ADVANCED CHARACTERIZATION TECHNOLOGIES FOR SECONDARY BATTERIES

Editors:
Tinglu Song
Fan Xu
Chunli Li

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Advanced Characterization Technologies for Secondary Batteries

Edited By

Tinglu Song
Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

Fan Xu
State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics & Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China

&

Chunli Li
State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China

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Editors: Tinglu Song, Fan Xu & Chunli Li

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Chunli Li, Hao Li, Guang Yang, Huiyu Li and *Yongjun Feng*

FOREWORD

The growing global demands for electric energy storage and renewable resources promote the development of various secondary batteries, including metal-ion batteries, metal-air batteries, etc. Despite significant progress obtained in recent decades, permanent goals exist in secondary batteries to continually improve their energy density and durability/safety. To achieve this, it becomes imperative to elucidate the relationship between micro-level structures/properties and device performance. However, conventional measurements may fail to meet such stringent requirements.

In this book, eight typical advanced characterization tools in battery research are introduced, including various microscopy, spectroscopy, and diffraction techniques. More importantly, it includes several attractive techniques that have been employed in battery studies yet have not been in-depth discussed, such as neutron diffraction and ultrasonic nondestructive testing. Furthermore, related applications and future prospects are reviewed and presented. I believe that this book will be an essential and important guide for the broad battery research community.

Congratulations to the editors and all authors for successfully accomplishing this book.

Gu Xu
Fellow of Canadian Academy of Engineering
Department of Materials Science and Engineering
McMaster University, Ontario, Canada

PREFACE

The development of high-energy density and stable secondary batteries fulfills the growing global demand for electric energy storage capacity. Although tremendous efforts have been devoted, further enhancement of battery performance will significantly rely on the precise unravelling of atomic-level structure and micro-properties in related materials/devices. Therefore, in this book, we would like to highlight several essential yet commonly employed characterization tools in secondary battery investigations.

In chapters 1 to 3, we focus on morphology measurements in secondary batteries, discussing basic structure, diverse accessories, sample preparation, recent research progresses, applications and current limitations of transmission electron microscopy (TEM), focused ion beam (FIB) methods, and atomic force microscopy (AFM) in related battery studies.

Chapters 4, and 5 present a discussion on X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), respectively, aiming to unravel the chemical states of electrode materials and solid electrolyte interphase/cathode electrolyte interphase (SEI/CEI) film.

In chapters 6-7, we review diffraction-related technologies (e.g., neutron diffraction, synchrotron-radiation X-ray tomography) in secondary batteries, which are commonly adopted to acquire chemical and crystallographic details.

The last chapter 8 introduces an emerging method, ultrasonic nondestructive testing technology, to probe defects in battery materials/devices.

We expect the above contents could promote future developments of both advanced characterization methods and secondary battery studies. The potential audience of this book includes the broad research community of secondary batteries and characterization, such as research scientists, professors, engineers, and students.

Tinglu Song
Experimental Center for Advanced Materials
School of Materials Science and Engineering
Beijing Institute of Technology
Beijing 100081, China

Fan Xu
State Key Laboratory for Artificial Microstructure and Mesoscopic Physics
School of Physics, Frontiers Science Center for Nano-optoelectronics &
Collaborative Innovation Center of Quantum Matter
Peking University, Beijing 100871, China

&

Chunli Li
State Key Laboratory of Chemical Resource Engineering
College of Chemistry, Beijing University of Chemical Technology
Beijing 100029, China

List of Contributors

Chuguang Yu	Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Chaoxiang Xie	Shanghai Institute of Space Power Sources, Shanghai, China
Chunli Li	State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China
Defeng Lu	Explorer Testing Technologies (Dongguan) Co., Ltd., Dongguan 523000, China
Fan Xu	State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics & Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China
Guoqiang Tan	Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Gang Xue	Suzhou MASRC Testing Technology Co., Ltd., Suzhou 215168, China
Guang Yang	Shanghai Aerospace Power Technology Co., Ltd. Shanghai, China
Huaqiang Zhu	Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Huiyu Li	State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing, China
Hao Li	Key Laboratory of Neutron Physics and Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Sichuan 621999, China
Jili Yue	College of Materials Science and Engineering, National Engineering Research Center for Magnesium Alloys, National Innovation Platform (Center) for Industry-Education Integration of Energy Storage Technology, Chongqing University, Chongqing 400044, China
Jun Wang	Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201204, China
Jie Zhang	Beijing dklead Technology Co., Ltd., Beijing 101318, China
Lixia Bao	Analysis & Testing Center, Beijing Institute of Technology, Beijing 102488, China
Lian Wang	Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401151, China
Liyuan Zhao	Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Meishuai Zou	Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Mengmeng Qian	Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Ni Yang	Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401151, China

Ruiwen Shao	Beijing Advanced Innovation Center for Intelligent Robots and Systems and Institute of Convergence in Medicine and Engineering, Beijing Institute of Technology, Beijing 100081, China
Shixiong Zhang	Beijing dklead Technology Co., Ltd., Beijing 101318, China
Shunzi Jiang	Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Shuo Wang	School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Tinglu Song	Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Xiaodong Li	Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Xingze Jia	State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China
Xinyu Yang	Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Yip Sheung Yuen Wensly	ULVAC PHI Instrument Co., Ltd., Nanjing 211102, China
Yong Yang	Shandong Meijiatu New Material Technology Co., Ltd., Jinan 250300, China
Yixiao Li	State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China
Yan Chen	Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Yali Li	Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401151, China
Yuefeng Su	Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401151, China
Yongjun Feng	State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China
Ziqi He	Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
Zhaoyu Xue	Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

CHAPTER 1

Transmission Electron Microscopy and its Applications in Secondary Batteries

Lixia Bao[1], **Ruiwen Shao**[2], **Tinglu Song**[3,*], **Yong Yang**[4] and **Fan Xu**[5,*]

[1] *Analysis & Testing Center, Beijing Institute of Technology, Beijing 102488, China*

[2] *Beijing Advanced Innovation Center for Intelligent Robots and Systems and Institute of Convergence in Medicine and Engineering, Beijing Institute of Technology, Beijing 100081, China*

[3] *Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

[4] *Shandong Meijiatu New Material Technology Co., Ltd., Jinan 250300, China*

[5] *State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics & Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China*

Abstract: Transmission electron microscopy (TEM) has been widely employed as an important technique for detecting morphology in various secondary battery applications. When integrated with diverse accessories, TEM could attain sub-angstrom level detection, cryogenic TEM (cryo-TEM), and other functionalities, which enables the observation and comprehension of the microstructure of secondary battery materials, as well as structural variations during battery charging and discharging processes. In this chapter, essential structures, main functions, and sample preparation methods of TEM are introduced. Additionally, applications of TEM in characterizing materials used in secondary batteries are discussed and summarized. The aim is to provide essential guidance for employing TEM and to facilitate its future development.

Keywords: TEM, Secondary battery, Sample preparation, Cryo-TEM, In-situ TEM.

1. INTRODUCTION

The growing demands for renewable energy and the rising concern over environmental pollution have created significant opportunities for the develop-

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[*] **Corresponding author Tinglu Song and Fan Xu:** Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China; and State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics & Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China; Tel. & fax number: +8613718876634: E-mails: song@bit.edu.cn, xufan@pku.edu.cn

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ment of secondary battery technology [1], including investigations for materials related to other optoelectronic devices [2 - 4]. The macroscopic performance of batteries, including capacity, density of energy, circulation life, safety performance, operating voltage, and operating temperature range, is closely related to the microstructures of assembled battery materials. These microstructures, such as size, surface morphology, surface reconstruction, crystal structure, and grain boundaries, exhibit a pivotal role in determining the overall performance of the battery. Therefore, it becomes imperative to gain a comprehensive understanding of the microscopic structural and chemical changes in electroactive materials during battery operation, which may be achieved *via* advanced techniques for in-depth characterization of electroactive materials [5]. Such an understanding not only enhances the accuracy of examining the correlation between microstructure and performance but also facilitates the fundamental understanding of high-performance batteries. Furthermore, it may function as a roadmap for battery design, thus advancing the overall development of secondary battery technology.

Various techniques, such as microscopes, X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), secondary ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS), have been utilized to investigate the structure of secondary battery materials. However, there is still a lack of powerful tools for atomic-level detection. TEM emerges as an indispensable tool to probe local atomic structures with high resolution, which also possesses multiple functions, providing valuable insights into real space, reciprocal space, or energy space, thus enabling an in-depth understanding of the mechanisms connecting microstructure changes to battery performance [6]. TEM has been used to characterize the microstructure of perovskite solar cells to better understand the macroscopic performance of batteries [7]. Moreover, TEM and high-resolution TEM (HRTEM) further allow for the observation of the surface and interface morphology of battery materials, as well as detailed information on the lattice structure. Spherical aberration-corrected TEM and scanning TEM (STEM) have been developed to reveal atom arrangements, atomic-level real-space imaging, and atomic occupancy. Furthermore, when configured with X-ray energy dispersive spectroscopy (EDS), TEM becomes a powerful tool for analyzing the types and distribution of elements. Electron energy loss spectroscopy (EELS) is particularly effective for light elements, even surpassing the resolution of EDS, making it highly relevant in lithium-ion batteries (LIBs) research. By fitting the EELS spectra with density functional theory (DFT), accurate information on the valence and even electronic states of elements could be obtained. The functionality of in-situ TEM is significantly more potent in battery investigations. By integrating in-situ batteries within the TEM column, it could achieve real-time measurement and analysis of the morphology and structural evolution of battery materials during cycling, which unveils critical information about the position, concentration, and chemical environment of lithium ions in electrode materials, offering insights into both static and dynamic conditions [8, 9]. With the development of electron microscopy technology, new TEM techniques have also rapidly evolved, including annular bright-field (ABF), integrated differential phase contrast (iDPC), and ptychography, which provide the possibility of directly imaging lithium ions, surpassing traditional annual dark field (ADF) and high-angle annular dark field (HAADF) methods [10, 11].

This chapter provides an in-depth review of three essential aspects of TEM, including the structure, functionality, and sample preparation procedures. Additionally, it delves into the practical application of TEM in characterizing battery materials, with a particular emphasis on secondary battery materials. The primary objective is to elevate the comprehension of the intricate interplay between microstructure and the performance of battery materials by presenting a detailed analysis of the microstructural characteristics inherent in these materials. This enhanced understanding is anticipated to advance the comprehension of battery failure mechanisms, as well as provide valuable insights that will guide the future development of high-performance batteries.

2. INTRODUCTION OF TEM

2.1. The Structure of TEM

TEM is an electron-optical instrument renowned for its high resolution and magnification, which utilizes an extremely short-wavelength electron beam as the illumination source and an electromagnetic lens to focus and image the transmitted electron beam. The TEM can be divided into four major components: the electronic optical system, the vacuum system, the power supply control system, and the additional instrument system.

(1) The electronic optical system comprises three essential components: the illumination system, the imaging system, and the observation and recording system. Functioning as the core of the TEM, the optical path diagram and cross-section diagram are shown in Fig. (**1**). The illumination system mainly consists of the electron gun, the condenser, the translation centering and tilt adjustment device, working as the primary light source for the imaging system. The electron gun, which is the source of the electron beam, may be categorized into thermionic and field-emission guns, respectively. These electron guns emit electron sources with distinct brightness, temporal coherence, special coherence, energy emissivity, and stability. Different electron sources are employed in TEM based on their performance characteristics. The performance comparison of various electronic guns is shown in Table **1**.

CHAPTER 2

Focused Ion Beam Methods and its Applications in Secondary Batteries

Ni Yang[1], **Yali Li**[1], **Lian Wang**[1], **Tinglu Song**[2] and **Yuefeng Su**[1,*]

[1] *Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401151, China*

[2] *Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

Abstract: This chapter discusses the major challenges of characterizing the microstructure and morphology of battery materials, as well as the limitations of current characterization techniques in lithium-ion batteries. To address these challenges, the dual-beam system of focused ion beam scanning electron microscopy (FIB-SEM) emerges as one promising solution. The FIB-SEM system enables accurate manipulation and analysis of battery materials from both micro- and nano-scale perspectives, thus providing valuable insights for the development of high-performance and safe lithium-ion batteries.

Keywords: Cryo processing, Focused ion beam-scanning electron microscope, Lithium-ion battery, Three-dimensional reconstruction.

1. INTRODUCTION

High-performance lithium-ion (Li-ion) batteries are essential parts of consumer electronics, electrical vehicles, electric transportation, and grid-scale storage. A typical Li-ion battery consists of a negative electrode (anode), a positive electrode (cathode), a polymer separator, and an organic liquid electrolyte, each of which functions together to store and release energy. The performance of the battery, such as cycle life, energy density, and safety, is closely related to the structural and mechanical evolution of battery materials during the electrochemical cycle. Therefore, an in-depth study of changes in the microstructure and macrostructure of lithium-ion battery materials is crucial for the development of high-performance and safe Li-ion batteries.

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[*] **Corresponding author Yuefeng Su:** Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401151, China; Tel: +8610-68918099; Fax: +8610-68918200; E-mail: suyuefeng@bit.edu.cn

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However, at present, there remain several problems in characterizing the microstructure and morphology evolution process of Li-ion battery materials. For example, several battery components, including charged electrode sheets, Li metal electrodes, organic liquid electrolytes, and solid-electrolyte interfaces (SEI), may not be resistant to electron beam irradiation, which compromises the authenticity and reliability of the obtained data and information. This is particularly significant as ambient factors during sample preparation and measurement may influent the accuracy of the results. On the other hand, conventional scanning electron microscopy (SEM) observes the state of Li-ion batteries after electrochemical cycling, which is usually semi-*in-situ*, *i.e.*, the battery after electrochemical cycling is disassembled, separated cleaned, and then characterized. During this process, it is facile to produce contamination and deviate from the most authentic reaction state. In addition, some commonly employed methods to characterize the microscopic morphology of the electrode, such as SEM, atomic force microscopy (AFM), *etc.*, are limited by their measurement principles, which could only probe the material surface, rather than obtaining the internal morphology and structure information of the electrode material. The difficulty in preparing Li-ion battery materials and the harsh environmental requirements put forward higher requirements for analysis and characterization equipment.

As an important micro-nano-scale fine processing equipment, the Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) dual Beam system could realize functions such as fixed-point etching, deposition, and *in-situ* analysis. It has been widely employed in various fields such as semiconductors, biology, analytical chemistry, *etc.* In recent years, FIB-SEM has developed rapidly in 3D reconstruction, cryo-processing technology, *etc.* Its flexible collocation with other accessories and equipment provides alternate solutions to the above problems. In this chapter, the basic principle and structure of the FIB-SEM dual beam system are introduced. The latest research progress of FIB-SEM in Li-ion battery, as well as its limitations are summarized and discussed, which is expected to provide essential guidance for further employment of FIB-SEM in the characterization of Li-ion battery materials.

2. INTRODUCTION AND RESEARCH STATUS OF FIB-SEM

2.1. Basic Introduction of SEM

Ordinary optical microscopes have limited magnification, but using electron microscopes allows us to acquire more clear insight into the microscopic world. Since its first introduction by Max Knoll and Vladimir Zworykin [1] in the 1930s and 1940s, SEM has gradually been used in microscopic imaging, composition and structure analysis, micro-nano manufacturing, *etc.*, owing to its high performance and efficiency, ease of use, economy and other advantages, and has become an indispensable tool in various research fields from materials science to biology.

In general, SEM mainly consists of an electron column, signal acquisition system, a sample table, and other accessories (*e.g.*, a vacuum system, a power system, *etc.*). As shown in Fig. (**1**), from top to bottom, the electron column is composed of the electron gun, condenser lens, scanning coil, and objective lens. The electron gun emits electrons to accelerate and form a pen-shaped electron beam under the action of anode voltage. The size and intensity of the electron beam are controlled through the condenser lens and aperture, and then the deflection coil scans the electron beam on the surface of the sample in a raster scanning mode (each line is scanned from left to right, then repeat downwards. The cycle continues to repeat until one frame is completed). Then the final beam spot, beam current, and convergence half angle are controlled through the objective lens and objective lens aperture. The electron beam interacts with the sample to generate signals, which will be collected by the detector and synchronously transmitted to the display *via* data processing. Eventually, the final image is obtained.

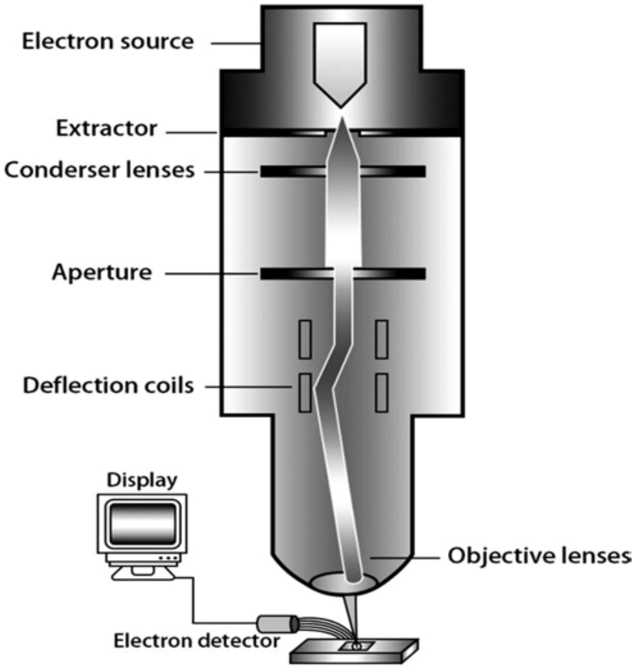

Fig. (1). Schematic sketch of the electron column.

CHAPTER 3

Atomic Force Microscopy and its Applications in Secondary Batteries

Jili Yue[1,*], **Chaoxiang Xie**[2], **Xingze Jia**[3], **Yixiao Li**[3], **Mengmeng Qian**[4], **Tinglu Song**[4] and **Chunli Li**[3,*]

[1] *College of Materials Science and Engineering, National Engineering Research Center for Magnesium Alloys, National Innovation Platform (Center) for Industry-Education Integration of Energy Storage Technology, Chongqing University, Chongqing 400044, China*

[2] *Shanghai Institute of Space Power Sources, Shanghai, China*

[3] *State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China*

[4] *School of Materials Science & Engineering, Beijing Institute of Technology, Beijing, China*

Abstract: Atomic Force microscope (AFM) not only reveals the surface morphology of substances at the nanoscale and molecular level but also enables the measurement of extremely weak forces, which allows for the study of weak interactions between molecules. Moreover, the AFM possesses certain spatial resolution ability. As a valuable tool in secondary battery research, AFM could reveal the surface microscopic morphology of the electrode in real time through the interaction between atoms from the tip and the electrode surface. It offers nanoscale surface information of the electrode from both chemical and physical perspectives, thus establishing essential guidance for further modification of electrode materials and electrolytes. This chapter reviews the state-of-art application progress of AFM in the study of secondary batteries, including cathode materials, anode materials and solid electrolyte interface.

Keywords: Anode, Atomic force microscopy, Cathode, Secondary batteries, Solid electrolyte interphase.

1. INTRODUCTION

In recent years, researchers have tried to find a way to explore the atomic and molecular structures and properties of matter. In 1982, Dr. Gerd Binnig and Dr. Heinrich Rohrer of the Zurich Laboratory developed the world's first surface

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[*] **Corresponding authors Jili Yue and Chunli Li:** College of Materials Science and Engineering, National Engineering Research Center for Magnesium Alloys, National Innovation Platform (Center) for Industry-Education Integration of Energy Storage Technology, Chongqing University, Chongqing 400044, China & State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China; Tel: +8613917312446: E-mails: jili.yue@cqu.edu.cn, lichunli@buct.edu.cn

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analysis instrument, the Scanning tunneling microscope (STM) [1]. Its introduction enables human beings for the first time to observe in real-time the arrangement of separate atoms on the surface of a substance and the physical-chemical properties surrounding the surface electron behavior. It provided scientists with an unprecedented ability to directly observe single atoms and single molecules, which fundamentally changed the level of human understanding of the micro and nano world. The unique advantages of STM compared with other analytical techniques have promoted its development within just a few years. At present, STM has been widely employed in various fields, including chemistry, physics, life science, and materials science [2]. Despite the numerous advantages of the STM, inherent limitations exist in its operational mode. One primary constraint is that the sample under observation must exhibit certain electrical conductivity. Since most biomaterials lack conductivity, a conductive layer should be applied to the sample surface for imaging. Due to the particle size and uniformity of the conductive layer, the image resolution to the actual surface is limited.

The Atomic Force microscope (AFM) was successfully developed in 1986, based on the previously established STM [3]. AFM could not only provide detailed information on the surface morphology of substances at the nanoscale and molecular level but also enable the measurement of extremely weak interactions between molecules. The chemical-functionalized AFM probe could be employed to study intermolecular or chemical functional group interactions. It has been widely used in both organic and inorganic materials and has played a pivotal role in promoting the development of material science and life science [4 - 14]. AFM is able to detect conductors, semiconductors, and insulators. Moreover, it can analyze different physical properties in diverse environments, including atmosphere, vacuum, and liquid, which makes AFM a valuable tool in surface science, material science, life science and other fields.

2. WORKING PRINCIPLE OF AFM

AFM was developed on the basis of STM. The sample surface morphology may be measured by testing the interaction force between atoms/molecules on the surface of the sample and the AFM microcantilever probe. The main difference between AFM and STM is that AFM uses a sharp needle tip with one end fixed and the other end mounted on an elastic micro-cantilever instead of an STM tunnel probe to detect the force of the micro-cantilever, and the tiny deformation generated instead of detecting the tiny tunnel current. Its working principle is shown in Fig. (**1**) [15]. A microcantilever, which is very sensitive to very faint forces, is anchored at one end and features a small needle tip at the other side, slightly contacting the sample surface. There is a tiny small repulsive force between the needle tip atoms and the sample surface atoms. By keeping this force constant while scanning, the cantilever with the tip of the needle causes the equipotential plane corresponding to the interatomic force to undulate perpendicular to the surface of the sample. The displacement variation corresponding to the scanning points can be observed by tunnel current detection or optical detection, and the signal is amplified and converted to obtain the atomic-level three-dimensional image of the sample surface.

AFM is mainly composed of a piezoelectric scanner that performs raster scanning and z positioning, a feedback electronic circuit, an optical reflection system, a probe, an anti-vibration system and a computer control system, as shown in Fig. (**1**). The piezoelectric ceramic tube (PZT) governs the sample's movements along the x, y, and z axes. When the sample is scanned in the x and y direction compared to the needle tip, the tip-to-sample distance varies as the surface rises and falls. As the laser beam illuminates the rear of the cantilever as well as interacts with the attached photodetector, variations in laser intensity across different quadrants of the detector correlate proportionally with the cantilever's shape variable. The surface topography is obtained by controlling the distance between the needle tip and the sample to retain a constant force. This measurement mode is called constant force mode. When the surface of the sample is known to be very smooth, the constant height mode can be used for scanning, that is, the distance between the needle tip and the sample remains constant, and the force between the needle tip and the sample directly reflects the surface topography image.

AFM images are detected by measuring the bending and degree of the cantilever force during sample scanning. There are three ways to bend the cantilever, namely the tunnel current method, capacitance detection method and optical detection method. At present, the optical detection method is commonly used to detect cantilever micro-deformation. Optical detection methods can be divided into two basic types: interference method and beam emission method. The related principle is illustrated in Fig. (**1**). A laser beam will be generated from the laser diode, which then is reflected through the cantilever into a position-sensitive photodetector (PSPD) with a photodiode. It will output a sensitive signal reflecting the position of the reflected light. The principle is that the laser light emitted from the laser is focused on the cantilever back and then reflected off the smooth surface of the cantilever. When scanning the sample, the properties of the sample surface will bend the cantilever by repulsive forces between atoms. This bending will shift the reflected angle of the laser beam from the cantilever. The related offset can be detected by a position-sensitive photodiode. Choosing the right distance between the cantilever and the PSPD is one of the important methods to improve sensitivity.

CHAPTER 4

X-ray Photoelectron Spectroscopy and its Applications in Secondary Batteries

Chuguang Yu[1], **Defeng Lu**[2], **Fan Xu**[3], **Liyuan Zhao**[1], **Yan Chen**[1], **Meishuai Zou**[1,*] and **Tinglu Song**[1,*]

[1] *Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

[2] *Explorer Testing Technologies (Dongguan) Co., Ltd., Dongguan 523000, China*

[3] *State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics & Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China*

Abstract: As an important surface analysis technique based on the photoelectric effect, X-ray Photoelectron Spectroscopy (XPS) enables both qualitative and semi-quantitative analysis of the elemental composition and chemical state of the solid material surface, and has thus been widely applied in secondary batteries. In this chapter, we first delve into a detailed introduction of the working principle, main functions, analytical capabilities and technical features of XPS. Following this, we outline various types of XPS spectral peaks and elucidate general principles for data analysis. Then, the preparation of diverse XPS specimens along with their packaging and transfer processes are introduced. Last but not least, we comprehensively summarize and discuss the application of XPS in secondary batteries, including the characterization of electrode material composition, charge/discharge mechanism, solid electrolyte interphase (SEI) structure, *etc.* Additionally, we provide examples of the insightful information acquired through XPS and demonstrate how this data aids researchers in achieving a more profound understanding of secondary batteries, which highlights the increasingly important role of XPS in the development of secondary batteries.

Keywords: Electrode materials, SEI, Secondary batteries, Surface characterization, XPS.

1. INTRODUCTION

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a vital surface analysis technique based on the

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[*] **Corresponding authors Meishuai Zou and Tinglu Song:** Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China; Tel. & Fax Number: +861068911306: E-mails: zoums@bit.edu.cn, song@bit.edu.cn

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photoelectric effect. This technique employs X-ray to excite the inner electrons of atoms on the sample surface (generally within a depth of 10 nm) and obtains an energy spectrum by analyzing the energy of these excited electrons. Through the energy spectrum, the elemental composition and chemical state of the sample surface may be derived, allowing for the quantitative characterization of the relative content of each element. Meanwhile, when coupled with ion etching techniques, XPS depth profiling may be carried out to reveal the chemical information of the material along its depth [1].

Currently, XPS has been widely applied and plays an increasingly important role in various fields, including metals, polymers, semiconductors, catalytics, ceramics, biological materials, and others. The significance of XPS is particularly emphasized in the investigation of secondary batteries.

2. WORKING PRINCIPLE OF XPS

The principle of XPS is based on Einstein's theory of the photoelectric effect. When an X-ray with a specific energy irradiates the sample surface, a photon could be absorbed by an electron in the atomic orbit of a particular element. Then, the electron will break free from the nuclear confinement and emit from the interior of the atom with certain kinetic energy as a free photoelectron, while the atom transforms into an excited ion (as shown in Fig. **1**) [2]. The energy conversion in the photoionization process can be described by the following formula:

$$E_b = \mathrm{h}\nu - E_k - \Phi_{\mathrm{sp}} \tag{1}$$

where E_b refers to the Binding energy (B.E.) of a specific atomic orbital, which is equal to the energy required to transfer the electron from its current energy level to the Fermi level. E_k refers to the energy of the emitted photoelectron. h refers to the Planck's constant. v refers to the X-ray frequency. hv refers to the energy of the photon from the X-ray source. Φ_{sp} refers to the work function of the spectrometer, which is equal to the energy required for the electron to enter the vacuum from the Fermi level to become a free electron. The work function of the spectrometer is mainly determined by the material and the state of the spectrometer, which can be considered as a constant for the same spectrometer with an average value of 3~4 eV.

XPS utilizes an X-ray excitation source to irradiate the sample surface. The commonly employed X-ray source is the Al Kα monochromatic X-ray source with an energy of 1486.6 eV. Due to the high energy of X-ray, the inner orbital electrons at the atomic core level could be excited. The energy of the emitted photoelectron is only related to the energy of the incident photon and the orbital binding energy of the atom. Consequently, with a specific monochromatic excitation source and atomic orbital, the energy of the emitted photoelectron becomes identical [3]. When the energy of the excitation source is constant, the energy of the emitted photoelectron is only influenced by the type of element and the atomic orbital excited by photoionization. By measuring the kinetic energy of the photoelectron, the binding energy of the electron in the atom can be calculated. Qualitative and quantitative analysis of the material is then feasible by examining the binding energy and peak intensity values, which reveal information about the elemental composition and chemical state of the sample.

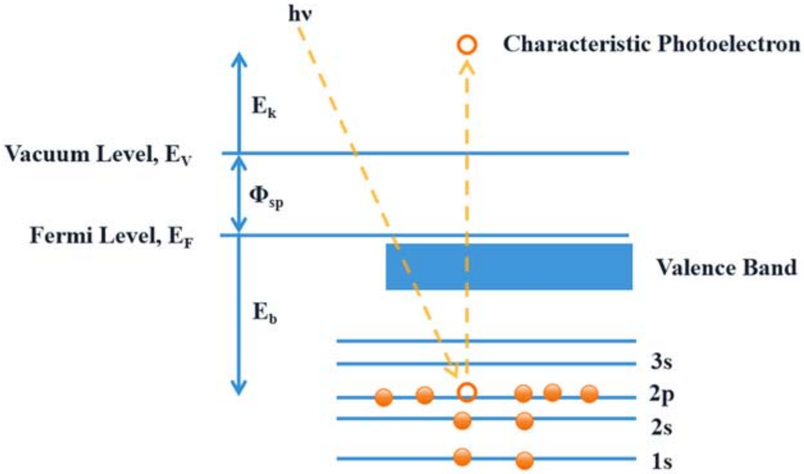

Fig. (1). Schematic of photoelectron excitation process.

The binding energy of the inner electrons is influenced not only by the strong Coulomb interaction of the atomic nucleus but also by the shielding effect of the outer electrons. As the density of outer electrons decreases, the shielding effect weakens, leading to an increase in the binding energy of inner electrons. Conversely, enhancing the outer electron density results in a reduction of binding energy. Therefore, when the oxidation state of the measured atom rises or when the atom forms compounds with higher electronegativity, the spectral peak will shift towards higher binding energy. This systematic shift of the spectral peak, caused by changes in compound structure and atomic valence state, is termed the chemical shift.

3. MAIN FUNCTIONS AND TECHNICAL FEATURES OF XPS

The analysis depth of XPS is generally considered to be less than 10 nm. XPS can be employed for both qualitative and quantitative measurements of the elemental

CHAPTER 5

Time-of-flight Secondary Ion Mass Spectrometry and its Applications in Secondary Batteries

Tinglu Song[1], **Huaqiang Zhu**[1], **Ziqi He**[1], **Yip Sheung Yuen Wensly**[2], **Chuguang Yu**[1], **Xinyu Yang**[1], **Shunzi Jiang**[1], **Fan Xu**[3,*] and **Xiaodong Li**[1,*]

[1] *Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

[2] *ULVAC PHI Instrument Co., Ltd., Nanjing 211102, China*

[3] *State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics & Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China*

Abstract: In recent years, Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) has been widely employed as a powerful surface characterization tool in secondary battery investigations. In this chapter, we introduced the essential working principle, fundamental functions, and basic components of TOF-SIMS, which hopefully could provide useful insights for potential users and readers with particular interests in TOF-SIMS measurement. Additionally, state-of-the-art practical applications and research progress of TOF-SIMS in secondary batteries, including electrode materials and electrode/electrolyte interfaces, were thoroughly reviewed and discussed.

Keywords: Depth profiling, Mapping, Secondary batteries, Three-dimensional reconstruction, TOF-SIMS.

1. INTRODUCTION

Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) has been considered one of the cutting-edge scientific technologies that combine secondary ion mass spectrometry with time-of-flight mass analysis. In 1979, German scientist Benninghoven and his research team [1] pioneered the development of TOF-SIMS I by conducting S-SIMS studies with a magnetic field deflection mass

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[*] **Corresponding authors Xiaodong Li and Fan Xu:** Experimental Center for Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China and State Key Laboratory for Artificial Microstructure and Mesoscopic Physics, School of Physics, Frontiers Science Center for Nano-optoelectronics & Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China; Tel. & Fax Number: +861068918075; Tel: +8613718876634;
E-mails: bitlxd@bit.edu.cn, xufan@pku.edu.cn

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analyzer and a four-bar mass analyzer. Subsequently, they constructed a reflective TOF-SIMS II. In 1985, the Benninghoven research team successfully integrated a laser-SNMS device into the TOF-SIMS instrument. Based on the Benninghoven theory, the University of Münster in Germany developed the world's first TOF-SIMS system.

As a sensitive surface analysis technology, TOF-SIMS could provide compositional information with submicron lateral resolution. For specific materials, TOF-SIMS offers unparalleled sensitivity and excellent reproducibility. Moreover, as a mass spectrometry technology, it also ensures outstanding specificity and is thought of as one of the most surface-sensitive analysis methods. In addition, TOF-SIMS is particularly suitable for the detection and analysis of elements such as Li, H, C, and O. As a result, TOF-SIMS has been widely employed in various fields including chemistry, materials science, and engineering.

This chapter will introduce the fundamental working principle, advantages and disadvantages, and essential components of TOF-SIMS. In addition, the state-of-art research progress of TOF-SIMS in secondary battery studies is reviewed and discussed, which is expected to provide future guidance toward employment and developments of such technology.

2. WORKING PRINCIPLE OF TOF-SIMS

Secondary Ion Mass Spectrometry (SIMS) is a surface analysis technology based on the interaction between primary ions and the sample surface. The related working principle is demonstrated in Fig. (**1a**). A primary ion beam with an energy of several thousand electron volts is incident on the sample surface, resulting in various particles generated from the action area, including secondary electrons, neutral particles, secondary ions, reflected ions, *etc.* Information could then be obtained by collecting different particles through detectors. The collection of secondary ions and subsequent analysis *via* a mass analyzer enable the acquisition of the mass spectrum, which contains compositional information at the sample surface.

Apart from the SIMS, the time-of-flight (TOF) technique is further integrated to form the completed TOF-SIMS instrument. When the surface of solid materials is bombarded with a single pulse ion, the mass of the secondary ions excited from the surface will be measured by the flight time to characterize their elemental composition, molecular structure, and molecular bonding. To summarize, TOF-SIMS is operated by measuring the flight times of secondary ions to obtain detailed information about the surface properties of solid materials.

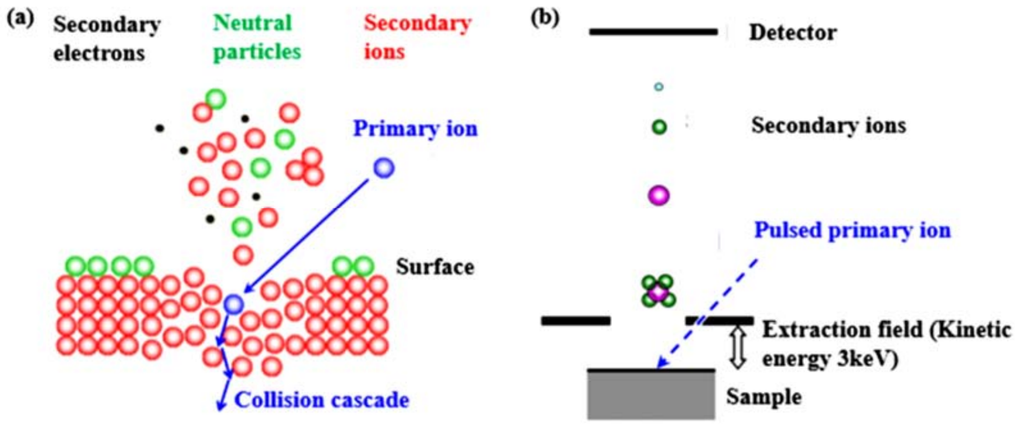

Fig. (1). (**a**) The principal diagram of SIMS and (**b**) a schematic diagram of how TOF-SIMS works.

As illustrated in Fig. (**1b**), TOF-SIMS mainly utilizes primary ion sources (*e.g.*, Ga^+, Au^+, Bi^+, Bi_3^{++}, C_{60}^+) to excite secondary ions, including both atomic and molecular ions, when being incident on the sample surface. All excited ion fragments will receive identical kinetic energy (in general, 3keV) to be accelerated, following the energy conservation formula (1):

$$3\text{KeV}=1/2mv^2$$

$$T\propto\sqrt{M} \tag{1}$$

T: Flight time of secondary ions, *M:* Mass weight

The speed of ions varies with their masses, with higher-mass ions exhibiting reduced flight speeds. Consequently, when the flight distance is fixed, heavier ions take longer flight time to reach the end (detector). By measuring the time each ion takes to reach the detector, the ion mass could thus be determined. In addition, since all ions must commence simultaneously during the process, the ion source must be operated in the pulse mode rather than the direct current (DC) mode. In the pulse mode, each pulse triggers a race, with the next pulse commencing only after all ions have reached the detector. In general, the pulse time lasts a few nanoseconds, leaving the remaining time for the collection of secondary ions. Notably, the excitation current of the primary ion source is also relatively small. Therefore, the above-mentioned TOF-SIMS refers to static SIMS, which enables sensitive surface analysis without inducing substantial damage.

CHAPTER 6

Neutron Diffraction and its Applications in Secondary Batteries

Chunli Li[1], **Hao Li**[2], **Guang Yang**[3], **Huiyu Li**[1] and **Yongjun Feng**[1,*]

[1] *State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China*

[2] *Key Laboratory of Neutron Physics and Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Sichuan 621999, China*

[3] *Shanghai Aerospace Power Technology Co., Ltd., Shanghai 201112, China*

Abstract: As a well-established method, neutron diffraction has been widely adopted to characterize the atomic structure of materials. One of the most distinct advantages of neutron diffraction refers to its high sensitivity to most light elements (*e.g.*, lithium), which could distinguish isotopes and identify adjacent elements. Moreover, magnetic structure may also be probed. More importantly, the penetration depth of neutrons is thick enough for battery detection with centimeter scales. For secondary batteries, neutron diffraction has shown advantages in determining phase structure and ion diffusion in active materials, which are critical issues in battery studies due to the dominant charge and energy transport functions of active ions. Moreover, neutron diffraction also exhibits superior performance in revealing lithium coordinates in lattice and related occupations, as well as visualizing the diffusion path of lithium atoms, which may not be completed *via* other characterizations. This chapter aims to comprehensively review the working mechanism and main research progress of neutron diffraction in secondary batteries. The essential background, working principle and practical applications of neutron diffraction on the cathode, anode, solid-state electrolytes and full batteries, as well as its data analysis, are introduced and discussed.

Keywords: Cathode materials, Graphite, Li-ion migration pathway, Light element substitution, Neutron tomography, Neutron diffraction.

1. INTRODUCTION

Diffraction is a standard technique for accurately determining crystal structure at an atomic scale, which is an essential tool in material research. In general, diffraction could be used to detect crystal structures such as lattice constant and

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[*] **Corresponding author Yongjun Feng:** State Key Laboratory of Chemical Resource Engineering, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China; Tel: +8613910075163; E-mail: yjfeng@mail.buct.edu.cn

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angle, atomic coordinate and occupation, composition, strain, slip system, texture, atomic thermal vibration, atomic density distribution in phase transition, mechanical distortion, thermodynamic process, etc. Various radiation types may be employed for diffraction, including X-rays, electrons, and neutrons. Among them, since neutron primarily interacts with atomic nuclei, while other radiations (*e.g.*, X-ray, electron) interact mainly with the surrounding electron cloud, the neutron exhibits high sensitivity to light elements, which makes it a particularly useful method to identify adjacent elements and isotopes. In addition, the carried magnetic momentum enables neutrons to be scattered by electrons with magnetic momentum. As a result, neutron diffraction could be adopted to investigate the structure of ferro-, ferri-, and antiferro-magnetic materials. Due to the above unique physical properties, neutron diffraction has been applied in several applications [1]. Especially in characterizations with specific requirements, *i.e.*, global detection of synchronized structural changes in different parts of lithium-ion batteries, as the good penetration offers one distinct advantage [2].

Ion diffusion is critical for secondary battery investigations because it cannot only govern the kinetics but also closely relate to the structural evolution of active materials. Information on content and position is essential to understand diffusion. Fortunately, diffraction methods could reveal atomic-scale position and content information from diffraction angle and intensity, respectively. In addition, intensity is related to the Coherence Elastic Scattering Length (CESL) of atoms. The X-ray Coherence Elastic Scattering Length (XCESL) is always positive and directly proportional to atomic number. The Neutron Coherence Elastic Scattering Length (NCESL) shows no order dependence on atomic number, with the NCESL for lithium being negative, while most other atoms are positive. Consequently, neutron diffraction exhibits excellent sensitivity to lithium ions, which is of great significance in studying lithium-ion batteries. Spinel lithium titanate ($Li_4Ti_5O_{12}$) is a good example to demonstrate the function of neutron diffraction. $Li_4Ti_5O_{12}$ could be lithiated to $Li_7Ti_5O_{12}$ with negligible variations in volume, which means that it is difficult to detect any diffraction peak shift during lithiation or delithiation. Therefore, information about lithiation states may only be acquired from diffraction intensity. Fig. (**1**) shows the calculated neutron powder diffraction and X-ray powder diffraction patterns of $Li_{4+x}Ti_5O_{12}$ at different lithiation states. Obviously, neutron diffraction patterns show enhanced intensity deviations for different lithium content.

Another important application of neutron diffraction in secondary batteries refers to the visualization of ion diffusion paths at the atomic scale, which is vital and essential for realizing diffusion mechanisms. Once the diffusion pathway is determined, the activation energy and diffusivity can be calculated. Neutron diffraction is considered the only method to experimentally reveal the details of the lithium-ion diffusion pathway in batteries. To obtain diffusion pathways through diffraction experiments, related information on atomic density distribution should be acquired. Fourier maps [3], probability distribution function [4], and maximum entropy method (MEM) are well-established methods to derive atomic density from diffraction results. In the latest investigations on lithium-ion batteries, the combination of neutron diffraction and MEM effectively unraveled the diffusion path of lithium ions in electrodes or electrolytes [5, 6].

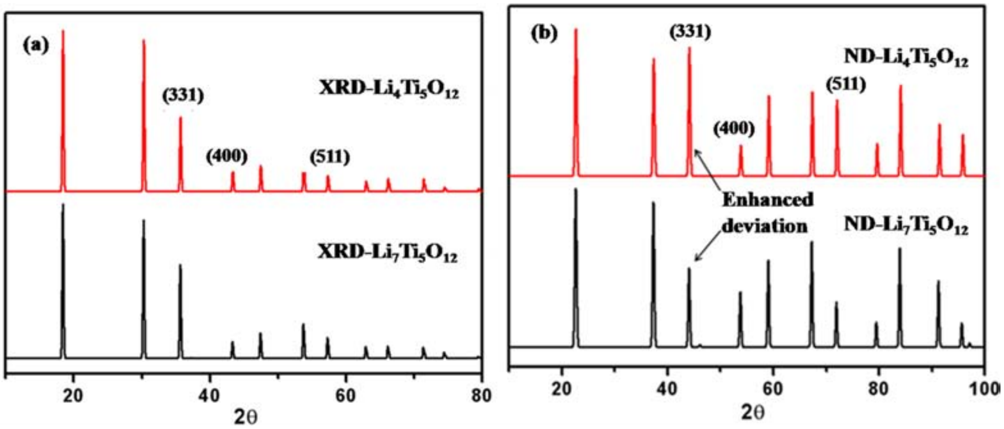

Fig. (1). Calculated profiles of (**a**) X-ray diffraction and (**b**) neutron diffraction patterns for $Li_{4+x}Ti_5O_{12}$. Neutron diffraction shows enhanced deviation for different lithium content.

Neutron diffractometer is the basic apparatus in neutron scattering science platform, such as D2B at Institute Laue-Langevin (ILL) [7], Structure Powder Diffractometer (SPODI) at Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) [8], BT-1 at NIST Center for Neutron Research (NCNR) [9], Echidna at Australian Nuclear Science and Technology Organisation (ANSTO) [10], Xuanwu and Fenghaung at China Mianyang Research Reactor (CMRR) [11, 12], GPND and Multi-Physics Instrument (MPI) at China Spallation Neutron Source (CSNS) [13, 14]. Normally, neutron counts are limited in diffraction experiments due to the penetration ability of neutrons and the rarity of neutron sources. Moreover, it may not be simple to obtain results with both satisfied neutron flux intensity and resolution. Therefore, it is imperative to select and set appropriate experimental conditions for specific cases. For example, high-resolution neutron diffraction is suitable for accurate determination of structural evolution and ionic diffusion, while high-intensity neutron diffraction is preferred for fast observation of phase transition during electrochemical cycling.

CHAPTER 7

Synchrotron Radiation X-ray Tomography Technique and its Applications in Secondary Batteries

Shuo Wang[1], **Xiaodong Li**[1], **Jun Wang**[2], **Gang Xue**[3] and **Meishuai Zou**[1,*]

[1] *Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

[2] *Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201204, China*

[3] *Suzhou MASRC Testing Technology Co., Ltd., Suzhou 215168, China*

Abstract: Electrode materials undergo complex structural variations during the operation of secondary batteries. Three-dimensional characterization of these changes offers researchers a more in-depth and comprehensive insight into the dynamically evolving complex interactions compared to the conventional two-dimensional characterization. Synchrotron radiation X-ray tomography technology, which is capable of non-destructively conducting multi-scale and 3D imaging of battery components in both static and operational states, has emerged as an indispensable tool for enhancing further understanding of secondary battery research in recent years. Here, in this chapter, the integration of synchrotron radiation X-ray tomography technology and pertinent knowledge within the context of secondary battery research is undertaken, which is aimed at advancing the application of synchrotron radiation X-ray tomography technology in future secondary battery research. This chapter initiates by elucidating the essential principles and experimental apparatus of synchrotron X-ray tomography technology, followed by exploring its applications in both positive and negative electrode materials of secondary batteries. Last, typical application software and cases of data processing are presented and introduced. We anticipate that this chapter will enhance the readers' understanding of synchrotron X-ray tomography technology, and provide novel insights to inspire its application in secondary battery investigations.

Keywords: Non-destructive characterization, Secondary battery, Synchrotron radiation, X-ray tomography, 3D reconstruction.

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[*] **Corresponding author Meishuai Zou:** School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China; Tel: +86-010-68910875; E-mail: zoums@bit.edu.cn

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1. INTRODUCTION

Energy remains an enduring concern in today's world, particularly as fossil fuel resources are increasingly depleted. The efficient storage and utilization of energy have become pivotal challenges to limit human development. As an efficient electric energy/chemical energy conversion device, a secondary battery has been recognized as a critical technology in addressing contemporary energy-related issues. To improve the overall performance of the secondary battery, researchers persistently endeavor to optimize both their system architecture and material composition. Conventional two-dimensional characterization methods such as SEM and TEM have proven inadequate in fulfilling the evolving requirements for the characterization of secondary batteries. Over recent decades, synchrotron radiation X-ray imaging technology has indeed become increasingly prominent in the field of secondary battery research.

Since Roentgen's groundbreaking discovery in 1895 that X-ray possesses the capability to penetrate objects, their extensive application across various industries has become increasingly apparent. X-rays exhibit the capacity to penetrate materials with distinct absorption characteristics, where the absorption coefficient is roughly proportional to the square of the atomic number, Z, raised to the fourth power. Consequently, the X-ray intensity received during imaging has been constrained by the inherently low energy of X-rays, posing challenges in meeting specific application requirements. After numerous attempts, synchrotron radiation X-ray was initially discovered in 1947 [1], offering the feasibility of utilizing high-energy X-rays for analysis and characterization. Synchrotron radiation X-rays are generated in a synchrotron radiation facility, which is a circular particle accelerator. Electrons are accelerated to relativistic speeds and guided along a circular path by strong magnetic fields. As they move through the curved trajectory, they emit intense beams of synchrotron radiation including X-rays. Specialized insertion devices, such as undulators or wigglers, enhance the production of synchrotron radiation. X-rays are emitted when circulating electrons undergo periodic oscillations or undulations.

With the advantages of high brightness, substantial flux, and precise collimation, synchrotron radiation X-rays could achieve high-resolution (submicron level) non-destructive three-dimensional microscopic imaging of the sample, which facilitates comprehensive three-dimensional characterization of both positive and negative materials within secondary batteries across diverse scales. In addition, it enables in-situ real-time characterization during the working process of the secondary battery, significantly expanding the scale and dimension of the secondary battery research. In conclusion, synchrotron radiation X-ray imaging technology has been widely employed in the analysis and characterization of secondary batteries, offering advanced methods for in-depth investigations. Therefore, this chapter mainly introduces the principles, classifications, and applications of synchrotron radiation X-ray imaging technology in the analysis and characterization of secondary batteries, to provide readers with valuable insights and inspiration for their research endeavors.

2. WORKING PRINCIPLE OF SYNCHROTRON X-RAY TOMOGRAPHY

2.1. Synchrotron Radiation

On November 8, 1895, a German scientist Roentgen discovered the X-ray (Fig. **1**), which has evolved into an indispensable characterization method in scientific research and has exerted a profound and far-reaching impact on the development of science and technology throughout the 20th century. X-ray absorption spectroscopy is currently employed in many fields, such as structural characterization and property studies. The most commonly adopted X-ray spectra come from X-ray tubes, in which high-energy electron beams bombard a target to generate X-rays. The characterization of synchrotron radiation X-rays is distinguished by their high-energy nature, improved accuracy, and microscopic resolution, as well as enhanced efficiency, which enables the realization of non-destructive stress measurement and in-situ characterization at key locations. Consequently, synchrotron radiation X-rays have been extensively applied across diverse fields including life sciences, materials science, physics, chemistry, medicine, *etc.*

Fig. (1). Wilhelm conrad röntgen and the first x-ray image in the world.

CHAPTER 8

Ultrasonic Nondestructive Technique and its Applications in Secondary Batteries

Liyuan Zhao[1], **Shixiong Zhang**[2], **Mengmeng Qian**[1], **Jie Zhang**[2], **Zhaoyu Xue**[1], **Guoqiang Tan**[1,*] and **Tinglu Song**[1,*]

[1] *Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China*

[2] *Beijing dklead Technology Co., Ltd., Beijing 101318, China*

Abstract: Secondary batteries have been widely studied due to their highly efficient electrical and chemical energy-converting performance. Further improvement of these batteries is expected to meet the growing demands of the economy and technology. Various advanced characterization techniques have been applied in secondary batteries to gain a deeper understanding of electrochemical evolution and detection in the discharge/charge process. The ultrasound technique, with its high sensitivity, low cost and real-time detection ability, shows great potential for the characterization of secondary batteries. In this chapter, we introduce the fundamental principles of the ultrasound technique and summarize its applications in secondary batteries.

Keywords: Mapping, Nondestructive characterization, Secondary batteries, Ultrasound technique.

1. INTRODUCTION

Secondary batteries, particularly lithium-ion (Li-ion) batteries, have been widely employed to promote developments of electric vehicles, mobile electronics and large-scale energy storage stations. To fulfill the growing daily demands, the battery performance still needs to be enhanced, such as capacity, cycle life, and rate capability. Numerous advanced characterization techniques have been employed to acquire in-depth information on the internal health status and failure mechanism. These techniques can be categorized as either destructive or non-destructive. Destructive characterization techniques have been widely employed in secondary batteries since components such as electrode materials and electro-

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[*] **Corresponding authors Guoqiang Tan and Tinglu Song:** Experimental Center of Advanced Materials, School of Materials Science and Engineering, Beijing Institute of Technology, Beijing 100081, China; Tel. & Fax Number: +861068911306; E-mails: tan123@bit.edu.cn, song@bit.edu.cn

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lytes could be facilely measured after disassembling batteries for post-modern analysis. However, the chemical status of these materials may be varied during the disassembling process, leading to potentially misleading results. Moreover, these materials are sensitive to air and water, which induces challenges for sample preparation and transformation. As a result, nondestructive characterization methods, such as X-ray tomography (XCT) and neutron diffraction attract much attention. However, such methods may not be able to meet the demands for real-time and rapid detection due to their time-consuming. Additionally, XCT lacks sensitivity to liquid electrolytes and internal gases, as these substances may not effectively scatter X-rays. Moreover, the high costs of X-ray and neutron-based techniques hinder their practical applications.

Therefore, it is imperative to develop inexpensive, convenient, and rapid characterization technologies to enable real-time detection and health monitoring of secondary batteries. The employment of the ultrasonic technique shows great potential to achieve such goals, as ultrasound transmission is highly sensitive to gas, porosity and mechanical properties of materials. Indeed, several researchers have already applied this technique to secondary batteries. In this chapter, we will introduce essential principles and common applications of ultrasonic technique in secondary batteries.

2. ESSENTIAL PRINCIPLE OF ULTRASONIC NONDESTRUCTIVE TECHNIQUE

The operation of the ultrasonic nondestructive technique is based on the interaction of ultrasonic waves with samples. By analyzing the reflection, transmission, and scattering waves, macro defects, geometric properties as well as mechanical properties of the sample can be detected. The essence of the ultrasonic wave is a mechanical wave, resulting from the high-frequency mechanical vibration generated by the piezoelectric chip of the ultrasonic probe when excited by electronic pulses. In addition to its strong penetrating and high energy, it also exhibits characteristic behaviors similar to mechanical waves, such as reflection, scattering, and refraction at heterogeneous interfaces. The ultrasonic nondestructive technique belongs to five conventional testing methods that have been widely employed in industry for quality control, raw material inspection, process improvement even equipment maintenance.

The ultrasonic nondestructive technique mainly involves the collection and analysis of transmission and reflection signals of ultrasonic waves to determine the location and size of defects. In the reflection method, defect size and position are determined based on changes in energy from the reflected echoes. As shown in Fig. (**1**), when defects are present within the specimen, some ultrasonic waves will be reflected by the defects. In terms of relatively large defects, all sound waves will be reflected, leading to the absence of a bottom wave reception.

Conversely, if there is no defect or imperfection in the sample, the initial wave reflection will receive a bottom echo. The transmission method is based on the attenuation of ultrasound waves after penetrating the specimen. Generally, two probes- one for emission and the other for reception- are placed on opposite sides of the specimen for detection. When defects exist within the specimen, ultrasound attenuation occurs, causing a decrease in the amplitude of received ultrasonic waves, which can be adapted to determine defect characteristics. As illustrated in Fig. (**2**), the receiving probe may not be able to receive the transmitted signal when defects are substantial or ultrasound attenuation is significant. When defects are small, the ultrasonic wave will exhibit certain attenuation, allowing the receiving probe to capture the transmitted signal. Further analysis of this signal could provide detailed information about the internal defects of the specimen.

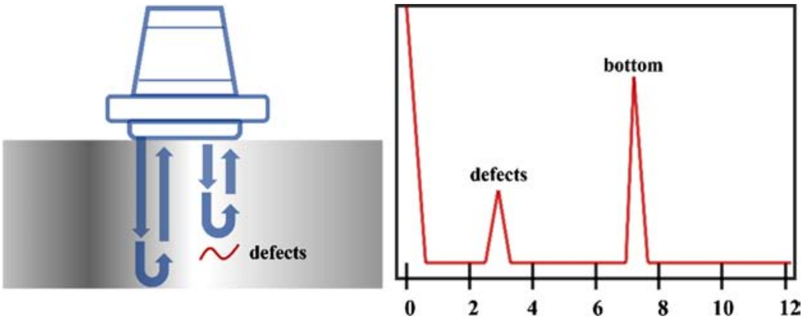

Fig. (1). Schematic diagram of the ultrasonic reflection detection.

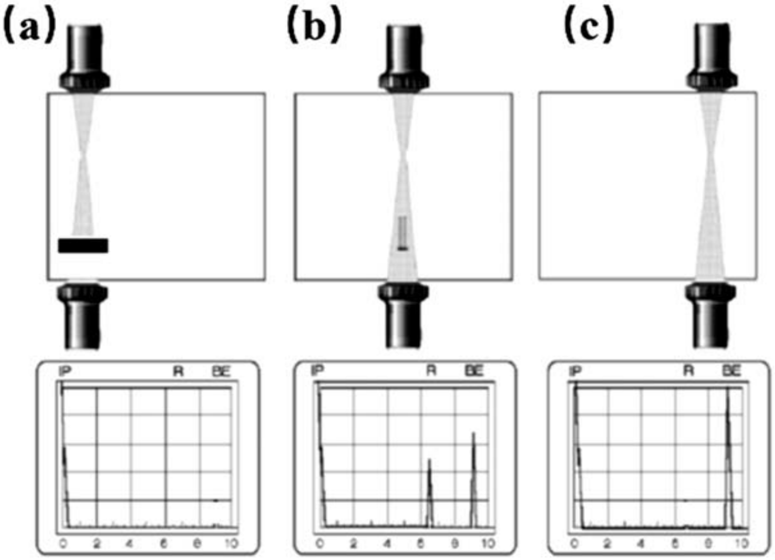

Fig. (2). Schematic diagram of the ultrasonic transmission detection with (**a**) large defects, (**b**) small defects and (**c**) no defects.

SUBJECT INDEX

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