EERA
European Energy Research Alliance

EERA Joint Program SP1 – Electrochemical Storage Fact Sheet

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Insights on *In Situ* and *Operando* Experiments

Evolution to ensure sustainability and long-term growth

According to McKinsey's forecast, battery demand is expected to grow by approximately 21% per year, reaching 5 TWh by 2030. This growth will be driven by a variety of battery chemistries, including sodium-ion (Na-ion) and lithium-sulphur (Li-S) batteries [1]. While lithium-ion batteries (LIBs) are approaching their theoretical limits, other chemistries are still in the early stages of development: Na-ion and Li-S batteries have not yet surpassed the 50-60% threshold. It is also anticipated that meeting the demand with supply will not be achieved through a revolution in new chemistries, but rather through an **evolution and a pivotal holistic strategy**. This strategy will integrate multiple characterization methods to identify previously neglected factors. For a comprehensive strategy that explicitly focuses on the electrode material inside the battery throughout its cycling process, consider the following approaches [2]:

- ***Ex situ / PostMortem:*** Samples are studied in their thermodynamic equilibrium, unaffected by other factors.
- ***In situ:*** Data is collected under stable conditions, with specific environmental parameters maintained within a controlled setting, such as a sample environment apparatus.
- ***Operando / quasi-operando:*** Samples are examined in a non-steady state, experiencing non-equilibrium and non-ambient conditions.

The reaction mechanisms of LIBs, Na-ion, and Li-S batteries often involve multiple reactions and adsorbed species, some of which are rate-limiting while others exhibit rapid kinetics. Consequently, there will be **significant reliance on *in situ* or *operando* "observer" techniques**. This is because the state of battery chemistry is determined by parameters such as scan rate, constant current, or frequency, as applied through conventional electrochemical methods like cyclic voltammetry, galvanostatic charge-discharge tests, or electrochemical impedance spectroscopy. During operational conditions, the **temporal and spatial resolution of the technique must be suitable for capturing the process of interest or the lifetime of the species we aim to observe under non-steady state conditions**. It's worth noting that lab-scale (up to TRL 4) experiments typically utilize a conventional two-electrode setup to model the entire battery system. Three- or four-electrode configurations are rare and usually reserved for focusing on electrode reactions at either the anode or the cathode specifically. Despite extensive research efforts aimed at developing affordable, high-performance, and sustainable batteries, progress is hindered by **the absence of standardized battery data, a common vocabulary, and machine-readable tools for interoperability** [3].

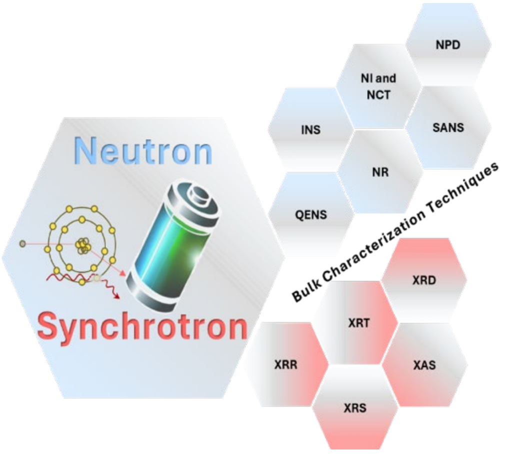

Figure 1. Neutron and synchrotron techniques offer unique benefits for enhancing battery performance by providing real-time, detailed insights into electrochemical processes and material behavior. Own picture, data from [4]

Importance of the characterization modality

Evaluating active materials via characterization modality in their initial state, as well as when integrated into cathodes/anodes and during electrochemical operation, requires the application of diverse, complementary techniques. These techniques need to examine different length scales, spanning from atomic to nanometer and micrometer scales [4]. Therefore, we observe localized electrochemically induced alterations in surface charge, which, for example, can change the chemical adsorption ability. This provides indirect insights into the effectiveness of modifying active materials' structure by altering the electrolyte solution's composition near the electrode.

However, tracking the contribution of a specific surface functional group to the reduction reaction (RR) or oxidation reaction (OR) mechanisms in real-time is exceptionally challenging for any ***in situ*** or ***operando*** **measurement**. One reason is that the electrolyte likely contributes significantly most of the time, even with methods designed for explicitly surface-sensitive characterization. Numerous considerations and challenging questions must be addressed when gathering and interpreting data. For instance, **is the technique capable of simultaneously detecting particles in both solid and liquid states?** A significant characterization challenge lies in the selected technique's ability to identify species during the process, including the phase transition from solid to liquid. Another important inquiry is **whether monitoring reduction reactions (RR) and oxidation reactions (OR) occur in real-time under actual cell charging and discharging conditions, with sufficient spatial and temporal resolution provided by the chosen observational technique.** Additionally, can we identify the formation of the solid electrolyte interphase, pseudo-metallic sodium storage, or trapped polysulfides, **and at what penetration depth?** Finally, **to what extent will the results be affected by collecting data after cell geometrical modification?** These are critical questions that must be considered to ensure accurate and meaningful data interpretation.

The ultimate question is whether the observations are made under *operando* conditions, both from an electrochemical perspective and in terms of the spectroscopy technique used.

Invaluable insights at the cost of beam damage, artifacts, and complex data analysis?

The challenges in studying battery materials using various techniques at large-scale facilities **(synchrotron- and neutron-based bulk techniques)** primarily stem from the need for a cell set-up compatible with instrumentation for a reliable signal [5]. Information obtained from **customized *operando* test cells**, whether through the drilled holes in current collectors or metal foil, the addition of windows (Kapton, Beryllium) for photon, X-ray or neutron penetration, extra membranes enabling observation of the electrolyte sample, or perforations in electrodes allowing signal passage, may **not consistently align with typical coin cell or pouch cell** systems. When utilising *operando* characterisation modality, it's essential to consider radiation damage [6], particularly at high flux instruments such as synchrotrons where beam intensities must be carefully controlled. Neutron penetration, higher than X-rays, allows using conventional battery cells like pouch or coin cells. However, thick samples may face limitations due to multiple scattering, potentially leading to data misinterpretation**.**

While advanced characterization techniques provide invaluable insights into battery performance and materials, they come with significant challenges. Addressing these requires careful planning, substantial resources, and interdisciplinary collaboration to mitigate issues related to beam damage, artifacts, and complex data analysis.

Comprehensive characterization, standards and knowledge transfer

Comprehensive Characterization

\- Requires suitable temporal and spatial resolution of the technique and compatibility with the process of interest or the lifetime of the species under study.

\+ Allow to observe and analyze dynamic processes (Immediate feedback)

Standardized Guidelines

\+ Establish uniform guidelines for conducting battery experiments.

\+ Facilitate the integration of new technologies with existing standard protocols.

\+ Implement common calibration practices for equipment.

Knowledge Transfer

\+ Create a unified framework for *operando* data collection and reporting Industry-relevant battery parameters

\+ Foster collaboration and data sharing across research institutions and industries

Figure 2. Comprehensive characterization, standards, and knowledge transfer ensure that innovations are well-understood, consistently developed, and widely disseminated, driving progress toward more efficient, reliable, and sustainable battery technologies.

Comprehensive characterization, standards and knowledge transfer are targeted within the SP1 of the EERA Joint Program on Electrochemical Storage, dealing with batteries and electrochemical storage systems.

The use of ***in situ*** and ***operando, quasi operando*** techniques with synchrotron X-rays and neutrons at large-scale facilities will be crucial for providing the temporal resolution and precise structural insights necessary for the development of high-performance, environmentally sustainable batteries and electrochemical storage systems. In the coming decades, the combined efforts of synchrotron and neutron facilities are expected to significantly drive advancements in battery research and industry [7]. As a result, the popularity of cross-disciplinary approaches in battery studies is increasing.

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Advantages

- Detailed insights of battery operation, degradation, and failure
- Holistic view from atomic-scale changes to macroscopic performance

Drawbacks / Challenges

- Long-term experimental time is needed
- Require sophisticated and expensive equipment
- Beam damage (X-rays)
- Artifacts / Customized test cells
- Complex analysis

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