

Lawrence Berkeley National Laboratory

LBL Publications

Title

Elemental-sensitive Detection of the Chemistry in Batteries through Soft X-ray Absorption Spectroscopy and Resonant Inelastic X-ray Scattering.

Permalink

<https://escholarship.org/uc/item/0922k78t>

Journal

Journal of visualized experiments : JoVE, 2018(134)

ISSN

1940-087X

Authors

Wu, Jinpeng
Sallis, Shawn
Qiao, Ruimin
[et al.](#)

Publication Date

2018-04-01

DOI

10.3791/57415

Peer reviewed

1TITLE:

2Elemental-Sensitive Detection of the Chemistry in Batteries Through Soft X-
3Ray Absorption Spectroscopy and Resonant Inelastic X-Ray Scattering

4

5AUTHORS & AFFILIATIONS:

6Jinpeng Wu, Shawn Sallis, Ruimin Qiao, Qinghao Li, Zengqing Zhuo, Kehua
7Dai, Zixuan Guo, Wanli Yang

8

9Jinpeng Wu

10Geballe Laboratory for Advanced Materials

11Stanford University

12Stanford, California

13Advanced Light Source

14Lawrence Berkeley National Laboratory

15Berkeley, California

16jinpeng@lbl.gov

17

18Shawn Sallis

19Department of Materials Science and Engineering

20Binghamton University

21Binghamton, New York

22Advanced Light Source

23Lawrence Berkeley National Laboratory

24Berkeley, California

25ssallis@lbl.gov

26

27Rumin Qiao

28Advanced Light Source

29Lawrence Berkeley National Laboratory

30Berkeley, California

31rqiao@lbl.gov

32

33Qinghao Li

34School of Physics, National Key Laboratory of Crystal Materials

35Shandong University

36Jinan, China

37Advanced Light Source

38Lawrence Berkeley National Laboratory

39Berkeley, California

40liqinghaosdu@163.com

41

42Zengqing Zhuo

43School of Advanced Materials

44Peking University Shenzhen Graduate School

45Shenzhen, China

46Advanced Light Source

47Lawrence Berkeley National Laboratory

48Berkeley, California

49zzhuo@lbl.gov

50

51Kehua Dai

52School of Metallurgy

53Northeastern University

54Shenyang, China

55Advanced Light Source

56Lawrence Berkeley National Laboratory

57Berkeley, California

58kdai@lbl.gov

59

60Zixuan Guo

61Department of Chemical Engineering

62University of California-Santa Barbara

63Santa Barbara, California

64Advanced Light Source

65Lawrence Berkeley National Laboratory

66Berkeley, California

67zixuanguo@umail.ucsb.edu

68

69Wanli Yang

70Advanced Light Source

71Lawrence Berkeley National Laboratory

72Berkeley, California

73wlyang@lbl.gov

74

75**CORRESPONDING AUTHOR:**

76Wanli Yang (wlyang@lbl.gov)

77

78**KEYWORDS:**

79Energy Storage, Li-ion Batteries, Na-ion Batteries, Soft X-ray absorption

80spectroscopy (sXAS), Resonant Inelastic X-ray Scattering (RIXS), Redox

81reactions

82

83**SUMMARY:**

84Here, we present a protocol for the typical experiments of soft X-ray

85absorption spectroscopy (sXAS) and resonant inelastic X-ray scattering

86(RIXS) with the application in the battery material studies.

87

88**ABSTRACT:**

89Energy storage has become more and more a limiting factor of today's

90sustainable energy applications, including electric vehicles and green electric

91grid based on volatile solar and wind sources. The pressing demand of

92developing high-performance electrochemical energy storage solutions, *i.e.*,

93batteries, relies on both the fundamental understanding and practical
94developments from both the academe and industry. The formidable
95challenge of developing successful battery technology stems from the
96different requirements for different energy-storage applications. Energy
97density, power, stability, safety, and cost parameters have to be all balanced
98in batteries to meet the requirements in different applications. Therefore,
99multiple battery technologies based on different materials and mechanism
100need to be developed and optimized. Incisive tools that could directly probe
101the chemical reactions in various battery materials become critical to
102advance the field beyond the conventional trial-and-error approaches. Here,
103we present detailed protocols of soft X-ray absorption spectroscopy (sXAS),
104soft X-ray emission spectroscopy (sXES) and resonant inelastic X-ray
105scattering (RIXS) experiments, which are inherently elemental-sensitive
106probes of the transition-metal $3d$ and anion $2p$ states in battery compounds.
107We provide the details on the experimental techniques, and demonstrations
108of revealing the key chemical states in battery materials through these soft
109X-ray spectroscopy techniques.

110

111INTRODUCTION:

112Developing high-performance batteries is one of the crucial requirements for
113realizing modern energy applications with environmentally benign resources
114and devices. Developing high-efficiency, low-cost and sustainable energy
115storage devices has become one of the key challenges more and more
116important critical for both electric vehicles (EVs) and electric grid, with
117projected market expansion of ten times in this decade. The ubiquitous Li-ion
118battery (LIB) technology remains a promising candidate for high energy-
119density and high power energy storage solutions¹, while Na-ion batteries
120(SIBs) hold the promise to realize low-cost and stable storage for green-grid
121applications². However, the overall battery technology level is well below
122what is required to meet the need of this new phase of mid-to-large scale
123energy storage^{1,3}.

124

125The formidable severe pressing challenge of developing high-~~performance~~
126~~battery energy-storage~~ system stems arises from the complication
127~~complicated~~ ex mechanical and electronic of battery characteristics in of the
128~~battery~~ operations, ~~both mechanically and electronically~~. Extensive efforts
129have focused on material synthesis and mechanical properties, however, the
130evolution of the chemical states of particular elements in battery electrodes
131is often under active debates for newly developed battery materials. In
132general, both LIBs and SIBs operate with evolving electronic states triggered
133by the transportation of the electrons and ions during the charge and
134discharge process, leading to the oxidation and reduction (redox) reactions
135of specific element(s). As the bottleneck for many performance parameters,
136battery cathodes have been paid much attention in research and
137developments^{4,5}. A practical battery cathode material is typically $3d$
138transition-metal (TM) oxide with particular structural channels for the ion

139 diffusion. Conventionally, the redox reaction is limited to the TM elements,
140 however, recent results indicate that oxygen could possibly be utilized in
141 reversible electrochemical cycling⁶. The redox mechanism is one of the most
142 critical information to understand the electrochemical operation, and a direct
143 probe of the chemical states of battery electrodes with elemental sensitivity
144 is thus highly desirable.

145

146 Synchrotron-based soft X-rays spectroscopy is an advanced technique that
147 detects the valence electron states in the vicinity of the Fermi level in
148 battery materials⁷. Because of the high sensitivity of soft X-ray photons to
149 the electrons of a specific element and orbital, soft X-ray spectroscopy could
150 be utilized as a direct probe of the critical electron states in battery
151 electrodes⁸, or at the interfaces in batteries⁹. Furthermore, compared with
152 hard X-rays, soft X-rays are lower in energy and cover excitations of the low-
153 Z elements, e.g., C, N, O, and of the *2p*-to-*3d* excitation in the *3d* TMs¹⁰.

154

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

174

175 sXES is a PIPO technique, corresponding to the decay of the excited state to
176 fill the core hole, leading to the by—along with emission of ting—an x-ray
177 photons at characteristic energies. If the core electron is excited to the high
178 energy—continuum electron state well, which is far away from above—the sXAS
179 threshold, it is a non-resonant X-ray fluorescence process corresponding to
180 the decay of occupied (valence-band) electrons to the core holes, i.e., sXES
181 reflects the DOS of the valence-band states. On the other hand Otherwise, if
182 the core electron is resonantly excited to exactly the absorption threshold by
183 tuning the excitation energy, the resulting emission spectra feature strong
184 excitation energy dependence. For such—this—resonant—emission—case, the

185 spectroscopy experiments are called resonant inelastic x-ray
186 scattering (RIXS). ~~if the emitted x-ray energy is not the same as that of the~~
187 ~~incident photon energy, we denote this type of emission experiments as~~
188 resonant inelastic x-ray scattering (RIXS).

189

190 Because sXAS and sXES corresponds to the unoccupied (conduction-band)
191 and occupied (valence-band) electron states, respectively, they provide
192 complementary information of the electron states involved in the reduction
193 and oxidation reactions in the battery electrodes upon electrochemical
194 operation¹¹. For low-Z elements, especially C^{12,13}, N¹⁴, and O¹⁵⁻¹⁷, sXAS has
195 been widely used for studying the critical electron states corresponding to
196 both the electron transfer^{12,13} and chemical compositions¹⁵⁻¹⁷. For 3d TMs,
197 sXAS of TM L-edges has been successfully demonstrated to be an effective
198 probe of the TM redox reactions of V¹⁸, Mn¹⁹⁻²³, Fe²³⁻²⁶, Co^{20,27}, and Ni^{20,28}.
199 Because the TM-L sXAS features are dominated by the well-defined multiplet
200 effect, which are sensitive to the different TM oxidation^{18-22,24-28} and spin
201 states^{14,29}, the TM sXAS data could enable even quantitative analysis of the
202 TM redox couples in LIB and SIB electrodes²⁷.

203

204 Compared with the popular employment of sXAS for battery material studies,
205 RIXS is relatively less utilized due to the complexity of both the experiments
206 and data interpretation for obtaining meaningful information related to
207 battery performance¹⁰. However, due to the extremely high chemical-state
208 selectivity of RIXS, RIXS is potentially a much more sensitive probe of the
209 chemical state evolution in battery materials with inherent elemental
210 sensitivity. Recent sXES and RIXS reports by Jeyachandran et al., have
211 showcased the high sensitivity of RIXS to specific chemical configurations in
212 the ion-solvation systems beyond sXAS^{30,31}. With the recent rapid
213 developments of high-efficiency RIXS systems³²⁻³⁴, RIXS has quickly shifted
214 from a fundamental physics tool to also a powerful technique for battery
215 researches, and sometimes becomes the tool-of-choice for specific studies of
216 both the cation and anion evolutions in battery compounds.

217

218 In this work, the detailed protocol of sXAS, sXES and RIXS experiments is
219 introduced. We cover the details on experimental planning, technical
220 procedures for carrying experiments, and more importantly, the data
221 processing for different spectroscopic techniques. Furthermore, three
222 representative results in battery material studies are presented to
223 demonstrate the applications of these three soft X-ray spectroscopy
224 techniques. We note that the technical details of these experiments could be
225 different at different endstations and/or facilities. Additionally, *ex-situ* and *in-*
226 *situ* experiments have very different setup procedures on the sample
227 handling due to the stringent requirements of ultra-high vacuum for soft X-
228 ray spectroscopy³⁵. But the protocol here represents the typical procedure
229 and could serve as a common reference for soft X-ray spectroscopy
230 experiments in various experimental systems at different facilities.

231

232 **PROTOCOL:**

233 **1. Experimental Planning**

234

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

240

241 1.1. Check facility website for beamline directory (e.g.,
242 <https://als.lbl.gov/beamlines/>) or contact scientists in charge of the interested
243 beamline(s), to determine the proper beamline for the scientific need.

244

245 1.2. Submit beamtime proposals to the facility and beamline(s) of
246 Advanced Light Source (ALS) through online submission system at
247 <https://als.lbl.gov/users/user-guide/>.

248

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

252

253 1.3. For safety controls, accomplishing any necessary safety trainings
254 according to the facility notification. Report chemicals, samples, and special
255 equipment required by experiments, and get inspections to guarantee the
256 safety.

257

258 1.4. Arrive at the facility ahead of their beamtime to get basic ideas on the
259 experimental setup and sample loading, especially as new users to a facility/
260 beamline.

261

262 **2. Sample Preparation**

263

264 2.1. Synthesize the samples of the LIB and SIB materials, and
265 electrochemically cycle to different state-of-charge (SOC).

266

267 2.2. Perform the following steps for air-sensitive samples:

268

269 2.2.1. Handle the air-sensitive samples without air exposure, *i.e.* open the
270 sample containers, and cut the samples with scissors and tweezers into size
271 fitting the experimental system under inert gas environment.

272

273 2.2.2. Mount the samples with an appropriate size onto sample holders by
274 using double-sided conductive tape under inert gas environment.

275

276 Note: If Carbon or Oxygen edges are to be measured, use soft metals such

277as Indium for sticking the powder samples on, for avoiding background C and 2780 signals from the organic compounds in conductive tape.

279

2802.3. Perform the following steps for non air-sensitive samples:

281

2822.3.1. Cut the samples to match the specific sample holder for experimental 283systems.

284

2852.3.2. Mount the samples with an appropriate size onto sample holders by 286using double-sided conductive tape. Use indium foil if collecting Carbon and 287Oxygen signals of power samples.

288

2892.4. For *in-situ* samples, prepare *In-situ* samples with specific cells that 290typically implement soft X-ray membrane. Check electric connections and 291cell integrity before loading into the experimental system.

292

293Note: Detail about *in-situ* cells is out of the scope of this typical work but 294could be found in previous publications³⁵⁻³⁷.

295

2963. Loading and Positioning Samples

297

298Note: Due to the requirement of ultra-high vacuum for soft X-ray 299spectroscopy experiments, sample loading typically takes multiple steps to 300go through a buffer vacuum chamber before entering main experimental 301chamber.

302

3033.1. Stop vacuum pumps, close vacuum valve between the sample loadlock 304and main experimental chamber, and vent the sample loadlock that is 305typically attached directly to the experimental system with N₂ gas.

306

3073.2. Use home-made sample grabber or a big tweezer to grab the sample 308holder and load it into loadlock.

309

3103.3. Start pumping the loadlock. Wait until the vacuum pressure gauge 311shows low enough vacuum for opening loadlock to main experimental 312chamber, typically around mid 10⁻⁷ Torr.

313

3143.4. Open the valve between loadlock and the main chamber. Transfer the 315sample holder onto the main manipulator of the main chamber by using 316transfer arm.

317

3183.5. Open the valve between the main experimental chamber and the 319beamline. Determine the beam spot by looking at a reference sample with 320visible-light fluorescence.

321

3223.6. Position the sample to the beam spot by changing the coordinates of

323the sample manipulator of the experimental endstation.

324

3254. **Set Up the X-ray Energy and Resolution**

326

3274.1. Change the values of the slits of the beamline monochromator,
328through the computer program or manual adjustment knob, to control the
329energy resolution of the incident X-ray beam.

330

3314.2. Set the incident beam energy to the desired value for accessing the
332absorption edge of the interested element(s), e.g., 290 eV for C-K, 530 eV for
333O-K edges³⁸.

334

3354.3. Connect signal cables of the X-ray beam flux (I-0) monitor, which is
336typically a clean Gold mesh in the beam route.

337

3384.4. Fix the beamline monochromator mechanism and collect the beam flux
339intensity upon the undulator gap. Determine a particular undulator gap value
340for the maximum possible beam flux.

341

342Note: Because sXAS requires a large energy range for different edges, an
343optimization of the undulator gap to obtain the maximum possible beam flux
344is often necessary.

345

3465. **Collect sXAS Data**

347

348Note: Total yield sXAS data are collected by recording the intensity of signals
349from both the sample current (TEY) and the channeltron or photodiode (TFY).
350Partial yield signals are typically collected through a gated channeltron and
351solid-state detector. Because RIXS system is introduced here, and RIXS
352covers all kinds of partial fluorescence yield (PFY) signals including PFY and
353inverse-PFY (iPFY), only the typical protocol for TEY and TFY data collection is
354described in this session.

355

3565.1. Connect the sample to the current amplifier, and feed the sample
357current signal (TEY) to the computer counter.

358

3595.2. Turn on power supplies and controllers of the channeltron or
360photodiode, feed the TFY signal to the computer counter.

361

3625.3. Start the LabVIEW sXAS data acquisition program "BL Control Main" to
363arrive the software interface (**Figure 2**), and then click the menu button
364"Scanning" → "Single Motor Scan" (**Figure 2**).

365

3665.4. Click the menu button "Scan Setup" (**Figure 3**) to setup the scan
367range of the incident (beamline) X-ray photons to match the interested sXAS
368edge, e.g., 280-300 eV for C-K edge.

369

3705.5. Click the button “Start Scan” (**Figure 3**) to record the intensity signals
371from i) the TEY, ii) the TFY, and iii) the I-0 channels simultaneously while
372scanning the incident X-ray photon energy.

373

374Note: Usually there would be a little shift of several eV on the incident X-ray
375photon energy. For calibration, collect sXAS data of one or more typical
376reference samples before collecting the battery material samples.

377

3786. Collect sXES and RIXS Data

379

380Note: Because sXES is technically one of the RIXS cut at the non-resonant
381(high) energy range, the data collection equipment and process are
382essentially the same.

383

3846.1. Collect sXAS first to define the excitation energy range and calibrate
385the energy values (refer to Section 5. Collect sXAS data).

386

3876.2. Turn on power supplies of the spectrometer detector of the sXES/RiXS
388system, and cool down soft X-ray detector to reduce the background noise
389per manufacture recommendations.

390

3916.3. Start the LabVIEW sXES/RiXS data acquisition program “BL Control
392Main” to arrive the software interface (**Figure 4**).

393

3946.4. Click the menu button “Motors” (**Figure 4**) to set the optical
395parameters of the spectrograph so the detector covers the energy range of
396the interested elements and edges (**Figure 5**).

397

3986.5. Click the menu button “Scanning” (**Figure 4**) → “CCD Instrument
399Scan” (**Figure 6**).

400

4016.6. Click the menu button “Scan Setup” (**Figure 6**) to setup the scan
402range of the incident (beamline) X-ray photon energy. If collecting sXES, set
403to a single value that is about 20-30 eV above the sXAS absorption edge;
404else if collecting RiXS, set the incident X-ray (beamline) energy to a range
405that covers the sXAS absorption edge.

406

4076.7. Select the icon “Apply Cosmic Ray Filter” (**Figure 6**) to remove the
408cosmic ray signals from the raw RIXS 2D images once collected from the
409spectrograph detector.

410

4116.8. Click the button “Start Scan” (**Figure 6**) to collect the fluorescence
412signals, which were diffracted and energy-resolved by optical grating, in the
413form of 2D image by the detector on the spectrograph for each excitation
414energy.

415

4167. **sXAS Data Process**

417

418Note: The experiment data, including sXAS as well as sXES and RIXS, is
419processed in Igor Pro program.

420

4217.1. Normalize sXAS TEY and TFY signals to the I-0 signals that are
422collected simultaneously.

423

4247.2. Calculate the energy error between the collected sXAS of the reference
425samples with the standard; calibrate sXAS signals by shifting the energies
426according to the calculated energy error.

427

4288. **sXES and RIXS Data Process**

429

4308.1. Integrate the intensity of the raw 2D image by summing up the photon
431counts along the angle-adjusted emission-energy channels to generate a
432single sXES or RIXS spectrum.

433

4348.2. Normalize the integrated 1D RIXS spectrum to both the incident beam
435flux monitored real-time during the data collection, and the collection time
436(in seconds).

437

4388.3. Plot the normalized 1D spectrum in color-scaled format.

439

4408.4. For RIXS data, repeat 8.1-8.3 for each excitation energy to obtain a
441series of 1D RIXS spectra upon emission-energy channels; and then stack all
442the color-scaled 1D RIXS spectra one-by-one into a 2D image map, with one
443axis along excitation energy, another axis shows the emission-energy
444channels.

445

4468.5. Calibrate the values of excitation energy of the sXES spectrum or RIXS
447maps by using sXAS calibration, typically through reference samples (refer to
448Section 7.2).

449

4508.6. Select a set of points (x = channel number, y = energy value) along
451the elastic features on the RIXS map, where the excitation and emission
452energies are the same; do linear curve fitting with the set of points to attain
453the formal energy value per channel; according to the relation, rescale x axis
454from channel to energy.

455

456**REPRESENTATIVE RESULTS:**

457The sample holder and pasted samples are shown in **Figure 1. Figure 7a** is
458a typical RIXS image collected at a particular excitation energy with
459spectrometer set to the interested edges. The image shown here is collected
460on a battery electrode material, $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, with excitation energy

461of 858 eV and detector set at about 500-900 eV range to cover the energy
462range of O-K, Mn-L, Co-L, and Ni-L, as indicated in the figure. Each peak on
463the 1D spectrum corresponds with one feature on the 2D map, which
464represents the occupied state of one specific element in the material. With
465the ultra-high efficiency of the newly commissioned iRIXS endstation³⁴, a full
466range sXES covering all these edges could be collected in 10 s with decent
467statistic (**Figure 7b**). This enables a high throughput experiment for
468chemical analysis of battery materials.

469

470**Figure 8** displays an example of the technical process for generating a Ni L-
471edge RIXS map of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$. It shows the procedure on how to
472process the raw RIXS image into one cut of the final RIXS map, and how the
473protocol described in this work is implemented. By using our new high
474throughput efficiency iRIXS system, collecting RIXS maps of TM L-edges with
475fine excitation energy steps in a reasonably short time has been
476practical become feasible~~The high throughput of our new iRIXS system makes~~
477~~it practical to collect RIXS maps of TM L-edges with fine excitation energy~~
478~~steps and within a reasonably short time.~~ Additionally, the large energy
479window of the spectrograph makes the a wide energy range RIXS mapping
480possible to contain include multiple emission features within a large energy
481range from different elements., by which ~~allows us to obtain~~ Two different
482types of absorption spectra could be attained through such RIXS maps;
483partial fluorescence yield (PFY) and inverse partial fluorescence yield (iPFY)³⁹;
484~~which makes use of the multiple emission features in the RIXS map with~~
485~~large energy window.~~ Note that iPFY is a bulk PIPO probe with signals
486corresponding directly to the intrinsic absorption coefficient³⁹. Such
487information is a bi-product of the RIXS mapping with high energy resolution.
488Detailed analysis of the Ni RIXS results of $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ displays that
489the Ni-L RIXS features are dominated by the excitations between the 3d
490states, the so-called “d-d excitations”. PFY, iPFY, and conventional TEY and
491TFY signals are simultaneously collected while RIXS maps are collected for
492detailed chemical state analysis³⁴.

493

494**Figure 9** shows three selected examples of quantitative analysis of the TM
495redox states based on sXAS of Mn, Fe, and Ni in various battery cathodes for
496LIBs and SIBs^{10,27}. **Figures 9a** and **9b** are the quantitative analysis of Mn L-
497edge soft XAS on a series of $\text{Na}_{0.44}\text{MnO}_2$ electrodes cycled to different SOC²¹.
498The solid lines are experimental spectra data, and dotted lines are simulated
499spectra ones. Simulations were done ~~through~~ by linearly combination
500combining of the three reference spectra of Mn^{2+} , Mn^{3+} and Mn^{4+} ^{22,40}, with
501two variables of the concentration percentage of the Mn states, *i.e.*, total
502concentration equals to 100%. All the high-resolution features in the
503measured sXAS spectra were completely reproduced by this linear-
504curve-fitting combination simulation, and thus the surface Mn valence distribution
505at different SOC could be precisely quantitatively determined. The
506~~simulation completely reproduces all the high-resolution features in the~~

507 ~~experimental sXAS data, which provides a precise determination of the~~
508 ~~surface Mn valence distribution at different SOC.~~ Details on scientific
509 discussions and the quantitative values of the fitted results are presented in
510 the Fig. 3 b-d in Reference²¹.

511 **Figures 9c** and **9d** demonstrate another perfect quantitative ~~fitting~~
512 ~~combination~~ of the ~~soft-XAS data taken/collected~~ on Li_xFePO_4 electrodes at
513 different SOC. ~~A linear combination of The~~ soft-XAS spectra of the two end
514 states, *i.e.*, one variable: $(x)\text{LiFePO}_4$ and $(1-x)\text{FePO}_4$, ~~are/were~~ used ~~as the~~
515 ~~benchmarks~~ for the quantitative fitting of the experimental spectra (solid
516 lines).

517 The ~~intermediate SOC of the intermediate states can be~~ precisely
518 ~~determined/attained~~, with fitting results marked directly in (d)²⁴. **Figures 9e**
519 and **9f** show the comparison of the theoretically calculated Ni^{2+} , Ni^{3+} , and
520 Ni^{4+} TFY spectra with ~~the sXAS data/experimental ones collected~~ in TFY mode
521 of ~~a/the~~ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material²⁸.

522 ~~By a linear combination of the calculated spectra (dotted spectra) of~~ Ni^{2+} ,
523 Ni^{3+} and Ni^{4+} , ~~the Ni-L-L-edge sXAS collected/measured~~ on a series of
524 ~~$\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at different SOC~~ could be perfectly fitted ~~by~~
525 ~~linearly combining the calculated spectra (dotted spectra) of~~ Ni^{2+} , Ni^{3+} and
526 Ni^{4+} (~~2-3~~ variables on concentration percentage with the sum of 100%)²⁷. The
527 theoretical multiplet calculation is consistent with the experimental result
528 and proves the distinctive feature arising from the Ni^{3+} state, suggesting ~~a~~
529 ~~single electron transfer mechanism and sequential redox reactions of~~
530 ~~$\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ ($\text{Ni}^{2+} \rightarrow \text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$) determined by the single electron~~
531 ~~transfer mechanism~~. Because of the lack of experimental reference data of
532 the Ni^{3+} XAS, theoretical calculations are used here for a quasi-quantitative
533 fitting. Nonetheless, the scientific focus here is to experimentally reveal the
534 single-charge-transfer redox reaction mechanism in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes,
535 and the assignment of the Ni^{3+} peak thus provides unambiguous evidence²⁸.

536

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

548

549 **FIGURE AND TABLE LEGENDS:**

550 **Figure 1. The sample holder and pasted samples.** The sample holder is
551 a copper cylinder with a height of 0.5 inch and a diameter of 1.0 inch. The
552 samples are ~~usually cut into small piece~~ typically several millimeters in size.

553

554 **Figure 2. The main-interface for sXAS equipment control and data**
555 **acquisition.**

556

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

558

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

561

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

563

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

565

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

573

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

583

584 **Figure 9. Demonstrations of quantitative analysis of TM redox**
585 **couples in battery electrodes based on sXAS.** In all panels, solid lines
586 are experimental data, and dotted spectra are simulation results. **(a)**
587 **$\text{Na}_{0.44}\text{MnO}_2$ electrode cycled to different electrochemical states, and (b) the**
588 **quantitative analysis of Mn L-edge sXAS. (c) Li_xFePO_4 electrode cycled to**
589 **different SOCs, and (d) the quantitative fitting of the sXAS data. (e)**
590 **$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode within the first electrochemical cycle, and (f) the**
591 **quantitative fitting of the Ni-L sXAS through the comparison between**
592 **experimental data and calculated Ni^{2+} , Ni^{3+} and Ni^{4+} spectra. This figure has**
593 **been modified from *Lin, F et al. Why LiFePO_4 is a safe battery electrode:***
594 ***Coulomb repulsion induced electron-state reshuffling upon lithiation.***

595

596 **DISCUSSION:**

597 The formidable challenge of improving the performance of energy storage
598 materials requires advances of incisive tools to probe directly the chemical

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.

603

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.

612

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.

620

621We 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-effeciency 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.

637

638While 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

645data analysis. In the meantime, theoretical interpretation of RIXS in a
646complex real-world system remains challenging for a complete
647understanding of RIXS features. Nonetheless, the last two decades have
648witnessed the rapid progress on the technical development of RIXS in both
649efficiency and resolution, we expect that this fundamental-physics tool will
650soon be employed for tackling the critical challenges for understanding and
651optimizing energy storage materials.

652

653ACKNOWLEDGMENTS:

654~~This work is supported by the~~The Advanced Light Source (ALS) of the
655Lawrence Berkeley National Laboratory (LBNL).~~The ALS~~ is supported by the
656Director, Office of Science, Office of Basic Energy Sciences, of the U.S.
657Department of Energy under Contract No. DE-AC02-05CH11231. Q.L. thanks
658the China Scholarship Council (CSC) for financial support through the
659collaboration based on China 111 project No. B13029. R.Q. thanks the
660support from LBNL LDRD program. S.S. and Z.Z. thank the support from the
661ALS Doctoral fellowship.

662

663DISCLOSURES:

664The authors have nothing to disclose.

665

666REFERENCES:

- 6671 Armand, M. & Tarascon, J. M. Building better batteries. *Nature*. **451**
668 (7179), 652-657, doi:10.1038/451652a, (2008).
- 6692 Yang, Z. *et al.* Electrochemical energy storage for green grid. *Chem*
670 *Rev.* **111** (5), 3577-3613, doi:10.1021/cr100290v, (2011).
- 6713 Dunn, B., Kamath, H. & Tarascon, J. M. Electrical energy storage for the
672 grid: a battery of choices. *Science*. **334** (6058), 928-935,
673 doi:10.1126/science.1212741, (2011).
- 6744 Ellis, B. L., Lee, K. T. & Nazar, L. F. Positive Electrode Materials for Li-
675 ion and Li-Batteries†. *Chemistry of Materials*. **22** (3), 691-714,
676 doi:10.1021/cm902696j, (2010).
- 6775 Goodenough, J. B. & Kim, Y. Challenges for Rechargeable Li Batteries†.
678 *Chemistry of Materials*. **22** (3), 587-603, doi:10.1021/cm901452z,
679 (2009).
- 6806 Grimaud, A., Hong, W. T., Shao-Horn, Y. & Tarascon, J. M. Anionic redox
681 processes for electrochemical devices. *Nat Mater*. **15** (2), 121-126,
682 doi:10.1038/nmat4551, (2016).
- 6837 Wanli Yang, R. Q. Soft x-ray spectroscopy for probing electronic and
684 chemical states of battery materials. *Chin. Phys. B*. **25** (1), 17104-
685 017104, doi:10.1088/1674-1056/25/1/017104, (2016).
- 6868 Yang, W. *et al.* Key electronic states in lithium battery materials probed
687 by soft X-ray spectroscopy. *Journal of Electron Spectroscopy and*
688 *Related Phenomena*. **190**, **Part A** 64-74,
689 doi:<https://doi.org/10.1016/j.elspec.2013.03.008>, (2013).
- 6909 Qiao, R. & Yang, W. Interactions at the electrode-electrolyte interfaces

- 691 in batteries studied by quasi-in-situ soft x-ray absorption spectroscopy.
692 *Journal of Electron Spectroscopy and Related Phenomena*. doi:10.1016/
693 j.elspec.2017.04.007, (2017).
- 69410 Lin, F. *et al.* Synchrotron X-ray Analytical Techniques for Studying
695 Materials Electrochemistry in Rechargeable Batteries. *Chem Rev.*
696 doi:10.1021/acs.chemrev.7b00007, (2017).
- 69711 Liu, X. *et al.* Why LiFePO₄ is a safe battery electrode: Coulomb
698 repulsion induced electron-state reshuffling upon lithiation. *Phys Chem*
699 *Chem Phys.* **17** (39), 26369-26377, doi:10.1039/c5cp04739k, (2015).
- 70012 Liu, G. *et al.* Polymers with tailored electronic structure for high
701 capacity lithium battery electrodes. *Adv Mater.* **23** (40), 4679-4683,
702 doi:10.1002/adma.201102421, (2011).
- 70313 Wu, M. *et al.* Toward an Ideal Polymer Binder Design for High-Capacity
704 Battery Anodes. *Journal of the American Chemical Society.* **135** (32),
705 12048-12056, doi:10.1021/ja4054465, (2013).
- 70614 Wang, L. *et al.* Rhombohedral prussian white as cathode for
707 rechargeable sodium-ion batteries. *J Am Chem Soc.* **137** (7), 2548-
708 2554, doi:10.1021/ja510347s, (2015).
- 70915 Qiao, R. *et al.* Distinct Solid-Electrolyte-Interphases on Sn (100) and
710 (001) Electrodes Studied by Soft X-Ray Spectroscopy. *Advanced*
711 *Materials Interfaces.* **1** (3), 1300115-n/a, doi:10.1002/admi.201300115,
712 (2014).
- 71316 Shan, X. *et al.* Bivalence Mn₅O₈ with hydroxylated interphase for high-
714 voltage aqueous sodium-ion storage. *Nat Commun.* **7** 13370,
715 doi:10.1038/ncomms13370, (2016).
- 71617 Qiao, R., Chuang, Y. D., Yan, S. & Yang, W. Soft x-ray irradiation effects
717 of Li₂O(2), Li₂CO(3) and Li₂O revealed by absorption
718 spectroscopy. *PLoS One.* **7** (11), e49182,
719 doi:10.1371/journal.pone.0049182, (2012).
- 72018 Bak, S.-M. *et al.* Na-Ion Intercalation and Charge Storage Mechanism in
721 2D Vanadium Carbide. *Advanced Energy Materials.* 1700959,
722 doi:10.1002/aenm.201700959, (2017).
- 72319 Zhuo, Z. *et al.* Effect of excess lithium in LiMn₂O₄ and Li_{1.15}Mn_{1.85}O₄
724 electrodes revealed by quantitative analysis of soft X-ray absorption
725 spectroscopy. *Applied Physics Letters.* **110** 093902,
726 doi:10.1063/1.4977502], (2017).
- 72720 Qiao, R. *et al.* Transition-metal redox evolution in LiNi_{0.5}Mn_{0.3}Co
728 0.2O₂ electrodes at high potentials. *Journal of Power Sources.* **360**
729 294-300, doi:10.1016/j.jpowsour.2017.06.009, (2017).
- 73021 Qiao, R. *et al.* Revealing and suppressing surface Mn(II) formation of
731 Na_{0.44}MnO₂ electrodes for Na-ion batteries. *Nano Energy.* **16** 186-
732 195, doi:http://dx.doi.org/10.1016/j.nanoen.2015.06.024, (2015).
- 73322 Qiao, R. *et al.* Direct evidence of gradient Mn(II) evolution at charged
734 states in LiNi_{0.5}Mn_{1.5}O₄ electrodes with capacity fading. *Journal of*
735 *Power Sources.* **273** (0), 1120-1126,
736 doi:10.1016/j.jpowsour.2014.10.013, (2015).

- 73723 Wu, J. *et al.* Modification of Transition-Metal Redox by Interstitial Water
738 in Hexacyanometallate Electrodes for Sodium-Ion Batteries. *Journal of*
739 *the American Chemical Society*. doi:10.1021/jacs.7b10460, (2017).
- 74024 Liu, X. *et al.* Phase Transformation and Lithiation Effect on Electronic
741 Structure of Li_xFePO_4 : An In-Depth Study by Soft X-ray and
742 Simulations. *Journal of the American Chemical Society*. **134** (33),
743 13708-13715, doi:10.1021/ja303225e, (2012).
- 74425 Liu, X. *et al.* Distinct charge dynamics in battery electrodes revealed by
745 in situ and operando soft X-ray spectroscopy. *Nat Commun*. **4** 2568,
746 doi:10.1038/ncomms3568, (2013).
- 74726 Zhuo, Z., Hu, J., Duan, Y., Yang, W. & Pan, F. Transition metal redox
748 and Mn disproportionation reaction in $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ electrodes cycled
749 with aqueous electrolyte. *Applied Physics Letters*. **109** (2), 023901,
750 doi:10.1063/1.4958639, (2016).
- 75127 Li, Q. *et al.* Quantitative probe of the transition metal redox in battery
752 electrodes through soft x-ray absorption spectroscopy. *Journal of*
753 *Physics D: Applied Physics*. **49** (41), 413003, doi:10.1088/0022-
754 3727/49/41/413003, (2016).
- 75528 Qiao, R. *et al.* Direct Experimental Probe of the Ni(II)/Ni(III)/Ni(IV) Redox
756 Evolution in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Electrodes. *The Journal of Physical*
757 *Chemistry C*. **119** (49), 27228-27233, doi:10.1021/acs.jpcc.5b07479,
758 (2015).
- 75929 Pasta, M. *et al.* Manganese-cobalt hexacyanoferrate cathodes for
760 sodium-ion batteries. *J. Mater. Chem. A*. **4** (11), 4211-4223,
761 doi:10.1039/c5ta10571d, (2016).
- 76230 Jeyachandran, Y. L. *et al.* Investigation of the Ionic Hydration in
763 Aqueous Salt Solutions by Soft X-ray Emission Spectroscopy. *J Phys*
764 *Chem B*. **120** (31), 7687-7695, doi:10.1021/acs.jpcc.6b03952, (2016).
- 76531 Jeyachandran, Y. L. *et al.* Ion-Solvation-Induced Molecular
766 Reorganization in Liquid Water Probed by Resonant Inelastic Soft X-ray
767 Scattering. *The Journal of Physical Chemistry Letters*. **5** (23), 4143-
768 4148, doi:10.1021/jz502186a, (2014).
- 76932 Fuchs, O. *et al.* High-resolution, high-transmission soft x-ray
770 spectrometer for the study of biological samples. *Rev Sci Instrum*. **80**
771 (6), 063103, doi:10.1063/1.3133704, (2009).
- 77233 Chuang, Y.-D. *et al.* Modular soft x-ray spectrometer for applications in
773 energy sciences and quantum materials. *Review of Scientific*
774 *Instruments*. **88** (1), 013110, doi:10.1063/1.4974356, (2017).
- 77534 Qiao, R. *et al.* High-efficiency in situ resonant inelastic x-ray scattering
776 (iRIXS) endstation at the Advanced Light Source. *Review of Scientific*
777 *Instruments*. **88** (3), 033106, doi:10.1063/1.4977592, (2017).
- 77835 Liu, X., Yang, W. & Liu, Z. Recent Progress on Synchrotron-Based In-
779 Situ Soft X-ray Spectroscopy for Energy Materials. *Adv Mater*. **26** (46),
780 7710-7729, doi:10.1002/adma.201304676, (2014).
- 78136 Guo, J. The development of in situ photon-in/photon-out soft X-ray
782 spectroscopy on beamline 7.0.1 at the ALS. *Journal of Electron*

- 783 *Spectroscopy and Related Phenomena.* **188** (0), 71-78,
784 doi:<http://dx.doi.org/10.1016/j.elspec.2012.12.007>, (2013).
- 78537 Blum, M. *et al.* Solid and liquid spectroscopic analysis (SALSA)-a soft x-
786 ray spectroscopy endstation with a novel flow-through liquid cell.
787 *Review of Scientific Instruments.* **80** (12), 123102,
788 doi:10.1063/1.3257926, (2009).
- 78938 Williams, G. P. X-RAY DATA BOOKLET. (2009).
- 79039 Achkar, A. J. *et al.* Bulk sensitive x-ray absorption spectroscopy free of
791 self-absorption effects. *Physical Review B.* **83** (8), 081106, doi:10.1103/
792 PhysRevB.83.081106, (2011).
- 79340 Qiao, R., Chin, T., Harris, S. J., Yan, S. & Yang, W. Spectroscopic
794 fingerprints of valence and spin states in manganese oxides and
795 fluorides. *Current Applied Physics.* **13** (3), 544-548,
796 doi:10.1016/j.cap.2012.09.017, (2013).