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Review

Experimental Investigations on the Chemo-Mechanical Coupling in Solid-State Batteries and Electrode Materials

Jiaxuan Wang [1,2] and Feng Hao [1,2,*]

[1] Shenzhen Research Institute of Shandong University, Shenzhen 515100, China
[2] Department of Engineering Mechanics, Shandong University, Jinan 250100, China
* Correspondence: fenghao@sdu.edu.cn

Abstract: Increasing attention has been paid to the safety and efficiency of batteries due to the rapid development and widespread use of electric vehicles. Solid-state batteries have the advantages of good safety, high energy density, and strong cycle performance, and are recognized as the next generation of power batteries. However, solid-state batteries generate large stress changes due to the volume change of electrode materials during cycling, resulting in pulverization and exfoliation of active materials, fracture of solid-electrolyte interface films, and development of internal cracks in solid electrolytes. As a consequence, the cycle performance of the battery is degraded, or even a short circuit can occur. Therefore, it is important to study the stress changes of solid-state batteries or electrode materials during cycling. This review presents a current overview of chemo-mechanical characterization techniques applied to solid-state batteries and experimental setups. Moreover, some methods to improve the mechanical properties by changing the composition or structure of the electrode materials are also summarized. This review aims to highlight the impact of the stress generated inside solid-state batteries and summarizes a part of the research methods used to study the stress of solid-state batteries, which help improve the design level of solid-state batteries, thereby improving battery performance and safety.

Keywords: solid-state batteries; electrode materials; chemo-mechanical coupling; in situ experiment

Citation: Wang, J.; Hao, F. Experimental Investigations on the Chemo-Mechanical Coupling in Solid-State Batteries and Electrode Materials. *Energies* **2023**, *16*, 1180. https://doi.org/10.3390/en16031180

Academic Editors: Paola Costamagna, Qibo Deng, Ying Zhao, Bo Lu and Wenshan Yu

Received: 2 December 2022
Revised: 5 January 2023
Accepted: 16 January 2023
Published: 20 January 2023

1. Introduction

Advanced energy storage technology plays an important role in the development of today's society. Lithium-ion batteries have been widely used in all aspects of our social life; from the energy storage of the space station to smartphones and electric vehicles around us, lithium-ion batteries can be seen. How to make the existing energy storage technology more economical, efficient, and safer is the development direction of this field today. Traditional commercial lithium-ion batteries are generally composed of lithium metal oxide cathodes, carbonate liquid electrolytes, and graphite anodes. Although liquid electrolyte batteries have made great progress in recent decades, there are still some insurmountable problems. For example, the organic electrolytes aggravate side reactions and oxidative decomposition, and increase the risk of combustion at high temperatures. The lithium dendrites generated during battery cycling can easily pierce the separator and cause a short circuit in the battery, and conventional batteries seem to be reaching their limits both physically and chemically. Compared with traditional lithium-ion batteries, the main difference of solid-state batteries is that the electrolyte is solidified, which fundamentally solves the problems of high-temperature decomposition, the combustion of electrolytes, and piercing of the separator by lithium dendrites, and significantly improves the energy density of the battery, marking the development direction of the next generation of power batteries. Due to the various advantages of solid-state batteries, more and more people have begun to focus on the study of solid-state batteries [1–9]. Gao et al., discussed the latest developments in solid-state electrolyte (SSE) and provided an outlook on the challenges and opportunities

for solid-state batteries [1]. Kim et al., provide a comprehensive review of all aspects of solid-state batteries [2]. Randau et al., identified research goals for high-energy, high-power, and practical all-solid-state batteries [3]. Wang et al., studied and focused on garnet-type solid-state electrolytes [4]. Wu et al., focused on solid-state ionics, providing insights into the development of solid-state thin-film mu-batteries [5]. Zhang et al., focused on sulfide solid electrolytes [6]. Zhang et al., reported a garnet ($Li_7La_3Zr_2O_{12}$)-based, hybrid, solid electrolyte (HSE) membrane, which enabled solid-state batteries to efficiently store pulsed energy [7]. Zhao et al., used cationic aluminium species to initiate ring-opening polymerization of molecular ethers inside an electrochemical cell to produce solid-state polymer electrolytes (SPEs) [8]. Chen et al., outlined the directions and challenges of solid-state battery development, focusing on solid-state electrolyte stability and related issues at the interface with electrode materials [9]. Solid-state batteries have problems, such as low ionic conductivity of the solid electrolyte and loose contact between the solid electrolyte and electrode. Therefore, solid electrolyte requires a certain pressure to ensure good contact with the electrode during operation, which can also minimize resistance, and, like liquid-electrolyte batteries, the electrode active materials of solid-state batteries undergo significant volume changes when lithium ions are deposited or stripped. With rigid contact of the solid-to-solid interface, the solid-state battery experiences significant stress fluctuations during operation. Koerver et al., emphasized the effect of the volume change of electrode materials in the solid-state battery environment. Most electrode materials experience volume changes during lithium intercalation and extraction, and the combination of electrode materials with different characteristics can effectively reduce the stress during cycling [10]. Due to this characteristic of solid-state batteries and electrode materials, it is important to study their stress changes during charging and discharging. Liu et al., summarized the electrical, chemical, electrochemical, and mechanical failure mechanisms of solid-state lithium batteries and provided insight into future research directions [11]. Hu et al., used Raman stress mapping to study the evolution of three-dimensional microscopic stresses in solid electrolytes during battery cycling [12]. Kodama et al., analyzed the ionic conductivity of all-solid-state cells by coupling non-linear stresses and electric fields [13]. Ahmad et al., summarized the relationship between the fabrication and processing of solid-state batteries and chemo-mechanical coupling [14]. Liu et al., summarized the application of cold sintering process (CSP) technology in different solid-state electrolytes, which helps to improve various properties of solid-state electrolytes [15]. By studying the SSE lithium amide-borohydride-iodide ($LiBH_4$-$LiNH_2$-LiI), Ebechidi et al., found that battery charging and discharging cycles lead to local strain buildup and failure of the solid electrolyte [16]. Glenneberg et al., investigated the correlation between the electrochemical aging and mechanical aging of solid-state, flexible lithium-ion batteries [17].

This review mainly introduces some in situ observational methods to study the stress development inside the battery or just the electrode material. In situ experiment means carrying out some characterization and measurement work without disturbing the dynamic process of the experimental sample and without moving the experimental sample [18–22]. The atmosphere inside the battery is demanding, and the battery assembled in the laboratory is generally completed in an argon glove box to ensure that the content of water and oxygen in the gas environment in the glove box is less than 1 ppm. Applying in situ experiments to study batteries and electrode materials can simulate the normal working state of batteries to the greatest extent. Specifically, the internal components of the battery can work under normal pressure and will not be damaged by exposure to high humidity and oxygen content. Therefore, the experimental data obtained can be close to the real working battery. In previous work, many people have used in situ optical methods to study chemo-mechanical coupling in liquid electrolyte batteries. Li et al. [23] designed and built a cantilevered silicon composite electrode structure and quartz cell and measured the curvature, elastic modulus, and stress evolution of Si/PVDF composite electrodes using an in situ method. Xie et al. [24] constructed a novel battery structure, in which the current collector, electrode material, and electrolyte were arranged in concentric circles on a plane, and through the in situ dual optical system,

measured the stress under the working state of the battery. Because of the difference in the structure and working conditions of the solid-state battery and the liquid electrolyte battery, more new methods are needed to measure internal stress. Different from previous reviews in this field, this review focuses on the latest experimental investigations on the chemo-mechanical coupling in solid-state batteries and electrode materials; thus, the advantages and disadvantages of various methods are summarized and compared.

In this article, some in situ chemo-mechanical characterization methods for full cells or electrode materials are introduced and summarized. From the traditional method using external mechanical sensors to the novel and difficult X-ray and internally embedded FBG fiber methods, their specific experimental device design and experimental methods are discussed. In addition, several methods for changing the properties of electrode materials and solid electrolytes to improve mechanical properties are also introduced. Finally, some existing challenges and future development directions in this research field are discussed.

2. Characterization Method

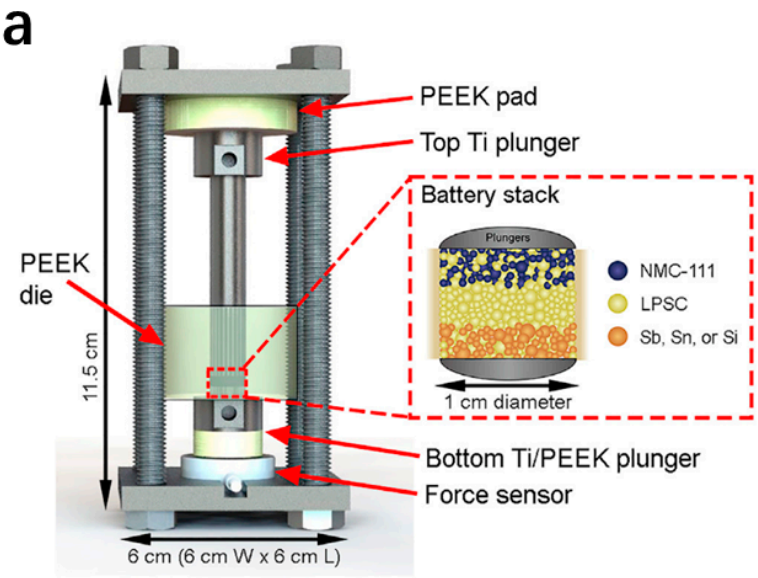
2.1. External Mechanical Measurement

Apart from traditional liquid electrolyte batteries, the solid electrolyte, electrode material, current collector, and battery shell of solid-state batteries are all in rigid contact. Therefore, due to the different partial molar volumes of lithium in different electrode materials, the volume change caused by the intercalation and deintercalation of lithium ions in the electrode material during battery cycling is particularly pronounced in solid-state batteries. The excessive internal pressure leads to material fracture and secondary particle fragmentation, which accelerates the capacity decay of the battery. Most electrode materials expand in volume when lithium ions are inserted and shrink in volume when lithium ions are extracted, that is, the partial molar volume is positive. However, there are some material exceptions, such as the frequently used lithium titanate (LTO), which is a zero-strain material with negligible volume change during cycling. Lithium cobalt oxide (LCO) exhibits a negative partial molar volume when the lithium content $x < 0.6$ (xLi in LixM). Therefore, using a reasonable combination of electrode materials can significantly reduce the internal stress of the battery, for example, 55:45 wt% NCM-811:LCO composite is used for the cathode [10]. Since the stress inside the solid-state battery is eventually transferred to the case, adding external force sensors can be used to obtain stress data inside the battery. However, the positive and negative battery cases must be separated, such as the mold of the piston structure [25]; otherwise, part of the stress may be offset by the deformation of the battery case and cannot be measured. As shown in Figure 1a–c, this kind of similar experimental setup has appeared in many articles, and their works have some things in common: they transmit the total internal stress of the solid-state battery directly to the force sensor through a plunger or a rigid cylinder, they use an external force sensor to measure the uniaxial stress, and all operations are done in an argon glove box. The advantage is that the accurate stress change inside the solid-state battery can be measured in real time. Combined with the data obtained by the external battery test system, an intuitive chemo-mechanical coupling phenomenon can be seen, which is conducive to later analysis.

In recent works, Lee et al., and Han et al., both used peek molds and titanium plungers to assemble solid-state batteries [25,26]. The radial strain of each component in the battery is limited, which can better simulate the real state of solid-state battery operation. However, only the uniaxial stress is measured, and the stress caused by the internal radial restraint is ignored. Lee et al., used two types of solid electrolytes with different properties to assemble a symmetric battery, and they studied the mechanical and electrochemical performance of solid-state batteries under different conditions by changing the external initial stacking pressure and solid-state electrolyte fabrication pressure [25]. Their work advances the understanding of the possible link mechanism between electrochemistry and stack pressure, and it also makes important contributions to the understanding of the interfacial evolution of two frequently used solid-state electrolytes. Among them, the LSPS solid electrolyte

is thermodynamically unstable when in contact with lithium, resulting in the formation of an interface, which makes it difficult for lithium dendrites to penetrate, while LPSC makes Li dendrites grow during the charging process and easily penetrate SSE particles, resulting in the short circuit of the battery. In addition, they believe that high stacking pressure can make the interface between Li and SSE uniform contact, but lithium can also be mechanically deformed and forced through micropores between the SSE particles to short-circuit the battery. Han et al., studied the stress evolution phenomenon produced by an NMC-111 cathode, solid electrolyte, and three different composite anode material combinations [26]. They also observed the effect of electrode material particle size on stress evolution during battery cycling. Specifically, the smaller the particle size of the electrode material, the smaller the stress generated, which has reference significance for the fabrication of solid-state electrode materials. In addition, Liang et al. [27] designed a rigid, stainless steel, Swagelok battery case, making all volume changes come from solid-state battery components. They mainly studied the stress evolution phenomenon of lithium metal in practical batteries, so they chose zero-strain material LTO as the cathode. They found that with the continuous increase of electrochemical cycles, the stress of the lithium metal anode continued to increase, and its volume also expanded irreversibly. They also believe that the changes in stress are mainly related to the amount of lithium plating and stripping, but not to the current density, electrolyte, and cathode mass loading. However, this external stress monitoring method also has certain disadvantages. The stress data is obtained from the volume change of the entire battery, but the stress evolution experienced by each component inside the battery during the battery cycle is different and non-uniform. The external stress sensor cannot measure the stress evolution of the electrode material, the solid electrolyte, and the interface between them alone.

In conclusion, the real-time stress evolution inside the solid-state battery during battery cycling can be accurately obtained utilizing external sensor measurement, and it can be coupled with electrochemical phenomena. This part of the chemo-mechanical coupling is mainly reflected in the coupling between the stress curve and the charge/discharge curve, providing an intuitive explanation for studying the chemo-mechanical coupling phenomenon inside solid-state batteries.



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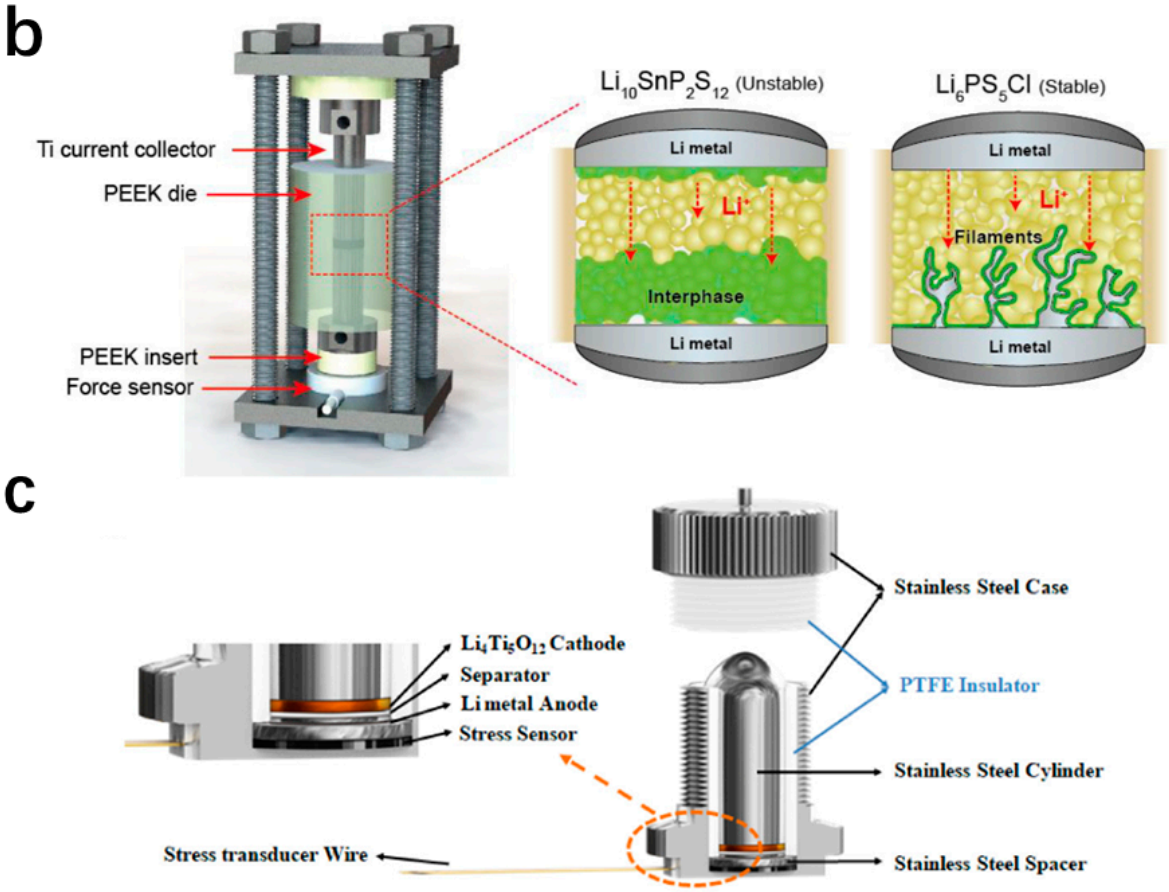


Figure 1. (**a**) Assembly of solid-state batteries and chemo-mechanical coupling experimental setup [25]. (**b**) Li-metal symmetric cells with two different solid-state electrolyte and chemo-mechanical coupling experimental setups [26]. (**c**) A rigid, stainless steel, Swagelok battery with a stress sensor inside [27].

2.2. Internal Mechanical Measurement

Different from traditional stress sensors, optical fiber sensors can be used to measure many physical quantities, such as sound field, electric field, pressure, temperature, etc. These external factors change the optical properties of light, such as the intensity, wavelength, frequency, and phase, to accurately measure their changes. In recent years, optical fiber sensors have been widely used to measure the stress changes of various batteries. For example, Ee et al. [28] and Peng et al. [29] both used optical fiber sensors to measure the surface strain of the pouch battery, which can accurately obtain the strain evolution of the aluminum plastic film surface of the flexible battery with the battery charging and discharging cycles, but it is still impossible to directly obtain the stress inside the battery. Liu et al. [30] implanted a FBG (Bragg fiber grating) sensor into a 18650 battery to measure the temperature change inside the battery. Nascimento et al., constructed a hybrid sensing network consisting of Bragg gratings to measure the strain and temperature evolution of a cell non-invasively [31]. Li et al., designed a smart lithium-ion battery with integrated FBG, where the FBG sensor can simultaneously monitor the temperature, force, and strain of the battery [32]. Xi et al., monitored the temperature changes inside a solid-state battery by embedding short FBG sensors inside the battery [33].

The external stress sensor cannot measure the stress evolution in the internal structure of the battery, which makes the external stress measurement method have great limitations. The optical fiber sensor is small in diameter, about 150 μm, and it has good chemical stability and electrical insulation characteristics [34]. This makes the fiber sensor the first choice for measuring the internal stress of the battery. First of all, because of its small diameter, the

impact on the internal structure of the battery can be ignored, and the internal environment of the battery under normal operation is restored to the maximum extent, which is non-invasive. Second, because of its chemical stability and electrical insulation characteristics, the optical fiber sensor is immune to the chemical reaction and electromagnetic interference inside the battery. Alberto Blanquer et al. [34] measured the internal stress of a liquid electrolyte battery and solid battery with an FBG sensor. When the light passes through the optical fiber, the FBG sensor acts as a reflector of a specific wavelength, that is, the Bragg wavelength (λB), which is defined as λB = 2 neffΛ. The change of the internal strain of the battery (ε) is eventually converted into the change of wavelength, which can be regarded as peak shift (ΔλB), so the internal stress evolution can be obtained by strain transformation. They first used the improved Swagelok battery to assemble a liquid electrolyte battery, as shown in Figure 2a. There are two opposite holes on the battery shell to pass through the single-mode optical fiber inscribed with the FBG sensor, and then they sealed the holes to ensure the normal working environment inside the battery. They set two positions for embedding optical fibers: one embedded on the electrode surface, the other in the electrode. When InLix is used as the anode and LTO is used as the cathode, they found that the maximum stress measured when the FBG sensor is embedded in the electrode is almost twice that when it is placed on the surface, and the FBG embedded in the electrode shows peak shift and spectral splitting. They attributed this phenomenon to the accumulation of transverse and axial stresses. Then they applied this work to solid-state batteries. Similarly, the FBG is set inside the electrode material or on the interface between the electrode and the solid electrolyte. When placed inside the electrode, they found that the results are similar to those of the liquid electrolyte battery. Meanwhile, they also added an external mechanical sensor to measure the stress and found that the stress value recorded by the external sensor was far lower than the internal sensor, which further explained the necessity of internal stress measurement and the complexity of the internal stress distribution of solid-state batteries. When the sensor is planted at the interface between the electrode and the solid electrolyte, the situation changes. Under low pressure (0–2.5 MPa), there is only one optical resonance peak (λB), then (2.5–9 MPa) it splits into two peaks (λx and λy), which is called the birefringence phenomenon. Through decoupling, the transverse interface stress (Δσ) of this specific InLix LPS interface can be calculated, which provides insight into the measurement of the anisotropy of the internal stress field of the battery. Miao et al. [35] mainly measured the internal stress of the lithium-sulfur battery directly by implanting the optical fiber sensor into the sulfur-based anode of the lithium-sulfur battery. They also used the FBG sensor; with the shift in the peak value (ΔλB), the strain data is obtained, and the stress evolution is finally calculated. They studied three different battery composition mechanisms, namely, the Solid-liquid-solid mechanism, Solid-solid mechanism, and Quasi solid mechanism. They found that the stress in the cathode under the Solid-solid mechanism has the largest change rate and amplitude, while the cathode under the Solid-liquid solid mechanism has the smallest mechanical change. Bae et al. [36] proved earlier that the FBG sensor can be used to directly detect the size change of a single battery electrode, in which the strain evolution leads to repeatable peak shift and peak splitting, and has a high accuracy, which provides some experience and ideas for later work.

In a word, the use of fiber Bragg grating sensors can directly measure the stress evolution of any component or interface inside the battery, and through the decoupling of the split two peaks, the axial and radial profitable evolution can be obtained, not just the uniaxial stress. This part of the chemo-mechanical coupling is mainly reflected in the relation between the amount of wavelength change and the amount of charging and discharging, which is important for the study of the uneven distribution of stress and stress anisotropy inside the battery, and has a good application prospect.

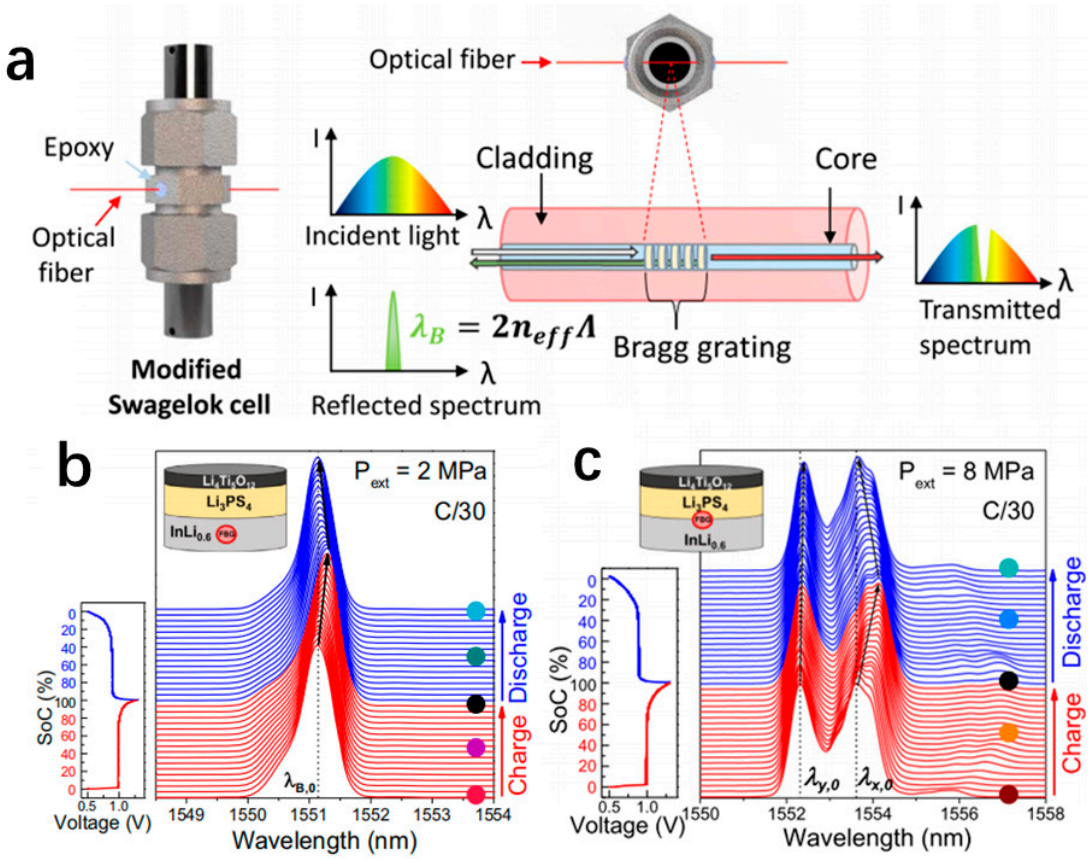


Figure 2. (**a**) Home-made Swagelok cell combined with FBG method to measure internal stress. (**b**) Peak displacement when FBG sensor is buried in the solid-state battery electrode material. (**c**) Splitting of peaks (λx and λy) [34].

2.3. Optical and X-ray Characterization Methods

Optical observation methods have been widely used to observe the strain and morphology evolution of lithium battery electrodes. CCD (charge-coupled device) cameras have high sensitivity, high spatial resolution, wide dynamic response range, and other advantages, and are often used to take photos of in situ battery experiments. A CCD camera combined with digital image correlation (DIC) technology to measure strain is also a common method [37,38]. Generally, the full field strain is measured by analyzing the speckle change in the image. This method is also commonly used to study the cracking of material surfaces and the evolution of cracks. Ogunfunmi et al., used a combination of in situ optical microscopy and digital imaging correlation (strain mapping) techniques to study compression deformation and cracking in solid electrolytes [39]. Hao et al., constructed an in situ experimental platform based on acoustic emission (AE) and three-dimensional digital image correlation (3D-DIC) methods to study 18650 batteries [40]. Luo et al., measured the changes in the morphology of pouch cells, including surface strain and volume changes, externally by the DIC technique, and observed the surface morphology of the cathode and anode before and after electrochemical cycling by tracing electron microscopy [41]. Chen et al., designed an in situ measurement platform and a 3D interpolation-induced expansion model to obtain the surface morphology of a cell and the multi-point strain distribution in three directions [42]. Leung et al., used 3D DIC technology in a pouch battery [43]. Mao et al., fabricated a freestanding V2O5 anode and placed it inside a transparent cell shell filled with electrolyte for DIC observation to analyze the strain evolution of the electrode [44]. In recent work, Chen et al. [45] used their chemo-mechanical coupling system to study the changes in elastic modulus, surface state, and stress relaxation of aluminum foil electrodes with lithiation (Figure 3a). The whole device can be divided into three main

parts. The first part is the mechanical part, which mainly provides tension; the second part is the electrochemical part, which is a self-made open liquid battery and an external electrochemical workstation; and the third part is the optical measurement system. In the self-made battery, aluminum foil is used as the working electrode, and lithium metal is used as both the counter electrode and the reference electrode. Because the aluminum foil needs to be stretched, the entire battery was designed to be open, and the whole experiment process needs to be carried out in the argon glove box. The aluminum foil is designed in the shape of a dog bone for easy stretching. They placed spray spots on the surface of the edge of the study area and measured the strain using the DIC method. They found that the elastic modulus of the aluminum foil increased first, and then decreased with the lithiation. They also measured with EIS (electrochemical impedance spectroscopy) spectra under different stress conditions to investigate the effect of mechanical stress on the electrochemical behavior of the battery. From Nyquist plots under different stress states, they found that the impedance response shows capacitive behavior. Based on previous work, He et al. [46] mainly studied the relationship between aluminum deposition and stress concentration. The experimental device is roughly the same as Chen et al. [45], and the symmetrical cell design is adopted. The difference is that they opened an elliptical hole in the tensile aluminum foil research area to produce an obvious stress concentration area (Figure 3b). They found that the aluminum deposition in the stress concentration area is significantly denser than that in the stress uniform area, in other words, stress concentration can promote the deposition of aluminum. In addition, they also analyzed the morphology changes of the aluminum foil surface under different loads through SEM (scanning electron microscope) and AFM (atomic force microscope) technology combined with mathematical model analysis. Koohbor et al. [37] measured the in situ strain in the Li-LAGP-Au solid-state lithium battery through full-field optical DIC and other methods. They designed a module by themselves, using a hollow stainless steel clamp to tighten the solid-state battery to make it work normally. The clamp also acts as a collector, while the hole in the middle of the clamp is used for in situ DIC observation. They found that after a complete charge-discharge cycle, the maximum strain on the surface of the gold electrode can reach 3%, which leads to the separation between the electrode and the solid electrolyte. Cho et al. [47] calculated the electrode change in the lithium metal layer through the in situ curvature measurement of the lithium metal electrode (Figure 3c). In the previous work, the method of obtaining the stress evolution through curvature measurement is usually used for the single electrode of the liquid battery. It is relatively novel to use the electrode material of the solid-state battery. They used LLZO as a solid electrolyte, and the research electrode and counter electrode were lithium metal. A layer of quartz glass is covered on the surface of the copper foil collector, with lithium metal to better measure the curvature change, and they found that it takes a long time (30–50 h) for the stress change in the lithium metal layer generated during the charging process to reach a stable state, which indicates that the stress evolution in the lithium metal is slow. In addition, through the disassembly and observation of the recycled battery, it is found that the direction perpendicular to the surface crack has the largest curvature, which means the maximum deformation. Through the analysis of experimental results and the simulation calculation, the electrode surface defects (crack) lead to greater lithium flux and greater plastic deformation, and thus a greater hydrostatic pressure is generated at the crack tip. In contrast to DIC techniques, there are techniques to study the evolution of electrode materials and particle morphology at a more microscopic scale, such as operando SEM/TEM, operando XPS, or IR (on beamline). These techniques are often used to study particles, voids, and lithium dendrite nucleation and growth in electrode materials [48–50]. The observation of the evolution of these morphologies is usually analyzed in combination with electrochemical measurements, such as CV curves and EIS curves [49,50]. The EIS curve, for example, is semi-circular at high frequencies, reflecting the charge transfer between the material and the electrolyte, and diagonal at low frequencies, reflecting the diffusion of lithium ions in the electrolyte.

The diameter of the semicircular part represents the resistance value of the battery material, and the smaller resistance indicates the better performance of the electrode material.

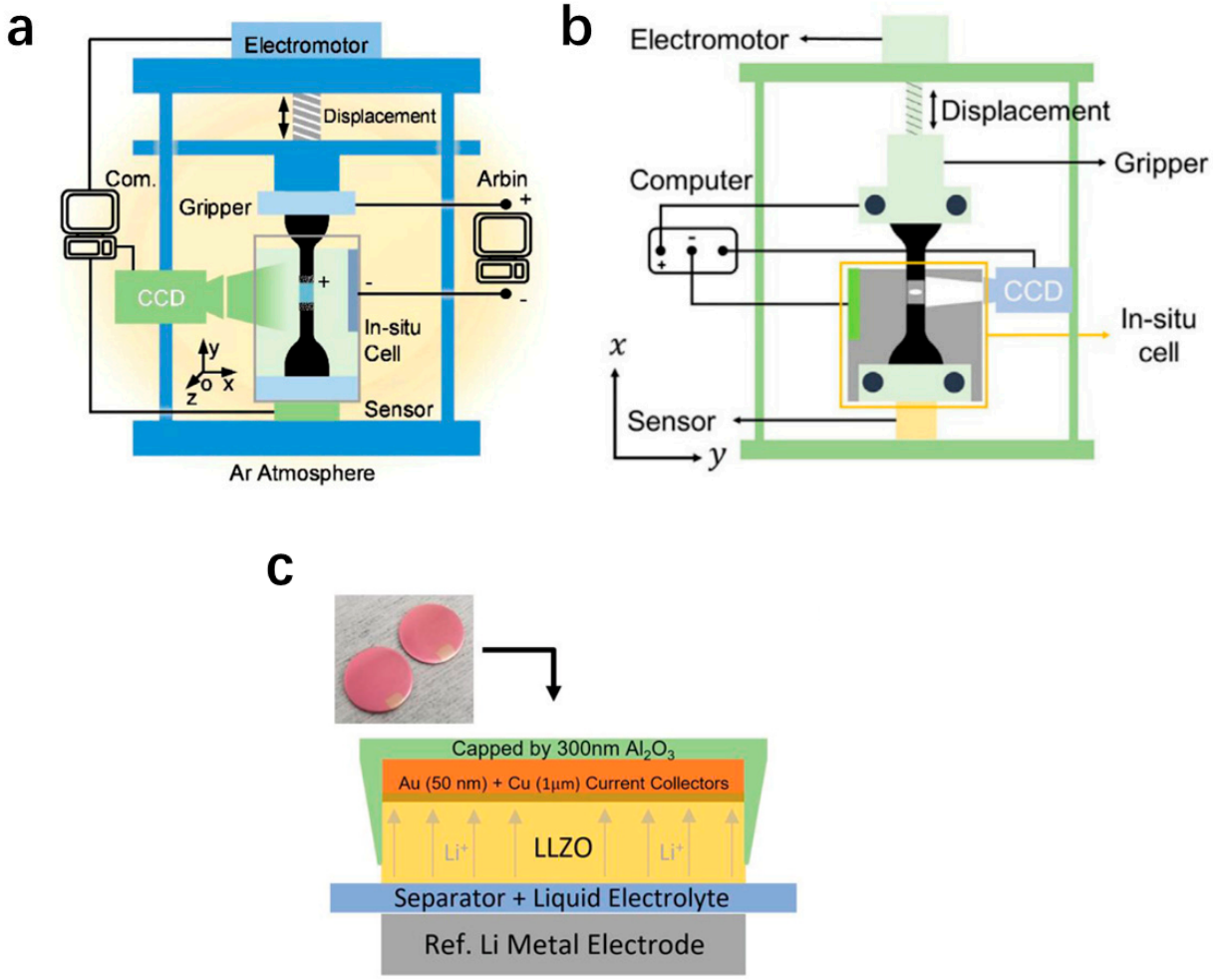
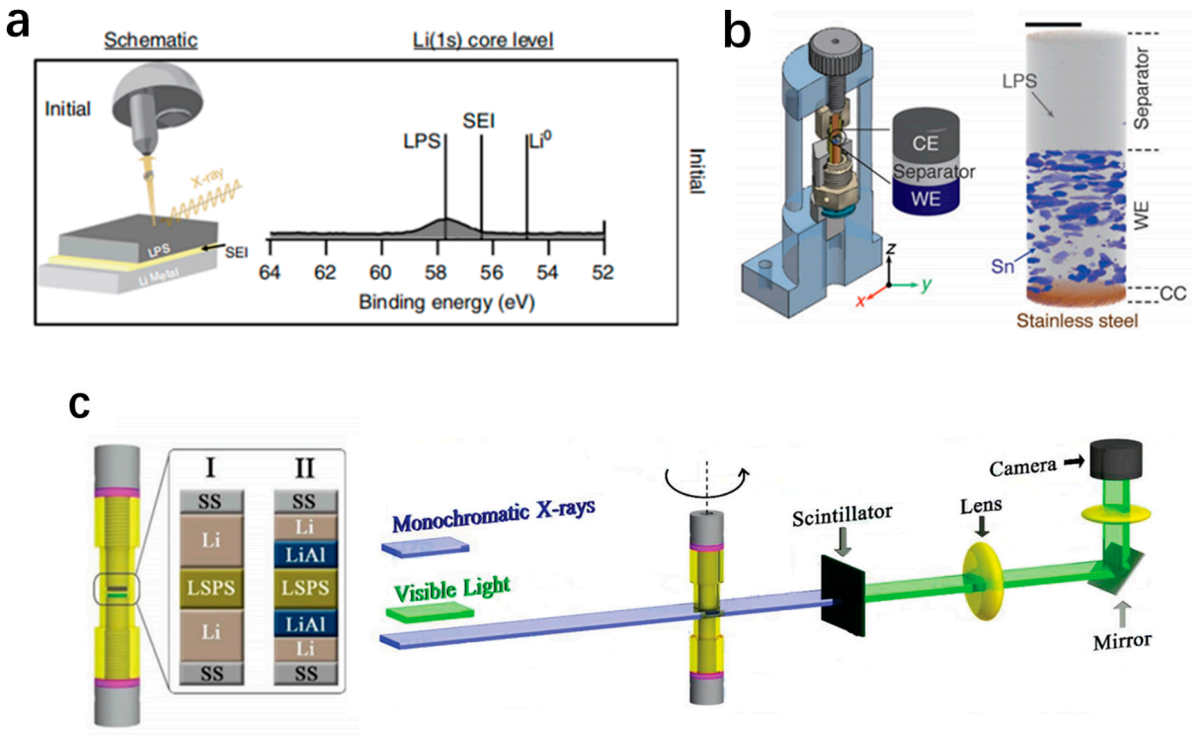


Figure 3. Several optical observation experimental setups: (**a**) In situ experimental setup for stretching aluminum foil [45]. (**b**) Tensile test device and elliptical hole reserved on aluminum foil [46]. (**c**) Solid-state battery assembly for measuring curvature [47].

X-ray technology can be used not only for defect detection inside batteries, but also for chemo-mechanical coupling experiments of batteries. At present, there are many battery experimental technologies based on X-ray, such as X-ray microscopy tomography [50], X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), synchrotron X-ray tomography [51–54], X-ray computed tomography [55,56], and X-ray diffraction [57–59]. No matter the optical observation method or X-ray characterization method, a homemade battery test device is required to achieve observation. Su et al. [60] modified a standard CR2016 battery, and they respectively punched a hole with a diameter of 3 mm in the positive and negative battery shell to prevent X-ray attenuation by the battery shell, and then sealed it with copper foil and aluminum foil. Combined with X-ray scattering and high-resolution transmission X-ray microscope (TXM) technology, the morphology evolution of $LiCoO_2$ particles in the cycle process was obtained intuitively. They found that $LiCoO_2$ particles experienced a process from cracking to crushing when lithiation occurred, and the larger the particles were, the better the crack resistance. This put forward new insights into the particle size of electrode materials used in battery manufacturing. In a recent study by Sun et al. [61], they mainly used (synchrotron) X-ray tomography technology. The schematic diagram of the solid-state battery assembly and X-ray experimental device is shown in Figure 4c,d. They studied the mechanical deformation and deforma-

tion evolution of the interface between the electrode material and the solid electrolyte in the solid-state battery due to the electrochemical reaction, including the cracks caused by lithium metal invading the solid electrolyte, the evolution of the interface, and the creep of lithium metal (Figure 4d). Their experimental results show that to maintain the normal operation and good performance of solid-state batteries, solid electrolytes with excellent mechanical properties must be selected, and the electrochemical stability of solid electrolytes is crucial. In addition, they also infer that the deformation degree of solid electrolytes increases with the increase of one-way discharge transport capacity, and they propose the electrochemical-induced mechanical stress distribution and its impact on the potential and ion distribution. It is worth mentioning that their method of combining X-ray tomography, EIS, TOF-SIMS (time of flight secondary ion mass spectrometry), and FEA (finite element analysis) technology to reveal the morphology evolution of the solid electrolyte and the internal interface region of the solid electrolyte is the first time for this method, which has far-reaching influence and significance on the research of solid-state batteries. X-ray tomography can also be combined with phase field simulation to study the fracture problems of electrode structures in solid-state batteries [62]. In some previous work, Wood et al. [63] used operational X-ray photoelectron spectroscopy and real-time in situ auger electron spectroscopy mapping to study the formation and evolution of the interface between lithium metal and solid electrolyte during the charge–discharge cycle of solid-state batteries (Figure 4a). Wu et al. [64] designed an X-ray observation device (Figure 4b). The anisotropy of active materials during expansion and contraction and the propagation mode of horizontal cracks in solid-state batteries were studied by using X-ray tomographic microscopy.

In general, the ordinary optical observation method device is more concise and can intuitively obtain strain data for chemo-mechanical coupling analysis, while the technology related to X-ray is more precise, which is conducive to the in-depth understanding of the solid battery electrode materials and the morphological evolution inside the solid electrolyte, but the stress-strain data are not easy to obtain. The chemo-mechanical coupling of these two parts is mainly reflected in the change of the external or internal morphology of the electrode material as the charging and discharging progresses.



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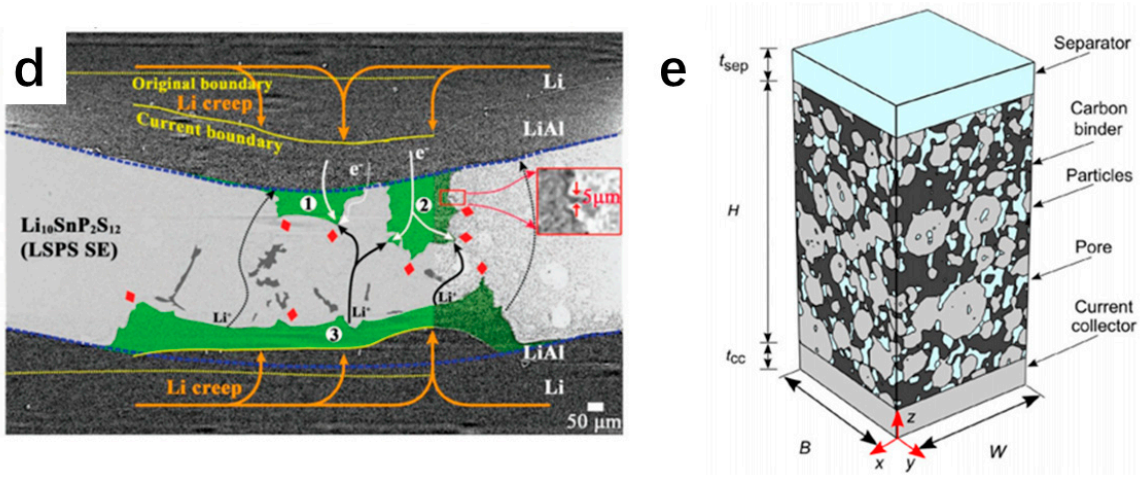

Figure 4. (**a**) OpXPS schematic and Li 1s core-level evolution of clean LPS surface [57]. (**b**) A design of operando SRXTM experimental [58]. (**c**) Schematic illustration of X-ray experimental battery assembly method and experimental set-up [55]. (**d**) SX-CT characterization results of the selected cross-section of the LSPS SE. (**e**) A 3D image-based microstructure obtained by X-ray CT [56].

3. Change the Structure or Mechanical Properties of Battery Components

In the previous sections, various experimental observation methods were used to study the mechanical chemo-mechanical coupling phenomena within solid-state batteries or electrode materials. The focus of the research approach was to use specific experimental setups and experimental techniques to study commonly used or highly researched electrode materials or full cells, but the studied electrode materials or cells themselves were not substantially changed or innovated. In some of the research work presented below, the study focus was placed on changing the properties of the electrode materials themselves as a way to improve the mechanical performance of the electrode materials during electrochemical cycling.

During the charge/discharge cycle of the battery, the electrode materials experience periodic volume expansion and stress evolution, which leads to cracks on the surface and inside of the electrode material. These cracks accelerate the capacity decay of lithium batteries, and the generation and development of such cracks should be minimized. In their recent work, Li et al. [65] proposed to improve the mechanical properties of electrodes during cycling by using undulating LiSn electrodes. They achieved the undulating electrode surface in two main steps, the first step using the mechanical imprinting method to produce undulating structures on the Sn foil electrode, and the second step using Naph-Li solution for pre-lithiation of the Sn foil (Figure 5a). The experimental results show that the capacity of the pre-lithiated undulating Sn foil electrode is significantly increased, while the resistance is significantly reduced. The simulation results show that this structure has much less stress compared to the plane electrode structure, which can effectively reduce the generation of cracks, which is consistent with the experimentally observed results. This structure of the electrode also allows for a more uniform reaction of the LiSn electrode alloying/de-alloying and, due to the increased surface area of the electrode, allows more lithium to participate in the alloying reaction at the same time, reducing the loss of lithium. Ren et al. [66] designed a sulfide solid electrolyte with a self-healing function, which has the function of reversible adaptation to the volume change of lithium metal electrode, and they found that the cycle life of lithium metal electrode using this solid electrolyte increased more than two times compared with the ordinary lithium metal electrode. In addition, the composite electrolyte can effectively prevent the formation of interface and lithium filament penetration due to the automatic repair of cracks, which is of great significance for the research of solid-state batteries. Kwon et al. [67] introduced a method of making electrodes using a sulfide binder that allows solid-state batteries to operate properly at much lower external stack pressures. Liu et al. [68] and Qian et al. [69] both changed the internal structure of the

battery, changing the traditional way of winding the battery cells and designing a battery with high mechanical flexibility by referring to the structure of crocodile skin and vertebrae.

Changing the structure or chemical and mechanical properties of the battery components can effectively improve the performance of the battery, and this method provides a new way of thinking for the development and innovation of the battery. This part of the chemo-mechanical coupling is mainly reflected in the improvement of the chemical or mechanical properties of the battery by changing the structural or mechanical properties.

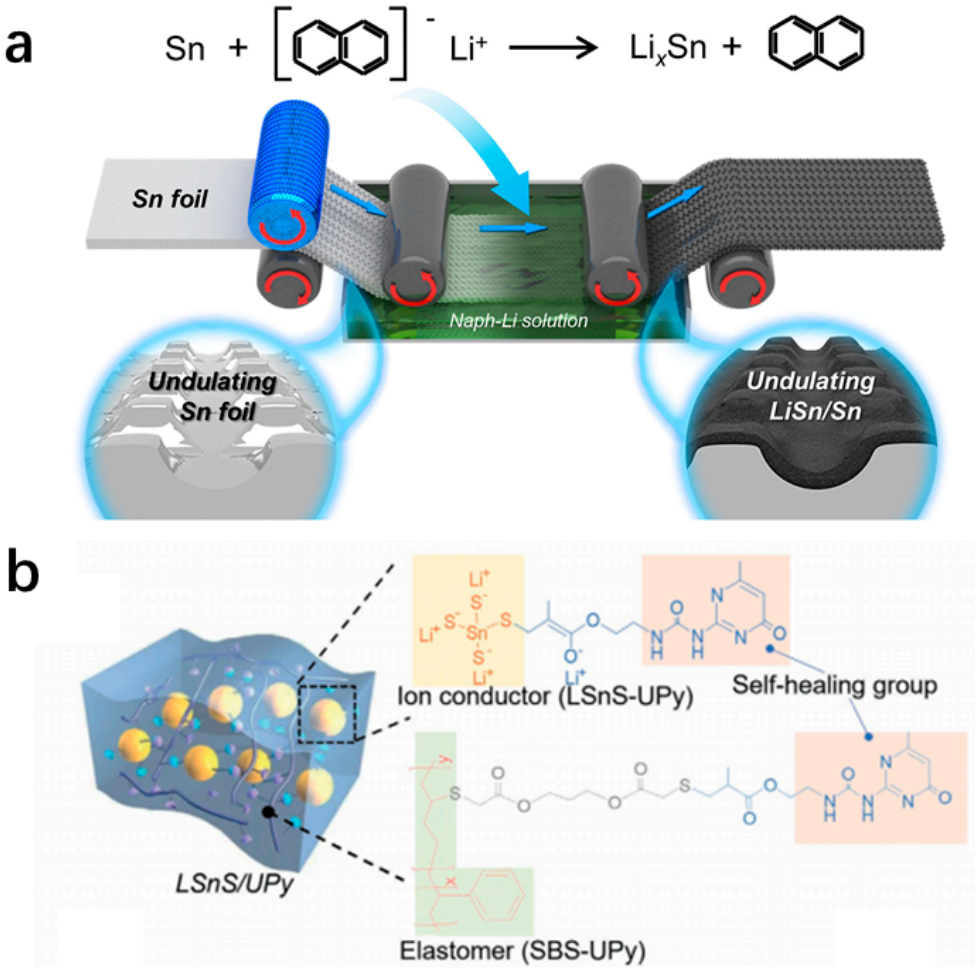

Figure 5. (**a**) Two main steps to obtain an undulating electrode [65]. (**b**) Solid electrolyte with self−healing ability [66].

4. Prospect and Summary

This review describes several experimental methods for observing chemo-mechanical coupling phenomena in cells or electrode materials, including direct stress measurement by external mechanical sensors, the internal burial of optical fibers, measurement of stress and strain in solid-state batteries using optical measurement methods, observation of the evolution of the interface between electrode materials and solid-state electrolytes in solid-state batteries using X-ray methods, and changing the structure and composition of the cell assembly itself. These methods have their focus on the research point, but also all have certain limitations. As summarized in Table 1, the first three methods can be used when the study focuses on stress, and the fourth method can be used to analyze the evolution of the internal morphology in the cell after charging and discharging cycles. To study the electrode material alone, for example, one can research a specific electrode material itself and chemo-mechanical coupling properties, and exclude the interference of other battery components, which has great significance for the progress and development of

the electrode material itself; but this method is challenging when put into a functioning battery. In the case of solid-state batteries, the interface evolution cannot be observed while using external/internal or optical methods to measure stress and strain. Meanwhile, it is difficult to directly measure the stress evolution using experimental methods with X-ray-related technology. The solid-state battery requires a certain external pressure to ensure the tight connection between the components during operation, which places high demands on the experimental setup, firstly, to ensure that a certain external stack pressure is provided, and also to facilitate the experimental observation operation. The future development direction of the experimental device should combine the previous methods while exploring new methods, focusing on how to ensure the non-invasive nature of the mechanical measurement device, without affecting the work of the battery itself, while directly obtaining the stress evolution of different internal components or interfaces. At the same time, the experimental device does not affect the X-ray observation, and the experimental method based on X-ray technology can be carried out to visualize the entire dynamic. In this way, it is possible to visualize the morphological evolution of the measured parts while obtaining the stress evolution inside the cell, which is a great contribution to the study of solid-state batteries. The method of changing the structure and composition of the cell components presented at the end of this paper also has great potential for development. It is worth mentioning that mathematical modeling can also be used to study solid-state batteries. For example, Li et al., proposed a reduced-order approach to simplify the PDE (partial differential equation)-based all-solid-state battery model to an ordinary differential equation (ODE) model [70]. Raijmakers et al., developed a model to describe the charge transfer kinetics at the electrode/electrolyte and interface, the diffusion and migration of mobile lithium ions in the electrolyte, and the diffusion and movement of lithium ions and electrons in the cathode [71]. Song et al., developed a battery model to study the chemo-mechanical coupling behavior in all-solid-state, thin film, Li-ion batteries (TFBs) [72]. The advantage of using mathematical models is that there is no need to place any physical sensors inside the battery, and this approach can be well combined with experimental methods to study solid-state batteries. In conclusion, it is important to use experimental methods to characterize and measure the chemo-mechanical coupling inside the cell, and innovations in observation and characterization methods contribute to the development of new electrode materials and the next generation of solid-state batteries.

Table 1. Advantages and disadvantages of four main experimental methods.

Experimental Method	Advantages	Disadvantages
External mechanical measurement	(1) Experiments are relatively easy to perform. (2) Uniaxial stresses of solid-state batteries can be obtained directly.	(1) Radial stresses and radially imposed restraint effects are neglected. (2) Internal components and stresses at the interface cannot be measured separately.
Internal mechanical measurement	(1) Sensors can be individually embedded in different components and interfaces. (2) Biaxial stress can be obtained.	(1) Internal sensors may have some effects on the battery.
Optical characterization methods	(1) Strain data and images of the evolution of each part of the cell can be obtained.	(1) Stress cannot be measured directly, but can only be calculated from strain or curvature change.
X-ray characterization methods	(1) The battery can be observed to check the evolution of each part and the interface.	(1) Inability to measure stress while observing internal evolution.

Author Contributions: Methodology, Formal analysis, Writing—original draft, J.W.; Conceptualization, Funding acquisition, Supervision, Writing—review & editing, F.H. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the GuangDong Basic and Applied Basic Research Foundation (Grant No. 2022A1515010950) and the Natural Science Foundation of Shandong Province, China (Grant No. ZR2020QA043).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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