

# Analysis and Characterization of Lithium Batteries and Recent Advancements

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**Abstract:** Advanced scanning transmission electron microscopy (STEM) and related instruments have significantly improved the characterization of all-solid-state (ASS) Li batteries. These tools provide localised information on the morphology, chemistry, structure, and electronic state of electrodes, electrolytes, and their interfaces at the nano and atomic scale. The rapid advancement of in situ technologies has enabled a comprehensive understanding of interfacial dynamic behaviour and heterogeneous characteristics throughout the cycling process. However, conducting thorough and reliable examinations of the structure and chemistry at the interface with an extremely high level of detail, without causing damage to the sample, is challenging due to the sensitivity of light components like Li and O in the interphases. This article covers the following topics: The current challenges in implementing this method, the novel advancements of advanced STEM in the study of ASS Li batteries, and the potential for integrating cold electron microscopy with STEM phase contrast imaging techniques.

**Keywords:** Battery management system, all-solid-state (ASS), scanning transmission electron microscopy

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## INTRODUCTION:

The all-solid-state (ASS) Li battery is a very promising electrochemical energy storage technology that offers several advantages compared to other batteries with similar capacities. The user's text is "[1-2]". Initially, ASS Li batteries address a crucial safety concern associated with conventional Li-ion batteries (LIBs) by using a solid-state electrolyte (SSE) in place of a combustible organic liquid electrolyte. The given text is [3,4]. Furthermore, Li metal may be used as an anode because the mechanical rigidity of the solid-state electrolyte (SSE) can prevent the formation of Li dendrites. The range of values from 5 to 7. Hence, the inclusion of alkali metals across the whole cell of the battery has the capacity to substantially enhance the energy storage density of lithium batteries.

However, because to the significant resistance at the interface and the low inherent ability of the electrolyte to conduct ions, it has not been possible to develop high-performance ASS Li batteries. The primary factors contributing to inter-face impedance are insufficient physical contact at the interface and undesired chemical interaction between the electrode and electrolyte. The user's text is "[7]". Furthermore, the progress of ASS Li batteries is impeded by the structural and chemical durability of electrode materials such as Li metal anodes. It is essential to examine the structural and chemical changes occurring inside ASS Li batteries and assess their influence on the battery's electrochemical performance. This is because the properties of the electrode material and the interaction between the electrode and electrolyte are critical factors affecting the performance of ASS Li batteries.

## II EXISTING WORK

The significant resistance at the interface and external properties of the electrolyte provides some obstacles for the practical use of the ASS Li battery. The range of values is between 8 and 9. Prior to addressing these concerns, it is essential to have a comprehensive understanding of the behaviour of the ASS Li battery material at the microscopic and/or atomic scale. The array

contains the elements 10 and 11. The Scanning/Transmission Electron Microscope (S/TEM) is very efficient and reliable equipment for this purpose. This section provides a summary of the progress made in utilizing Scanning/Transmission Electron Microscopy (S/TEM) to gain a deeper understanding of the changes in structure and chemical stability at the interfaces between the cathode and solid-state electrolyte, the Li metal anode and solid-state electrolyte, and the ion transport behaviour in solid-state electrolyte battery performance.

Another significant factor that contributes to below-average battery performance is the chemical interaction between cathodes and solid-state electrolytes (SSEs). This interaction leads to the mutual diffusion of elements and the production of inter-phases, which ultimately results in the deterioration of the electrodes and/or electrolytes. The array contains the elements 12 and 13. The presence of a space charge layer at the interface between the oxide electrode and sulphide electrolyte may contribute to a significant interfacial resistance. The text is referencing pages 14-15. Transmission electron microscopy (TEM) is considered a critical tool for investigating interfacial difficulties in solid-state Li batteries because it allows for the observation of contact between electrolytes and cathodes at the Nano scale level.

## 2.2. Solid-State Electrolytes

### 2.2.1. Ion Mobility of Grain Interior

The solid-state electrolytes (SSEs) may be classified into three categories: organic polymer solid electrolytes, inorganic solid electrolytes, and organic-inorganic composite solid electrolytes. Currently, due to the sensitivity of other species in the solid-state electrolyte (SSE), the focus of high-resolution transmission electron microscopy (TEM) investigation is mostly on inorganic solid oxide electrolytes. Transmission electron microscopy (TEM) has been widely used in the study of common oxide solid electrolytes, such as LLTO and LLZO, which exhibit excellent environmental stability and ion conductivity. The LLTO compound has a perovskite structure, namely  $ABO_3$ , where there are vacancies and the

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elements Li and La cohabit at the A-site. The crystal structure, composition (including factors such as the concentration of vacant sites, order of cations on the sites, and presence of dopants), and structural distortion all play a crucial role in determining the behaviour of Li-ion conduction inside the grain of LLTO. LLZO, a kind of garnet oxide, may exist in two different forms at room temperature: a tetragonal phase with lower conductivity and a cubic phase with very high conductivity. Comprehensive comprehension of lithium-ion conductivity, specifically regarding its relationship with atomic-level structure and phase transition, is crucial for the development of a highly conductive solid electrolyte. The scanning/transmission electron microscope (S/TEM) has been extensively used to achieve atomic-scale phase differentiation and directly see the crystal structure.

2.2.2. Ion Mobility of Grain/Domain Boundaries (GBs/DBs)

The resistance at the interface between grains in a solid electrolyte is a crucial factor that influences the ability of ions to conduct electricity. The ion mobility at the border is regulated by structural distortion, domain size, and chemical changes, as opposed to the ion mobility inside the grain core. Hence, in order to create a thorough model of Li-ion conductivity, it is necessary to have a profound understanding of the ion migration process occurring at the grain boundaries (GBs).

2.3. Anode/Electrolyte Interface

The use of Li metal as an anode material in high-energy ASS Li battery systems has been considered suitable because of its low density, low negative electrochemical potential, and high theoretical specific capacity. The use of the Li/SSE contact has been hindered due to interfacial resistance and chemical instability. The primary factor contributing to the elevated interfacial resistance is often the inadequate affinity between the Li metal and the solid-state electrolyte (SSE). The occurrence of chemical or electrochemical instability may result in the creation of an interphase layer at the interface between lithium and solid-state electrolyte (SSE), which hinders the mobility of lithium ions and causes a decline in battery performance.

In order to verify the presence of Li-filled voids located at the boundaries of LLZO:Ta grains, Tsai et al. [20] used transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). Lithium (Li) has been identified, showing that after a short circuit, lithium dendrites form in the grain boundaries. The researchers determined that the growth of Li dendrites was a result of the uneven contact between the Li electrodes and the LLZO solid electrolyte. The addition of a thin layer of gold (Au) improved the connection between the lithium (Li) electrodes and the LLZO:Ta electrolyte. This led to a reduction in the resistance at the interface and prevented any short circuits in the cell. Therefore, it is necessary to meticulously design the interface in order to minimize the resistance at the contact, thereby enhancing the performance of ASS Li batteries.

III STRUCTURAL AND PHASE TRANSFORMATION DYNAMICS

Electrode

ASS Li batteries have also used LiCoO<sub>2</sub>, a conventional cathode material. Unlike traditional liquid lithium-ion batteries (LIBs),

there is little research on the structural changes and phase transition of the LiCoO<sub>2</sub> cathode in all-solid-state (ASS) lithium batteries. Gong et al.[23] constructed a LiCoO<sub>2</sub>/LLZO/Au ASS battery (Figure 1a) employing focused ion beam (FIB) on an electrically biased chip. The behaviour of LiCoO<sub>2</sub> throughout the delithiation process was subsequently examined in situ using TEM.

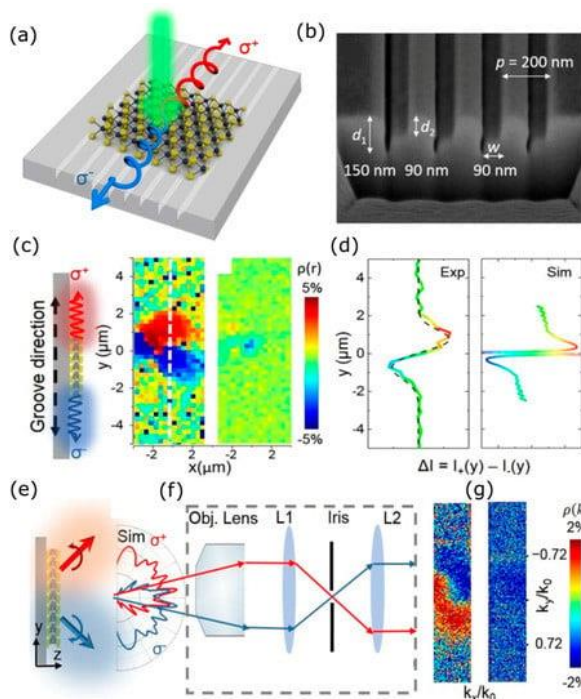


Figure 1. a) An LCO/LLZO/Au nanobattery fabricated by FIB, b) nanosized polycrystal with different orientations were colored using GPA, c) HAADF-STEM and ABF-STEM images of the delithiated LCO. A–c Reproduced with permission. d) Schematic of in situ experimental setup for biasing a Nano battery and e) Li distribution at LCO/LiPON interface revealed by STEM-EELS. d,e) Reproduced with permission. f) Thickness-dependent self-discharge behavior of solid-state 3D nanowire battery. Reproduced with permission. g) Formation mechanism of stable Li/LLZO interface.

After undergoing a high-voltage delithiation process, the original LiCoO<sub>2</sub> single crystal changed into smaller poly-crystals that are connected by coherent twin boundaries and antiphase domain boundaries. This transformation is evident in the HAADF-STEM and ABF-STEM images (Figure 1b,c). Unlike liquid LIBs, the electrode-SSE interface in this case mostly consists of point contact and has the ability to initiate the growth of grain boundaries. Their research demonstrated that the optimization of the solid-solid interface state is crucial for achieving optimal performance in ASS Li batteries. This was achieved by establishing a correlation between atomic structure alterations and the performance of ASS batteries. To understand the process of delithiation, similar methods were used to analyse the changes in the atomic and electronic structures of a LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode.

Cathode/SSE Interface

Because many SSEs have ion conductivities that are similar to liquid organic electrolytes, electrode/electrolyte interfacial resistance has been identified as a significant barrier to enhancing the performance of ASS batteries. Meng et al. investigated the

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interfacial phenomena of LiCoO<sub>2</sub>/LiPON/Si ASS batteries during charging using in situ STEM-EELS (Figure 1d). Using the FIB manufacturing process, electrochemically active Nano batteries were created and galvanostatically biased in the TEM column.

**Anode/Electrolyte Interface**

The anode/electrolyte interaction has a substantial influence on the performance of ASS Li batteries. The use of high specific capacity Li metal anodes is hindered by the inadequate conductivity and instability at the interface between the anode and solid electrolyte. Ma et al.[24] generated and fabricated a Li/LLZO interface in its original position (Figure 1g) and investigated the progression of the chemical composition and structure at the interface to determine the process of creating the Li/SSE interface. Before conducting in situ STEM measurements, the Li and cubic-LLZO (c-LLZO) samples, both protected by dry helium, were individually transferred into the microscope.

**IV PERSPECTIVE**

The primary goal of using TEM in ASS battery research is to see conductive ions and atoms in real-time throughout the native state electrode heterostructure. Furthermore, it seeks to tackle significant concerns with the electrodes, electrolytes, and interfaces of rechargeable batteries. Electrons interacting with electrolytes, Li metal, and associated intermediates cause significant damage during high-resolution imaging, which hinders the use of TEM for this purpose. Diagnosing Li metal or similar interphases without leaving any atomic artefacts behind is a difficult task.

To effectively tackle significant concerns related to rechargeable battery materials and get precise information about the atomic structure of the crystal, it has become imperative to exercise control over and minimize electron beam damage. This will aid in elucidating the correlation between the structure and properties of ASS Li batteries, as well as the process of ion transport. The primary mechanisms via which an electron beam may cause damage to materials, whether they are inorganic or organic, are typically as follows: (1) atomic displacement; (2) electron-beam sputtering; (3) electron-beam heating; (4) electrostatic charging; and (5) radiation analysis. In essence, the periodic lattice undergoes point defects and atom displacement. The damage caused by radiation breakdown occurs when incoming electrons interact with valence electrons in the sample, leading to the disruption of chemical bonds by ionisation. Moreover, if the sample is not able to conduct electricity and has poor ability to transfer heat, when the electron interacts with the sample, it will cause the sample's temperature to rise in that specific area. Additionally, there will be a build-up of electrostatic charge due to the loss of secondary electrons that are expelled when the electron beam interacts with the sample in an elastic manner. The usual approach to reducing electron-induced sample damage is to do imaging at a low dosage. Nevertheless, using lower electron doses leads to images with a subpar signal-to-noise ratio due to the inadequate electron scattering of low atomic number elements like Li and O. Consequently, the electron doses are either sufficiently enough to provide a satisfactory signal-to-noise ratio but lead to unacceptable levels of specimen damage, or they

are sufficiently low to prevent radiation damage but result in images with a high degree of noise. The biology community successfully handled a similar issue by using three distinct approaches that used modern "high-resolution" electron microscopy techniques. The first technique is referred to as "cryo-electron microscopy," where frozen samples are visualized and maintained at very low temperatures, namely either liquid helium or liquid nitrogen cold.

**4.1. High-Sensitive Phase Contrast Imaging in STEM**

The correction for aberration refers to the adjustment made to compensate for the distortion or deviation from normal behaviour in an optical system. STEM has become an indispensable technique for characterizing materials at the atomic level due to its ability to perform STEM-HAADF imaging and spectroscopic mapping simultaneously. Although TEM bright field (BF) imaging may frequently achieve equal phase contrast imaging, the study and application of phase contrast imaging and its associated theories have not been extensively explored or used compared to TEM. The discovery has shown that STEM-BF offers significant benefits for doing research that involves both biological samples and materials. With the advancement of fast segmented and pixelated detectors, there is a growing development of strategies aimed at enhancing the utilisation of BF-STEM.

Nevertheless, the dose effectiveness of STEM-BF is low, resulting in a higher level of noise compared to other STEM imaging techniques due to the limited utilisation of the incident probe current for image generation. Recent developments in fast electron detectors and advanced algorithms have enabled the development of innovative STEM phase contrast imaging methods, such as electron ptychography. This has greatly enhanced the capacity to distinguish light parts from heavy components in a single image. Therefore, STEM phase contrast imaging has great potential, especially for analysing ASS batteries. Ptychography was first proposed based on the observation of a 2D diffraction pattern being captured at each spatial location inside a 2D array of points. These points exhibit substantial overlap in the adjacent illuminated areas (Figure 2c). The overlapping of the illuminated areas offered redundancy, enabling it to determine the phase of the specimen. Electron ptychography has several advantages.

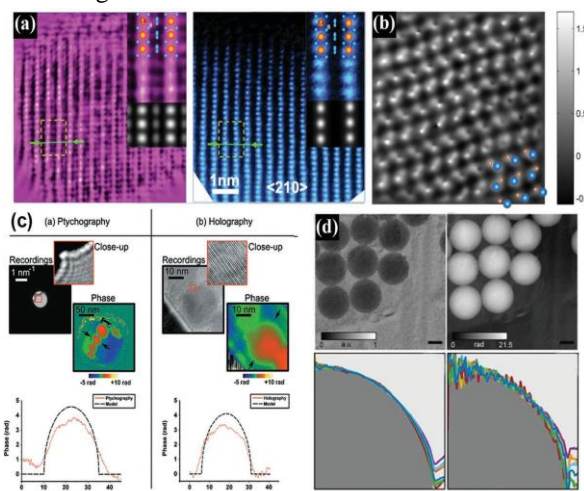


Figure 2. a,b) Ptychographic reconstructed images of LaB<sub>6</sub> and GaN where light elements can be clearly resolved. a) Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0



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International License (http://creativecommons.org/licenses/by/4.0/). b) Reproduced with permission. c,d) Comparison between the reconstructed phase profiles and theoretical profile. c) Reproduced with permission. d) Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0.

Furthermore, the use of electron ptychography has the potential to enhance the transmission of phase contrast and optimise the imaging efficiency of light elements via its integration with a phase plate. Furthermore, studies conducted by Maiden et al. [198] (Figure 2d) and Hüe et al. [26] (Figure 2c) demonstrate that the ptychographic phase image exhibits a high level of accuracy when it comes to quantification. Finally, these quantitative phase signals may be used, similar to holography, for the examination of electric and magnetic fields. Through the use of conventional electron holography in TEM mode, we were able to identify fluctuations in potential across the solid electrolyte interface and electrodes of similar magnitude (refer to the review in Section 3). Ptychography eliminates the need for a reference beam by using the sample as an interferometer. Additionally, ptychography has the advantage of not needing an electrostatic bipolar probe or specific sample preparation for its use.

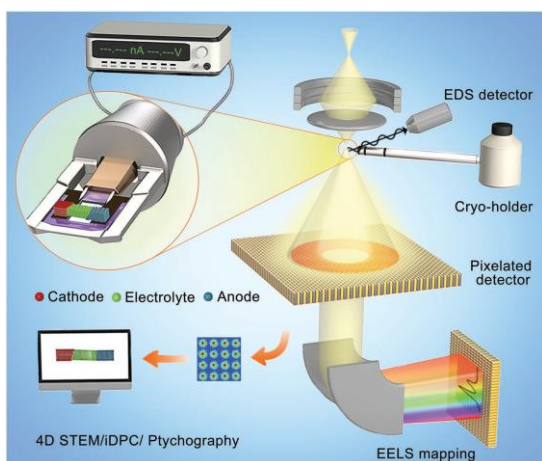


Figure 3. Illustration of experiment setup where cryogenic technique, in situ technique, EELS, and hollow pixelated detector are combined.

Focused probe ptychography has the unique capacity to integrate with existing atomic-resolution imaging methods, including as ADF-STEM, ABF-STEM, BF-STEM, and DPC, concurrently, in contrast to defocused probe ptychography, which has significant promise in the low dosage application. Additionally, as seen in Figure 3, a hollow ptychographic imaging configuration presented by Song et al. can provide the simultaneous coupling of focused probe ptychography and spectroscopic methods (e.g., EELS, etc.) via a rapid hollow detector. This geometry allows for simultaneous, correlative analysis using Z-contrast, phase imaging, and chemical mapping, which makes multiple channels of information about the specimen available with highly efficient use of the electron dose. Fast hollow detectors that are compatible with EELS spectrometers have made this possible. For the specific goal in certain investigations, a compromise between focused and defocused probe ptychography must be made, but we

anticipate that the battery community will gain a great deal from the progress in STEM phase contrast imaging utilizing either one or combining the two approaches.

4.3. Future Instrument for ASS Li Batteries Research

By integrating phase contrast imaging techniques like ptychography with cryogenics, which takes inspiration from cryo-EM in biology, we may achieve the most effective method for visualising battery materials in their original state. This approach will provide a high level of contrast for lithium atoms at the atomic level. The presence of artefacts may be introduced into the image when electrons undergo diffraction in the multichannel STEM mode, while simultaneously using imaging techniques like as ptychography, HAADF-STEM, and DPC, as well as spectroscopic techniques like EDS and EELS.

V CONCLUSION

The characterization of device-scale in battery research may be significantly improved by monitoring long-range fields. However, performing ptychography across large fields of view remains challenging. Recent advancements in the use of large defocused probes and selected area ptychography have shown potential in addressing the problem. By employing a system that integrates cryogenic, in situ, and multichannel characterization, we can gain a comprehensive comprehension of the dynamic transformations taking place within batteries. This knowledge will enable us to effectively control the dynamic phenomena necessary for the development and production of advanced energy storage materials in the future.

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