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**Interfacial properties in energy storage
systems studied by soft X-ray absorption
spectroscopy and resonant inelastic X-ray
scattering**

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Abstract

Interfacial behaviors and properties play critical roles in determining key practical parameters of electrochemical energy storage systems, such as Lithium-ion and sodium-ion batteries. Soft X-ray spectroscopy exhibits shallow penetration depth and demonstrates inherent surface sensitivity to characterize the

interfacial behavior with elemental and chemical sensitivities. In this review, we present a brief survey of modern synchrotron-based soft X-ray spectroscopy of the interface in electrochemical energy storage systems. The technical focus includes core-level spectroscopy of conventional X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS). We show that, while conventional techniques remain powerful for probing the chemical species on the surface, today's material researches have triggered much more demanding chemical sensitivity that could only be offered by advanced techniques like RIXS. Another direction in the field is the rapid developments of various *in-situ/operando* characterizations of complex electrochemical systems. Especially, the solid-state battery systems provide unique advantages for future studies of both the surface/interface and the bulk properties under *operando* conditions. We conclude with perspectives on the bright future of studying electrochemical systems through these advanced soft X-ray spectroscopic techniques.

Introduction

Electrochemical energy storage systems, such as lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) play a significant part in sustainable energy applications^{1, 2}. In prevailing

electrochemical energy storage devices, the functionality and stability of the interfaces and interphases between the electrodes and electrolyte have been one of the central topics³⁻⁷. For example, in LIBs, the so-called solid electrolyte interphase (SEI) between the carbonate electrolyte and the graphite anode has been critical for the life time of commercial LIBs. For the other electrode, the cathode, the surface activities have been paid relatively less attention for long; however, the transition metal (TM) dissolution and surface reconstruction have been known detrimental to the battery operations for various electrode materials⁸. These interface behaviors are directly related to impedance increase, capacity decrease, and exothermal reactions correlated with battery safety concerns. The issues related with surface properties of the pairing electrodes become more and more important in recent years, due to the demand of high-capacity and high-energy battery systems. The high operation voltage required for high-energy batteries often leads to electrolyte decomposition beyond electrochemical stability window, as well as the cathode instability issue from oxygen release and structural collapse. More importantly, at the charged state, the interactions between the highly oxidized cathode and electrolyte may lead to cycling instability, battery decay, and safety issues. As a result, the surface and interface properties often define the

stability of battery operation, and determine the practicability of the high-energy battery systems.

Note that the interfacial behavior mostly involves complicated physical and electrochemical processes, which makes this research topic a daunting challenge⁶. Up to now, although with lots of progress and achievements on understanding and controlling the anode SEIs⁹⁻¹², a comprehensive and clear picture of the interface on electrodes has not yet been established on the detailed interfacial composition and structure, formation mechanism, functionality, and its influence on electrochemical performances. Over the years, tremendous and extensive interface investigations have been carried out with various techniques. Soft *X-ray* generally exhibits shallow penetration depth, corresponding soft *X-ray* spectroscopy techniques become suitable choice for interface investigations¹³, such as soft *X-ray* photoelectron spectroscopy (XPS)^{14, 15}, soft *X-ray* absorption spectroscopy (XAS)¹⁶ and etc. Particularly, the ambient pressure *X-ray* photoelectron spectroscopy (APXPS) enables direct detection across liquid-electrode interface under external bias¹⁷, which demonstrates bright potential in energy storage devices investigations. sXAS functions based on the core level excitation and subsequent decay process, which exhibits elemental/orbital/chemical sensitivity. The energy range of soft *X-ray*

covers transition metal (TM) L edge and O-K edges, as a result sXAS can directly probe valence band related TM 3d and O 2p states and fingerprint detailed chemical species evolution. Based on different data collecting modes, sXAS offers two different probing depths of several nanometers from total electron yield (TEY) and hundreds of nanometers from total fluorescence yield (TFY) modes, which can be collected simultaneously and present contrast between the interface and bulk behaviors¹⁸. These characteristics and advantages make soft X-ray absorption spectroscopy a powerful tool for interface research.

The interface reactions in electrochemical energy storage devices can be characterized through specific sXAS experiments. For example, on the anode surface, the formed SEI could be measured through O-K or C-K edge sXAS¹⁹. Interfacial reaction products, such as carbonate species formation can be well detected. On the cathode, surface passivation demonstrates TM valence states evolution, which could be detected by TM-L edge sXAS. Especially, at high voltages, oxygen participation in charge compensation, known as anionic redox reaction (ARR), further complicates the interfacial reactions and makes a clear characterizations challenging. Compared with conventional XAS, recently developed resonant inelastic soft X-ray scattering (RIXS)

mapping provides much improved chemical sensitivity by collecting the energy distribution curves of emitted photons²⁰⁻²⁴. The fundamental physical process and general comparison between sXAS and RIXS are shown in **Figure 1**. For XAS, the unoccupied electronic states are mapped out by emitted photon counts or compensate current, which lead to the TFY and TEY data collection modes respectively. While for RIXS, the energy distribution of emitted photons is recorded while the incident excitation energy is scanning through the absorption edges. Through the excitation and decay process, the changes in photon energy, momentum and polarization can be transferred to intrinsic excitations of materials²⁵. At each excitation energy, RIXS further resolves the single data point in XAS into an energy distribution curve, which hence provides a new dimension of information along emission energy²⁶. Note that the photon-in-photon-out (PIPO) data collection mode makes RIXS mostly bulk sensitive. But RIXS has been quickly established as a superior technique beyond conventional XAS in many aspects of battery studies. For example, RIXS has revealed the monovalent Mn in battery electrode that cannot be detected by XAS²⁷, it could also distinguish the intrinsic state of the oxidized oxygen in battery electrode cycled at high potentials²⁸⁻³⁰. Note that such signals are mixed together with transition-metal characters in conventional

sXAS results³¹. Because this review focuses on the interfacial studies, the examples on RIXS studies in this manuscript is mainly for discussing the superior chemical sensitivity of RIXS for interfacial properties. Nonetheless, we note that the rapid development of RIXS technique in the last couple years has opened up new opportunities for employing this advanced tool for energy material studies, and the combined tool chest of conventional XAS and modern RIXS mapping often provides a powerful combination for interface properties in energy storage systems.

Other than the technical advances on the signal collection, *in-situ* and *operando* soft X-ray spectroscopic measurements have also been much developed and become essential for studying the interface involving solid/liquid phases with dynamic response³²⁻³⁵. For *in-situ* soft X-ray spectroscopy characterization, since soft X-ray spectroscopy exhibits shallow penetration depth and can only be conducted in vacuum chambers, specially designed cells are needed to seal liquid electrolyte³⁶. Many works have showcased the advantages and power of *in-situ* soft X-ray for interface study³⁷. Nevertheless, those works are generally challenging to handle experimentally and can not exclude potential radiation damage effect from long time data collection. The rapid development of solid state batteries provides new opportunities for *in-situ* soft X-ray

characterization^{38, 39}, but corresponding research still needs more efforts. Overall, conventional *ex-situ* characterizations have the advantages of better data quality, especially for quantitative analysis⁴⁰, and relatively clean signal contributions, especially for elements such as O and C. However, samples for *ex-situ* experiments need to be carefully controlled so they could represent the true electrochemical states. On the other hand, *in-situ/operando* experiments could maintain the non-equilibrium states, e.g., states that require an applied potential. As a result, we would like to stress the importance of both the *in-situ* and *ex-situ* characterizations, as each has its own technical advantages. We also note that protecting the samples from degradation, e.g., changes upon air or humidity exposure is essential for many battery material studies. Additionally, *ex-situ* experiments also require samples with locked electrochemical states with systematically evolving signals^{41, 42}, while *in-situ* studies could be from one cell at different electrochemical states. In reality, however, *ex-situ* studies of multiple samples, if properly controlled, are often more straightforward and less demanding compared with *in-situ/operando* measurements of soft X-ray spectroscopy.

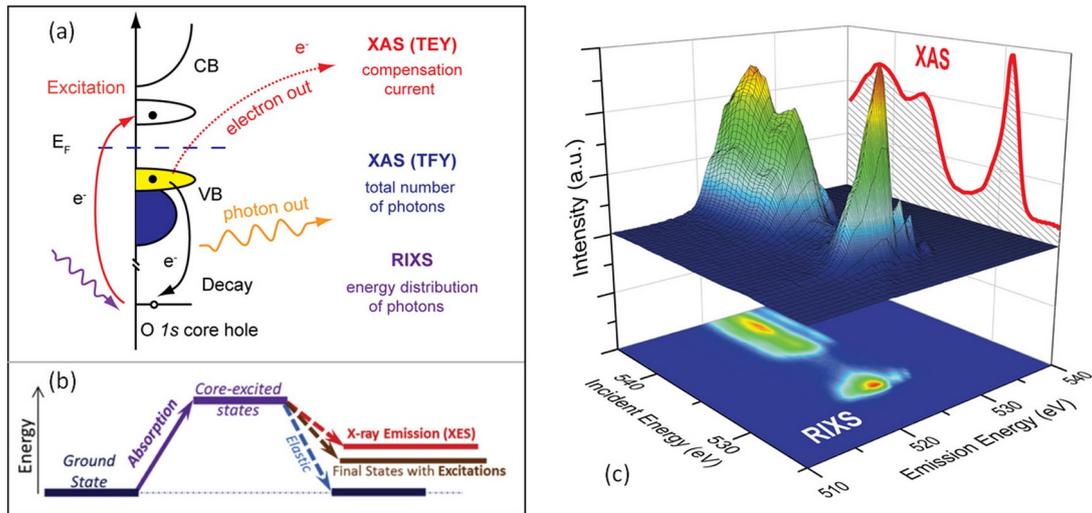


Figure 1. Schematic diagram of (a) fundamental physical process and data collection modes of XAS and RIXS. (b) Different states involved in the RIXS process upon energy scale. Reprinted with permission from reference ²⁶. (c) Direct comparison between RIXS mapping and XAS.

In this review, we provide a brief summary of different topics and applications regarding utilizing soft X-ray spectroscopy to study surfaces and interfaces in LIBs and SIBs, mostly focusing on sXAS and RIXS. Here, we first discuss the anode SEI characterizations, where the electrolyte decomposition and SEI layer formation have attracted much attention for decades. Then we will move onto the cathode-electrolyte interface, where the intrinsic electrode fatigue from structural collapse, gas release and etc are the research focus. Additionally, we show that, although conventional XAS is capable of

detecting many reaction products on the surface of battery and supercapacitor electrodes, it lacks the chemical sensitivity to measure the subtle effect at the interface if the signals are dominated by the signals from bulk materials that are always in the vicinity of the interface. We present a representative example of a model system on how RIXS could meet such a technical demand through its much improved chemical sensitivity. At the end, we provide our perspective of the technical developments and great potentials of advanced soft X-ray spectroscopy for studying interfacial problems in both liquid and solid state systems.

Anode SEI studies based on sXAS and RIXS

Since conventional anodes (e.g. graphite) exhibit Li chemical potential higher than LUMO (lowest unoccupied molecular orbital) of carbonate electrolyte, continuous electrolyte reduction and interface reactions may well take place on anode surface. Such thermodynamic instability on anode was once the bottleneck challenge for the practical development of LIBs. To overcome the problem, a stable solid electrolyte interphase (SEI) layer formation is essential or even prerequisite to enable long cycle of LIBs¹⁰. However, the interface reaction between anode and electrolyte is

very complicated. Building up the full picture of SEI layer then calls for systematic and comprehensive characterizations. In the past decades, XPS has been widely utilized to investigate SEI layer composition and its evolution with battery cycle, the influence of electrolyte additives on the stability of SEI can be further established⁴³. By combining the ion etching strategy or selecting the excitation X-ray energy, XPS can be further utilized to present the SEI components distribution with depth profiles. Based on the extensive efforts, the so-called “mosaic model” of SEI has been widely accepted presently, but it is still not fully established experimentally and faced with many challenge⁶.

With the elemental and surface sensitivity, soft X-ray absorption spectroscopy can provide unique and valuable insights to disentangle factors determining the interface reactions. One typical example is clarifying the influence of crystal orientation on SEI formation. By comparing the sXAS collected on two types of Sn single crystal, (100) oriented Sn and (001) oriented Sn, distinguished SEI components can be detected (**Figure 2a, 2b**)⁴⁴. While SEI on Sn (100) mostly consists of porous Li_2CO_3 , which mainly results from LiPF_6 salt decomposition on surface, SEI on Sn (001) are mostly LiF and organic molecules, which can be attributed to carbonated electrolyte decomposition. The distinguished SEI

components and morphology demonstrates different electrochemical behavior during long cycle. While the dense LiF can act as a passivation layer, porous Li_2CO_3 can not prevent further electrolyte decomposition.

With the deepening of the investigation, it was further found that CEI demonstrate dynamic response with charge-discharge process, called “breathing effect” (**Figure 2c, 2d**). With selected Cu electrode as a model template, the SEI formation and evolution can be investigated⁴⁵. By comparing with reference spectra from lithium ethylene dicarbonate (LEDC) and lithium acetate ($\text{H}_3\text{C-COO-Li}$), the carbonyl formation on Cu anode can be verified experimentally, such as semi-carbonate, oxalate or carboxylate species. As verified from the C-K edge and O-K edge absorption peak evolution, carbonate species get decomposed from SEI during delithiation and reformed during subsequent lithiation. The redox reversibility of nascent carbonate species in SEI leads to thickness oscillating with cycle, which is also supported by TOF-SIMS. Moreover, sXAS demonstrates that the overall SEI thickness gradually increases and the surface gets passivated with extended cycles. Such dynamic response and chemical profile of SEI layer was also verified on C- ZnFe_2O_4 electrode by comparing XAS and XPS with different probing depth⁴⁶. Partial reversible alkyl lithium carbonates (~5-7 nm)

formation at SEI can act as Li reservoir and contribute to extra capacity of electrodes.

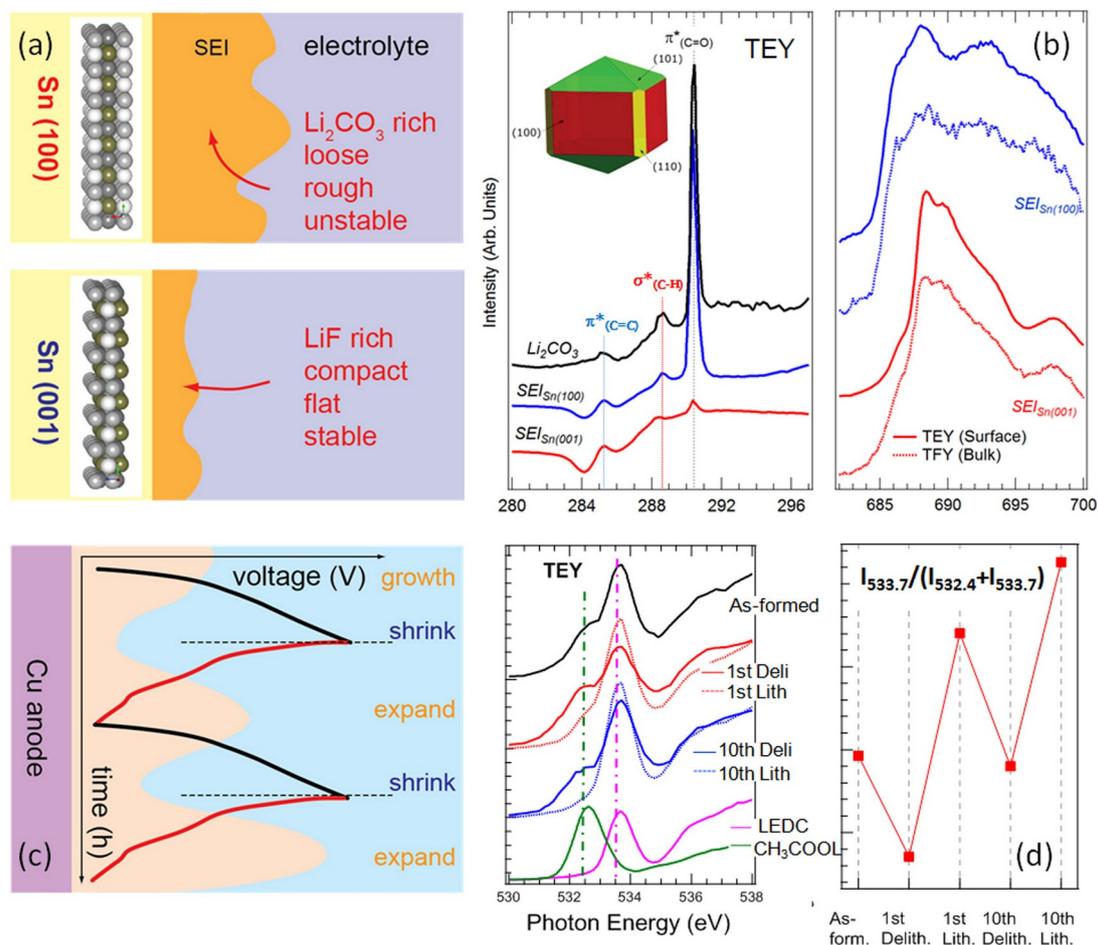


Figure 2. Soft X-ray spectroscopy on anode electrolyte interface research. (a) Schematic diagram of CEI evolution on Sn anode with different orientation. (b) C-K edge and F-K edge XAS of SEI grown on single crystal Sn anode with different orientation. Inset, Equilibrium shape of β -Sn, where (100) is the preferred surface. Reprinted with permission from reference ⁴⁴. (c) Schematic diagram of CEI evolution on Cu anode with cycle. (d) O-K edge XAS of SEI grown on Cu anode and the characteristic peak intensity evolution

upon lithiation and delithiation. Reprinted with permission from reference⁴⁵.

Besides XAS, RIXS provides further energy resolution along the emission energy scale at resonant energy, which can be well utilized for SEI research. A. Augustsson et al utilized RIXS to investigate SEI layer on graphite anode cycled in different electrolytes¹⁹. With selective excitation energy, RIXS spectra of SEI can be well matched with reference compounds including lithium oxalate ($\text{Li}_2\text{C}_2\text{O}_4$), lithium succinate ($\text{LiO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Li}$) and lithium methoxide (LiOCH_3). By specially designed background subtracting and quantitative fitting, C-K edge emission of SEI species can be well separated from graphite and further simulated by using 0.1 Li-oxalate, 0.45 Na-succinate and 0.45 Li-methoxide. Liang Zhang et al further utilized RIXS to study the electronic structure and chemical bonding of graphene oxide-sulfur (GO-S) nanocomposite⁴⁷. GO is verified to partially reduce from S incorporation and the interaction between GO and S can further stabilize S bonding during cycle. These pioneering works demonstrate the power of RIXS in detailed and insightful SEI research. With the further development of synchrotron techniques, it is foreseeable that RIXS will play a more significant role for future SEI research not only qualitatively but also

quantitatively. Meanwhile, with the utilization of synchrotron based X-ray micro fluorescence (uXRF)⁴⁸, 2 dimensional spatial resolved RIXS mapping across anode surface can be even anticipated for SEI research.

sXAS and RIXS study of cathode surface upon electrochemical potentials

Early studies of “conventional” voltage range typically suggest that cathodes do not suffer much parasitic reactions on the surfaces, because the lithium chemical potential of most prevailing cathodes lie within the electrochemical stability window of carbonate electrolyte⁴⁹. However, recent push towards high voltage batteries has led to fervent debates on the cathode electrolyte interphase (CEI) layer formation, which demonstrates as dramatic structural reconstruction at particle surface, electrolyte decomposition as well as distinguished TM valence states between cathode surface and bulk⁵⁰⁻⁵³. Moreover, high voltage cycling may further trigger oxygen participation in charge compensation, the chemically active high valence oxygen makes the cathode interface reaction even more complicated^{54, 55}. These interface instability issues and induced CEI layer formation are found directly related to

the electrochemical performances, such as internal impedance increase, voltage fade and capacity decay.

In previous reports, TM mostly demonstrates lower valence state at cathode surface compared with that of bulk, which indicates surface redox reaction against carbonate electrolyte. The sXAS characterizations further indicate that CEI layer demonstrates dynamic TM valence variation upon charge-discharge, which can be quantified with delicate spectra fitting. In spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, lower valence Mn^{2+} at cathode surface is quantified to flourish during charge and decrease during discharge^{56, 57}. Particularly, Mn^{2+} increase accompanies high valence Mn^{4+} at electrode facing electrolyte, indicating that surface Mn^{2+} is correlated with the interface reactions between higher valence Mn^{4+} and liquid electrolyte at charge state (**Figure 3a, 3b, 3c**). These findings are in contrary to conventional scenario that Mn^{2+} comes from Mn^{3+} disproportion reaction, which mostly take place at discharge state. However, in the case of $\text{Na}_{0.44}\text{MnO}_2$, Mn^{2+} evolution at cathode surface is quite different, which increases dramatically at discharge state below 2.6 V but decreases at charge state (**Figure 3d**)⁴¹. Regulating the cycling voltages can well improve the electrochemical cycling stability of assembled battery. Such behavior has also been found in $\text{NaLi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ electrode, which

agrees with Mn^{3+} disproportionation scenario and is in contrary to spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ case. The contrasting results can be attributed to detailed cathode properties differences including crystal structure, chemical composition or even cycle parameters; which indicate the complexity of interface reactions in various systems. Furthermore, dynamic TM ions dissolution from cathode, migration in electrolyte and redeposition on anode/cathode has been verified in past years⁵⁸. Such dynamic response may further affect the experimental results and more in-depth studies are hence necessary on the surface TM states variation mechanism.

In recent years, reversible ligand oxygen participation in charge compensation, known as anionic redox couple (ARR), has attracted wide attention, which demonstrates extraordinary capacity ~ 250 mAh/g⁵⁹. The novel reaction scheme has made interface reactions even more complicated. Previously, oxygen participation at high voltage is widely believed harmful to battery cycle since higher valence oxygen are chemically unstable and may trigger oxygen gas release from crystal lattice. Such radical oxygen release mostly occurs at cathode surface, which further leads to structural collapse, TM dissolution, cation migration or even safety concern. On the other hand, high valence oxygen may further trigger interface reactions. Particularly, the redox reaction between oxidative high

valence oxygen and reductive carbonate electrolyte may well take place. Moreover, high voltage cycle upon ARR involves higher valence TM, which may further bring about potential catalytic effect on electrolyte decomposition or trigger redox reactions at interface between cathode and electrolyte. Note that it is challenging to experimentally characterize ARR, conventional XAS cannot disentangle the signals of intrinsic oxidized O in the lattice from the strong TM-O hybridization. In contrast, RIXS provides extra sensitivity to chemical states with a new dimension of information along emission energy⁶⁰. A specific RIXS feature can be directly verified fingerprinting the bulk oxygen redox, which could be completely buried in conventional sXAS^{21, 61, 62}. Presently, Li rich cathodes are still hindered by several application-wise issues, such as sluggish kinetics, large hysteresis and voltage fade, where ARR play a significant role^{63, 64}. While strategies including surface modification are demonstrated effective to stabilize surface oxygen and benefit electrochemical cycle performances⁶⁵, further indicating the key role of surface effect in ARR exploitation. As can be inferred, RIXS will play an increasingly important role in the future development of ARR-active cathodes, in accompany with its rapid development on synchrotron facilities worldwide^{66, 67}. With the pursue of next generation of LIBs with higher working voltage and

larger Li capacity, the interface reactions on cathode maybe even more serious. The detailed reactions can be influenced by cathode structure, chemical composition and the activated ARR at high voltage. Furthermore, the cathode surface reaction can be entangled with anode surface reactions in the well sealed battery⁶⁸. Such correlation has been verified in the case the TM dissolution-migration-redeposition procedure between cathode and anode, and the dynamic and integrated interface layer evolution still calls for more research^{58, 69}.

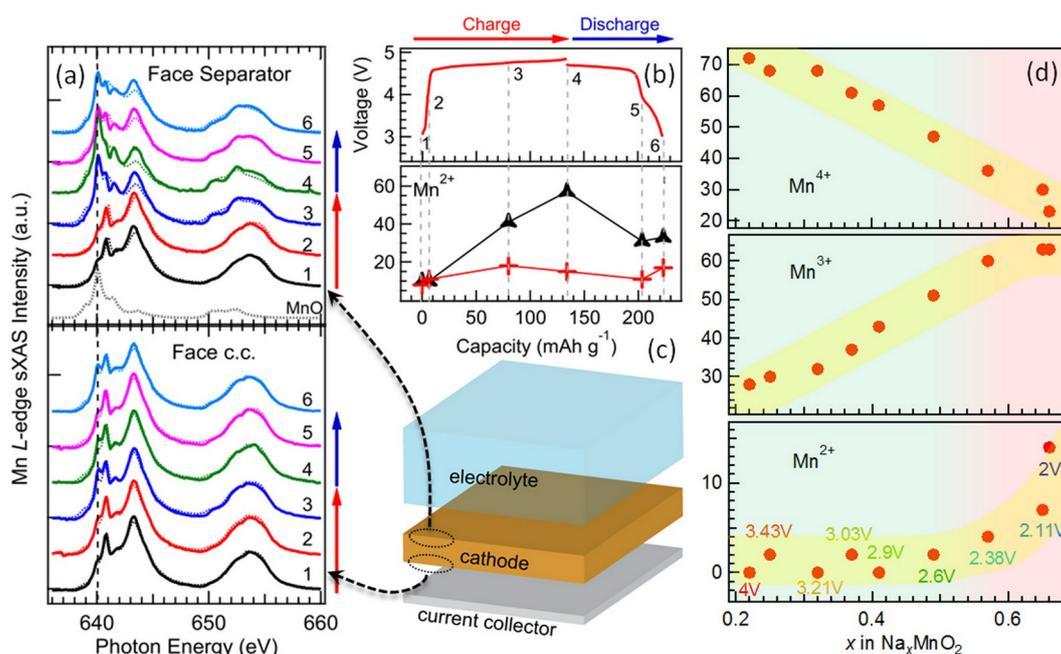


Figure 3. soft X-ray spectroscopy on cathode electrolyte interface research. (a) Mn valence state evolution of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode surface facing separator (up) and facing current collector (down) upon battery cycle. (b) Corresponding voltage profiles and Mn^{2+} concentration variation. (c) Schematic diagram of sXAS

detecting surface. Reprinted with permission from reference ⁵⁷. (d) Quantified Mn concentration at different valence states with varying Na concentration in $\text{Na}_{0.44}\text{MnO}_2$. Reprinted with permission from reference⁴¹.

Distinguishing interfacial signals from bulk signals

In addition to LIBs and SIBs discussed above, soft X-ray spectroscopy can be widely utilized for studying the surfaces and interfaces in other electrochemical devices, such as fuel cells, solar cell, electro-catalysis study^{70, 71} and etc. A striking example is on revealing an intriguing interface on the electrode surface of a supercapacitor with aqueous electrolyte. Aqueous electrochemical devices exhibit high safety, low cost and environmental friendly, but is limited by narrow potential window within HER (Hydrogen evolution reaction) or OER (oxygen evolution reaction)⁷². With layered Mn_5O_8 , Xiaoqiang Shan et al obtained pseudocapacitor electrode with wide and stable potential window ~ 3.0 V (**Figure 4a**). With the surface and elemental sensitive O-K edge sXAS, hydroxylated species formation and Mn-O coordination change on electrode surface can be verified. By virtue of Mn_5O_8 background subtracting, sXAS of surface hydroxylated layer can be further

obtained. Compared with reference samples and theoretical calculations, the obtained surface hydroxylated layer demonstrates strong ice-like ordering with perfectly aligned H-bond and O-O direction, but presents much longer O-O distance after cycle. Based on their research, the interplay between Mn^{2+} terminated surface and hydroxylated interface layer favors mitigating gas evolution and leads to the wide stability window, meanwhile provide facile pathway for sodium-ion transport. Such interface layer formation finally demonstrates high energy and power performances and long cycle retention of 85% after 25,000 cycles.

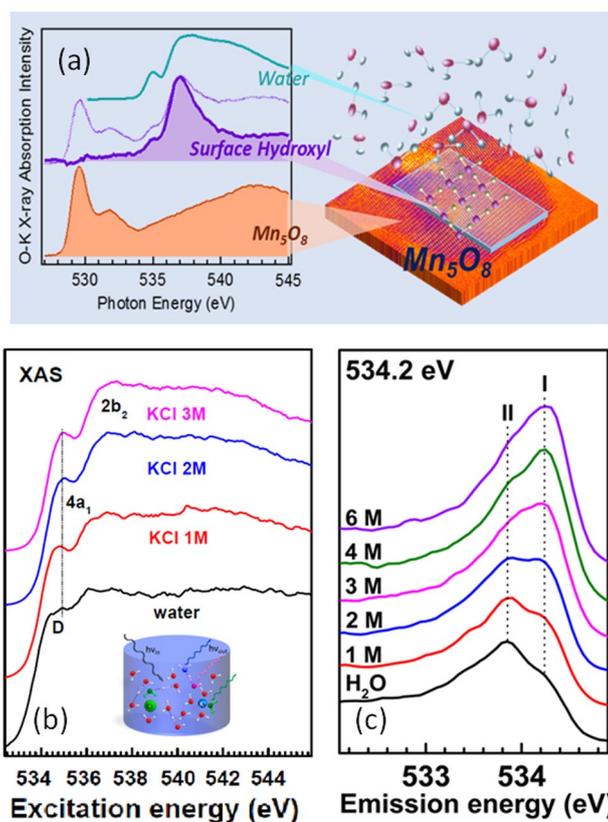


Figure 4. soft X-ray spectroscopy on typical electrochemical devices. (a) O-K edge XAS of Mn_5O_8 based pseudocapacitor

electrode. Reprinted with permission from reference ⁷². b) O-K edge XAS, (c) RIXS cut at 534.2 eV and O-K edge RIXS map on KCl solution with changing KCl concentration. Reprinted with permission from reference ⁷³.

Liquid electrolyte in typical batteries consists of Alkali salt dissolved in organic or aqueous solvents. In these electrolytes, the solvation shell can be viewed as the intrinsic interface between alkali ion and solvent molecules, which is directly related to the intercalation and deintercalation process and fundamentally determines the interface reactions¹⁰. However, detecting such an “interface” of solvation shell is extremely difficult because they are buried in the electrolyte solvent, and more importantly, the shell consists of exactly the same chemical components as in the bulk material surrounding it. **Figure 4b** shows the sXAS results of KCl solution in water with different salt concentration. Indeed, not much difference can be detected from sXAS although with different salt concentration. The overall consistency in sXAS is because the “interface signal” from solvation shell is well buried in signal from the overwhelming non-coordinated solvent molecules. With the photon-in-photon-out scheme, *in-situ* RIXS can be conducted in the sealing cells, which directly probes the local electronic structure of

aqueous KCl solutions. The effect of ion solvation on the reorganization of hydrogen bond network can be directly detected through the clear variation of the RIXS spectra (**Figure 4c**), which is correlated with ultrafast molecular dissociation of H₂O molecules and gradual slow-down of proton dynamics in KCl solution⁷³. The molecular level probe via soft X-ray spectroscopy provide valuable information on detailed solvent molecular configuration in liquid electrolyte, and such information is key to understand the dynamic electrochemical process with battery cycle. These findings from RIXS open up new opportunities for studying Li salt solvation and desolvation in liquid electrolyte, which are fundamentally and practically significant for future electrochemical energy storage devices development.

In-situ and operando soft X-ray spectroscopy

Compared with *ex-situ* characterizations, *in-situ* studies can mimic the real-world chemistry in batteries if handled properly. *In-situ* characterization exhibits unique advantage in probing solid-liquid interfaces, or even solid-liquid-gas interfaces^{13, 15, 74-76}. *In-situ* soft X-ray spectroscopy experiments are generally more challenging compared with hard X-ray techniques^{77, 78}. This is because the

energy range of soft X-ray is ~ 200 eV to 2000 eV, which has shallow penetration depth in atmosphere and can only be conducted in vacuum chamber. Since liquid electrolyte evaporates easily and is incompatible with vacuum atmosphere, well sealed model cells can be one promising choice. Note that conventional cells for *in-situ* hard X-ray spectroscopy cannot be directly transferred to *in-situ* soft X-ray characterization, and the X-ray transmission window selection becomes the key. This window not only separates liquid electrolyte from vacuum atmosphere, but also allow the soft X-ray penetration. With specially designed thin film windows of Si_3N_4 , Carbon, Aluminum etc., which typically have a thickness of tens of nanometers, a “static cell” or “flow cell” can be assembled for *in-situ* soft X-ray characterizations (**Figure 5a, 5b**)^{36, 78-81}. Several works have been reported with *in-situ* soft X-ray absorption spectroscopy. With a UHV-compatible *in-situ* static cell, Timothy S. Arthur et al studied the Mg deposition behavior with Mg-K edge XAS, the presence of an interfacial Mg intermediate can be verified at voltage below equilibrium Mg/Mg^{2+} potential⁸². Note that the photon-in-photon-out fluorescence mode can be directly probed within the well-sealed cells, but achieve mostly bulk information. Meanwhile, the extraction of pure interface layer signal via electron yield is very challenging and needs detailed experimental design. With the

combination of piezo chopper and lock-in amplifier scheme, the electric double layer across Au-H₂O interface can be obtained which evolves with bias voltage. Base on the *in-situ* interface probe, the hydrogen bonding direction at interface region can be statistically calculated³⁷.

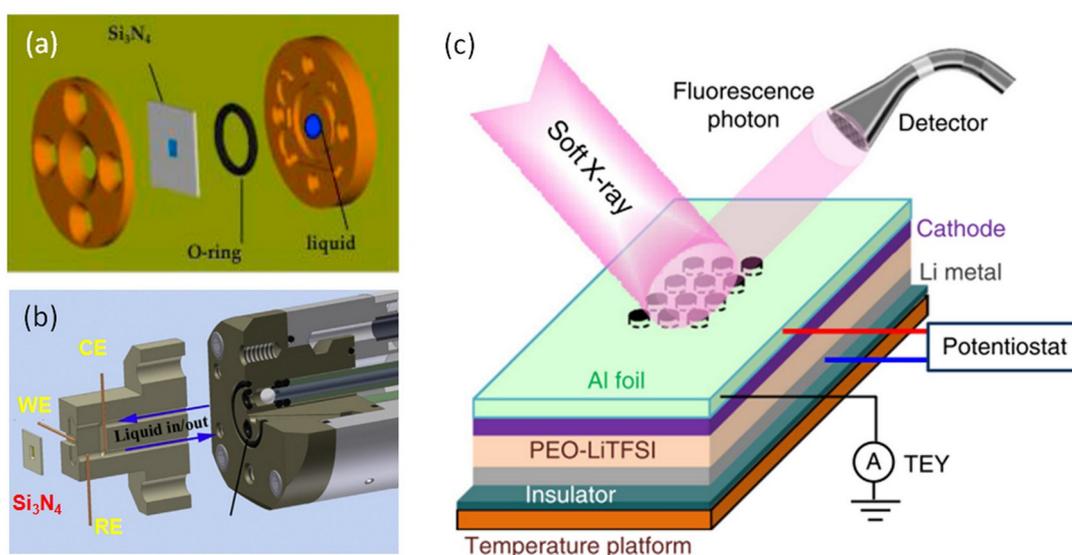


Figure 5. *in-situ* and operando soft X-ray spectroscopy.

Schematic diagram of (a) static cell, (b) flow cell and (c) *in-situ* XAS on solid state batteries. Reprinted with permission from reference³⁶,

83 .

With the development of diverse solid state electrolytes (SSEs), solid state batteries (SSBs) become promising choice for future applications⁸⁴. SSBs avoid flammable carbonate electrolyte and favor superior safety performances, which is key to future large

scale applications. Meanwhile, SSEs demonstrate large electrochemical stability window (there are still some dispute on this topic), which is widely accepted to support cathodes to even higher voltage. More importantly, SSEs exhibit larger mechanical shear modulus, which may well suppress Li dendrite growth. Therefore, higher voltage cathodes and Li metal anode can be utilized in SSBs, which favors high energy density batteries far beyond conventional LIBs.

Due to these advantages, SSBs have attracted wide attention, but are still hindered with various obstacles such as poor interface contact and large surface resistance^{85, 86}. SSEs further confront chemical instability and interface reactions against both electrodes⁸⁷⁻⁸⁹. Soft X-ray spectroscopy can play a significant role in fingerprinting interface reactions in SSBs. One example is the chemical reaction of garnet LLZO against moisture air⁹⁰. Li_2CO_3 formation at LLZO surface can be detected by sXAS and verified to be the fundamental origin of large interface resistance. With the contrast from difference probe depth, Li_2CO_3 thickness can be further estimated below 100 nm. Surface polishing can effectively remove Li_2CO_3 and dramatically improve interface properties. With sXAS, the same research group further found that interface resistance of LLZO is correlated with grain size and Al dopant

distribution⁹¹, and the reaction path can be established by combining theoretical calculations.

In the meantime, SSBs provide promising model systems for *in-situ* investigations because it does not require the specific cell for conceal the liquid and/or gas in the soft X-ray vacuum systems, which make SSBs great candidates for *in-situ* soft X-ray characterizations. *In-situ* sXAS experiment has been demonstrated in SSBs system with polymer PEO as SSE many years ago (**Figure 5c**)⁸³. With *in-situ* and *operando* sXAS, distinguished dynamic response can be detected on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) and LiFePO_4 (LFP). Whereas NMC response immediately to electrochemical cycle and follow the overall state of charge (SOC), LFP demonstrate strong relaxation and SOC gradient effect. The *in-situ* characterizations provide valuable insights on dynamic response of battery operation and the set-up can be well utilized for investigating other electrodes. The employment of SSBs makes various experiments possible for *in-situ* soft X-ray studies of some challenging issues, e.g., the buried solid-solid interface between electrode and electrolyte. With controlled thin film deposition, electrode thickness matching probe depth of soft X-ray could be designed and manufactured, both electrode materials and the interfacial behaviors in SSBs could be detected through *in-situ/operando* experiments. This also provides

unique opportunities for RIXS experiments to detect the bulk states of electrode materials under *in-situ/operando* conditions²⁶.

Conclusion

In this review, we provide an overview of soft X-ray spectroscopy on the interfacial researches in electrochemical energy storage devices. We focus on four different topics on studying interfacial phenomena in battery systems through sXAS and RIXS techniques: i) the anode SEI, ii) the cathode surface, iii) the liquid electrolyte system, and iv) *in-situ/operando* experiments. For the anode SEI studies, we show that sXAS could detect the surface chemical species, through which, different SEI formation mechanism and its dynamics could be detected. For the cathode surface, we argue that recent efforts towards high-energy batteries drive the surface of transition-metal oxide based electrode unstable and behave distinctly from the bulk electrode behavior. In particular, at the highly charged/oxidized states, the surface of the oxide cathode often displays the counter-intuitive low oxidation state of the TMs. This is associated with the fervent debates on the oxygen oxidation reactions at high potentials, which triggers different kinds of reactions and remains elusive. We then demonstrates that RIXS,

through its new dimension of information of the emission photon energy, provide superior chemical sensitivity for detecting the subtle changes of the solvation shell, which consists of the same solvent molecules as in the bulk electrolyte and is thus undetectable through conventional sXAS. At the end, we discuss the developments of *in-situ/operando* soft X-ray experiments and provide our perspective on the bright future of sXAS/RIXS techniques for studying SSB systems. The soft X-ray spectroscopic technique has witness significant improvements over the last two decades since the third generation synchrotron light source becomes available. At this time, the new generations of synchrotron light source with high-brightness diffraction-limited storage ring have been planned in many countries, which will further advance the technical capabilities of synchrotron techniques for tackling the grand challenges in energy storage materials.

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