.rossi@elettra.eu

Brief introduction to the technique and its application to battery studies

The IUVS beamline is dedicated to the study of inelastic scattering with ultraviolet radiation, in the time-space domain.

Incident photons have an energy in the range 5 ÷ 11 eV. The photons diffused inelastically by the sample can be analysed with two different and complementary UV Brillouin and UV Resonant Raman scattering instruments probing, respectively, the acoustic and optical phonons propagating in the sample. This allows the acquisition of information about the structure and dynamics of matter over different length scales, through the analysis of its collective and molecular vibrations.

The Brillouin setup, with scattering angle θ of 178° , allows measuring exchanged momenta in the range of $2 \cdot 10^{-2} \div 2 \cdot 10^{-1} \text{ nm}^{-1}$, enabling the investigation of a kinematic region not presently accessible with other experimental techniques, such as Brillouin scattering with visible light, X-Ray scattering and neutron scattering.

In the Raman range, the setup performs UV Resonant Raman spectroscopy using synchrotron radiation in the range of wavelengths 200 ÷ 270 nm, thus providing a finely tuneable source in the deep-UV for mapping a wide resonance range in diverse types of samples: from nanostructures and strongly

correlated materials to biophysical and biochemical systems.

Independently from the synchrotron source, laser beams of 244, 266, 532 and 633 nm are also available.

UV-Raman has been recently employed to investigate the surface anode chemistry and to characterize the SEI. Specifically, Si [97] and C anodes for LIB,[98] N-doped CNT anode for Na batteries [99] were studied.

Description of the Instrument

IUVS is composed by two separate branch-lines, devoted to UV Brillouin and resonant Raman scattering, respectively. An undulator provides photons in the tunable range of 5÷11 eV, by a proper selection of the undulator gap. Two grazing-incidence mirrors remove high-order energetic harmonics, after which the beam is delivered to either of the setups by a removable grazing incidence silicon mirror.

➤ **Resonant Raman setup**

After the switching mirror, the beam is brought out from the UHV ambient through a fused silica viewport, after which the UV-beam can be handled optically as a conventional laser beams.

At this point, the beam has by a bandwidth of ~ 20 nm, and is monochromatized with a Czerny-Turner spectrometer before use for Raman spectroscopy.

The spectrometer is equipped with three holographic UV-optimized gratings of 1800 g/mm, 2400 g/mm and 3600 g/mm, allowing a final bandwidth in the range 10 ÷ 50 cm⁻¹.

After the monochromator, the beam is collimated by a spherical lens and brought to the sample through a 45° mirror. A spherical lens with a focal length of 100 mm, acts as focusing and collecting lens, thus providing a backscattering configuration. The analyser system is composed by three interconnected Czerny-Turner spectrometers with focal lengths of: 500, 500 and 750 mm, coupled to work both in additive and subtractive configurations. The first one enables Raman measurements with very high resolution (up to 0.3 cm⁻¹ at 633 nm), the second one allows strong reduction of the elastic component without using notch or longpass filters, making it possible to measure Raman peaks up to ~ 50 cm⁻¹.

The set-up is complemented by a micro-Raman system based on the 266 nm laser. The backscattering configuration and the geometrical characteristics of the Raman set-up allow the use of a large variety of sample environments, including standard electrochemical cells with a quartz window.

For measurements of liquids and/or aqueous solution, a thermostatic specific sample holder is available, able to fix the sample temperature in the range 5 ÷ 120o C.

➤ **Brillouin setup**

The inelastic light scattering spectrometer uses an incident photon energy tuned in the 5 ÷ 11 eV range by a monochromator, with relative energy resolution in the range 10⁻⁵ ÷ 10⁻⁶ range. The analyzer separates the energy of the photons diffused by the sample, with an energy loss or an energy gain in the region typical of phonon-like excitations in the considered momentum region. The momentum transfer, Q, is in the range 0.02 ÷ 0.25 nm⁻¹, depending on the incident photon energy, the choice of the scattering angle, and the refractive index of the sample. The momentum resolution is typically ~ ΔQ/Q = 0.05.

The Brillouin branchline is also equipped for temperature-scans on solid and liquid samples in the range

–20 ÷ 120° C, with an accuracy of less than 0.5° C. A liquid nitrogen cryostat is also available to cool the sample down to 77 K. Moreover, a pressure cell is available, allowing to reach pressures up to 4 Kbar.

Key activities of Instrument

The experimental setup for UV Brillouin experiments allows measuring the dynamic structure over the intermediate, mesoscopic, region of exchanged-energy / exchanged-momentum, giving access to the frequency range required for studying the structural relaxation processes in H- bonding systems, as molecular liquids and water solutions.

The UV Resonant Raman scattering setup enables to gain additional information on samples whenever the complexity of the system analysed does not allow a straightforward interpretation of spontaneous Raman spectra. The tunable radiation source in the deep-UV range (4 ÷ 6 eV, 200 ÷ 300 nm) gives the possibility of finely mapping a resonance range that is diagnostic for widely different systems, ranging from graphene and carbon-related materials, to DNA, proteins and aromatic compounds.

Typical research projects at the IUVS beamline include the characterization of dynamics of systems in scientific fields, such as: water and liquids, polymers and gels, drug-carriers, bio- logical molecules such as proteins and DNA, nanostructures and archaeometry.

Actual state of the art of battery studies

A few experiments have been carried out, aimed at disclosing structural aspects of ionic liquids and deep-eutectic solvents of interest for battery electrolytes that have generated a recently published paper [100].

Possible adaptation of the facility to battery

In principle, the beamline, in its standard configuration, both in the synchrotron-based and offline modes, is ready to accept battery-relevant materials and cells for both ex situ and in situ experiments, without need of special adaptation. Development of specific electrochemical cells by users would be welcome and would receive support by the beamline staff.

Interest of the facility in prospective battery studies

The Beamline Responsible is open to developing battery-related studies and willing to support them.

2.5.6. Materials Characterisation by X-ray diffraction (MCX) beamline

Responsible: Jasper Rikkert Plasier – jasper.plaisier@elettra.eu

Description of the facility:

The MCX beamline is a general purpose X-ray diffraction beamline with a large useful energy range from 4 to 21 keV and equipped with a four circle goniometer, allowing a wide range of non-single crystal diffraction experiments: grazing angle diffraction and reflectivity, residual stress and texture analysis, phase identification and structural studies and kinetic studies. Systems that can be investigated vary from organic and inorganic thin films, to thermally and/or mechanically modified surfaces of mechanic components, to polymers, catalysts and highly disordered materials in the form of films, powders, fibers.

The research carried out at MCX concerns fields related to materials science, archaeometry, geophysics, solid state and superconductors physics, catalysis, solid state chemistry, energy materials.

Actual state of the art of battery studies:

The beamline has already a lively activity in the field of batteries, mostly concentrated on the study of positive electrode materials such as LiMO₂ (layered transition metal oxides) with S. Brutti (Univ. Roma "La Sapienza"), Prussian Blue analogues with M. Giorgetti (Univ. Bologna) [101], Li-V₂O₅ cathodes [102] and Li-O₂ systems with D. M. Itkis (Lomonosov Moscow State University), Li- and Na- Fullerene negative electrodes with D. Pontirolli (Univ. Parma), and K-KTiPO₄ F with S. S. Fedetov (Skolkovo Institute of Science and Technology, Moscow)[103].

In the last semesters, in a total of about 15 experiments at MCX, there are 5 on batteries:

3 operando (about 20%) and 2 ex situ (13%). In the last semester, 2 operando studies have come through CERIC, and most operando proposals are awarded beamtime.

Possible adaptation of the facility to battery studies

There is a clear need of creating an infrastructure at Elettra to provide the users an adapted sample environment to work with batteries, especially for operando studies (i.e., potentiostat, glove box, etc.) Only a holder for different cells is available, whereas no in house in situ cell has been actually developed.

There are plans for buying a new detector Mythen-120° for faster measurements in the next two years.

Interest of the facility in battery studies and perspectives

The beamline staff is strongly interested in potentiating the activity in the field of batteries. The acquisition of the new Mythen detector will allow improving the analytical potential of the beamline towards fast kinetics and the rapid collection of high resolution patterns, allowing the study of battery system in shorter times.

2.5.7. Nanospectroscopy beamline

Responsible: Andrea Locatelli – andrea.locatelli@elettra.eu

Description of the facility:

The Nanospectroscopy beamline operates a state-of-the-art spectroscopic photoemission and low energy electron microscope (SPELEEM). This instrument offers a wide range of complementary methods providing structural, chemical and magnetic sensitivity.

The lateral resolution of the microscope currently approaches few tens nm. The microscope is served by a high photon flux beamline, which can deliver elliptically polarized photons in the range 50 eV to 1000 eV.

A small preparation chamber allows simple treatments such as annealing and exposure to gas. A small heating facility allows annealing and flash up to temperatures of about 2000 K. An Ar ion gun facing the sample is provided for sputtering.

The main chamber is equipped with 6 ports for e-beam evaporators, and 1 port for illuminating the

sample with Hg-lamp. Available facilities are a gas line with precision leak valves, e-beam evaporators (Focus - Omicron GmbH), a quadrupole mass spectrometer, a magnetization stage, and a sample parking stage.

Research takes place in fields such as surface physics and chemistry, magnetism, materials science and nanotechnology, exploiting the high surface, chemical and electronic structure sensitivity of core level and valence band XPEEM.

Actual state of the art of battery studies:

Only one proposal selected by the Elettra Review Panel was related to batteries. This study aimed to characterize the electronic structure and chemical composition of epitaxial LiCoO₂ (LCO) films as a function of Li content on single grains, in order to understand the lithiation/delithiation process and the nature of the electronic and structural changes that LCO undergoes as a function of different conditions (annealing in O₂, UHV, etc.). Such study was NOT a real "operando" investigation, but rather a surface science approach.

The most difficult challenge to overcome concerns the preparation of suitable samples and cartridges for operating the photoemission electron microscopy (PEEM). The application of voltage potentials/currents to the sample collides with the limitations of cathode lens microscopy, making imaging extremely difficult. Further, the presence of contact pads and bonding wires (on the specimen) would favor high voltage discharges between sample and objective lens, resulting in sample or instrumental damage.

Possible adaptation of the facility to battery studies

A feasibility study on solid state battery would be mandatory to assess whether these experiments can be actually performed with the PEEM.

Interest of the facility in battery studies and perspectives

The Nanospectroscopy beamline, together with the Surface Laboratory, has recently submitted a proposal for a PhD fellowship to the CERIC-ERIC consortium. The purpose was to investigate multiscale architected materials, with a finely designed and controlled structure at the atomic and meso-scale, in order to optimize the concurrent mechanisms taking place at different scales in the electrochemical storage processes.

2.5.8. SISSI - Synchrotron Infrared Source for Spectroscopy and Imaging & SISSI-offline

Responsibles: Lisa Vaccari – lisa.vaccari@elettra.eu, Giovanni Birarda – giovanni.birarda@elettra.eu

Brief introduction to the technique and its application to battery studies

The SISSI infrared beamline employs the IR and visible components of synchrotron emission to perform spectroscopy and microspectroscopy.

A close-knit group of papers from the Canadian Synchrotron appeared, that has pioneered in situ IR electrochemical microspectroscopy:

- In situ synchrotron IR microspectroscopy and time-resolved (range of a few s) spectroscopy were demonstrated with a thin-cavity external reflectance cell, employed to study the diffusion controlled redox of a ferrocyanide solution. [104]
- The time resolution was pushed down to fractions of a second by performing step-scan spectroelectrochemistry with an IR microscope using synchrotron IR radiation. The external reflectance cell features 25 μm gold ultramicroelectrodes. [105]
- Electrochemical adsorption of a monolayer of 4-methoxypyridine (MOP) with a gold film electrode, was studied in situ with Attenuated Total Reflection – Surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) [106]. In this study the authors could measure high quality IR spectra of 2.5 fmol of molecules confined to a 125 μm^2 beam spot.
- The high spatial resolution provided by synchrotron generated infrared (IR) radiation was employed to map in situ spatio-temporal concentration profiles in the diffusion layer around a working electrode, during reduction of ferricyanide and the oxidation of hydro-quinone. An improved cell design was also proposed, based on a band-type electrode. [107]
- A similar approach was also used for a combinatorial electrocatalytic study consisting in mapping the activity of a Pt-Ni alloy electrode, exhibiting a linear metal concentration gradient, towards methanol oxidation, spectroscopically determined by measuring the rate of CO₂ production as a function of position. [108]

Description of the Instrument

The SISSI beamline implements two branchlines, aimed at Materials and Life Science, respectively. Radiation for the SISSI beamline is collected from a bending magnet with a wide acceptance angle and comprises a broad range of emissions. The extracted radiation is transferred by gold-coated mirrors in HV, and finally focused at the SISSI-endstations; a CVD diamond window separates the HV of the beamline from the low vacuum of the interferometers and the ambient pressure of the IR-Vis microscopes:

- The Material Science branchline (SISSI-Mat) is equipped with a spectrometer for spectroscopy and spectromicroscopy measurements over a broad spectral range can mount different detectors on the infrared microscope, allowing to exploit a diffraction-limited beam from the visible down to the terahertz. This branchline is also equipped with cryostats and diamond anvil cell, permitting to explore the behaviour of matter at extreme conditions of temperature and pressure.
- The Chemical and Life Sciences branchline (SISSI-Bio) is optimized for FTIR spectroscopy, microscopy, and imaging in the mid-IR and targets chemical and biomedical applications, cultural heritage, geological science and biophysics. A state-of-the-art interferometer and IR microscope, equipped with appropriate accessories, give access to the full FIR-MIR range. The SISSI-Bio branchline offers full support for chemical, biophysical and biomedical applications as well as for studies in the fields of geology and cultural heritage.

Key activities of Instrument

SISSI-Bio Mainly targets life science and biochemistry studies, including cell biology, protein folding and biomedical diagnostics. Other common applications cover the fields of: surface and material science, microanalysis, forensics, geology, microfluidics and cultural heritage. In addition, high-pressures and time resolved IR can be performed. IR microscopy experiments are now well established and the beamline

scientists are currently focusing on the development of nanoscopy.

Actual state of the art of battery studies

So far, SISSI has never hosted any electrochemical experiment, but the first application for beamtime in the field of battery studies has been submitted at the last call, and is presently under evaluation.

Possible adaptation of the facility to battery

Limited electrochemical IR-imaging activity is documented to date (see first paragraph of this Section), and the beamline scientists are keen on developing novel and better approaches, in collaboration with users who are experts in electrochemistry. Specifically, the key desideratum is the development of a system for time-resolved IR micro-spectroelectrochemical measurements. Cell-design will be the first activity to be launched. As far as wet cells for in situ work, an advantage of the SISSI setup is that the sample does not need a vacuum ambient. The next most crucial issue will be to assess the better responsive class of battery materials to be investigated. In IR microscopy, a potential limitation for in operando work, could be the acquisition rate, in the case of electrodynamic kinetics experiments: this aspect will probably require the implementation of dedicated data-acquisition protocols

Interest of the facility in prospective battery studies

The beamline staff is willing to extend SISSI activities to battery-related topics and to run feasibility experiments. They regard the topic as a strategic and they are convinced that IR imaging can contribute unique information to the field.

This beamline participates in a CERIC PhD grant for battery studies, in which the main proposer is TwinMic@Elettra: the related activities will start in November 2020.

2.5.9. Spectromicroscopy beamline

Responsible: Alexey Barinov – alexey.barinov@elettra.eu

Description of the facility:

The beamline houses unique microscope designed for studies of the local band structure of materials. A low photon energy beam (below 100 eV) is focused into a submicrometre spot and electrons arising from the photoemission process are collected and analyzed in terms of their angular and energy distributions (ARPES).

The final focusing is obtained by multilayer coated optics of Schwarzschild objectives. The use of multilayers required for high reflectivity at a certain wavelength restricts the photon energy range available after the monochromator (20-200 eV) to specific narrow lines. Currently the beamline is equipped with two Schwarzschild objectives designed for 27 and 74 eV of photon energy.

ARPES is then performed by means of internal movable electron energy analyzer mounted on precision two axes goniometer setup. The sample can be measured in the temperature range of 40-470 K and the sample focusing and imaging are performed thanks to the XYZR scanning stage on which the sample manipulator is mounted.

Spectromicroscopy is devoted to a user community working in the field of surface and material science

(strongly correlated materials, topological insulators, etc.) with particular emphasis on electronic structure phenomena such as electronic phase transitions and electronic structure of small – down to sub micrometer size – objects.

Actual state of the art of battery studies:

Currently there are no proposals submitted regarding batteries. In the past, one experiment aiming to study the Li distribution on graphene positive electrode for Li-air battery was performed, thanks to the spatial resolution and energy range available on the beamline [109].

Possible adaptation of the facility to battery studies

The beamline works in HUV environment, therefore the batteries based on liquid electrolyte technology cannot be studied in operando conditions. Solid samples with a flat surface are also suitable for this technique.

Since it is possible to mount integrated chip equipped with electric connections on the manipulator, some investigations on solid state batteries in operando conditions could be possible in the future.

Interest of the facility in battery studies and perspectives

Thanks to the sub-micron spot available on the beamline, a mapping of the Li distribution on the pristine materials can be performed even if the sample surface is not perfectly flat. However, due to the low photons energy, the sample surface needs to be clean or cleavable.

2.5.10. SuperESCA beamline

Contact for battery-related activities (n.b.: this is not a formally defined task, all contacts can be found on the beamline webpage): Luciano Lizzit – luciano.lizzit@elettra.eu

Brief introduction to the technique and its application to battery studies

The SuperESCA beamline implements high-resolution core-level photoemission spectroscopy (HR-XPS). This method allows in-depth investigations on the electronic and structural properties of a variety of samples, ranging from single crystals to thin films and nanostructured materials. The beamline has been designed primarily for soft X-ray photoemission experiments on surfaces. SuperESCA combines high resolution capabilities with a high flux of linearly polarised photons in the 90 to 1500 eV range, allowing to obtain high-resolution spectra also for low-density systems and to follow in real-time surface processes and reactions. Moreover, the beamline has XPD capabilities.

Attention of the battery community to high-resolution, synchrotron-based XPS has been recently called.[110] Only limited amount of XPD work has appeared in the literature directly addressing battery materials (graphite anode lithiation,[111]) but the importance of achieving site-sensitivity in XPS by XPD for spinel-based LIB cathodes has been recently emphasized in the framework of methodological work on spinels.[112]

Description of the Instrument

In order to achieve high energy-resolution, keeping at the same time a high photon flux, the light

produced by the insertion device is collected, monochromatized and brought to the experimental station following a prefocusing-monochromator-refocusing scheme.

SuperESCA and ESCA Microscopy beamlines share the same insertion device: a linear planar undulator (for more details, see section on ESCAMicroscopy@Elettra).

The radiation is dispersed with a plane grating monochromator (resolving power $(E/\Delta E \sim 10^4)$) and focused into the exit slit, the aperture of which can be adjusted to optimize energy resolution and flux. The energy resolution can be further improved by acting on a set of baffles placed along the optical path inside the monochromator, in order to reduce stray light.

The end-station consists of two UHV preparation and analysis chambers. The preparation chamber hosts a sputter gun (ion beam energy $0.1 \div 3$ keV) and a gas line for standard cleaning procedures. The chamber is also equipped with a plasma source that can be employed for sample functionalization. Moreover, a number of ports is available for the installation of evaporation systems, giving the possibility to prepare samples, such as thin-films or supported nanoparticles. The analysis chamber is made of μ -metal and it is equipped with a 150 mm HSA with variable entrance slit and a custom-developed delay line detector. A LEED system, a monochromatized electron gun, a gas inlet system and a mass spectrometer are also available.

Two different sample environments are available:

1. A manipulator with 5 degrees of freedom, generally used for angle resolved measurements (XPD). It is equipped with a liquid N₂ cryostat and an electron-bombardment heating system, which allow heating the sample in the range $120 \div 1500$ K.
2. A liquid He cryostat with xyz translations and 1 rotational axis. The sample is heated by electron bombardment and temperature can be stabilized in the range $15 \div 1500$ K.

SuperESCA also features a branch-line - currently under construction - hosting the Combined Spectroscopy and Microscopy on Surfaces (CoSMoS) end-station, including:

1. A photoemission chamber equipped with an electron energy analyzer with spin detection system and standard preparation tools and lab sources: sputter and flood guns; monochromatized Al K α /Ag L α (~ 2.98 keV); high power UV-lamp). The sample is supported by a five-axis manipulator with cooling capabilities down to 80 K and heating up to about 1300 K;
2. A variable temperature ($80 \div 600$ K) STM;
3. An MBE system with LEED, RHEED, thickness monitor, RGA, 6 evaporation cells, and a RF discharge plasma source.

Key activities of Instrument

SuperESCA is an excellent tool for XPS investigations of the correlation between structural and electronic properties of surfaces and nanostructured materials surface and for the structural determination of thin-film, using X-ray photoelectron diffraction. Typical research topics range from surface physics and chemistry to material science and nanotechnology. Specifically: catalytic reactions on single crystals and model catalysts; growth and characterization of low-dimensional systems (graphene, hexagonal boron nitride and supported nanoclusters), including hydrogen-storage materials; ferroelectric, photovoltaic and photoelectronic materials.

Actual state of the art of battery studies

Over the last few years only a limited number of applications has been received for the battery community that have not been granted beamtime. Confidentiality makes this information reserved prior to the publication of the related studies. Apart from the received proposals, no other contacts have been established regarding electrochemical topics.

Possible adaptation of the facility to battery

The beamline staff would be interested in developing electrochemical cells and instrumentation, in particular with e-transparent graphene window. See Section on ESCAMicroscopy for more details.

Interest of the facility in prospective battery studies

The beamline staff expresses interest for future research in the field of batteries or related topics.

2.5.11. TwinMic beamline

Responsible: Alessandra Gianoncelli – alessandra.gianoncelli@elettra.eu

Brief introduction to the technique and its application to battery studies

TwinMic is a soft-X ray microscope that integrates the advantages of complementary scanning and full-field imaging modes into a single instrument. The uniqueness of X-ray microscopy results from the combination of different features:

1. Shorter wavelengths allow higher optical resolution (typically, 10 times higher) compared to visible light microscopy;
2. High X-ray penetration power gives deeper insight into samples, avoiding in many cases specimen slicing, that is generally required for TEM;
3. The electronic structure of atoms provides element-specific fingerprinting, allowing to combine X-ray microscopy with X-ray spectroscopies.

TwinMic has already hosted several investigations related to electrochemistry for energy, and to batteries in particular (see dedicated Section below).

Description of the Instrument

The light source is a 1m short undulator, featuring a brilliance similar to that of conventional undulators, but higher in angular divergence, highly suited for the twin microscope concept and facilitating the combination of complementary imaging and spectromicroscopy modes.

The beamline is equipped with a variable-angle plane grating monochromator, with high energy resolution in the range 400 ÷ 2200 eV.

The end station TwinMic has the unique capability to operate both as a transmission X-ray microscope (TXM) and as a scanning TXM (STXM). Both modes can be employed to implement coherent diffractive imaging approaches.

Key activities of Instrument

TwinMic combines high lateral resolution with X-ray absorption contrast, in particular between organic matter and water that allows imaging of specimens in their natural liquid environment. The highest lateral resolution can be achieved with the full-field imaging mode, which is currently about 20 nm using special objective lenses. Other imaging modes require optimization of X-ray intensity and chemical sensitivity, and generally allow micrometric and sub-micrometric lateral resolution. Typical research fields are: biotechnology; nanotechnology; environmental science and geo-chemistry; clinical and medical applications; novel energy sources; biomaterials and cultural heritage and archaeometry.

Actual state of the art of battery studies

TwinMic systematically hosts electrochemical work, including investigation of batteries. Battery studies have concentrated on zinc-air systems that have been investigated both by direct-space [113, 114] and coherent diffraction imaging [115, 116] approaches. Other electrochemical topics comprise: electrocatalysis, [117] fuel cells, [118, 119] electrodeposition [120] and corrosion [121].

Possible adaptation of the facility to battery

TwinMic staff is highly interested in improving and engineering the electrochemical wet cells that have been pioneered at this beamline [122] and to implement microfluidic capabilities. Moreover, there is high motivation to further develop the in situ CDI approach that, again, has been pioneered in this laboratory [123, 124]. As far as the beamline is concerned, a desirable upgrade may include a multilayer monochromator or a new grating for imaging and spectroscopic modes requiring higher flux and lower energy resolution (dynamic imaging and X-ray micro-tomography).

Interest of the facility in prospective battery studies

TwinMic is already actively involved in battery studies, and is strongly motivated to continue and extend them. This beamline has been granted a CERIC PhD scholarship for battery studies: the related activities will start in November 2020.

2.5.12. X-ray Absorption Fine Structure (XAFS) beamline

Responsible: Giuliana Aquilanti – giuliana.aquilanti@elettra.eu

Description of the facility:

The XAFS beamline is dedicated to x-ray absorption spectroscopy. It is installed on a bending magnet source and it was designed to cover a wide energy range, from 2.4 to 27 keV.

Being site selective and having local character, this technique provides information at the same time on the electronic structure and on the local environment of the absorbing atom.

Different collection modes are available. Transmitted photons are measured using three ionization chambers in series, allowing to record simultaneously the XAS spectrum from the sample and from a reference. A Silicon drift detector is used to collect the fluorescence photons, in case of diluted or too concentrated samples. Moreover, a converter total electron yield can allow collecting the secondary electrons and therefore to have access to the surface information.

Several sample environments are available (including furnace, liquid-N₂ cryostat and cells for liquid samples). In this way, XAFS beamline meets the needs of a large number of researchers in the area of conventional x-ray absorption spectroscopy.

Actual state of the art of battery studies:

The XAFS beamline has been widely exploited by the battery community, as more than 1/3 of the users in the last 3 years have used the beamline to carry out experiments regarding battery research. In particular, four different CERIC-ERIC users (R. Dominko, M. Giorgetti, L. Stievano and S. Brutti) performed operando XAS experiments, often coupled with XRD on the MCX beamline [101].

Those users have a long-date fruitful collaboration with the beamline staff, participating to the technical improvements as for example in the framework of the EuroLis project, where a special setup for Sulphur K-edge (2.4 KeV) XAS measurements has been developed [125].

Possible adaptation of the facility to battery studies

A better performing fluorescence detector, such as a Si drift with 7 channels, could improve data quality and speed-up data acquisition.

Interest of the facility in battery studies and perspectives

Thanks to the accessible energy range, the XAFS beamline covers the principal needs for battery research. In particular, XAFS has played an important role in supporting the research on the Li-S batteries due to its high stability and reproducibility at S k-edge energy.

The beamline has recently submitted 2 proposals for a PhD fellowship, one dedicated to recovery and characterization of layered oxides materials from spent batteries, and another for the characterization of newly synthesized Prussian blue analogues for battery applications.

2.5.13. X-Ray Diffraction 1 (XRD1) beamline

Responsible: Maurizio Polentarutti – maurizio.polentarutti@elettra.eu

Description of the facility:

The XRD1 beamline has been designed in collaboration with the Istituto di Cristallografia - CNR primarily for macromolecular crystallography, but the characteristics of the beamline permit to perform a wide variety of experiments. The light source is a multipole wiggler with a useful range from 4 to 21 keV, allowing the optimization of the anomalous signal of several heavy atoms (up to the calcium edge), and offering the enhancement of the Sulphur anomalous signal. Moreover, such wide energy range allows both reflection and transmission geometry, for a tunable penetration depth.

The experimental setup consists in a Huber goniometer with θ geometry fully controllable from remote.

An Oxford Cryostrem 700 allows cooling the sample in the temperature range 80–400 K.

Two XRD detectors are available. A classical MAR165 with 2.5 s readout is offline, but still working. A 2D PILATUS detector with 3 ms readout at 12 Hz frame rate, allows following structural transition, preferential orientation and degree of order in the material. In addition, a Si drift detector for fluorescence measurements is installed.

A high-throughput data acquisition is achieved using the mechanical robot developed on the beamline to

change automatically the capillaries under the beam.

The beamline hosts small molecules, protein crystallography, powder diffraction, high-pressure physics and solid-state experiments.

Actual state of the art of battery studies:

The XRD1 beamline has been highly demanded by the CERIC-ERIC users but not for battery research. At present, Elettra users have performed experiments on the structural evolution upon charge/discharge in battery.

Possible adaptation of the facility to battery studies

Thanks to the energy range and 2D detector, the beamline can be exploited for operando XRD studies on batteries.

A multi-holder dedicated to electrochemical cells could be developed for collecting data on different cells during the same experiment.

Interest of the facility in battery studies and perspectives

The beamline staff is interested in developing the battery research activity.

2.6. Poland

Directors: Marek Stankiewicz – M.J.stankiewicz@uj.edu.pl

Deputy director: Michał Młynarczyk – michal.mlynarczyk@uj.edu.pl

Responsible for Cryo-EM: Sebastian Glatt - sebastian.glatt@uj.edu.pl

The polish partners contribute to the offer of CERIC-ERIC via three instruments located at synchrotron SOLARIS: a Cryo-EM and two operating beamlines.

2.6.1. Cryo-Electron Microscope

Responsible: Sebastian Glatt - sebastian.glatt@uj.edu.pl

Description of the facility:

State-of-art cryo transmission electron microscope FEI Titan Krios 3Gi enables researchers to look at the frozen macromolecules with resolution of about 2Å.

Actual state of the art of battery studies:

The laboratory is dedicated to biological samples, therefore no proposals have been received from the battery community.

Possible adaptation of the facility to battery studies

Some recent studies [126] show that the cryo-EM can be also applied to electrode materials, as the low temperature reduces the radiation damage due to the 300 KV electron beam.

Interest of the facility in battery studies and perspectives

The instrument staff is not interested in developing battery research, as the instrument is massively required for biological studies.

2.6.2. Ultra Angle Resolved Photoelectron Spectroscopy beamline

Responsible: Jacek Kolodziej – jacek.kolodziej@uj.edu.pl, Natalia Olszowska natalia.olszowska@uj.edu.pl

Description of the facility:

The UARPES beamline is an experimental installation for studies of the electronic band structure of solid surfaces. The beamline is designed for the energy range 8 – 100 eV, providing high photon flux, high resolution, and variable polarization, with minimalized harmonic contamination.

The experimental end-station is composed of several ultrahigh vacuum chambers for sample processing and analysis, as well as devices for sample storage and transfer. Cryogenic, 5-axes manipulator is capable of stabilizing the sample temperature in wide range, as well as of precise positioning of the sample surface for experiments.

State-of-the-art electron energy spectrometer VG SCIENTA DA 30L is capable of massively parallel recording data with a resolution of 1.8 meV. Low energy electron diffractometer (LEED), with an image amplifier, is available for a precise sample orientation and for surface structure studies.

The beamline's staff is working to extend the photons energy range up to 400 eV.

Actual state of the art of battery studies:

An experiment from CERIC-ERIC users was performed in 2018 but it was not related to batteries.

The technique is not suitable for studies on battery materials, which are polycrystalline.

2.6.3. Photoemission Electron Microscopy / X-ray Absorption Spectroscopy beamline

Responsible: Marcin Zajac – mar.zajac@uj.edu.pl

Description of the facility:

The PEEM/XAS beamline is dedicated to microscopy and spectroscopy in the absorption of soft X-rays (200–2000 eV) and is equipped with two end-stations: a photoemission electron microscope (PEEM), and a universal station for X-ray absorption spectroscopy (XAS).

- The PEEM end-station is a fully equipped "surface science laboratory". It includes a load- lock and an entrance chamber for fast sample transfer from air into the ultrahigh vacuum (UHV) environment, a preparation chamber, the main microscopic chamber.
- The XAS end-station is a UHV system equipped with two-chambers (one for spectroscopy and other for preparation). Total electron yield, partial electron yield and total fluorescence yield detectors are available.
- The preparation chamber includes LEED and Auger spectrometers, several evaporation sources, an ion sputtering source, and a gas dosing system, thermal annealing process up to 2000 K. An

additional evaporation source is mounted in the main chamber for real time microscopy during the deposition.

Actual state of the art of battery studies:

Up to now there were only few applications in the batteries and solar cells field. Two proposals were from CERIC consortium and two as part of Solaris call.

From CERIC groups one proposal was related with photovoltaic material (it was performed in November 2018). The experimental group were well prepared and the samples were deeply pre-characterized. The second proposal topic (related with battery research) was not accepted due to lack of the beamtime available at XAS beamline.

There is not dedicated laboratory or equipment for the batter research at the beamline. Basic equipment at the facility (like glove-box and laboratory for sample preparation) will be probably available in the next year time period.

Possible adaptation of the facility to battery studies

The soft-XAS technique is interesting for battery studies.

Interest of the facility in battery studies and perspectives

The beamline staff is interested to potentiate the battery research activity, by providing in the next year some equipment dedicated to sample preparation.

2.7. Romania

Director: Ionut Enculescu – encu@infim.ro

Deputy director: Corneliu Ghica – cghica@infim.ro

2.7.1. Laboratory of Atomic Structures and Defects in Advanced Materials (LASDAM)

Responsible: Corneliu Ghica – cghica@infim.ro

Description of the facility:

As part of the National Institute of Materials Physics, the LASDAM has a strong expertise in solid state physics and materials science, with a research activity related to the study of the physical properties (structural, optical, electrical) of advanced materials (dielectrics, semi-conductors, alloys, ceramics) for various applications (semiconductor technology, gas sensing, radiation detectors, telecommunications).

A wide variety of investigation techniques materials synthesis, processing and characterization are available at LASDAM, such as:

- Transmission Electron Microscopy (TEM/HRTEM, STEM, EFTEM, EELS, EDS).
- Scanning Electron Microscopy and Focused Ion Beam (SEM-FIB, EDS, EBSD).
- Powder, thin film and single crystal X-ray diffraction (XRD).

- Multifrequency Electron Spin/Paramagnetic Resonance (ESR/EPR) spectroscopy.
- Mössbauer spectroscopy (57Fe, 151Eu, 119Sn, TMS, SMS and CEMS) techniques.
- Optical spectroscopy (absorption and emission).

The LASDAM offers the possibility of open access through CERIC to only two of the experimental facilities available at the laboratory, namely TEM and EPR facilities. The Mössbauer and X-ray diffraction facilities are not included in the agreement with CERIC.

Actual state of the art of battery studies:

At this moment, TEM and EPR facilities are not involved locally in projects dedicated to batteries. However, they had some contributions in projects not strictly related to batteries, but to the general topic of electrical energy storage and conversion (piezoelectric materials, capacitors, fuel cells, hydrogen storage, etc.).

Concerning specifically the batteries topic, two TEM investigations have come via CERIC: one application by Marco Giorgetti (Univ. Bologna) entitled "High energy cathode material at work: structure and morphology checked by in situ XAS, in situ XRD and TEM" (proposal no. 20172042) was already carried out, while a second proposal by Mohamed Al-Hada (Univ. Cambridge, proposal no. 20197115), entitled "*In situ laterally resolved photoemission spectroscopy characterization of LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811) positive electrodes for lithium ion batteries (LIB)*" is scheduled for the current semester.

Other techniques available at LASDAM (such as, for instant, Mössbauer spectroscopy and X-ray diffraction) could be also applied to the study of battery, especially for in situ studies of battery materials in the development of an adapted sample environment and in situ electrochemical cells.

Possible adaptation of the facility to battery studies

Actual appropriateness of the techniques: both TEM and EPR are both techniques of interest for the study of battery materials. Even though this field of research is not among those developed originally at LASDAM, some of the proposals that are arriving through CERIC- ERIC are concentrated on the use of TEM for batteries.

Actual appropriateness of the sample environment: The LASDAM does not actually provide an appropriate sample environment for battery research. No dedicated glove box, potentiostats or in situ cells are currently available.

Interest of the facility in battery studies and perspectives

No specific interest in this field of research was underlined, but the facility is open to host studies on new research themes.

2.8. Slovenia

Director: Janez Plavec – janez.plavec@ki.si

Deputy director: Primoz Sket – primoz.sket@KI.si

Responsible solid state NMR: Gregor Mali – gregor.mali@ki.si

Slovenia participates to CERIC-ERIC by sharing several NMR spectrometers hosted by the Slovenian

NMR Centre in Ljubljana.

2.8.1. Slovenian NMR Centre (Ljubljana, Slovenia)

Responsible: Janez Plavec – janez.plavec@ki.si

Description of the facility:

The Slovenian NMR Centre is a national facility that offers infrastructure and expertise in the field of liquid and solid state NMR spectroscopy to scientists and researchers in academic and industrial institutions. NMR centre was founded by Ministry of Higher Education, Science and Technology of the Republic of Slovenia on 17th of November 1992.

The Slovenian NMR centre is open to academic researchers and researchers from industrial partners. Research program of NMR centre includes data acquisition and interpretation for those who apply NMR in their research as part of basic and applied research projects or in industry itself. Annual research program is discussed and approved by the scientific council of NMR centre.

Actual state of the art of battery studies:

Continuous collaboration with Robert Dominko (same institute) for more than 10 years (1-2 common papers per year). This research touches many different areas of battery research (many different types of batteries), from various oxides, phosphates, silicates and sulfur-based batteries to organic batteries or their components.

Through CERIC, the Slovenian NMR Centre has been involved in 4 projects until now. Three were led by dr. Anastasia Vyalikh (TU Bergakademie Freiberg), and one by dr. Daniil Itkis (Lomonosov Moscow State University).

The research group around the facility (Department of inorganic chemistry and technology) does study energy storage based on water sorption in microporous materials.

The current solid-state NMR equipment comprises a standard-bore magnet and MAS probes with different rotor diameters (1.6 mm, 3.2 mm, 6 mm). The NMR centre itself does not own a glove box, but if necessary has access to the nearby glove boxes of the battery group.

The current solid-state NMR equipment comprises a standard-bore magnet and MAS probes with different rotor diameters (1.6 mm, 3.2 mm, 6 mm). The NMR centre itself does not own a glove box, but if necessary has access to the nearby glove boxes of the research group on batteries at KI.

Possible adaptation of the facility to battery studies

At the moment, no in situ /operando equipment is available for NMR measurements (all the measurements are performed ex situ). However, there are plans for upgrading the sample environment. For instance, the topic of the last "CERIC PhD proposal" submitted by the research group at the Slovenian NMR center was about developing operando NMR spectroscopy of batteries through the purchase of an in situ /operando probe (e.g., such as the one offered by the NMR service (see here for more details).

The Slovenian NMR Centre is actually in the middle of a large upgrade of the set of spectrometers. Included in this upgrade is the purchase of a new liquid NMR 600 MHz spectrometer and a new 400 MHz spectrometer, which is expected to perform both liquid and solid state NMR. The latter spectrometer can

in principle be efficiently coupled with the abovementioned in situ probe. According to the original plan, this upgrade should be finished within a few months, but because of the corona virus pandemic, it is actually in stand-by.

An additional upgrade is also planned in the long-term, involving the acquisition of two new spectrometers: a wide-bore 800 MHz solid-state NMR spectrometer, very convenient for in situ measurements, and of a 1GH z liquid NMR spectrometer, which could be useful for the study of liquid battery components.

Interest of the facility in battery studies and perspectives

The facility is already active in the field of battery studies, and is strongly committed in improving the analytical possibility in this field.

3. Techniques and facilities that should be included for the study of batteries that are not actually available in CERIC

3.1. Techniques

In this section, we propose some techniques that should be potentiated or included in the CERIC-ERIC consortium, both at laboratory and synchrotron.

3.1.1. Near-Ambient Pressure X-ray Photoelectron Spectroscopy

NAP-XPS is a characterization tool already available in the CERIC-ERIC consortium for battery research, but the dedicated staff is mostly involved in gas sensing, electrocatalysis and solar cell studies. Being so highly-demanded, the pressure for a proposal submission is quite high and only few shifts are distributed for allocated beamtime. For this reason, a second instrument committed by a new staff, would boost the battery research activity by proposing new technical developments and participating to the commissioning of new equipment.

3.1.2. Hard X-ray Photoelectron Spectroscopy

The application of photoelectron spectroscopy using hard X-rays (HAXPES) is becoming increasingly popular as a powerful spectroscopic tool in materials science. The success of HAXPES lies in the fact that, owing to its increased bulk sensitivity compared to classical XPS, the established strengths of conventional photoelectron spectroscopy for electronic and chemical structure investigations can now be applied to real functional materials. By increasing the inelastic mean free path of photoelectrons from 10–25 Å to 100–200 Å, this technique is particularly suitable to investigate battery electrodes showing anionic redox activity, where the charge compensation mechanisms are due to both cationic and anionic active sites, in order to minimize the surface contribution. [127, 128] On the other hand, the formation and growth processes of thick SEI - as a function of the potential and kinetics of electrolyte oxidation - can be directly studied using HAXPES, as proposed recently by Takahashi and coworkers [129].

The abovementioned studies were performed on *ex situ* electrodes, transferred from the glove box to the introduction chamber using a small SAS in order to prevent the air exposure. However, *in situ* / *operando* HAXPES measurements could be also done on a complete all solid state battery or micro-battery, where no liquid electrolyte is used. In this case, an appropriate cell holder needs to be design and developed to fit the manipulator constraints. While this technique is widely available in several synchrotron facilities (SOLEIL, ESRF, BESSY, PETRAIII), recently ScientraOmicron has proposed its own laboratory HAXPES setup, equipped with a Ga Kalpha source to achieve 9.25 KeV working energy.

Moreover, SPEC group proposes hemispherical energy analyzers with 2D Phoibos detector for photo- electron spectroscopy measurements in the pressure regime from UHV to near ambient pressure (NAP) and with a working energy up to 7 KeV, allowing therefore NAP-HAXPES measurements in *in situ* / *operando* conditions using a liquid electrolyte.

HAXPES is not available in the CERIC-ERIC consortium, neither as a synchrotron beamline nor a

laboratory equipment. It could be implemented as a future beamline in the framework of the Elettra upgrade or as a further instrument in the NAP-XPS laboratory, while in the first case the advantage of a tunable incident energy at synchrotron and the opportunity of a dedicated beamline staff will be beneficial for the battery research activity.

3.1.3. Beyond conventional soft-XAS

Soft X-ray absorption spectroscopy (sXAS) is an effective tool for quantitative analysis of the transition-metal states and surface chemistry, thanks to the surface sensitivity achieved by Total Electron Yield (TEY) measurements and the bulk information obtained in Total or Partial Fluorescence Yield (TFY, PFY) mode. However, the advent of anionic redox based compounds for battery materials has evidenced the limitation of conventional sXAS, because anions and cations have different atomic number with associated different probability of the decay channel, favoring Auger electrons for light elements and lower energy and promoting radiative decay for higher Z number and energy. Moreover, the fluorescence XAS measurements on too thick samples are highly affected by self-absorption effect, which determines a deformation of the spectrum. For those reasons, new approaches based on photon-in-photon-out technique are mandatory to fully explore the electrochemical mechanisms occurring in bulk as well as at the interphase.

Resonant and non-resonant inelastic X-ray scattering (RIXS and IXS) are a powerful probe of battery chemistry with superior sensitivity [130]. Such photon hungry technique has seen a rapid development with the advent of third generation synchrotron radiation facilities, and several RIXS beamlines operating in the soft X-ray are currently open to users. However, each beamline is designed to track a well-defined decay channel of the excited state with an energy ranging from meV (phonons, spin flip) to eV (charge transfer), which determines the energy resolution and acceptance of the installed spectrometer. Thanks to the high-efficiency full-energy-range RIXS spectrometer available on the 8.0.1 beamline at ALS synchrotron (USA) [131], mapping RIXS (mRIXS) has been successfully applied to battery studies. This technique has been able to carefully monitor the charge transfer excitation in ex situ cathodes, allowing to shed light on the complex charge compensation mechanism driven by both anionic and cationic redox activities [132, 133, 61, 134]. It is important to recall that, being based on the photons detection, mRIXS provides a bulk information compared by XPS. Moreover, the spectrum obtained by integrating the mRIXS intensity along the emission energy is not distorted as in conventional TFY [130].

Another interesting application of mRIXS is to detect the subtle chemical composition of the SEI, which governs the electrochemical performances in battery. Usually a combined approach based on TEY and TFY allows discriminating the composition of the SEI as a function of the different probe depths. However, the chemistry at the interface of two chemical species only shows subtle but critical difference compared with the bulk materials involved. For example the ion-solvation shell in liquid electrolyte, where the molecules in the solvation shell (the "interface" between ions and liquid) are essentially the same as in the bulk electrolyte, is technically challenging to detect by conventional TFY. In this case, the emission spectra collected by RIXS are more sensitive to the difference between the solvent and the ion in the solvation shell [135] while conventional sXAS spectral lineshape does not change.

While inherent requirement of ultrahigh vacuum for most soft X-ray experiment makes difficult the operando studies, the presence of a solid electrolyte in all-solid state battery is naturally a blessing for real-world experiment. In addition to the redox activity of electrodes, if the electrode deposition is

controlled to achieve an electrode thickness of less than 100 nm, in-situ/operando experiments could reach the electrode-electrolyte interface directly [136].

An elegant and reliable method to probe bulk-sensitive soft edges for elucidating anodic and cathodic charge compensation contribution via IXS so-called also Raman X-ray scattering spectroscopy. By using a hard X-ray incident beam, this technique circumvents surface limitations and is practically free of self-absorption due to its non-resonant nature. In addition, it does not require complex sample preparation or experimental setups, making it an ideal tool for potential in situ analysis of the electronic structure of electrode materials. In a recent study, bulk soft edges of both oxygen and transition metal (iron) of the cathode material $\text{Li}_2\text{FeSiO}_4$ was performed during one complete electrochemical cycle concurrently, showing that the redox mechanism relies primarily on the iron contribution. Nevertheless, a change in electron confinement of the oxygen suggests its active involvement in the charge compensation process (anodic) [137].

Being photon hungry technique, RIXS and generally all the techniques based on second order process need the high brilliance of third and fourth generation synchrotron radiation sources. For this reason, the Elettra Upgrade is a breeding ground for a brand new RIXS/IXS beamline dedicated to battery research.

3.1.4. X-ray Computed Micro-Tomography (XCMT)

In the last decade XCMT has progressively emerged as a powerful method to study batteries, in principle allowing nondestructive imaging of intact devices at any stage of their operational life, with in situ and in operando. XCMT enables analyses of structure at scales ranging from submicron to fractions of millimeter, with spatial resolution that anticorrelates with the probed sample volume. A potential CERIC partners based at the Elettra site, could be the synchrotron beamline SYRMEP@Elettra (coordinator: Giuliana Tromba – giuliana.tromba@elettra.eu) and the offline TomoLab laboratory (coordinator: Lucia Mancini – lucia.mancini@elettra.eu)

Pioneering XCMT studies addressed ZEBRA [138] and alkaline Zn [139] systems, while more recently much work has been devoted to the more popular LIB (for an overview, see [140, 141]). The structure of LIB has been studied, both statically and dynamically, at the following specimen lengthscales: whole cell (ca. 1 cm), electrode (ca. 100 μm) and single-particle of cathodic material (ca. 10 μm). The key topics investigated at the cell scale include: arrangement and degradation of components [142]; electrode thickness and its variations [143]; formation of hot spots [144]. A novel “virtual unrolling” methods has been developed for the investigation of commercial batteries, allowing to gain quantitative information about local mechanical conditions and detachment of active components at the device scale [73]. Microscopic studies have addressed both electrode and single-particle structures. In particular, research has focused on the characterization and tracking of particle packing and porosity with battery operation, quantifying changes in particle volume, particle shape, pore volume, surface area and tortuosity [145, 146, 147]. Moreover, the mutual adhesion of active particles, electronically conducting additives and binder has been investigated [148]. Dynamic investigations at the electrode scale have involved: crack formation [149, 150], delamination [151], the differentiation of the behavior of active material between the electrode/electrolyte and electrode/current collector interfaces [152, 153] and growth of Li dendrites [154]. As far as dynamical studies of single particles are concerned, lithiation has been followed by monitoring the expansion [150] and phase changes [149] of single host particles. Special attention has been devoted to the analysis of degradation, with studies of: thermal runaway

[155]; gas evolution [156] and elemental segregation in cathodic compounds [157].

A close-knit group of mainly very recent publications has demonstrated that XCMT can provide powerful handles to gain insight into a range of materials science aspects of Zn-based batteries. Primary [140] and secondary [158] commercial Zn–MnO₂ alkaline batteries were investigated *in situ* at different depths of discharge (DOD) at the mesoscopic and full-cell scales. Manke et al. [139] used synchrotron-based XCMT to highlight the spatial and size distribution and oxidation progress of zinc particles and the swelling and breaking of cathodic MnO₂, while Osenberg et al. [105] used lab-based XCMT to observe changes in 3D morphology of the zinc anode and the MnO₂ cathode, in dependence of the position inside the cell. Variations of zinc particle size, involving layer-by-layer dissolution and progressive cycling-induced shrinking were disclosed. In addition, cycling leads to MnO₂ cracking and changes in separator shape. Artl et al. [159] and Schmitt et al. [160] studied commercial button-cell ZABs at different DODs with lab-based XCMT and used imaging results to validate multi-physics mathematical models of material evolution and cell voltage. The former work is centred on discharge and presents a pointwise model, while the latter subjected a primary cell to cycling and describes a 2D model. Artl et al. [159] followed the Zn oxidation-rate distribution at battery and single-grain scales: Zn particle oxidation was found to proceed according to shrinking-core mode. Schmitt et al. [160] used XCMT mainly for model validation in terms of distribution and fraction of Zn particles with DOD. ZABs were studied also in cells specifically designed for *in situ* XCMT. [161, 162, 163, 164] Schröder et al. [161] carried out *in situ* lab-based XCMT analyses of a primary ZAB, with the main purpose of imaging the penetration of electrolyte in the GDL, as a function of DOD. Battery end of life was shown to be due to blockage of oxygen transport path caused by electrolyte flooding. Franke et al. [162] as well as Christensen et al. [163] followed the cycling of secondary ZABs by *in situ* XCMT at the mesoscopic and mm scale: the former study employed a lab-based device and the latter used synchrotron radiation-based instruments. Franke et al. [162] reports that cycling causes changes in morphology of zinc and air electrodes. In addition, electrolyte loss, zinc movement into the catalyst layer and gassing, were imaged and correlated with the progress of cycling. Christensen et al. [163] combined *in situ* XCMT with X-ray diffraction to monitor the space- and time-dependent conversion of Zn and ZnO during cycling. Titscher et al. [164] worked with a model ZAB whose anode consisted of zinc particles supported onto copper foam and Ni-cloth O₂ electrode, and followed with a lab-based XMCT system the evolution on the cell scale of zinc and zinc oxide components, resulting from a charge/discharge cycle. Bozzini et al. [165] studied the anodic hopper and the air cathode of a Zn-air fuel cell by lab-based XCMT. Pore occlusion of the gas-diffusion cathode was observed, due to the accumulation of zincate- related precipitates, deriving from the electrolyte crossing the separator. Moreover, by imaging the whole anode–cathode interface, the changes in size distribution was evaluated of residual, initially monodisperse anodic Zn particles, caused by the details of the current density heterogeneities of the anodic hopper. Yufit et al. [166] employed *in situ* synchrotron XCMT for a multiscale analysis of Zn dendrite formation, that allowed to pinpoint the local dendrite growth rates and shapes peculiar to initial growth, regrowth after dissolution, and growth through a porous separator. Recently, the morphochemical changes of Zn-sponge anodes upon cycling was followed *in situ* by lab-based XCMT. [167]

A similar approach has also been applied to the study of other battery systems [168, 169, 170, 171].

3.1.5. Mössbauer spectroscopy

Among the various characterization tools, Mössbauer spectroscopy is a well-known technique to provide

valuable information about valence state and bonding within a material as well as to study Li-driven local structural change in electrode materials. Therefore, this requires that the studied materials contain the right chemical elements. This turns out to be the case with:

1. The many different Sn-, Sb- and Fe-based negative electrode materials that can react towards Li at low potential with staggering capacity gains as compared to today carbon-negative electrodes;
2. The advent of positive electrode materials based on Li such as $\text{Li}_2\text{FeSiO}_4$ or LiFeP_2O_4 with the latter being amongst the most praised materials for high volume storage applications;
3. The development of alternative battery systems, such as Na-ion or Mg-ion batteries, which might also employ such Sn-, Sb- and Fe-based electrode materials.

A few of the aforementioned materials have reached market places, and it is not overstated to say that their rapid implementation was made possible owing to the great help already provided by Mössbauer spectroscopy in tuning their synthesis process or tracking their local structural changes during their electrochemical reaction towards Li (or Na). Examples enlisting the benefits of Mössbauer spectroscopy to the field of Li-battery research are many, and among them one can remember:

- The iron phosphate- and iron sulphate based positive electrode materials for Li- and Na-ion batteries, mostly working on the iron redox couple $\text{Fe}^{3+}/\text{Fe}^{2+}$; [172, 173, 174, 175, 176, 177, 178, 179].
- The iron-containing layered oxides, including the Li-rich ones, used as positive electrode materials, where Mössbauer spectroscopy helped unveiling the participation of iron to the redox mechanism and following its evolution along different oxidation states varying between Fe^{2+} and Fe^4 ; [180, 181, 182, 183].
- The tin containing negative electrode materials, based on alloy and/or conversion reactions. [184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197].

Based on the vast literature, it is clear that Mössbauer spectroscopy has already been of great help to the battery community to study the electrochemical mechanisms of these materials, unveiling the formation of transient or parasite species, providing vital information on their cycle life behaviour and relaxation, helping optimising both the synthesis techniques and the electrode materials performance. The use of high energy γ -rays enables the complete monitoring of complete cells when used *in situ* or *in operando* configurations. Moreover, it enables gathering basic structural/textural/ physical information at the atomic scale that provides a solid and valuable scientific ground to better predict/optimize and design highly performing nano-electrodes/ electrolytes components to use in the next generation of LIB and post-Li-ion batteries.

One of the drawbacks of Mössbauer spectroscopy is the long time scale requested for collecting a spectrum with a satisfying signal-to-noise ratio. For example, the measurement of an *in situ* ^{57}Fe Mössbauer spectrum of a battery containing a very thick positive electrode (about 20 mg cm^{-2}) of LiFePO_4 naturally enriched in ^{57}Fe (about 2 % of the total Fe) requires at least 2 hours. This means that, to perform such measurements along a charge/discharge process, it is necessary either to stop the electrochemistry for measuring enough spectra, or to use samples enriched in ^{57}Fe , which are more expensive and complicated to produce. A possible alternative is also the use of synchrotron radiation

techniques based on the Mössbauer effect, which provide similar information, such as Nuclear Forward Scattering. [198, 199] Unfortunately, only few synchrotrons allow accessing this kind of techniques (such as, for instance, the Nuclear Resonance Beamline ID18 at ESRF).

Mössbauer spectroscopy is currently not available in the CERIC-ERIC consortium, neither as a synchrotron beamline nor as laboratory equipment. This technique is however available at LASDAM, at least concerning the measurements of ^{57}Fe Mössbauer spectra. It could be thus implemented, at least for ex situ measurements. Even though this laboratory has no known experience in the study of battery materials using the Mössbauer effect, such new application skills could be developed in the future through adapted collaborations with institutes already mastering its application in the field of batteries (and already possessing adapted in situ tools). The availability of such a lab-based technique will be surely beneficial for the development of the battery research activity in Eastern Europe countries.

3.2. New support laboratories

Supporting laboratories dedicated to the samples and electrochemical cell preparation have a central role in boosting the battery research activity. In fact, being the electrodes and the electrolytes air sensitive, they need to be manipulated in a controlled atmosphere environment, such as an argon-filled glove-box with an accurate check of oxygen and moisture content. Moreover, each technique available in CERIC-ERIC requires a specific sample preparation and cell assembling due to the geometrical and environmental constraints (UHV environment, energy range, detection mode, sample position, etc.), therefore the presence of well-equipped laboratories improves the synergy between the user and the facility, yielding a successful experiment.

It present, some CERIC-ERIC facilities can benefit of the presence of supporting laboratories in their institutions, as in case of the NMR laboratory at the Ljubljana Chemistry Institution and the SAXS laboratory at TU Graz; probably a chemistry laboratory will be available next year at SOLARIS synchrotron, serving also the two beamlines included in the consortium. However, an appropriated supporting laboratory is still missing at Elettra synchrotron, while several beamlines are currently involved in battery research: the users bring their own potentiostat and cells; when a controlled atmosphere is required for cell assembling or sample handling, no glove-box is easily reachable.

Therefore, one supporting laboratory should be available for each institution, in order to fulfil the needs of the groups hosted in the same institution.

As a minimal equipment for an effective supporting laboratory, we suggest to install a glove-box, a potentiostat (with low current and high current channels), and an oven to dry the components to assemble the cell. A survey among the potentially interested users and the instruments staff is suggested to have a complete list of desired equipment.

As previous mentioned, the development of performing electrochemical cell strongly depends on the applied characterization technique and is a crucial point to boost the research on battery. [200, 201, 202, 203, 136]. In particular, the cell design is driven by the constraints imposed by the technique fitting the electrochemical performances, leading for example to specific X-ray transparent windows, geometry and printed circuit for electrolyte flowing. It is important therefore to create a link between the groups, which have complementary skills in fabrication of electrochemical cells, in order to promote their synergy and to develop new or more suitable electrochemical cells. With this aim, a supervisor (internal or external to CERIC-ERIC) having experience in electrochemistry and characterization techniques can

coordinate such activity: he would be always aware about the current and future developments and ready to share its expertise and competences. As first initiative in this direction, a sort of "cell pool" within the CERIC- ERIC consortium would promote the development of multi-techniques cells, which can be adapted from one technique to another one with similar constraints without major changes.

3.3. Calculation needs and facilities

3.3.1. Data reduction

The rapidly growing number of operando spectroscopy analyses has helped unravelling the electrochemical mechanism of lithium and post-lithium battery materials. The corresponding experiments usually produce large datasets containing many tens or hundreds of spectra. A suitable strategy for their treatment in a reliable way and within reasonable time frame is based on an innovative chemometric approach, allowing one to extract all meaningful information from such data by a combination of Principal Component Analysis (PCA) and multivariate curve resolution (MCR) [204, 205]. Since only the bilinearity assumption is required, this approach is not depending on the experimental details and can be applied to any dataset from a wide range of spectroscopy techniques, as already reported for battery studies using Mössbauer spectroscopy, X-ray absorption spectroscopy or transmission soft X-ray microscopy [206]. Some MATLAB routines with a user-friendly interface are available for PCA and MCR-ALS analysis [207].

However, before moving to the chemometric analysis, the raw data needs to be treated in order to obtain a suitable data matrix, which represents the input of PCA and MCR-ALS methods. Unfortunately, this step is still depending on the applied technique and specific tools are required.

3.3.2. Theoretical calculations

The deeper understanding of the electrochemical mechanisms can be achieved by combining the experimental results with theoretical calculations. For example, the emerging of anionic redox has asked for a new theoretical paradigm based on the reductive coupling between the cationic and anionic site [208, 209, 210]. Molecular dynamics simulations have better explained the electrical double layer behaviour than standard mean-field theories [211], which is of capital importance to understand the electrode-electrolyte interaction [212]. Multiscale physical modelling techniques, spanning scales from few atoms to the device level, can advise about the materials behaviour and aging and how components with optimal specifications could be made and how they can be integrated into operating devices [213]. A theoretical support proposed by the CERIC-ERIC consortium would bring added value to the experimental studies, since actually it depends only on user individual collaborations.

For the sake of completeness, innovative approaches based on integrated high-throughput methods and artificial intelligence have gaining ground for accelerating the discovery of new materials for batteries.

Machine learning based methods are exploited for a screening among the possible structures and related chemical properties; only the most promising materials are synthesized and tested in a battery, avoiding time-consuming experiments; moreover, the high-throughput approach brings out the most relevant hidden features for each dataset, allowing to discriminate between the different functionalities [214, 215,

216].

For this goal, sophisticated data infrastructure and interchange platforms are necessary, requiring a massive technological and financial support.

3.4. Communication and user assistance

The key point that emerged from the present Battery Expert Group survey, is that there is **much scope as well as much potential interest** in battery work at the CERIC partner facilities, but, on the one hand **coordination**, and on the other hand **synergy** are still significantly **wanting**. In particular, the **multi-technique approach that is the unique to CERIC has been poorly exploited** in this field, so far.

What CERIC would need, is a series of clear and simple actions able to **turn this potential into action**.

As detailed in this Report, most of the available Instruments and Beamlines implement techniques that can potentially strongly contribute to cutting-edge battery research. Nevertheless only 21% have actually carried out directly battery-related work, 26% have made experiments in fields indirectly related to them, but only 13%, combining both these categories, gained access through the CERIC scheme. In particular, only exceptional cases (8% of Instruments) have been reported successful multi-laboratory CERIC proposals from this community.

This situation seems to stem from the fact that battery Scientists, who are also users of a close-knit group of Instruments/Beamlines that are involved in the CERIC scheme, maintain well-established collaborations outside the CERIC network. These Colleagues are not particularly motivated to ease the access through the Consortium to a wider number of users in this field.

Establishment of a Technical Battery Advisory Board

During this survey, we have developed the conviction that the simplest and most effective approach to foster multi-technique access to Consortium Facilities from new members of the battery community, would be to **establish a Technical Battery Advisory Board (TBAB)**, that can offer **concrete support** to both users who are not converse with the methods, and, on the other hand, to Beamline/Instrument Scientists who are not electrochemists. TBAB members should be colleagues that have personal hands-on expertise with electrochemical work and experiments at relevant, or related, facilities.

From the users' side, the TBAB can advise battery groups that would need the kind of information provided by the available methods, but have limited in-house knowledge of the relevant technicalities (e.g., opportunities / constraints / requirements of in situ and in operando measurements, cells, sample environment) and help them to interact with the Beamline/Instrument Scientists, to prepare and organize their experiments and to write their proposals. Special emphasis should be placed on suggesting multi-technique approaches, which are more and more necessary in cutting-edge research on batteries. Hopefully, this will create a CERIC Battery Network: at a later stage, if this concretely

happens, CERIC will find ways to formalize/strengthen it.

From the partners' side, the TBAB can help the Beamline/Instrument Scientists in developing cells or sample environments that can be attractive for battery researchers. In view of cooperation among CERIC partner Instruments these actions should favour access to multiple techniques (e.g., develop cells for different Instruments that will have the same electrochemical performance and generate comparable results).

Finally, the TBAB might play a role in attracting industrial users to the Consortium and related Battery Network.

Communication actions

Further to TBAB, other useful communication and user-support initiatives that we can foresee are listed below.

- i. A webpage of CERIC dedicated to battery work, presenting in a very light and legible way the kind of scientific information that can be achieved with the available techniques, and in particular with a multi-technique approach. Offer of help from the TBAB should be advertised.
- ii. The webpage could contain a series of virtual workshops (perhaps a YouTube channel) presenting CERIC's activities in the field of batteries and advertising synergistic use of CERIC's techniques. The same platform could contain videos with few-minute (less than 4 minutes, to be lightly accessible) presentations of battery papers based on CERIC facilities. CERIC users can be encouraged to produce their videos right from the proposal stage. This can be done, e.g., by notifying in the proposal form their availability to produce such a video in case results from a granted beamtime are published. We believe that virtual workshops would be much more effective than *de visu* ones, for obvious reasons of time and costs.
- iii. The webpage should also contain a complete and updated list of papers published under the CERIC access scheme. Of course, this option can extend to topic different from batteries, even though the existence of a dedicated "battery library" would help. An efficient search tool for the publication database would be extremely helpful to spot specific topics.
- iv. CERIC should endeavour to make presentations of the suite of facilities it can offer, at the main battery conferences / battery sessions of major electrochemistry congresses. This could go through two channels: an institutional one, i.e., CERIC people presenting the Consortium as such, and an indirect one, CERIC users presenting their results could be encouraged to add a couple of slides to their talks, in which they describe/advertise the Consortium.
- v. We have discovered that it is not easy to track CERIC-based experiments in published papers: users who have been granted CERIC beamtime should be more strongly encouraged to notify this in the Acknowledgment section of their papers. This requirement should be made mandatory by asking applicants to declare their acceptance of this condition in the proposal forms.

Funding actions

Funding of specific activities could foster battery activities at CERIC partner facilities.

➤ **Personnel costs: scholarships**

We believe that the recently activated scheme of funding a group of PhD scholarships for battery work across CERIC facilities is definitely worth continuing, because it helps creating/consolidating the network and forming research students who combine electrochemical and instrument skills, and will most probably continue this approach in their academic or industrial destinations after completion of their PhDs.

In addition to PhDs, post-doc scholarships would also be strongly effective in consolidating cross-technique activities and projecting young scientists towards scientific independence with the interdisciplinary culture that is, on the one hand, specific of CERIC and, on the other hand, unavoidable for next-generation battery research.

➤ **Funding for sample-environment development**

It would be very helpful to fund instrument-oriented activities aimed at battery work. These activities should favour in situ work, primarily in terms of fabricating cells and secondly of improving sample stages / end-stations and/or detectors. Ideally, the existence of adequate tools and of an experimental environment allowing in situ measurements that are available to users are likely to strongly enhance access of battery scientist who are not experts in specific techniques and do not possess in-house skills to design and fabricate their own sample environments.

CERIC might propose an internal competitive scheme to their facilities for access to this type of funding, perhaps in collaboration with Academic Colleagues that they can get involved with this aim. If funding is proposed to groups that can contribute in-house manpower, we think that grants of the order of EUR 50,000 could be a reasonable support for a single action.

Miscellaneous comments on communication

It is perhaps useful to note that, during our survey, we found varied scenarii of ease of access to facility information. In most cases, the websites were clear, informative and updated, but in some others, outdated information and inactive contacts could be found, which slowed our work. We can foresee that potential new users would find the same difficulties that we experienced.

As far as the responsivity of Instrument Scientists is concerned, in general the feedback to our requests of contact and information was immediate, while in a few cases it was sluggish or even completely missing. Also the quality and degree of informativeness of their replies were diverse. The average response was kind and timely, but manifested rather limited proactivity and efforts to give details and think ahead. In a few cases the responses were rich and insightful. In a few other cases they were just formal replies, essentially devoid of technical content. Kind, replicated reminder messages with tailored requests did not trigger better input. This outcome is, of course, statistically and sociologically predictable, but it might also give some information on the perception of the Consortium from the facility staff. We sometimes got the impression that, for some of them, CERIC is just one among the many things they have to handle and they are centred on the "local" scale, perhaps missing part of the global-scale vision opportunity CERIC is offering.

Surely, this survey has been a strong opportunity to raise interest and attention to this issue. Further to this, perhaps the CERIC Local Contacts might find ways to favour a stronger Consortium motivation in their Colleagues. Reporting locally the outcomes of this battery survey could be a simple and good opportunity in this sense. Furthermore, future TBAB members may be asked to be available for agile and informal contact (e.g., with video/teleconferences) with groups of Instrument Scientists of a given facility, to expound the relevant present and future scenarios within the Consortium.

4. Conclusions

The suite of CERIC partner Instruments, in its present configuration, offers an **outstanding opportunity** for state-of-the-art and next-generation battery research. Moreover, the cornerstone of CERIC, *i.e.*, fostering complementary, **multi-technique studies**, is especially crucial to electrochemical energetics, **battery science and technology**, in particular.

The current attention of CERIC to battery studies is particularly timely, because the potential of CERIC in this field has been **only partially exploited**. This is particularly true for the multi-technique approach.

In fact, **several CERIC techniques have been involved in battery research**, but **seldom in conjunction**. Some **other methods** have simply **never been exposed** to this field of research, but the respective Responsibles are keen on getting involved. In a limited number of cases, the Instrument Scientists have hardly manifested interest, for two main reasons: their focus is on completely different science (notably biosciences or fundamental solid-state physics) or manpower is worryingly wanting. Lack of interest from some Instrument Scientists, on the one hand, and scanty applications from new users might be due to limited **interaction with battery experts**. This **interdisciplinary contact** can be favoured by the establishment of an agile and operative **Technical Battery Advisory Board**, the characteristics of which have been detailed in Section 3.4.

In addition, notwithstanding the rich suite of Instruments available in the Consortium, **some techniques are missing**, that would result in a stronger appeal for the battery community: these are presented in Section 3. Moreover, some of the **existing techniques can be adapted** in view of the use for in situ or operando electrochemical applications. It is worth noting that the upgrade of Elettra could be a good opportunity to implement these actions.

In conclusion, the balanced mix of techniques that CERIC presently offers, integrated along the lines expounded in this report (in particular the **concrete recommendations** specified in Section 3.4.), can **fit ideally in the framework of recently launched EU initiatives** to foster battery studies through synergy among European analytical facilities, computing centres and industry. By strengthening battery activities the Consortium will be in a position to **strongly contribute to the BATTERY 2030+ roadmap** and related common efforts to develop a strong European route to next-generation batteries.

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