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REVIEW ARTICLE

Application of X-ray imaging technology in energy materials research

Yuxin Gong, Zhenjiang Yu, Jiajun Wang*

School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China. E-mail: jiajunhit@hit.edu.cn

ABSTRACT

With the increasing demand for sustainable energy, advanced characterization methods are becoming more and more important in the field of energy materials research. With the help of X-ray imaging technology, we can obtain the morphology, structure and stress change information of energy materials in real time from two-dimensional and three-dimensional perspectives. In addition, with the help of high penetration X-ray and high brightness synchrotron radiation source, in-situ experiments are designed to obtain the qualitative and quantitative change information of samples during the charge and discharge process. In this paper, X-ray imaging technology based on synchrotron and its related applications are reviewed. The applications of several main X-ray imaging technologies in the field of energy materials, including X-ray projection imaging, transmission X-ray microscopy, scanning transmission X-ray microscopy, X-ray fluorescence microscopy and coherent diffraction imaging, are discussed. The application prospects and development directions of X-ray imaging in the future are prospected.

Keywords: Synchrotron Radiation; X-ray Imaging; In Situ; Attenuation Mechanism

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1. Introduction

With the rapid development of the world economy and the gradual depletion of fossil energy, finding a sustainable energy as its substitute has become a major issue in the development of the new era. At present, rechargeable batteries, solar cells, fuel cells and other new energy devices are the focus of researchers in related fields. However, in addition to the exploration in the field of design and preparation of new energy devices, the research in the field of characterization means is also essential to explore the characteristics of new materials, which clarifies the attenuation mechanism of electrode materials in the process of charge and discharge, clarifies the operating mechanism of devices, and improves the performance of new energy devices.

Common characterization methods mainly include nuclear magnetic resonance (NMR), X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), neutron imaging technology and X-ray imaging technology based on synchrotron radiation (SR)[1]. Compared with spectral characterization techniques such as infrared spectroscopy, imaging technology has the advantage of providing more intuitive information. It can clearly capture the microstructure of samples and accurately describe their characteristics.

At present, the commonly used imaging technologies include electron microscope and X-ray imaging technology. Electron microscope

has the characteristics of high resolution. However, conventional electron microscope can only observe the surface characteristics of materials, and cannot characterize the internal morphology of materials with three-dimensional structure. In addition, due to the high brightness, high flux and good stability of synchrotron radiation light source, X-ray technology based on synchrotron radiation can provide high-resolution images. Therefore, compared with other characterization methods, it can collect data quickly and accurately[2,3]. This paper will focus on the application of synchrotron radiation X-ray imaging technology in the qualitative and quantitative characterization of energy materials.

2. X-ray projection imaging

X-ray projection imaging is mainly composed of X-ray source, sample stage, X-ray area detector and CCD or CMOS detector coupled with scintillator, as shown in **Figure 1**. Unlike other X-ray imaging systems, there are no other X-ray optical devices behind the sample stage of the X-ray projection imaging system. X-rays pass through the sample and are directly projected onto the detector. Imaging relies on the different contrast of the sample itself to analyze its structure. Absorption X-ray imaging relies on the attenuation of the incident X-ray beam to form a projected image on the detector.

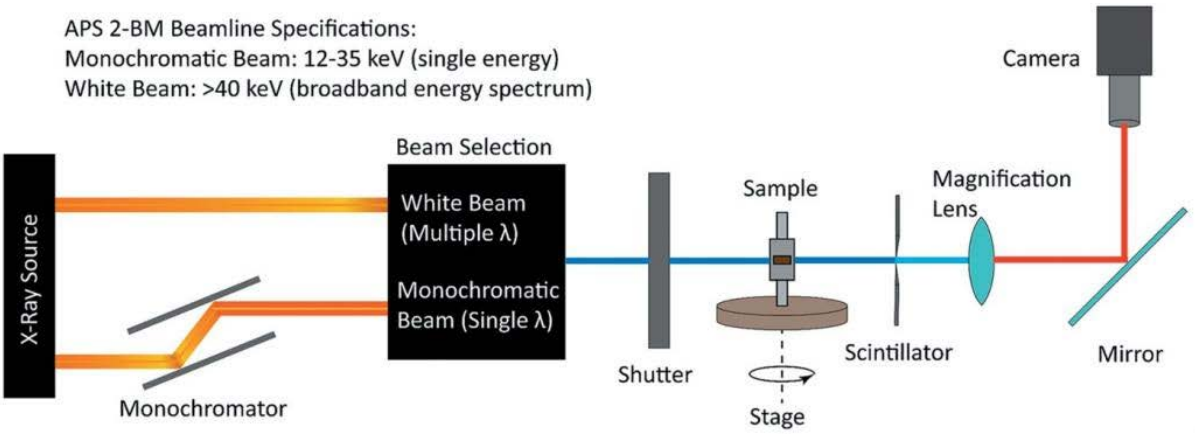


Figure 1. Diagram of the synchrotron X-ray projection imaging setup[4].

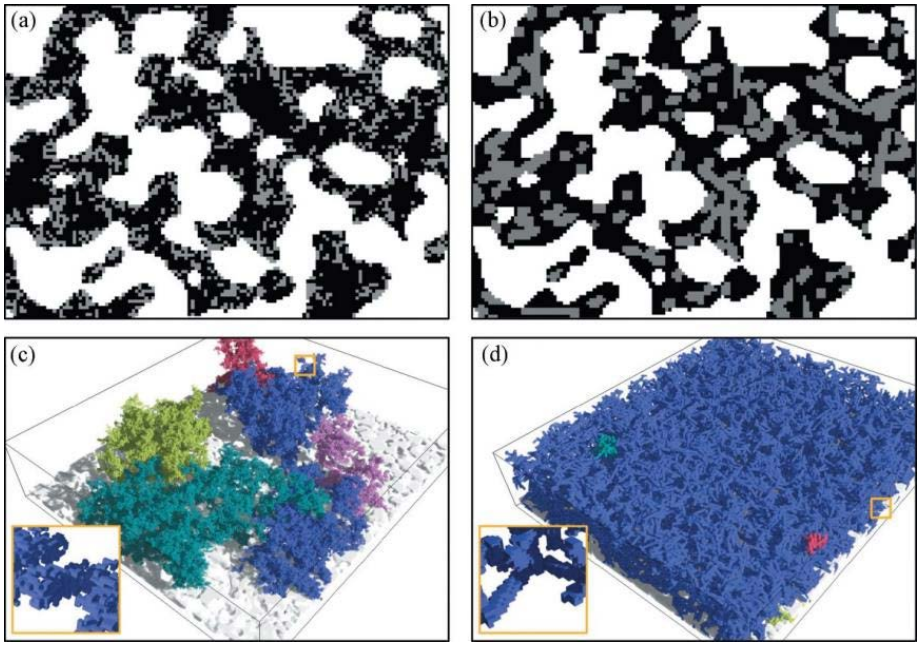


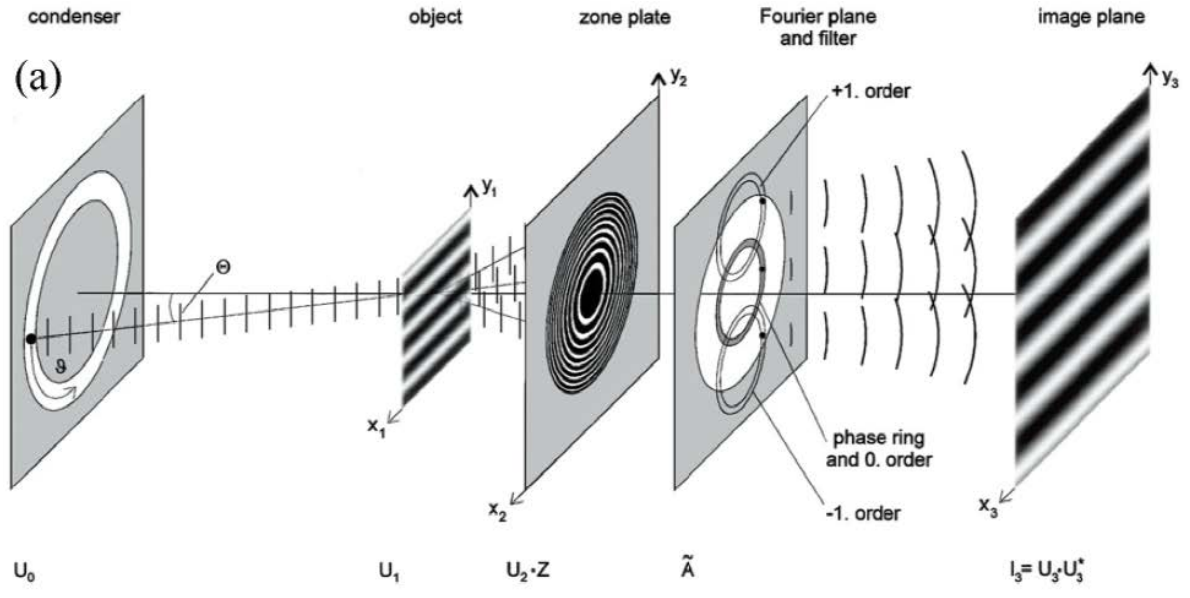
Figure 2. (**a**) Image of the reconstructed active-material domain (white) and the inserted CBD (gray), using the random cluster model; (**b**) the CBD inserted with the fiber model; (**c**, **d**) the five largest connected CBD clusters in the representations corresponding to 29% carbon binder content in the pore space for the random cluster model (**c**) and the fiber model (**d**)[7].

In terms of application, Shearing *et al.*[5] obtained the first high-resolution image of lithiumion battery electrode structure through X-ray projection imaging. Through this image, a series of parameters such as porosity, tortuosity and surface parameters were quantified, and the specific characterization of the heterogeneous microstructure of conventional graphite electrode was obtained for the first time. At present, X-ray tomography derived from X-ray projection imaging has become a conventional means to analyze battery structure and diagnose battery fault. At the same time, the combination of X-ray tomography and computer three-dimensional modeling can quantify the relationship between the structure and performance of energy materials, further expanding the application range of X-ray tomography[6 - 8]. Zielke *et al.*[7] combined the X-ray tomographic image data of active substances with the computer model of carbon binder domain (CBD), and compared the cathode transmission parameters during charging and discharging of two different CBD morphology models, random cluster model and fiber model. The modeling graph is shown in **Figure 2**.

Although X-ray projection imaging has the advantage of non-destructive detection of dynamic structure evolution with high time resolution, it still has some limitations. Firstly, the high-throughput synchrotron radiation X-ray beam may cause radiation damage to the sample. For example, when proton exchange membrane fuel cell (PEMFC) is exposed to X-ray beam, the electrochemical performance degradation of the cell caused by X-ray can be observed in the in-situ experiment[9]. Secondly, the resolution of X-ray projection imaging is insufficient. The best spatial resolution of X-ray projection imaging is about submicron, which is not enough to detect the structural changes of single electrode particle energy levels and the crystal structure and chemical state distribution in the samples. Therefore, in order to make up for the limitations of X-ray projection imaging, other X-ray imaging systems are still needed.

3. Transmission X-ray microscopic imaging

The imaging principle of transmission X-ray microscope (TXM) is similar to that of electron microscope. The difference is that most TXM use hard X-rays with shorter wavelength. In TXM, the X-ray is focused by the focusing lens and irradiated on the sample. The transmitted x-ray is amplified by the Fresnel zone plate and projected onto the detector to form a projection image (as shown in **Figure 3a**)[10]. TXM is a full field imaging technology, which can generate a single image with high resolution, and its maximum spatial resolution is determined by the region outside the Fresnel zone plate[11]. At present, the precision Fresnel zone plate can achieve a two-dimensional spatial resolution of 20 ~ 30 nm[12,13].



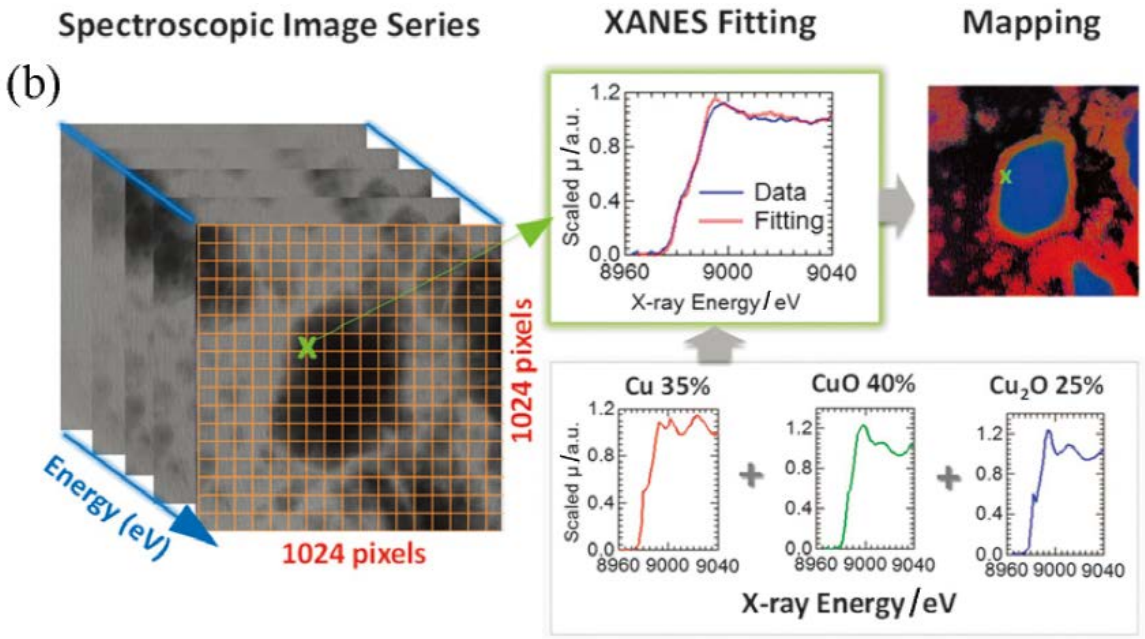


Figure 3. (**a**) Illustration of the TXM experimental setup[10]; (**b**) working principles and data processing of TXM-XANES experiment on CuO anode[12].

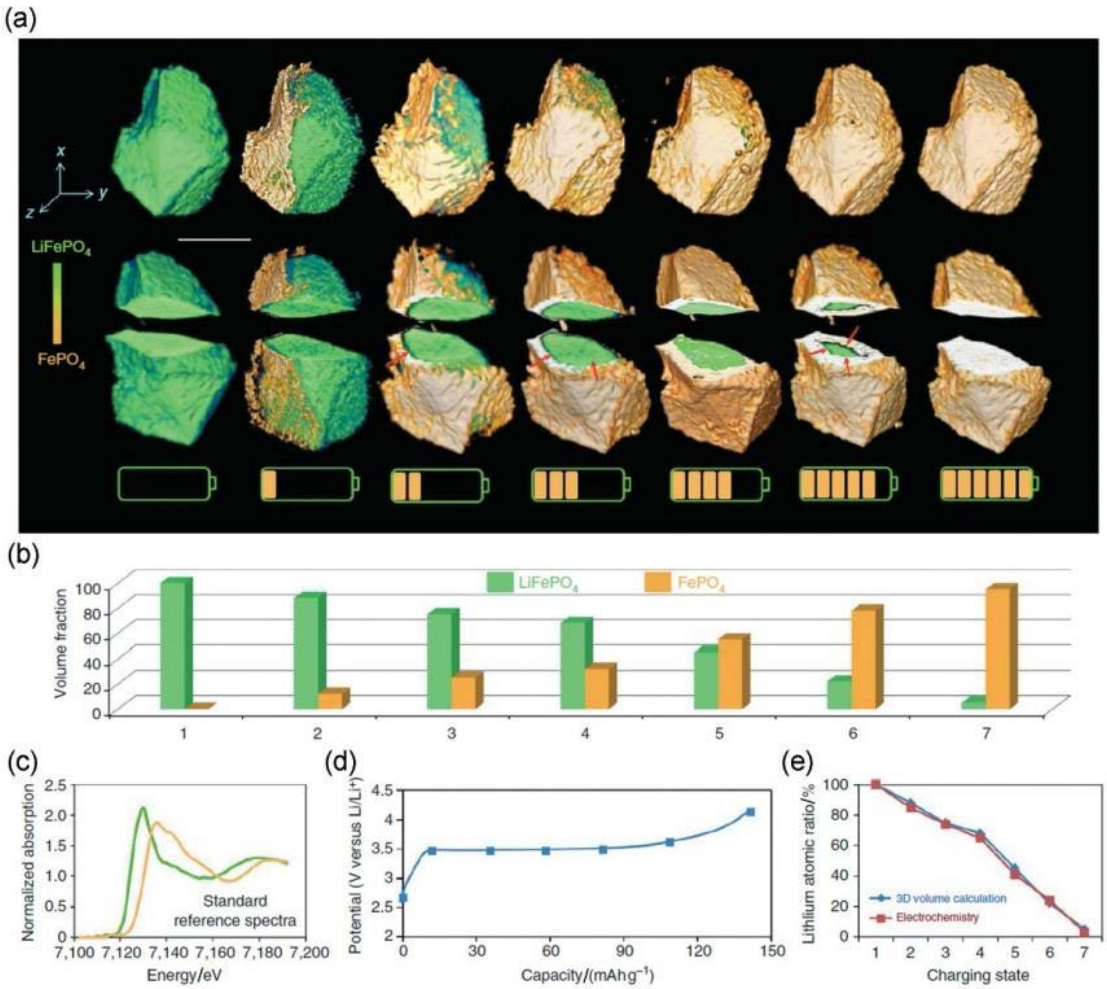


Figure 4. (**a**) Phase distribution as a function of charging time; (**b**) Phase volume fraction obtained from 3D quantitative analysis; (**c**) Standard XANES spectra for lifepo4 And fepo4; (**d**) The charging profile of lifepo4 Battery; (**e**) Agreement between lithium atomic ratio obtained from electrochemical measurement and from 3D volume analysis[14].

In the research of energy materials, the absorption contrast mode is often used to characterize the materials. The X-ray absorption degree is also different with the thickness and chemical composition of the materials. Therefore, in order to obtain high-quality absorption images, the thickness or particle size of samples are often adjusted according to their chemical composition. Wang *et al*.[13] selected CuO as the research material to demonstrate the core-shell conversion model and the interface phase after the lithium insertion/de lithium process for the first time. By combining X-ray imaging and synchrotron radiation X-ray absorption near edge structure (XANES) technology, the products at different discharge stages were quantified (**Figure 3b**). In addition to chemical component analysis, another unique feature of TXM technology is 3D imaging. Based on a series of two-dimensional X-ray projection images from different angles, X-ray 3D tomography technology can realize three-dimensional visual characterization of local morphology, chemical composition and crystal structure by revealing the internal characteristics of samples[14]. The high sensitivity and strong penetrability of imaging make TXM a reliable tool in battery research. In addition, the author's research group used the full field hard X-ray microscopic imaging technology to show an application case of in-situ XANES nano tomography technology, which can establish a five-dimensional (three-dimensional space, time and energy) data set to track the evolution of the phase transition of a single lithium iron phosphate particle with the charging time in the process of lithium removal (**Figure 4**)[14].

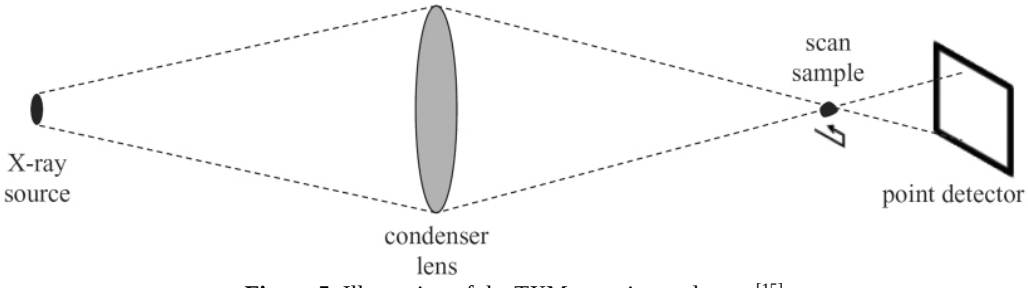


Figure 5. Illustration of the TXM experimental setup[15].

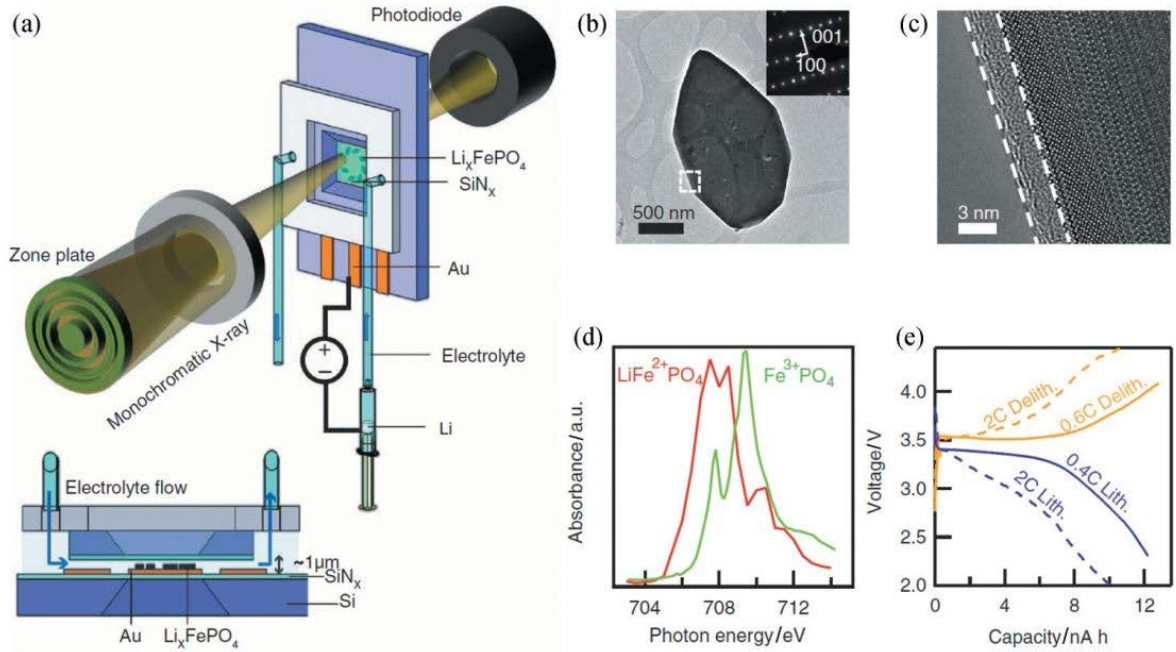


Figure 6. (**a**) Schematic of the operando liquid imaging platform; (**b**) bright-field TEM and electron diffraction of a typical $LiFePO_4$ Platelet particle; (**c**) high-resolution TEM of the carbon coating (outlined)of a $LiFePO_4$ particle; (**d**) typical x-ray absorption spectra of $LiFePO_4$ and $FePO_4$ particles in liquid; (**e**) electrochemical cycling of $LixFePO_4$ particles in the microfluidic liquid cell.

4. Scanning transmission X-ray microscopy

One limitation of TXM is the low X-ray absorption and poor image contrast of light elements (such as Li, etc.) in the hard X-ray energy range[12]. Similar to TXM, scanning transmission X-ray microscopy (STXM) also irradiates the sample with focused X-rays, and generates an image by analyzing the X-ray transmission intensity passing through the sample (**Figure 5**). Unlike TXM, STXM uses soft X-ray imaging to further improve the resolution. Therefore, compared with TXM, STXM has higher imaging resolution for light elements (Li, etc.), more flexible imaging area and lower X-ray dose. However, STXM also has some disadvantages, such as the need for imaging in vacuum environment, higher requirements for sample thickness, slow imaging, and small field of vision (tens to hundreds of nanometers)[12,16]. In terms of application, Lim *et al*.[17] used STXM to draw the dynamic image of Li component and intercalation rate in Li_XFePO_4 (**Figure 6**). The spatial change of nano spatial rate and composition controls the lithium path on the length scale of sub particles. This coupling of lithium component and surface reaction rate controls the dynamics and uniformity of ion insertion process in electrochemical reaction.

5. X ray fluorescence microscopy

In partially modified energy materials, such as doped or surface modified samples, the content of elements used for modification or doping is often very small, so the detection of these trace elements is difficult, and the detection equipment with high sensitivity is required. X-ray fluorescence microscopy (XFM) has a powerful function. Trace elements in samples can be mapped to ppm level through spectral analysis of secondary photons emitted. XFM has recently been used in battery research for element analysis under electrochemical test[18,19]. Combined with X-ray absorption spectroscopy, XFM can also be used to analyze trace chemical components in batteries. Yu *et al*.[18] combined in-situ XFM with XAS technology to monitor

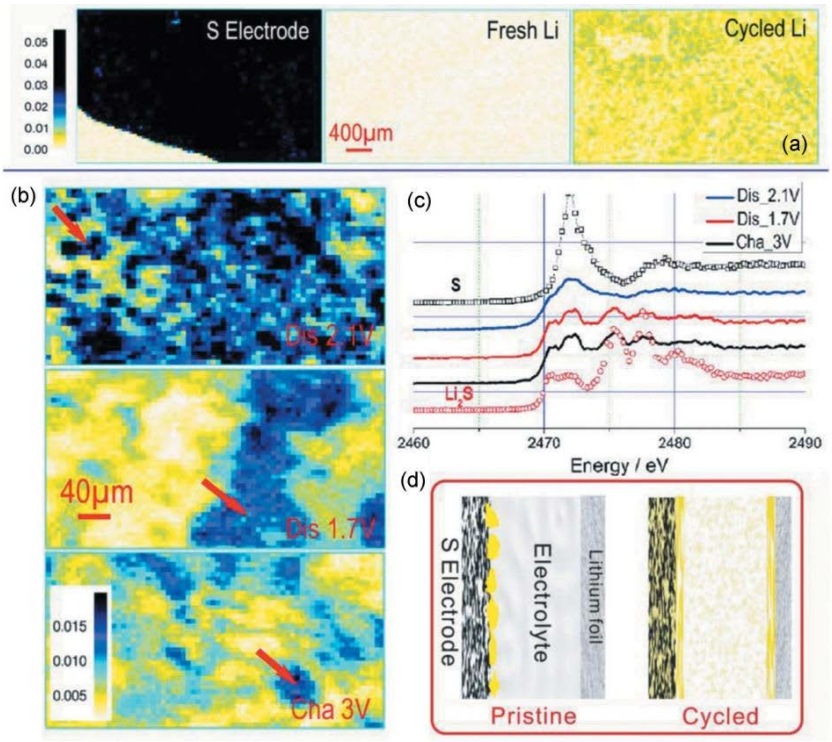


Figure 7. (**a**) XRF images collected on Sulfur/Ketjen black electrode, fresh Li foil, and Li foil harvest from the Li|Sulfur/Ketjen black cell after one cycle; (**b**) XRF images collected on lithium anode electrodes harvested from the Li|Sulfur/Ketjen black cells at discharged 2.1V, discharged 1.7V, and re-charged 3V states; (**c**) XAS spectra collected at the selected area as marked by red arrows shown on the images; (**d**) Schematic to illustrate sulfur dissolution and redistribution after initial cycle[18].

the morphological changes of sulfur electrode and the redistribution of sulfur and polysulfides in real time through XFM images, and characterized the changes of sulfur compounds through XAS, so as to detect the morphological evolution of Li-s battery during the first charge and discharge cycle of the battery (**Figure 7**).

At present, it is still difficult to study battery electrochemistry with XFM. Firstly, the spatial resolution of XFM is low (micron or submicron). It can only image large-scale electrode particles, but cannot clearly distinguish single nano particles. Second, XFM takes a long time. Because XFM is imaged by scanning, it usually takes a long acquisition time to achieve a reasonable signal-to-noise ratio for each pixel, which limits its application in the in situ battery electrochemical experiment[16]. The development of x-ray focusing optics, multi-element detectors and low radiation next-generation X-ray sources is expected to significantly improve the temporal and spatial resolution in the near future.

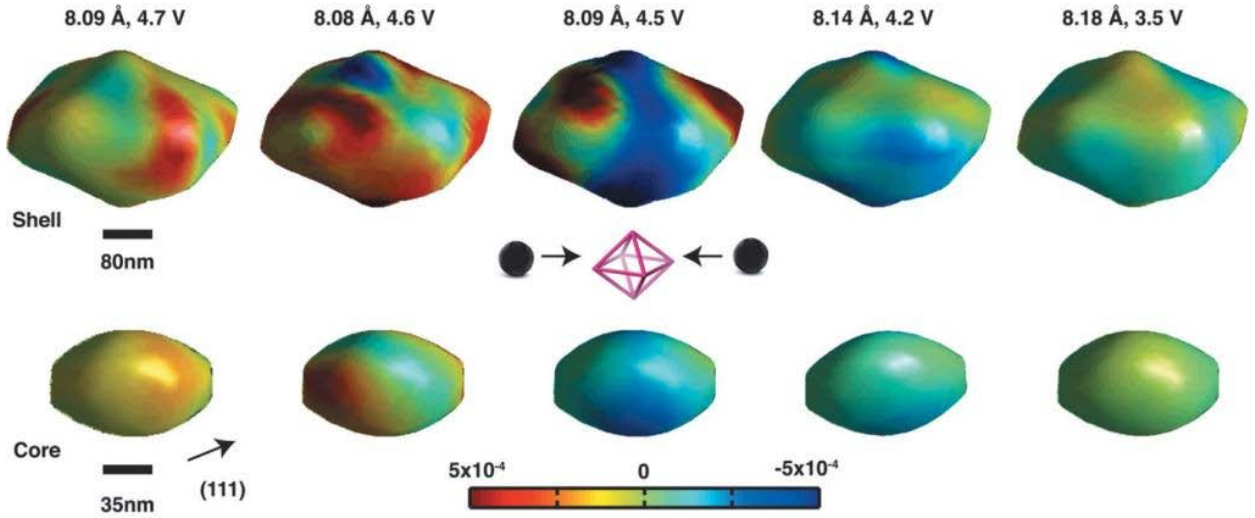


Figure 8. The in operando CXDI experiment shows inhomogeneous strain evolution during discharge of a single $LiNi_{0.5}$ $Mn_{1.5}O_4$ nanoparticle. Images are labeled by their respective lattice constant values and open circuit voltages[23].

6. Coherent X-ray diffraction imaging

Unlike the above lens based X-ray imaging system, coherent X-ray diffraction imaging (CXDI) does not need to be imaged through a lens, but uses the scattered light of the sample to form an image through the coherent characteristics of the incident beam. At the same time, due to the coherence between different scattered light, each scattered ray has a fixed phase relationship with each other ray, thus forming an interference pattern in the far field. The interference pattern is determined by the structure of the scattering object. Therefore, CXDI has many advantages that lens based X-ray imaging systems do not have. For example, very high spatial resolution imaging can be achieved by using high penetration X-rays[20]; for conventional X-ray imaging systems, Only using extremely high precision lenses can achieve similar resolution[21]. The X-ray imaging system with such lens usually has a very short working distance, which makes the in-situ imaging experiment more difficult[22]. Ulvestad *et al*.[23] for the first time to apply the in-situ CXDI operation technology to the research of such energy materials. They tracked the evolution process of 3D defects in $LiNi_{0.5}Mn_{1.5}O_4$ cathode particles, and found uneven stress distribution during the electrochemical cycle (**Figure 8**).

Recently, according to the scale of the detected object, the development of coherent diffraction X-ray imaging has been divided into two directions[24]: an imaging system whose target object size is completely consistent with the X-ray used for detection, also known as traditional coherent diffraction imaging; the object scale is large and needs scanning imaging. The imaging system in which data from different areas of the sample are superimposed in the calculation algorithm used to gener-

ate the image is called “stack imaging”.

7. Conclusion

X-ray imaging technology plays a key role in understanding the reaction mechanism of energy materials. We reviewed the main X-ray imaging technologies and introduced their working principles and their applications in energy materials research. The main features of the X-ray imaging technology discussed are summarized in **Table 1**.

X-ray imaging can provide two-dimensional and three-dimensional shape information of energy materials in various scales ranging from tens of nanometers to tens of microns. Taking time, temperature and pressure as other dimensions except two-dimensional/three-dimensional space can more accurately and comprehensively study the structure and changes of energy materials in the multi-dimensional space[25]. X-ray microscopic imaging technologies such as TXM and STXM, combined with absorption spectrum, have the ability to image chemical components, and can detect the distribution and heterogeneity of phase and oxidation states. CXDI combines microscope technology with diffraction technology to achieve high spatial resolution. In addition, the non-destructive, high penetration and high time resolution of X-ray imaging technology make the in-situ characterization experiment possible. This in-situ experiment can track the structural and chemical changes of devices in real time. It has been successfully applied in a variety of energy materials, which is very important to understand the working mechanism of energy materials. In recent years, the continuous progress of X-ray imaging technology has promoted the rapid development of energy materials. With the development of hardware (focusing lens, detector, etc.) and software (data collection, storage and analysis), the factors hindering the development of X-ray imaging are being overcome. We believe that the X-ray imaging technology based on synchrotron radiation will bring more possibilities to clarify the complex electrochemical processes in various battery systems, thus prompting researchers to better design and develop advanced materials to meet the human requirements for the continuous improvement of battery performance.

Table 1. Summary of the X-ray imaging methods[12]

Technology	Function	Spatial resolution	Time resolution	Energy level range	Sample thickness	Advantage	Shortcoming
X-ray projection imaging	Two dimensional imaging	10 μm		>5 keV		Full field view; fast imaging speed	Low spatial resolution
TXM	Elemental analysis, chemical analysis, 2D/3D imaging	20 ~ 30 nm	Seconds to minutes	5 ~ 11 keV	Tens of nanometers to tens of microns	Chemical analysis possible	Poor contrast of light element imaging
STXM	Elemental analysis (including light elements Element)	12 ~ 40 nm	Hundreds of seconds to hours	<2 keV	Tens to hundreds Nanometer	Light element imaging	It needs to be carried out under vacuum; slow imaging speed
XFM	Elemental analysis, chemical analysis, 2D/3D imaging	Submicron level	Minutes to hours	20 ~ 60 keV	Tens of microns	It can be used to detect trace elements	Low spatial resolution
CXDI	2D/3D imaging, electron density, stress analysis	Several nanometers	Seconds	5 ~ 15 keV	Hundreds of nanometers to tens of microns	Available for stress and structural analysis	Amorphous material not applicable

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Conflict of interest

The authors declared no conflict of interest.

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