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TITLE:
Elemental-Sensitive Detection of the Chemistry in Batteries Through Soft X-Ray Absorption Spectroscopy and Resonant Inelastic X-Ray Scattering

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80
81SUMMARY:
82Here, we present a protocol for the typical experiments of soft X-ray absorption spectroscopy (sXAS) and resonant inelastic X-ray scattering (RIXS) with the application in the battery material studies.
83
84ABSTRACT:
85Energy storage has become more and more a limiting factor of today’s sustainable energy applications, including electric vehicles and green electric grid based on volatile solar and wind sources. The pressing demand of developing high-performance electrochemical energy storage solutions, i.e.,
batteries, relies on both the fundamental understanding and practical developments from both the academe and industry. The formidable challenge of developing successful battery technology stems from the different requirements for different energy-storage applications. Energy density, power, stability, safety, and cost parameters have to be all balanced in batteries to meet the requirements in different applications. Therefore, multiple battery technologies based on different materials and mechanism need to be developed and optimized. Incisive tools that could directly probe the chemical reactions in various battery materials become critical to advance the field beyond the conventional trial-and-error approaches. Here, we present detailed protocols of soft X-ray absorption spectroscopy (sXAS), soft X-ray emission spectroscopy (sXES) and resonant inelastic X-ray scattering (RIXS) experiments, which are inherently elemental-sensitive probes of the transition-metal 3d and anion 2p states in battery compounds. We provide the details on the experimental techniques, and demonstrations of revealing the key chemical states in battery materials through these soft X-ray spectroscopy techniques.

INTRODUCTION:
Developing high-performance batteries is one of the crucial requirements for realizing modern energy applications with environmentally benign resources and devices. Developing high-efficiency, low-cost and sustainable energy storage devices has become critical for both electric vehicles (EVs) and electric grid, with projected market expansion of ten times in this decade. The ubiquitous Li-ion battery (LIB) technology remains a promising candidate for high energy-density and high power energy storage solutions, while Na-ion batteries hold the promise to realize low-cost and stable storage for green-grid applications. However, the overall battery technology level is well below what is required to meet the need of this new phase of mid-to-large scale energy storage.

The formidable challenge of developing high-performance battery energy-storage system stems—arises from the complication of mechanical and electronic characteristics of battery operations, both mechanically and electronically. Extensive efforts have focused on material synthesis and mechanical properties, however, the evolution of the chemical states of particular elements in battery electrodes is often under active debates for newly developed battery materials. In general, both LIBs and SIBs operate with evolving electronic states triggered by the transportation of the electrons and ions during the charge and discharge process, leading to the oxidation and reduction (redox) reactions of specific element(s). As the bottleneck for many performance parameters, battery cathodes have been paid much attention in research and developments. A practical battery cathode material is typically 3d transition-metal (TM) oxide with particular structural channels for the ion...
diffusion. Conventionally, the redox reaction is limited to the TM elements, however, recent results indicate that oxygen could possibly be utilized in reversible electrochemical cycling. The redox mechanism is one of the most critical information to understand the electrochemical operation, and a direct probe of the chemical states of battery electrodes with elemental sensitivity is thus highly desirable.

Synchrotron-based soft X-rays spectroscopy is an advanced technique that detects the valence electron states in the vicinity of the Fermi level in battery materials. Because of the high sensitivity of soft X-ray photons to the electrons of a specific element and orbital, soft X-ray spectroscopy could be utilized as a direct probe of the critical electron states in battery electrodes, or at the interfaces in batteries. Furthermore, compared with hard X-rays, soft X-rays are lower in energy and cover excitations of the low-Z elements, e.g., C, N, O, and of the 2p-to-3d excitation in the 3d TMs.

The excitations of soft x-ray spectroscopy first involve electron transitions from a particular core state to an unoccupied state by absorbing the energy from soft X-ray photons. The intensity of such soft X-ray absorption spectroscopy thus corresponds to the density of state (DOS) of the unoccupied (conduction-band) states with the existence of the excited core-holes. The X-ray absorption coefficient can be measured by detecting the total number of the photons or electrons emitted during the decay process. The total electron yield (TEY) counts the total number of emitted electrons and is thus a photon-in-electron-out (PIEO) detection mode. TEY has a shallow probe depth of several nanometers and therefore is relatively surface sensitive, due to the shallow escape depth of electrons. However, as a photon-in-photon-out (PIPO) detection mode, the total fluorescence yield (TFY) is a photon-in-photon-out (PIPO) detection mode and measures the total number of emitted photons in the sXAS process. TFY has a probe depth of is about hundreds of nanometers, which is deeper than that of TEY depending on the photon energies. Due to the difference in probe depths, the contrast between TEY and TFY often could provide valuable information for a comparison between the surface and bulk of the material.

sXES is a PIPO technique, corresponding to the decay of the exited state to fill the core hole, leading to the by along with emission of at characteristic energies. If the core electron is excited to the high energy continuum electron state well, which is far away from above the sXAS threshold, it is a non-resonant X-ray fluorescence process corresponding to the decay of occupied (valence-band) electrons to the core holes, i.e., sXES reflects the DOS of the valence-band states. On the other hand, if the core electron is resonantly excited to exactly the absorption threshold by tuning the excitation energy, the resulting emission spectra feature strong excitation energy dependence. For such this resonant emission case, the...
Spectroscopy experiments are called defined noted as resonant inelastic x-ray scattering (RIXS) if the emitted x-ray energy is not the same as that of the incident photon energy, we denote this type of emission experiments as resonant inelastic x-ray scattering (RIXS).

Because sXAS and sXES corresponds to the unoccupied (conduction-band) and occupied (valence-band) electron states, respectively, they provide complementary information of the electron states involved in the reduction and oxidation reactions in the battery electrodes upon electrochemical operation. For low-Z elements, especially C, N, and O, sXAS has been widely used for studying the critical electron states corresponding to both the electron transfer and chemical compositions. For 3d TMs, sXAS of TM L-edges has been successfully demonstrated to be an effective probe of the TM redox reactions of V, Mn, Fe, Co, and Ni. Because the TM-L sXAS features are dominated by the well-defined multiplet effect, which are sensitive to the different TM oxidation and spin states, the TM sXAS data could enable even quantitative analysis of the TM redox couples in LIB and SIB electrodes.

Compared with the popular employment of sXAS for battery material studies, RIXS is relatively less utilized due to the complexity of both the experiments and data interpretation for obtaining meaningful information related to battery performance. However, due to the extremely high chemical-state selectivity of RIXS, RIXS is potentially a much more sensitive probe of the chemical state evolution in battery materials with inherent elemental sensitivity. Recent sXES and RIXS reports by Jeyachandran et al., have showcased the high sensitivity of RIXS to specific chemical configurations in ion-solvation systems beyond sXAS. With the recent rapid developments of high-efficiency RIXS systems, RIXS has quickly shifted from a fundamental physics tool to also a powerful technique for battery researches, and sometimes becomes the tool-of-choice for specific studies of both the cation and anion evolutions in battery compounds.

In this work, the detailed protocol of sXAS, sXES and RIXS experiments is introduced. We cover the details on experimental planning, technical procedures for carrying experiments, and more importantly, the data processing for different spectroscopic techniques. Furthermore, three representative results in battery material studies are presented to demonstrate the applications of these three soft X-ray spectroscopy techniques. We note that the technical details of these experiments could be different at different endstations and/or facilities. Additionally, ex-situ and in-situ experiments have very different setup procedures on the sample handling due to the stringent requirements of ultra-high vacuum for soft X-ray spectroscopy. But the protocol here represents the typical procedure and could serve as a common reference for soft X-ray spectroscopy experiments in various experimental systems at different facilities.
PROTOCOL:

1. Experimental Planning

Note: While sXES could be performed through lab-based equipment, sXAS and RIXS are synchrotron-based experiments, which requires the access to the beamtime of a synchrotron facility. The procedure for applying for beamtime and running experiments could be different at different facilities, but they all follow a similar basic procedure.

1.1. Check facility website for beamline directory (e.g., https://als.lbl.gov/beamlines/) or contact scientists in charge of the interested beamline(s), to determine the proper beamline for the scientific need.

1.2. Submit beamtime proposals to the facility and beamline(s) of Advanced Light Source (ALS) through online submission system at https://als.lbl.gov/users/user-guide/.

Note: The beamtime proposal will be reviewed based on the policy of the synchrotron facility, and authors of successful proposals will be notified by the facility for experimental scheduling.

1.3. For safety controls, accomplishing any necessary safety trainings according to the facility notification. Report chemicals, samples, and special equipment required by experiments, and get inspections to guarantee the safety.

1.4. Arrive at the facility ahead of their beamtime to get basic ideas on the experimental setup and sample loading, especially as new users to a facility/beamline.

2. Sample Preparation

2.1. Synthesize the samples of the LIB and SIB materials, and electrochemically cycle to different state-of-charge (SOC).

2.2. Perform the following steps for air-sensitive samples:

2.2.1. Handle the air-sensitive samples without air exposure, i.e. open the sample containers, and cut the samples with scissors and tweezers into size fitting the experimental system under inert gas environment.

2.2.2. Mount the samples with an appropriate size onto sample holders by using double-sided conductive tape under inert gas environment.

Note: If Carbon or Oxygen edges are to be measured, use soft metals such
as Indium for sticking the powder samples on, for avoiding background C and O signals from the organic compounds in conductive tape.

2.3. Perform the following steps for non air-sensitive samples:

2.3.1. Cut the samples to match the specific sample holder for experimental systems.

2.3.2. Mount the samples with an appropriate size onto sample holders by using double-sided conductive tape. Use indium foil if collecting Carbon and Oxygen signals of power samples.

2.4. For in-situ samples, prepare In-situ samples with specific cells that typically implement soft X-ray membrane. Check electric connections and cell integrity before loading into the experimental system.

Note: Detail about in-situ cells is out of the scope of this typical work but could be found in previous publications 35-37.

3. Loading and Positioning Samples

Note: Due to the requirement of ultra-high vacuum for soft X-ray spectroscopy experiments, sample loading typically takes multiple steps to go through a buffer vacuum chamber before entering main experimental chamber.

3.1. Stop vacuum pumps, close vacuum valve between the sample loadlock and main experimental chamber, and vent the sample loadlock that is typically attached directly to the experimental system with N₂ gas.

3.2. Use home-made sample grabber or a big tweezer to grab the sample holder and load it into loadlock.

3.3. Start pumping the loadlock. Wait until the vacuum pressure gauge shows low enough vacuum for opening loadlock to main experimental chamber, typically around mid 10⁻⁷ Torr.

3.4. Open the valve between loadlock and the main chamber. Transfer the sample holder onto the main manipulator of the main chamber by using transfer arm.

3.5. Open the valve between the main experimental chamber and the beamline. Determine the beam spot by looking at a reference sample with visible-light fluorescence.

3.6. Position the sample to the beam spot by changing the coordinates of
the sample manipulator of the experimental endstation.

4. **Set Up the X-ray Energy and Resolution**

4.1. Change the values of the slits of the beamline monochromator, through the computer program or manual adjustment knob, to control the energy resolution of the incident X-ray beam.

4.2. Set the incident beam energy to the desired value for accessing the absorption edge of the interested element(s), e.g., 290 eV for C-K, 530 eV for O-K edges.

4.3. Connect signal cables of the X-ray beam flux (I-0) monitor, which is typically a clean Gold mesh in the beam route.

4.4. Fix the beamline monochromator mechanism and collect the beam flux intensity upon the undulator gap. Determine a particular undulator gap value for the maximum possible beam flux.

Note: Because sXAS requires a large energy range for different edges, an optimization of the undulator gap to obtain the maximum possible beam flux is often necessary.

5. **Collect sXAS Data**

Note: Total yield sXAS data are collected by recording the intensity of signals from both the sample current (TEY) and the channeltron or photodiode (TFY). Partial yield signals are typically collected through a gated channeltron and solid-state detector. Because RIXS system is introduced here, and RIXS covers all kinds of partial fluorescence yield (PFY) signals including PFY and inverse-PFY (iPFY), only the typical protocol for TEY and TFY data collection is described in this session.

5.1. Connect the sample to the current amplifier, and feed the sample current signal (TEY) to the computer counter.

5.2. Turn on power supplies and controllers of the channeltron or photodiode, feed the TFY signal to the computer counter.

5.3. Start the LabVIEW sXAS data acquisition program “BL Control Main” to arrive the software interface (Figure 2), and then click the menu button “Scanning” → “Single Motor Scan” (Figure 2).

5.4. Click the menu button “Scan Setup” (Figure 3) to setup the scan range of the incident (beamline) X-ray photons to match the interested sXAS edge, e.g., 280-300 eV for C-K edge.
5.5. Click the button “Start Scan” (Figure 3) to record the intensity signals from i) the TEY, ii) the TFY, and iii) the I-0 channels simultaneously while scanning the incident X-ray photon energy.

Note: Usually there would be a little shift of several eV on the incident X-ray photon energy. For calibration, collect sXAS data of one or more typical reference samples before collecting the battery material samples.

Collect sXES and RIXS Data

Note: Because sXES is technically one of the RIXS cut at the non-resonant (high) energy range, the data collection equipment and process are essentially the same.

6.1. Collect sXAS first to define the excitation energy range and calibrate the energy values (refer to Section 5. Collect sXAS data).

6.2. Turn on power supplies of the spectrometer detector of the sXES/RiXS system, and cool down soft X-ray detector to reduce the background noise per manufacture recommendations.

6.3. Start the LabVIEW sXES/RiXS data acquisition program “BL Control Main” to arrive the software interface (Figure 4).

6.4. Click the menu button “Motors” (Figure 4) to set the optical parameters of the spectrograph so the detector covers the energy range of the interested elements and edges (Figure 5).

6.5. Click the menu button “Scanning” (Figure 4) → “CCD Instrument Scan” (Figure 6).

6.6. Click the menu button “Scan Setup” (Figure 6) to setup the scan range of the incident (beamline) X-ray photon energy. If collecting sXES, set to a single value that is about 20-30 eV above the sXAS absorption edge; else if collecting RiXS, set the incident X-ray (beamline) energy to a range that covers the sXAS absorption edge.

6.7. Select the icon “Apply Cosmic Ray Filter” (Figure 6) to remove the cosmic ray signals from the raw RIXS 2D images once collected from the spectrograph detector.

6.8. Click the button “Start Scan” (Figure 6) to collect the fluorescence signals, which were diffracted and energy-resolved by optical grating, in the form of 2D image by the detector on the spectrograph for each excitation energy.
sXAS Data Process

Note: The experiment data, including sXAS as well as sXES and RiXS, is processed in Igor Pro program.

1. Normalize sXAS TEY and TFY signals to the I-0 signals that are collected simultaneously.
2. Calculate the energy error between the collected sXAS of the reference samples with the standard; calibrate sXAS signals by shifting the energies according to the calculated energy error.

sXES and RIXS Data Process

1. Integrate the intensity of the raw 2D image by summing up the photon counts along the angle-adjusted emission-energy channels to generate a single sXES or RIXS spectrum.
2. Normalize the integrated 1D RIXS spectrum to both the incident beam flux monitored real-time during the data collection, and the collection time (in seconds).
3. Plot the normalized 1D spectrum in color-scaled format.
4. For RiXS data, repeat 8.1-8.3 for each excitation energy to obtain a series of 1D RIXS spectra upon emission-energy channels; and then stack all the color-scaled 1D RIXS spectra one-by-one into a 2D image map, with one axis along excitation energy, another axis shows the emission-energy channels.
5. Calibrate the values of excitation energy of the sXES spectrum or RIXS maps by using sXAS calibration, typically through reference samples (refer to Section 7.2).
6. Select a set of points (x = channel number, y = energy value) along the elastic features on the RIXS map, where the excitation and emission energies are the same; do linear curve fitting with the set of points to attain the formal energy value per channel; according to the relation, rescale x axis from channel to energy.

Representative Results:
The sample holder and pasted samples are shown in Figure 1. Figure 7a is a typical RIXS image collected at a particular excitation energy with spectrometer set to the interested edges. The image shown here is collected on a battery electrode material, LiNi_{0.33}Co_{0.33}Mn_{0.33}O_{2}, with excitation energy...
of 858 eV and detector set at about 500-900 eV range to cover the energy range of O-K, Mn-L, Co-L, and Ni-L, as indicated in the figure. Each peak on the 1D spectrum corresponds with one feature on the 2D map, which represents the occupied state of one specific element in the material. With the ultra-high efficiency of the newly commissioned iRIXS endstation, a full range sXES covering all these edges could be collected in 10 s with decent statistic (Figure 7b). This enables a high throughput experiment for chemical analysis of battery materials.

Figure 8 displays an example of the technical process for generating a Ni L-edge RIXS map of LiNi_{0.33}Co_{0.33}Mn_{0.33}O_{2}. It shows the procedure on how to process the raw RIXS image into one cut of the final RIXS map, and how the protocol described in this work is implemented. By using our new high throughput iRIXS system, collecting RIXS maps of TM L-edges with fine excitation energy steps in a reasonably short time has become feasible. The high throughput of our new iRIXS system makes it practical to collect RIXS maps of TM L-edges with fine excitation energy steps and within a reasonably short time. Additionally, the large energy window of the spectrograph makes the a wide energy range RIXS mapping possible to contain multiple emission features within a large energy range from different elements. By which allows us to obtain two different types of absorption spectra could be attained through such RIXS maps—partial fluorescence yield (PFY) and inverse partial fluorescence yield (iPFY) which makes use of the multiple emission features in the RIXS map with a large energy window. Note that iPFY is a bulk PIPO probe with signals corresponding directly to the intrinsic absorption coefficient. Such information is a bi-product of the RIXS mapping with high energy resolution. Detailed analysis of the Ni RIXS results of LiNi_{0.33}Co_{0.33}Mn_{0.33}O_{2} displays that the Ni-L RIXS features are dominated by the excitations between the 3d states, the so-called “d-d excitations”. PFY, iPFY, and conventional TEY and TFY signals are simultaneously collected while RIXS maps are collected for detailed chemical state analysis.

Figure 9 shows three selected examples of quantitative analysis of the TM redox states based on sXAS of Mn, Fe, and Ni in various battery cathodes for LiBs and SIBs. Figures 9a and 9b are the quantitative analysis of Mn L-edge soft XAS on a series of Na_{0.44}MnO_{2} electrodes cycled to different SOCs. The solid lines are experimental spectra, and dotted lines are simulated spectra ones. Simulations were done throughaby linearly combination combining of the three reference spectra of Mn^{2+}, Mn^{3+} and Mn^{4+}, with two variables of the concentration percentage of the Mn states, i.e., total concentration equals to 100%. All the high-resolution features in the measured sXAS spectra were completely reproduced by this linear-curve-fitting combination simulation, and thus the surface Mn valence distribution at different SOCs could be precisely quantitatively determined. The simulation completely reproduces all the high-resolution features in the
experimental sXAS data, which provides a precise determination of the surface Mn valence distribution at different SOCs. Details on scientific discussions and the quantitative values of the fitted results are presented in the Fig. 3 b-d in Reference 21.

Figures 9c and 9d demonstrate another perfect quantitative fitting combination of the soft-XAS data taken collected on Li$_x$FePO$_4$ electrodes at different SOCs. A linear combination of the soft-XAS spectra of the two end states, i.e., one variable: (x)LiFePO$_4$ and (1-x)FePO$_4$, were used as the benchmarks for the quantitative fitting of the experimental spectra (solid lines).

Figures 9e and 9f show the comparison of the theoretically calculated Ni$^{2+}$, Ni$^{3+}$, and Ni$^{4+}$ TFY spectra with the sXAS data experimental ones collected in TFY mode of a LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode material. By a linear combination of the calculated spectra (dotted spectra) of Ni$^{2+}$, Ni$^{3+}$ and Ni$^{4+}$, the Ni-L$_\text{L}$-edge sXAS collected measured on a series of Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$ electrodes at different SOCs could be perfectly fitted by linearly combining the calculated spectra (dotted spectra) of Ni$^{2+}$, Ni$^{3+}$, and Ni$^{4+}$ (2-3 variables on concentration percentage with the sum of 100%) [27]. The theoretical multiplet calculation is consistent with the experimental result and proves the distinctive feature arising from the Ni$^{3+}$ state, suggesting a single electron transfer mechanism and sequential redox reactions of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ (Ni$^{2+}$→Ni$^{3+}$→Ni$^{4+}$) determined by the single electron transfer mechanism. Because of the lack of experimental reference data of the Ni$^{3+}$ XAS, theoretical calculations are used here for a quasi-quantitative fitting. Nonetheless, the scientific focus here is to experimentally reveal the single-charge-transfer redox reaction mechanism in Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$ electrodes, and the assignment of the Ni$^{3+}$ peak thus provides unambiguous evidence [28].

In general, these demonstrations show the sensitivity of the soft X-ray spectroscopy to the different oxidation (redox) states in SIB and LIB materials with inherent elemental sensitivities. Analysis based on soft X-ray spectroscopy could be performed carried out for different types of phase transformations and SOCs, with both surface and bulk sensitivity, and under in-situ/operando and ex-situ and in-situ conditions, and for different types of phase transformations. We also note that, although examples are not shown in this technical report, sXAS and RIXS results of low-Z element, e.g., C, N, O, also provide critical information on the critical chemical states in battery compounds, as demonstrated in many previous publications [12-14,30,31].

FIGURE AND TABLE LEGENDS:

Figure 1. The sample holder and pasted samples. The sample holder is a copper cylinder with a height of 0.5 inch and a diameter of 1.0 inch. The samples are usually cut into small piecestypically several millimeters in size.
Figure 2. The main-interface for sXAS equipment control and data acquisition.

Figure 3. The sub-interface for sXAS data acquisition.

Figure 4. The main-interface for sXES/RiXS equipment control and data acquisition.

Figure 5. The sub-interface for sXES/RiXS equipment control.

Figure 6. The sub-interface for sXES/RiXS data acquisition.

Figure 7. Ultra-high efficiency sXES spectrum of the O-K, Mn-L, Co-L and Ni-L edges of LIB electrode material LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$. (a) shows a typical 2D image collected through a RIXS spectrometer with a 858 eV excitation (beamline) energy. (b) displays the sXES spectra of all the 570 edges involved in LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$ electrode materials. The spectrum shown here was taken in 10 s with 900 eV excitation energy with all the 572 edges collected simultaneously.

Figure 8. Schematic and demonstration of RIXS mapping of Ni-L RIXS of LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$ electrode material. (a) Raw RIXS image data collected at a particular excitation energy. (b) Integrated RIXS spectrum with one particular excitation energy after angle adjustment and intensity integration. (c) The spectral intensity is plotted in color scale as one of the cuts for the RIXS map in (d). (e) shows a typical RIXS map of Ni L-edge after all the data process steps. Scientific analysis is typically done by zooming in particular emission energy range of such a map. Protocol numbers introduced in this work are marked in the figure.

Figure 9. Demonstrations of quantitative analysis of TM redox couples in battery electrodes based on sXAS. In all panels, solid lines are experimental data, and dotted spectra are simulation results. (a) Na$_{0.44}$MnO$_2$ electrode cycled to different electrochemical states, and (b) the quantitative analysis of Mn L-edge sXAS. (c) Li$_x$FePO$_4$ electrode cycled to different SOCs, and (d) the quantitative fitting of the sXAS data. (e) LiNi$_{0.5}$Mn$_{1.5}$O$_4$ electrode within the first electrochemical cycle, and (f) the quantitative fitting of the Ni-L sXAS through the comparison between experimental data and calculated Ni$^{2+}$, Ni$^{3+}$ and Ni$^{4+}$ spectra. This figure has been modified from Lin, F et al. Why LiFePO$_4$ is a safe battery electrode: Coulomb repulsion induced electron-state reshuffling upon lithiation.
599evolutions in battery compounds upon electrochemical operation. Soft X-ray 600core-level spectroscopy, such as sXAS, sXES, and RIXS, is a tool-of-choice for 601detecting the critical valence states of both the anions and cations involved 602in LIBs and SIBs.

604Core-level spectroscopy techniques involves the strong excitation of core 605electrons to unoccupied states following the dipole selection rules. Compared 606with hard X-rays, the low energy of soft X-rays enables dipole-allowed 1s-2p 607excitations for low-Z anion elements, such as C, N, and O K-edges, as well as 608the 2p-3d excitations for 3d TM elements. The strong dipole-allowed 609excitations make soft X-ray techniques unique for probing directly the 610valence states of the 2p states in anions, and 3d states in cations, of battery 611materials.

613With the recent developments of soft X-ray spectroscopy instrumentation, 614sXAS, sXES and RIXS experiments could be performed at unprecedented 615efficiency for revealing both the conduction-band (sXAS) and valence-band 616(sXES) states in the vicinity of the Fermi level. This work provides a general 617protocol for typical sXAS, sXES and RIXS experiments. We cover common 618procedures of the data collection and analysis of these techniques without 619involving too much specific details of a particular experimental endstation.

620We demonstrate that, due to the high sensitivity to the TM valence states in 622battery materials, sXAS could be used for a quantitative analysis of the 623chemical state of TMs in battery electrode at different electrochemical 624states. We also showcase that state-of-the-art high-efficiency sXES could be 625performed in a much faster speed now compared with conventional sXAS 626and XPS experiments that are popular for chemical analysis. Additionally, 627RIXS mapping of interested elements could provide much more detailed 628information on the specific electron state configuration because RIXS reveals 629the correlation between different states through low-energy excitations. 630Particularly for revealing the chemical states in battery materials, RIXS 631provides extra sensitivity by uncovering the underlying decay process 632beyond sXAS. Because of the extra dimension of the emission energy, the 633low energy excitations in RIXS results often correspond to specific chemical 634information that does not manifest in sXAS experiments31. This is critical for 635studying some novel valence state that cannot be reliably probed by sXAS, 636especially on the recently proposed anionic redox in batteries6.

637While sXAS has been extensively employed for studying LIB and SIB 639materials, and our demonstrations have shown that high-quality sXAS results 640could be quantitatively analyzed for TM states, sXES and RIXS have seen 641only limited applications in the field of energy storage materials. This work 642shows that the barrier of the low statistic in these PIPO experiments has 643been broken through by state-of-the-art RIXS instrumentations34. Still, 644establishing a reliable data bank of sXES and RIXS is required for detailed
In the meantime, theoretical interpretation of RIXS in a complex real-world system remains challenging for a complete understanding of RIXS features. Nonetheless, the last two decades have witnessed the rapid progress on the technical development of RIXS in both efficiency and resolution, we expect that this fundamental-physics tool will soon be employed for tackling the critical challenges for understanding and optimizing energy storage materials.

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