Exploring Battery Material Failure Mechanisms through Synchrotron X-ray Characterization Techniques

Lingzhe Fang,[a] Xiaozhao Liu,[a] Tao Li[a,b,*]

[a] *Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA*

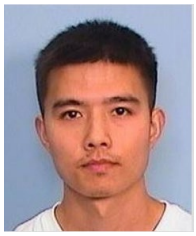
[b] *X-ray Science Division and Joint Center for Energy Storage Research, Argonne National Laboratory, Lemont, IL 60439, USA*

[*]Corresponding author.
E-mail address: tli4@niu.edu; taoli@aps.anl.gov (Tao Li)

ABSTRACT

Rechargeable battery cycling performance and related safety have been persistent concerns. It is crucial to decipher the capacity fading induced by electrode material failure via a range of techniques. Among these, synchrotron-based X-ray techniques with high flux and brightness play a key role in understanding degradation mechanisms. In this comprehensive review, we summarized recent advancements in degradation modes and mechanisms that revealed by synchrotron X-ray methodologies. Subsequently, an overview of X-ray absorption spectroscopy and X-ray scattering techniques are introduced for the characterizing failure phenomena at local coordination atomic environment and long-range order crystal structure scale, respectively. At last, we envision the future of material failure mechanism exploration.
Keywords: Battery failure; Synchrotron-based techniques; X-ray scattering; X-ray absorption spectroscopy

Lingzhe Fang is currently a Ph.D. candidate under the supervision of Dr. Tao Li at the Department of Chemistry and Biochemistry at Northern Illinois University. He obtained his M.S. degree in 2019 in materials science from Nanjing University of Science and Technology in China. His research focuses on the single atom catalysts for energy storage and conversion.



Xiaozhao Liu earned his bachelor's degree in safety engineering from North University of China in 2020 and a master's degree from South China University of Technology in 2023. He is currently a Ph.D. student in Prof. Tao Li's group at Northern Illinois University. His research focuses on the high-throughput screening and data-driven design of electrolytes for energy storage and conversion systems.

Tao Li is an associate professor in the Department of Chemistry and Biochemistry at Northern Illinois University and holds a joint assistant scientist position at the Advanced Photon Source at Argonne National Lab. His research interests focus on using advanced X-ray techniques to study nanoparticles and energy materials' self-assembly, including catalyst and battery. Dr. Li completed his Ph.D. in the Department of Chemistry and Biochemistry at the University of South Carolina-Columbia in 2009.

1. Introduction

The urgency of addressing environmental and climate concerns highlights the critical role of energy storage technology. Lithium batteries have expanded across a wide range of applications [1-3]. However, besides high energy/power density, the requirement for

prolonged lifecycles without safety concerns have not yet been satisfied[4-6]. The factors that contribute to performance deterioration are diverse, including the inherent physicochemical properties of battery materials and the complexities of fabrication procedures/operational parameters under utilization and storage phases[7]. Primarily, the origin of battery failure can be traced back to the failure of active materials.

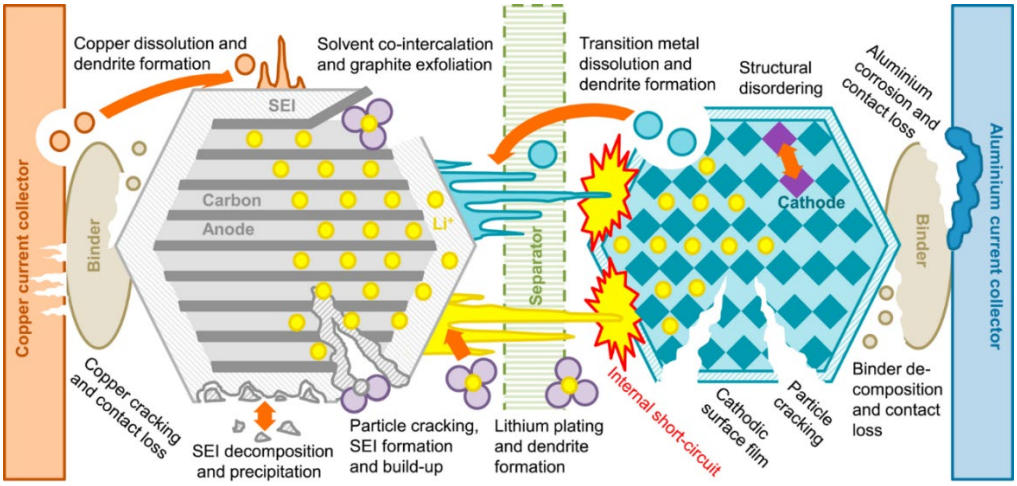


Fig. 1. Illustration of degradation mechanisms in liquid lithium ion batteries[8]. Copyright 2017, Elsevier.

Typically, battery active material failure triggers performance degradation and even safety concerns (**Fig. 1**) [8]. Performance degradation manifests as capacity decay, elevated internal resistance, voltage attenuation, and power loss. More severe degradation appears under work conditions like extreme temperatures and rapid charging. Moreover, safety failures encompass thermal runaway, short circuits, liquid/gas leakages, lithium plating, and corrosion. These two facets represent the dominant degradation modes encountered in battery systems. Battery failure mechanisms include four primary categories[9]: electrical, chemical, electrochemical, and mechanical. In lithium metal batteries, electrical failure is intricately linked to plating/stripping behaviors influenced by physicochemical properties and interfacial chemistry. Chemical failure stems from interfacial reactions occurring between electrode and electrolyte. Electrochemical failure results from sluggish diffusion and

transportation processes within both the bulk and interfaces, leading to poor dynamic behaviors. Mechanical failure are reflected in cracking, strain, and volume changes. Comprehensive solutions have been proposed to address these challenges including the modification of cathodic, anodic, and electrolytic components, along with the intricate interfaces.

To unravel the failure mechanisms within battery materials, synchrotron X-ray characterization techniques exhibit unique features in operando/ex situ measurements. As non-destructive techniques, X-ray characterization plays an indispensable role in energy storage research. Compared to the laboratory X-ray source, synchrotron X-ray present the exceptional brightness and high flux. The former radiation results from a deceleration of high voltage electrons as they pass by atomic nuclei. However, the synchrotron radiation is the electromagnetic emission produced when charged particles are accelerated along curved paths. Disregarding the concerns of limited beamtime and high costs of synchrotron light, synchrotron radiation provides high quality data with high resolution, short measuring time, good penetration. Significantly, the simultaneous operation of two X-ray techniques is possible by using synchrotron radiation, such as the simultaneous using of small-angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) at 12-ID beamline, the combination of small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) at 9-ID beamline at Advanced Photon Source. The advent of fourth-generation light sources has ushered in a new era, promising vast application potential across numerous scientific fields[10].

In this review, we summarized the application of cutting-edge synchrotron X-ray characterization techniques in lithium battery materials failure analysis. Specifically, our attention is centered on X-ray scattering (power X-ray diffraction (PXRD), X-ray pair distribution function (PDF), SAXS) and X-ray absorption spectroscopy techniques.

By utilizing these techniques (ex-situ, in-situ, and operando), a comprehensive understanding of both local and global intricacies, spanning both bulk and surface/interface domains, is achieved during failure analysis. This knowledge guides strategies to mitigate failures, ensuring the development of more durable, safer, and resilient battery systems.

2. X-ray scattering

The X-ray scattering technique is unique in capturing the bulk structural evolution and reaction mechanisms during electrochemical operations and temperature variations[11-14]. PXRD is widely employed for long-range order crystal structure analysis; As a complementary technology, PDF offers short-range insights into amorphous materials. This capability enables us to uncover the failure mechanisms of active materials, including phase transition, lithium plating, and volume change.

2.1 Phase transition

PXRD has been extensively employed to analyze the crystalline structural alterations in materials. Numerous in-situ/operando SR-PXRD studies have been conducted on cathode materials. In a study by Nam et al.[15], in-situ heating time-resolved SR-PXRD was utilized to investigate the thermal decomposition behaviors of overcharged $Li_xNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM) cathodes. NCA underwent structural transformations from rhombohedral to spinel and subsequently to rock-salt phases upon heating. In contrast, NCM exhibited structural changes from rhombohedral to spinel and then to Co_3O_4-type spinel structure, leading to a delayed phase transition to rock-salt. By integrating SR-PXRD with mass spectroscopy (MS), the gas species such as O_2 and CO_2 released from overcharged cathode materials can be monitored. This combined approach provides valuable insights into phase transitions and gas evolution during thermal decomposition processes[15-18]. Xu et al. [19]

employed SR-PXRD to elucidate a structure-driven degradation mechanism in Ni-rich cathodes. The study shows that the emergence of fatigued phases during cycling is attributed to interfacial lattice strain between the bulk structure and reconstructed surface layers, rather than bulk NCM phase transformations or increased Li/Ni anti-site mixing. Notably, this fatigue was observed not only in polycrystalline NCM materials but also in single-crystal counterparts.

Ryu et al.[20, 21] studied the capacity fading mechanisms in both polycrystalline and single-crystal Ni-rich cathodes with varying Ni content using SR-PXRD (**Fig. 2a,b**). The study reveals that in polycrystalline Ni-rich cathodes with Ni content below 0.8, capacity loss predominantly results from surface degradation. Conversely, a phase transition near the end of charging triggers a sudden anisotropic shrinkage/expansion when Ni content is higher than 0.8. This transition-induced stress destabilizes internal microcracks, which enables their propagation to the surface, leading to pathways for electrolyte attack and subsequent degradation. In contrast, single-crystal Ni-rich cathodes exhibits inferior electrochemical performance due to spatially inhomogeneous lithium concentrations and coexistence of phases within particles, especially under high C-rates and high Ni compositions. Optimizing particle sizes for single-crystal cathodes is essential to enhance lithium-ion diffusion kinetics, while stable polycrystalline cathodes could be achieved through microstructural modifications. Alternatively, mixing single-crystal and polycrystalline particles could be considered as a viable option.

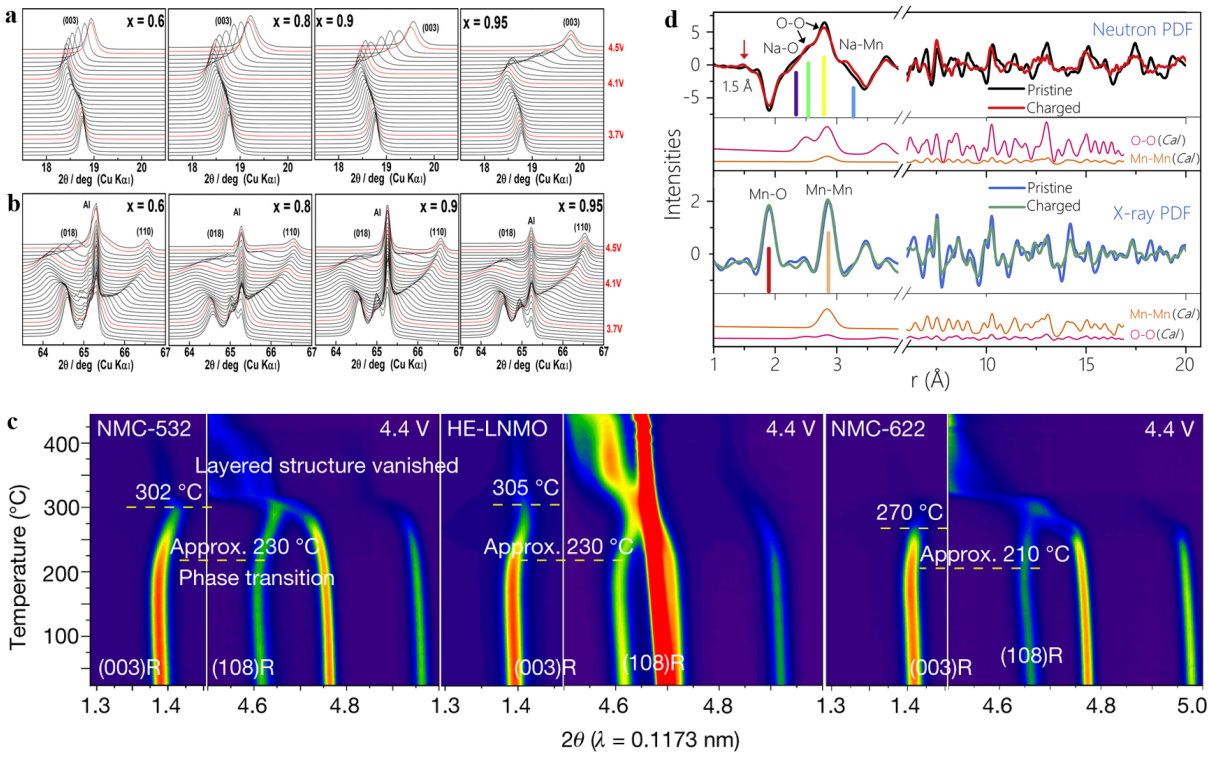


Fig. 2. (a) and (b) Structural evolution of Ni-rich cathodes during cycling[20]. Copyright 2018, American Chemical Society. (c) Thermal stability analysis of cathodes[22]. Copyright 2022, Springer Nature Limited. (d) Local structure analysis of desodiation[24]. Copyright 2017, Elsevier.

In addition to NCM cathode, Zhang et al.[22] applied SR-PXRD to uncover the transformation of new layered high-entropy cathodes (HEC) into a spinel structure at 230 °C and rock salt at 305 °C, highlighting the outstanding thermal stability than NCM (Fig. 2c). Additionally, their study revealed minimal lattice changes in HEC during delithiation, emphasizing HEC's superior structural stability. Xu et al.[23] emphasized the pivotal role of synthesis-induced intrinsic lattice strain in the swift deterioration of sodium-layered oxide cathodes during cycling. This inherent lattice strain initiates sudden structural deterioration, which is unaffected by charge cut-off voltage but highly influenced by operational temperature and charge/discharge rates. Strategies like surface coatings or electrolyte modifications prove ineffective in halting this fundamental lattice strain relaxation process. Rong et al.[24] conducted a detailed analysis of the local structures in charged and discharged $Na_{0.6}[Li_{0.2}Mn_{0.8}]O_2$ samples

using X-ray and neutron PDF techniques. As shown in Fig. 2d, the charged sample revealed a subtle O-O peroxide pair and diminished Na-O bonds, suggesting efficient sodium extraction and potential alterations in particle size or increased disorder. Upon discharging, the structure returned to a state resembling the pristine sample, underscoring the material's robust lattice oxygen and structural stability during oxygen redox processes. Wu et al.[25] designed a setup that combines SR-PXRD and SAXS, enhancing measurement accuracy and frequency. This setup is ideal for researching time-resolved dynamic processes such as chemical reactions, particle growth, and structural evolution.

2.2 Li plating

SR-PXRD also plays a crucial role in visualizing lithium plating in full cells, making it invaluable for industrial applications[26-30]. Charalambous et al.[29] employed SR-PXRD to investigate lithium plating in a NCM-523/graphite pouch cell under fast-charging conditions. As shown in **Fig. 3**, the study precisely quantified the processes of lithium plating and stripping, analyzing their impact on graphite intercalation of lithium. The growth of lithium plating exhibited a two-stage nucleation and autocatalytic growth mechanism. Heterogeneous lithiation of graphite grains was observed to be correlated with plating sites, suggesting that the over-lithiation of graphite might precede the initiation of lithium plating. Additionally, the study identified partial lithium stripping, with efficiency decreasing exponentially over cycles. Similarly, Paul et al.[28] introduced a method using SR-PXRD to quantitatively analyze diverse components at both localized and global scales, including Li plating on the anode, all without the need for device dismantling. When applied to pouch cells, this method elucidates the heterogeneous Li plating on the anode, showing a correlation with anode lithiation. This innovative approach offers non-destructive insights into multiscale degradation

processes in energy-storage devices.

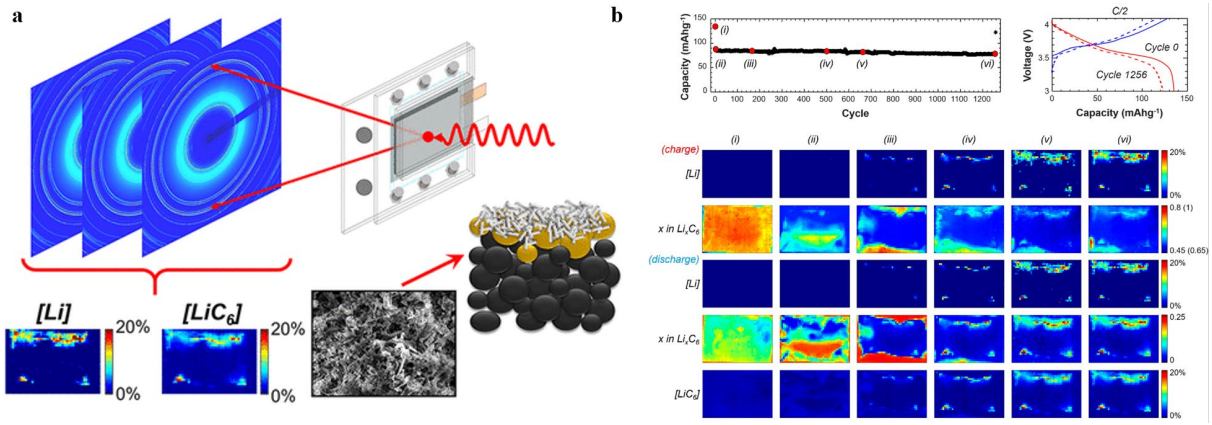


Fig. 3. (a) Schematic of XRD mapping for lithium plating. (b) Electrochemical performance and related color maps of lithium plating[29]. Copyright 2021, American Chemical Society.

2.3 Volume change

Conversion-type materials such as silicon, oxides, sulfides, and fluorides are potential electrodes used in batteries. However, these materials undergo significant volume changes during the conversion process. The severe and heterogeneous volume expansion of active materials leads to particle cracks, pulverization, and additional electrolyte consumption. These irreversible changes ultimately lead to a decrease in capacity and battery failure. Different from the local structure that observed by transmission electron microscopy (TEM), SAXS provides a size/morphology/pore information of materials within a micrometer sized beam. SAXS technique plays a crucial role in revealing the volume changes by providing statistics structural information of electrode materials.

Park et al.[31] probed the volume changes of several mesoporous oxide electrodes using SAXS during cycling, providing valuable insights into the electrode failure process (**Fig. 4a**). Wiaderek et al.[32] examined the impact of anion chemistry and reaction temperature on the formation mechanism of metallic iron in various iron compounds, employing SAXS and PDF techniques. As shown in Fig 4b, anion

chemistry significantly affects atomic defects, particle size, shape, and particle interactions, thereby influencing electrode performance and reaction kinetics. This research underscores the superiority of SAXS and PDF analyses in studying structural evolution when compared to electron microscopy methods, which can potentially damage materials through electron beam exposure.

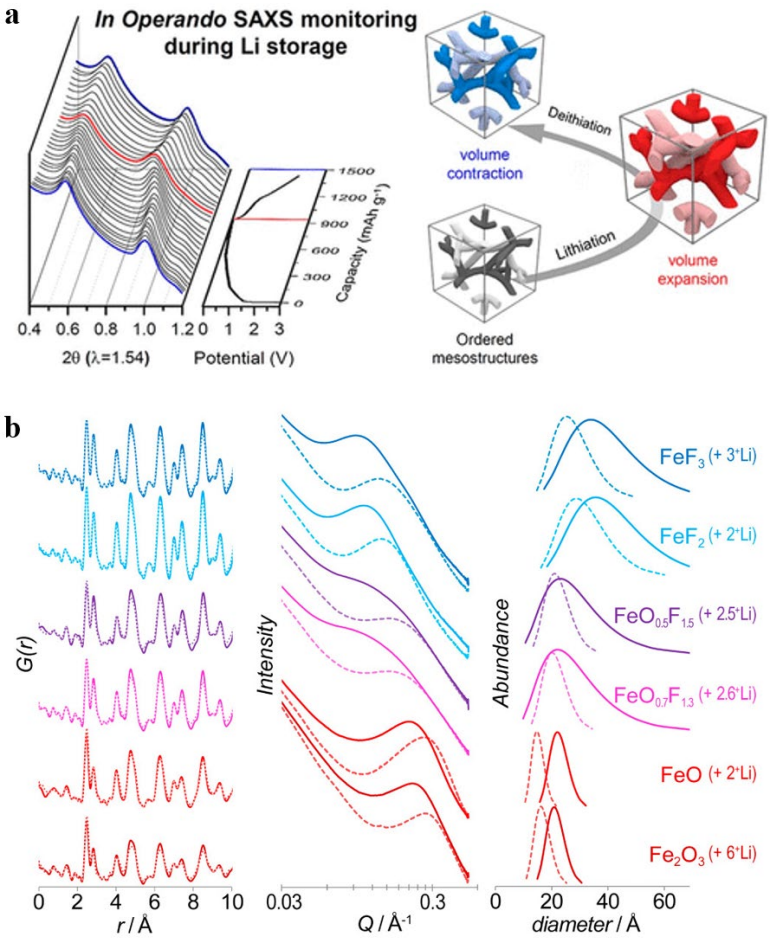


Fig. 4. (a) Illustration of SAXS used for volume change analysis[31]. Copyright 2015, American Chemical Society. (b) The PDF (left), SAXS (middle) data, and particle size distribution of a series of Fe electrodes[32]. Copyright 2014, American Chemical Society.

Different from transmission feature of SAXS, grazing-incidence SAXS (GISAXS) operates in reflection mode, showing surface-sensitive property. This enables the application of GISAXS in the surface structure information study. Bhaway et al.[33]

explored the influence of nanopore size on the atomic and nanoscale structural evolution of conversion-type ordered mesoporous $NiCo_2O_4$ (m-NC) anode by employing GISAXS and grazing-incidence XRD (GIXRD) techniques during battery operation. Their results reveal that m-NC with smaller mesopores collapses during the initial cycles due to irreversible electrochemical reactions, leading to a loss in capacity. In contrast, m-NC with larger mesopores experiences reduced distortion in the first two cycles, enhancing capacity retention. However, m-NC with larger mesopores also degrades during subsequent cycles due to structural deformations. This study highlights the impact of atomic-scale changes, such as lithium insertion and de-insertion, on the nanostructure, ultimately influencing battery performance over time.

Lithium-suffer batteries is regarded as the promising next-generation batteries because of high theoretical energy density of 2500 $Wh\,kg^{-1}$ and the earth-abundant sulfur. However, expect the volumetric expansion of S after lithiation ($\approx$80%), the insulating property solid discharged products (Li_2S_2/Li_2S) and their sluggish nucleation growth leads to insufficient sulfur utilization and poor rate performance. Prehal et al.[34] employed SAXS in conjunction with other advanced techniques to investigate the Li_2S formation mechanism. Their research unveiled the precipitation of Li_2S_2, succeeded by its conversion to Li_2S through solid-state electroreduction. Notably, their findings indicated that the limiting factors for discharge capacity and rate performance are primarily associated with mass transport, rather than electron transport through a passivating film. This study offers insights for designing and optimizing the performance of Li-S cells. In addition, SAXS has found application in the realm of solid-state electrolytes (SSEs)[35]. The research disclosed that batteries incorporating electrolytes with undefined structures exhibited commendable performance compared to those featuring precisely organized electrolyte architectures. Interestingly, annealed

polymer electrolytes displayed diminished performance due to structural disparities, yet this mismatch might serve as an intrinsic safety feature, preventing the battery from functioning when its temperature surpasses a specific threshold. This study sheds light on the significance of comprehending electrolyte morphology in solid-state batteries, illuminating pathways for future advancements in battery technology.

3. X-ray absorption

XAS serves as a powerful tool for elucidating the coordination environment and electronic structure of target element. Different from the PDF technique, the element-specific feature of XAS makes it able to monitor the local structure evolution of interested element under operando or ex suit conditions. In addition, XAS can be classified into hard XAS and soft XAS based on the incident X-ray energy. The hard XAS uncovers the bulk redox behaviors. In contrast soft XAS can provide us with an understanding of surface/interface redox processes. Hard XAS is suitable for analyzing high atomic number elements and the K-edges of 3d transitional metals (TMs), while soft XAS is applicable for analyzing low atomic number elements and the L-edges of 3d TMs[34].

3.1 Bulk redox

Ma et al.[36] utilized Quick XAS (QXAS) to investigate redox mechanism in Ni-rich cathodes, which offers intricate insights into electronic and local structural details. The findings revealed the prevalence of nickel in electrochemical reactions, the inertness of cobalt in these processes, and the reversible migration of nickel ions between TM sites and lithium sites. Assat et al.[37] explore cationic-anionic redox processes in Li-rich layered oxides using operando hard XAS coupled with principal component analysis (PCA) and multivariate curve resolution-alternating least-squares (MCR-ALS) analysis. A complex three-component reaction mechanism was

demonstrated, providing valuable insights into long-term reversibility, voltage hysteresis, and kinetics in electrochemical systems. Zhang et al.[22] employed a comparative analysis of the structural stability of cycled HEC and NCM-811 materials. The XANES analysis shows that HEC retained its structural integrity, whereas NCM-811 exhibited shifts in the Ni K-edge spectra, indicating diminished internal volumes, likely due to hindered Li^+ diffusion. Fourier-Transformed EXAFS (FT-EXAFS) analysis elucidated shortened coordination distances in NCM-811, implying lattice shrinkage and the formation of defects. Conversely, HEC exhibited consistent and stable coordination environments, wherein oxygen vacancies were confined around specific dopants, effectively preventing crack formation. Bak et al.[17] conducted XANES and EXAFS analyses on charged NCA cathodes at varying temperatures. As the temperature increased, Ni ions shifted to lower energy states, signifying a reduction in their oxidation state. This reduction plays a significant role in the thermal decomposition of charged cathodes. Although the spectra for Co exhibited similarities with those of Ni, Co ions began to shift at higher temperatures and to a lesser extent. Interestingly, Co ions demonstrated greater stability, showing a tendency to form a Co_3O_4 spinel-like structure before transitioning to a rock-salt structure at elevated temperatures. Xu et al.[23] investigated the evolution of redox couples in strained $NaNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ cathodes during charge/discharge processes, employing in situ Ni K-edge XANES. As shown in **Fig. 5**, the Ni K-edge spectra shifted to higher energy levels, reflecting the oxidation of Ni^{2+} to Ni^{3+}/Ni^{4+} during charging. Conversely, during discharging, the energy levels shifted back to lower values, indicating the reduction of Ni^{3+}/Ni^{4+} to Ni^{2+}. This suggests a reversible oxidation/reduction process for Ni within the voltage range of 2.0–4.4 V. Notably, despite significant capacity degradation over 10 cycles, Ni still displayed reversible redox reactions.

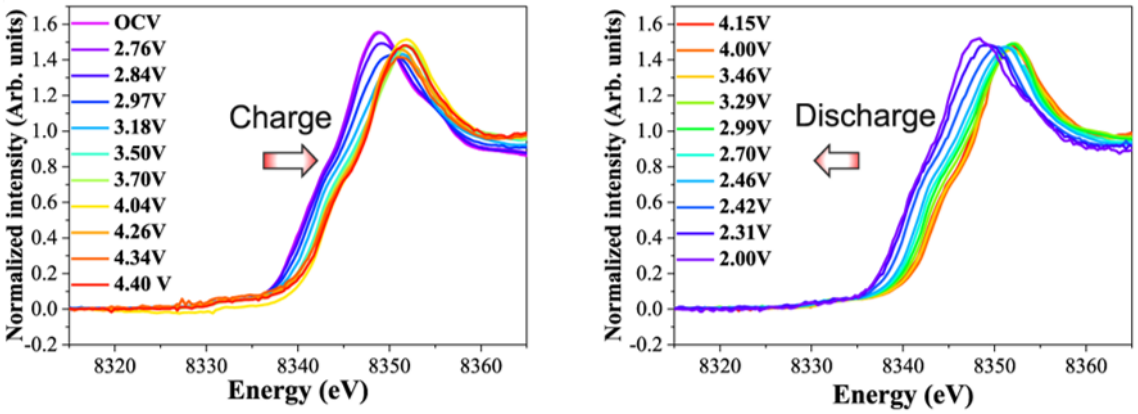


Fig. 5. In situ Ni K-edge XANES of $NaNi_{0.4}Mn_{0.4}Co_{0.2}O_2$[23]. Copyright 2022, UChicago Argonne, LLC, Operator of Argonne National Laboratory.

3.2 Surface/interface transformations

In addition to the study of bulk oxidation state of transition metal in cathode by using hard XAS, surface/interface-sensitive methods like sXAS and resonant inelastic X-ray scattering (RIXS) are potent tools for exploring oxygen redox processes. Liu et al.[38] utilized in-situ and operando techniques to unravel the intricate charge dynamics within cathode materials. Through meticulous comparisons of various cathode materials, such as NCM-111 and $LiFePO_4$, this study underscores the critical significance of factors such as charge transport, mesoscale morphology, and phase transformation in shaping these dynamics. Liang et al.[39] investigate the charge mechanisms of NCM cathodes during deep charging through a combination of sXAS and XRD. Elevated potentials exacerbate phase transitions and oxygen release, intensifying instability due to deeper lithium vacancies, higher Ni^{4+} content, and robust orbital hybridization. Analysis of TM L-edge sXAS spectra reveals that Ni predominantly contributes to charge compensation, whereas Co exhibits significant redox activity at elevated potentials. Additionally, examination of O K-edge spectra highlights increased oxygen hole formation and intricate metal-oxygen orbital hybridization involving TM 3d−O 2p orbitals. Another study[40] conducted within their group explored the influence of cation reduction on the surface in the formation of nanovoids, utilizing sXAS. They analyzed the valence

states of Ni and Co cations at different temperature stages. The findings indicated that a pronounced reduction of TM cations on the surface during thermal degradation led to the formation of visible nanovoids, especially in materials with lower Ni content, signifying a greater depletion of lattice oxygen at the surface.

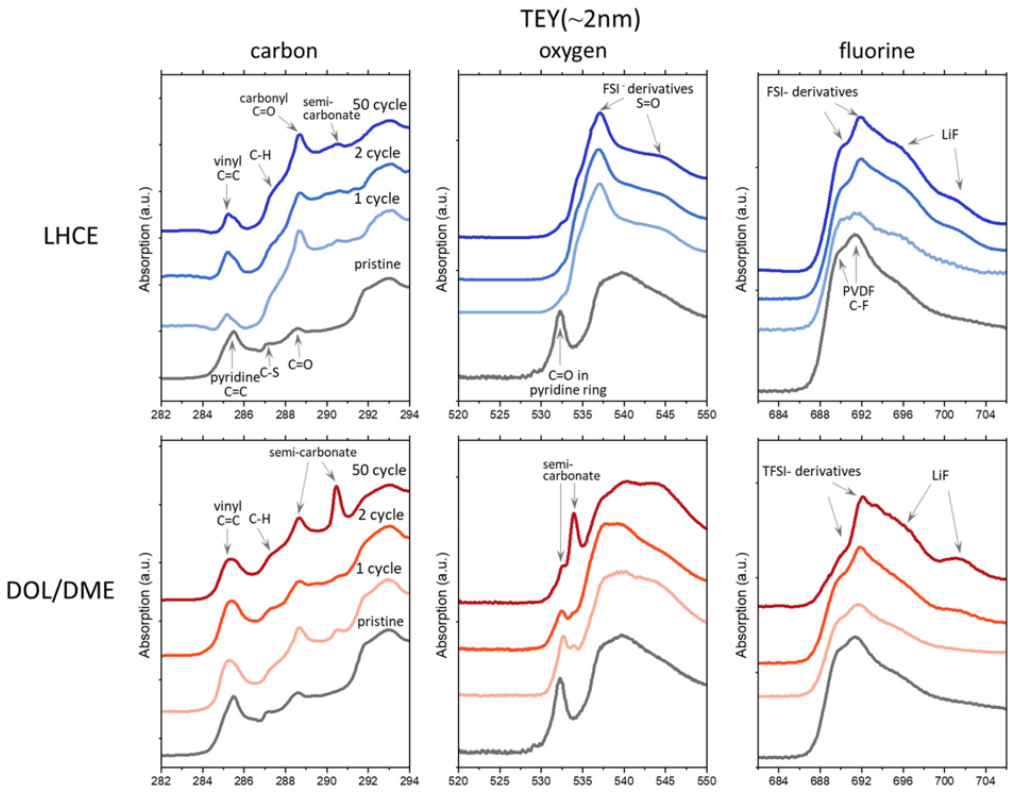


Fig. 6. sXAS results of pristine and cycled SPAN in different electrolytes[41]. Copyright 2023, American Chemical Society.

Tan et al.[41] investigated the structural and interphase transformations occurring in Sulfurized Polyacrylonitrile (SPAN) cathodes utilizing sXAS and PDF analysis (**Fig. 6**). PDF identified crucial features such as C−S bonds and sulfur dimers, which underwent conversion into short sulfur chains during the cycling process. Meanwhile, sXAS detected alterations in surface composition, highlighting the formation of a stable cathode electrolyte interphase (CEI) in the localized high concentration electrolytes, contrasting with the unstable CEI observed in ether-based and carbonate systems, attributed to persistent solvent and salt decomposition. Oxygen redox activities can lead

to undesirable outcomes during battery operation, including gas emissions, surface reactions, voltage fluctuations, and slow reaction rates. Although sXAS has been employed to investigate oxygen redox, its reliability is questionable[42]. RIXS emerges as an effective tool in this field. Yang et al.[43] have systematically reviewed the application of RIXS in the analysis of oxygen redox processes, offering a comprehensive understanding of this field.

4. Summary and outlook

With the widespread adoption of battery technology, numerous safety issues have occurred. The urgent need to decouple the materials-failure-mechanism correlation in battery materials cannot be overlooked. However, traditional characterization techniques face challenges related to efficiency and accuracy, making the process time-consuming and costly when attempting to decipher degradation mechanisms. Fortunately, synchrotron X-ray techniques, renowned for their exceptional brightness and high flux, present a potent solution for unveiling microscopic structures and redox changes within a shorter timeframe and with greater precision. In this context, we propose exploring diverse avenues to develop a cutting-edge FMMEA methodology (**Fig. 7**).

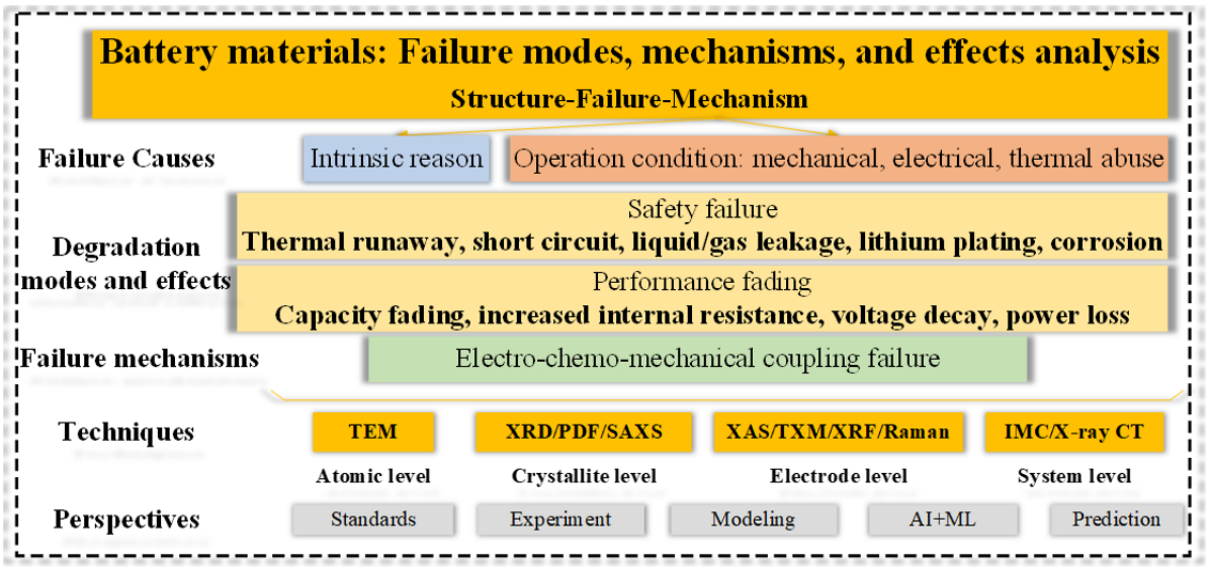


Fig. 7. Mechanisms and characterization scale perspectives for battery materials failure analysis.

Electro-chemo-mechanical coupling degradation mechanisms. In battery operations, material failures are not singular events; rather, they often result from the intricate interplay of multiple degradation modes, each influenced by a complex array of causes and effects. It is essential to discern the relationships among these degradation modes, meticulously identifying the primary factors contributing to battery material failures. This in-depth understanding is paramount for developing precise preventive measures and formulating targeted mitigation strategies, ensuring a proactive and effective approach to accident prevention.

Multiscale characterization methods. The mechanisms underlying battery failures are intricate and typically involve multiple time and space scales. Each characterization technique has its advantages and limitations. To comprehensively decipher battery material failures at atomic, crystallite, electrode, and system levels, it is imperative to integrate a combination of characterization tools such as X-ray methods, neutron-based techniques, electron microscopy, spectroscopy, and isothermal microcalorimetry, along with advanced modeling approaches. Only by employing this comprehensive toolkit can we construct a comprehensive map of the entire failure mechanism. When utilizing synchrotron-based techniques, careful consideration must be given to potential beam damage, which can significantly impact the analysis results.

Failure analysis process. Battery failure analysis constitutes a complex system engineering endeavor. To enhance our comprehension of failures and effectively mitigate accidents, the establishment of standardization protocols is imperative, normalizing practices within the industry. Furthermore, a comprehensive understanding of fading mechanisms necessitates the integration of both experimental and theoretical analysis.

Artificial intelligence. The brilliance and flux of synchrotron beams continually advance, enabling the acquisition of highly precise data within shorter time frames. Efficient processing of this acquired data is paramount. Artificial intelligence (AI) is reshaping various sectors worldwide, profoundly impacting the realm of science. It can be employed not only for predicting battery performance failure and safety monitoring and warnings but also for accelerating the battery materials failure characterization and analysis, both experimentally and theoretically. Furthermore, the integration of AI can significantly enhance synchrotron-based characterization processes, encompassing data collection, management, processing, analysis, and interpretation.

Declaration of Competing Interest

The authors declare no competing interests.

Acknowledgments

T. Li is thankful for the supported by U.S. National Science Foundation (Grant Nos. 2208972, 2120559, and 2323117). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility, operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02–06CH11357.

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