A Perspective on Studying Electronic Structure of Batteries through Soft X-ray Spectroscopy[①]

ZHUO Zeng-Qing[a]   PAN Feng[a②]   YANG Wan-Li[b]

[a] (*School of Advanced Materials, Peking University,*

Shenzhen Graduate School, Shenzhen 518055*, China*)

[b] (*Advanced Light Source, Lawrence Berkeley National Laboratory,*

1 *Cyclotron Road, Berkeley CA* 94720*, United States*)

ABSTRACT   Understanding electronic structure is crucial to enhance the battery performance. Soft X-ray spectroscopy (SXS) is one of the most effective methods to provide direct probe of electronic states. Here, spectroscopic measurements of transition metal $3d$ and oxygen $2p$ states are simply reviewed. Then, we mainly focus on the perspective of the development direction of modern SXS techniques. Although the true power of recently developed high efficiency mapping of resonant inelastic X-ray scattering (mRIXS) has been apparent for materials and chemistry studies, great challenges remain for mRIXS spectroscopic interpretation, and the understanding of the battery materials on novel redox activities remains elusive.

Keywords: electronic structure, soft X-ray spectroscopy, oxygen redox, O-*K* mRIXS;

Electronic structure determines the intrinsic physical and chemical properties of battery materials, which is related with the electrochemical performance, e.g., lithium ion intercalation/extraction potential, the voltage and capacity decay mechanism during cycling. Thus, it is crucial to provide the direct probe of the electronic structure through advanced experimental characterizations. Soft X-ray spectroscopy (SXS) stands out as one of the most effective methods detecting electronic state in the vicinity of Fermi level through photon-matter interactions. SXS is a direct probe of the relevant transition metal (TM) $3d$ and oxygen $2p$ states in battery materials with elemental, chemical, and orbital sensitivity, which has been demonstrate to be valuable for understanding and optimizing the battery performance. Details of SXS[2, 3] for battery studies have been previously reviewed. This perspective focuses on the directions of modern SXS techniques, especially the recently developed high efficiency mapping of resonant inelastic X-ray scattering (mRIXS).

SXS covers various core level spectroscopy tools[2, 3], e.g., soft X-ray absorption spectroscopy (sXAS), X-ray emission spectroscopy (XES), and resonant inelastic X-ray scattering (RIXS). It is noted that *soft X*-ray refers to X-ray photon energy at the range with tens of electron volts (eVs) to about 1 keV, which covers the low Z elements (C, N, and O) K edge and $3d$ TM L edge. Fig. 1 displays the scheme of the sXAS, XES, and RIXS. The spectroscopic process starts with the absorption of tunable incident photons

to excite a core electron to an unoccupied state. Subsequently, the excited state would decay to fill the core hole through different decay channels (electron and fluorescence), and the emitted photons would be probed through counts or energy distribution for XAS, or XES/RIXS, respectively. sXAS provides the information about the unoccupied electronic state with core hole existence through dipole allowed excitation, which fingerprints the formal valence, spin state, and chemical bond configuration. XES directly corresponds to the occupied valence-band state due to the band electron decay to fill the generated core hole. The combination of sXAS and XES probe band structure includes both the unoccupied and occupied states. RIXS was often used in fundamental physics for detecting

low-energy excitations involved in the spectroscopic process[5]; however, recent developments of ultra-high efficiency mRIXS have opened up this powerful technique for material and chemistry studies[2]. Technically, mRIXS reveals the energy of the outgoing photons after absorption process, thus providing a completely new dimension of information along the so-called emission energy at each single data point of an sXAS spectrum. Such a new scale of detection enabled superior chemical sensitivity over conventional sXAS in its bulk-sensitive photon-in-photon-out (PIPO) mode. Indeed, shortly after the mRIXS demonstrations, mRIXS has been recognized as the "tool-of-choice" for detecting the novel states of both TMs[6] and oxygen[7].
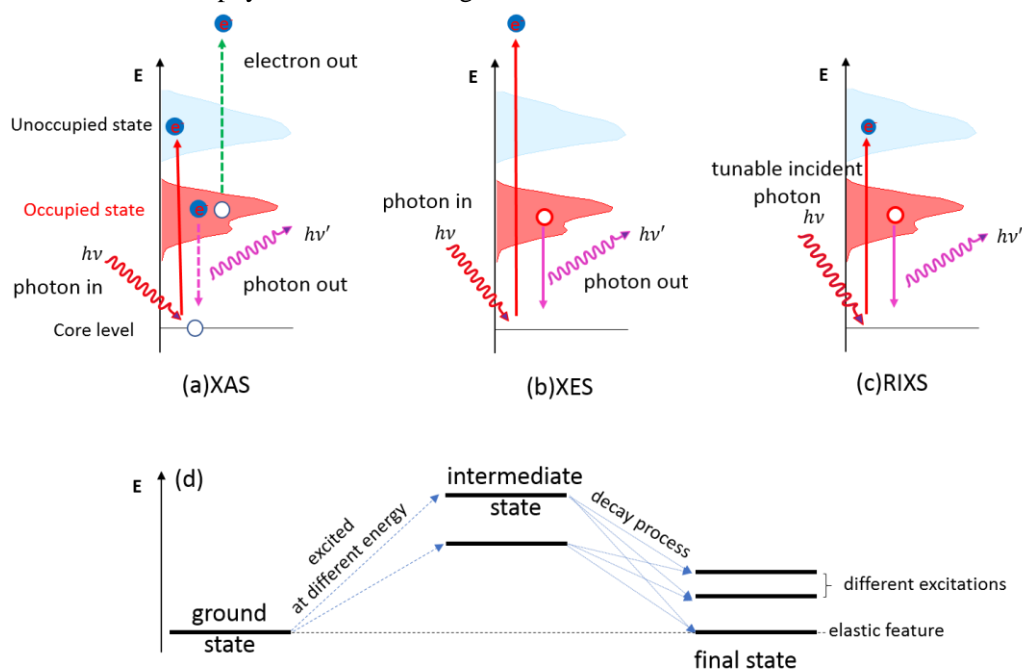

**Fig. 1.   Schematic of simplified model of (a) XAS, (b) XES, and (c) RIXS spectroscopic process.
(d) displays the RIXS process with different excited energy upon energy scale (vertical),
which are involved in different final states corresponding to various excitations**

The TM $3d$ states are the most sensitive states to the electronic properties in battery related with cation redox in battery material studies. TM $3d$ valence states could be directly probed by the TM L-edge sXAS through dipole allowed TM $2p$-$3d$ transitions[8, 9]. The quantitative analysis based on TEY lineshape variation has been proved to be a useful tool to understand the surface TM valence, spin state, and

the interphase behavior[10]. However, great caution needs to be taken to perform analogous quantitative analysis on TFY because of perishing line shape distortions from self-absorption effect. Fortunately, inverse partial fluorescence yield (iPFY)[1] based on mRIXS has been recently developed to potentially solve the distortion problem in fluorescence yield signals. Moreover, mRIXS-iPFY could provide high

energy resolution on all edges covered by soft X-rays. The iPFY provides the opportunity of a quantitative analysis of the TM oxidation states in the bulk materials at different electrochemical stages. sXAS provides the difference between the surface and the bulk of battery materials through comparison of quantitative analysis of TEY and iPFY.

The TM *L*-edge XAS spectral lineshape is domina- ted by the so-called multiplet features, which is strongly affected by the crystal field. Therefore, TM-L is highly sensitive to the crystal field that is associated with the local structure. Fig. 2 displays Fe *L*-edge sXAS lineshape evolution during (de)lithiation process (Fig. 2(a)) and the corres-ponding Fe 3*d* crystal field diagrams (Fig. 2(b)) of

Li_xFePO_4[4]. In general, the octahedral FeO_6 local structure determines a crystal field potential, leading to 3*d* state splitting into two groups, t_{2g} and e_g. The *z*-axis of the FeO_6 octahedron in $LiFePO_4$ is elongated compared with $FePO_4$. Such a local structural difference leads directly to the significant drop of all the 3*d* states involving d_z orbitals, resulting in a complete reconfiguration of all the 3*d* states (Fig. 2(b)). As the Fe *L*-edge corresponds to the excitations to 3*d* states, the spectra thus display distinct features of the Li_xFeP_4 electrode materials, serving as a sensitive probe of both the TM states and the local structural distortions upon electro-chemical cycling[4].
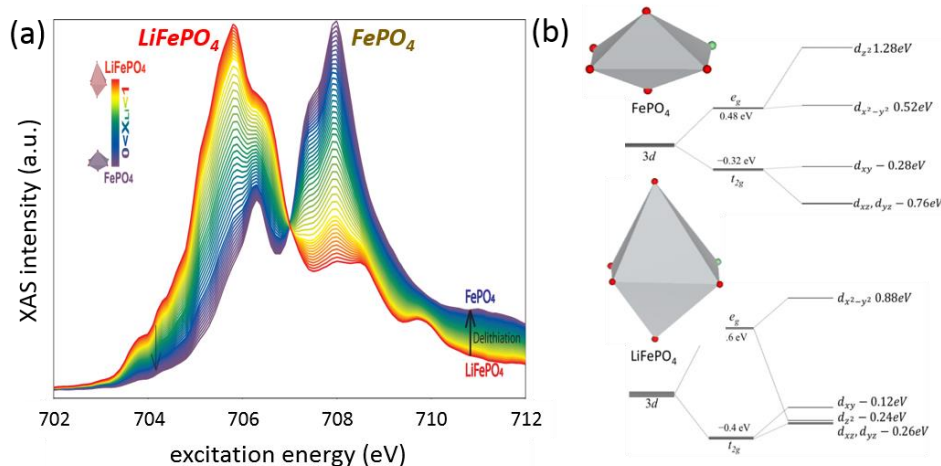

Fig. 2.   (a) Fe *L*-edge sXAS lineshape evolution of Li_xFePO_4 (0<*x*<1) during electrochemical cycling process, where the two end materials are $LiFePO_4$ and $FePO_4$. (b) Crystal filed diagram of $FePO_4$ (upper) and $LiFePO_4$ (lower) derived from the multiplet calculation. Reproduced from Ref.[4]

Such a sensitivity of TM 3*d* states to the crystal field could often change the electrochemical profile completely because these are the electronic states that define the charge/discharge process in electrochemistry. This is beautifully demonstrated in a seemingly subtle but strong effect of interstitial water molecules in a battery compound[11]. In $Na_xMnFe(CN)_6$ systems, C-coordinated Fe is at low spin (LS) state, while N-coordinated Mn is at high spin (HS) state. The valence concentrations of Fe^{3+} and Mn^{3+} upon electrochemical process in the two comparative systems are directly obtained through comprehensive quantitative analysis of the TM *L*-

edge sXAS[11]. For the hydrated system, $Fe^{2+/3+}$ and $Mn^{2+/3+}$ redox reactions take place separately at the low and high potential voltage plateaus, while, for the anhydrated system, a mixed Fe/Mn redox reaction takes place throughout the electrochemical process as one charging plateau. This distinct TM redox sequence in the contrasting systems is due to the competing effect from the ligand field stabilization energy (LFSE) with spin states and the ionization energy with TMs. And most importantly, these competing factors would be heavily affected by the crystal field variation, such as interstitial water.

The O 2*p* state investigation has been on the

central part of understanding the oxygen redox, which has been crucial for battery performance improvements. In virtue of the elemental and chemical sensitivity, O *K*-edge sXAS has been extensively utilized to detect the oxygen electronic states through the dipole transition from the O 1s to unoccupied O 2*p* state. It is noting that the states in the unoccupied bands just above Fermi level in transition metal oxide systems are dominated by TM *d* characters[12]. The hybridization of oxygen and TM gives rise to the dominating so-called *pre-edge* feature in O *K*-edge sXAS (Fig. 3 right panel). Thus,

the intensity and lineshape analysis of sXAS *pre-edge* feature mainly indicates TM oxidization states evolution and the overall covalency variation, which does not represent the intrinsic oxygen states[2]. Due to this intrinsic limitation of O-*K* sXAS of TM oxides, sXAS has been argued to be not reliable for detecting lattice oxygen redox states[2]. A direct and reliable probe of the oxidized oxygen state in battery materials should be able to rule out the TM-O hybridization effect from the intrinsic oxygen redox feature.
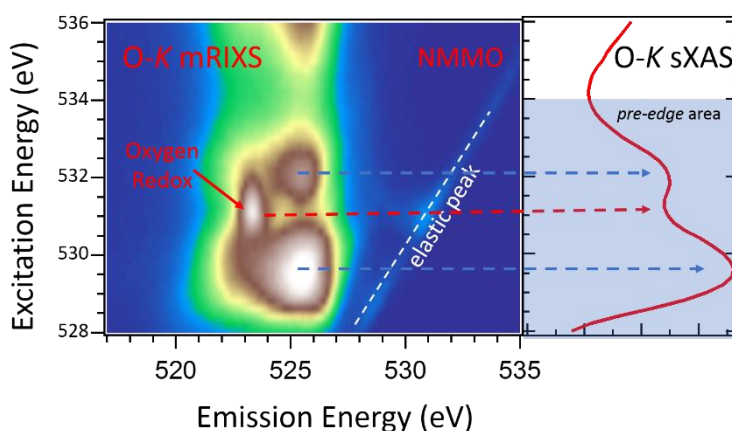

Fig. 3.   O *K*-edge mRIXS (left panel) and sXAS (right panel) result of Na$_{2/3}$Mg$_{1/3}$Mn$_{2/3}$O$_2$ (NMMO)[1] at full charged state. Specific mRIXS feature marked by the red solid arrow centered at 531 eV excitation energy (vertical axis) and 523.7 eV emission energy (horizontal axis) is observed, corresponding to the bulk oxygen redox feature. The shadow area in the O *K* sXAS is the so-called *pre-edge* area, which is dominated by the hybridization feature of TM 3*d* and O 2*p*. The dashed arrows clearly show that mRIXS deciphers the fluorescence signals in sXAS along the emitted photons energy, and provides a unique opportunity to resolve the entangled oxygen feature with the dominating TM characters in the *pre-edge* region. NMMO data reproduced from Ref. [9]

By further deciphering the fluorescence signals in sXAS along the emitted photons energy, mRIXS provides a unique opportunity to resolve the entangled oxygen feature with the dominating TM characters in the *pre-edge* region. Fortunately, the new dimension of the emission energy in O *K*-edge mRIXS turns out to be superiorly sensitive to the chemical state of oxygen. Experimental results have shown that the emission energies of the oxygen redox feature and TM-O hybridization feature are clearly separated in mRIXS results. Furthermore, as a two-dimensional intensity plot as a function of both excitation and emission energies, mRIXS provides

the full spectroscopic profile of non-divalent oxygen states, which holds the potential to quantitatively analyze oxygen redox during the electrochemical process[1].

While the development of high-efficiency mRIXS has been quickly reorganized as a powerful tool for materials and chemistry studies, at this time, however, formidable challenges remain for both the understanding of battery materials on novel redox activities, as well as the RIXS spectroscopic interpretation.

First, understanding the nature of oxygen redox states is still a highly debated topic and is often

considered under a simple scenario of oxygen molecular configurations[13-15]. In the meantime, it is clear that TM plays a key role in the oxygen redox behavior[16]. The specific mRIXS feature (Fig. 3 left panel) is the key to reveal the fundamental mechanism of oxygen redox. However, the theoretical simulation of oxygen redox related specific mRIXS feature remains challenging, and the intrinsic nature of oxygen redox remains elusive. In a recent study, excitonic features at the same emission energy 523.7 eV with the broader excitation energy distribution present at Li_2O_2 O *K*-edge mRIXS[7], which originates from intra-band excitations to unoccupied O $2p$ orbitals. This was verified through the theoretical simulation. It provides crucial hints for understanding the oxidized oxygen state, i.e., with unoccupied $2p$ orbitals, however, the system of TM oxides is fundamentally different and requires significant future works in both fundamental physics and material sciences.

Second, a reliable detection of the chemical states related with redox reactions in batteries requires XAS/mRIXS experiments with further improved detection efficiency and energy resolution. High detection efficiency allows XAS/mRIXS experiments accomplished within a reasonable time scale, which becomes a feasibility issue due to the radiation sensitivity of chemical systems. Radiation effects or radiation damage, introduced by materials exposure to the high-intensity X-ray, induce feature intensity evolution and lineshape change[17]. Thus, improving the detection efficiency of RIXS experiments becomes the only choice, with controlled sample transfer, cooling, and manipulating during experiments. Unfortunately, high energy resolution is also necessary to distinguish and investigate the fine feature in the O *K*-edge mRIXS signals related with oxygen redox, especially the low-energy excitations close to the elastic line in mRIXS results with 0~2 eV energy loss range. These weak features provide indicator of oxygen redox reactions, and suggest that the oxidized oxygen states spontaneously trigger low-energy excitations likely through electron-

phonon coupling. Again, these studies should not be taken for granted as simple indications of particular O molecular systems. Instead, significant efforts in theory should follow with considerations of the complex TM oxide systems. The dilemma of high detection efficiency and high energy resolution is yet to be solved.

Third, performing mRIXS experiments under *in-situ/operando* conditions will be indispensable to understand electronic structure of battery materials, especially the oxygen state related with anionic redox. The *in-situ/operando* experiments provide the comprehensive information of how the electrochemical process affecting the battery materials under real-world conditions. However, typical soft X-ray in-situ/operando setups are often complicated in O and C signals due to the multiple contribution sources. At this time, reliable data sets rely on careful sample handling of eX-situ experiments, especially on avoiding air exposure, and it is hard to obtain high quality *in-situ/operando* spectra of some critical edges, including O-*K* and C-*K*. A solid-state battery is a promising approach to solve this problem by exposing a relatively clean surface of the interested material.

Fourth, the multimodal study with a combination of different characterizations and simulations is always necessary for obtaining a comprehensive understanding of the electrochemical process. It is also worth noting again that RIXS is a complex spectroscopic process and often requires significant theoretical efforts for a reliable interpretation. Unlike sXAS, one cannot conclude easily on the nature of a state by a simple comparison of mRIXS data with reference compounds. TM oxide is a complex system, and the highly oxidized states need extensive mRIXS characterizations to build up the database, close inspections upon electrochemical profile, and theoretical calculations. Often the structural and indirect chemical probes are popular in material studies, especially the elemental sensitivity falls into soft X-ray range, e.g., oxygen. The relatively less popular employment of soft X-ray spectroscopy as a

direct chemical probe is partially due to the missing link between fundamental physics and practical material researches. One of the purposes of this perspective in a structural chemical journal is to promote such multidiscipline collaborations on grand challenges in the battery field.

REFERENCES

(1)   Dai, K. H.; Wu, J. P.; Zhuo, Z. Q.; Li, Q. H.; Sallis, S.; Mao, J.; Ai, G.; Sun, C. H.; Li, Z. Y.; Gent, W. E.; Chueh, W. C.; Chuang, Y. D.; Zeng, R.; Shen, Z. X.; Pan, F.; Yan, S. S.; Piper, L. F. J.; Hussain, Z.; Liu, G.; Yang, W. L. High reversibility of lattice oxygen redox quantified by direct bulk probes of both anionic and cationic redox reactions. *Joule* **2018**, 3, 1–24.

(2)   Yang, W.; Devereaux, T. P. Anionic and cationic redox and interfaces in batteries: advances from soft X-ray absorption spectroscopy to resonant inelastic scattering. *J. Power Sources* **2018**, 389, 188–197.

(3)   Yang, W. L.; Liu, X. S.; Qiao, R. M.; Olalde-Velasco, P.; Spear, J. D.; Roseguo, L.; Pepper, J. X.; Chuang, Y. D.; Denlinger, J. D.; Hussain, Z. Key electronic states in lithium battery materials probed by soft X-ray spectroscopy. *J. Electron Spectrosc.* **2013**, 190, *Part A* 64–74.

(4)   Liu, X. S.; Liu, J.; Qiao, R. M.; Yu, Y.; Li, H.; Suo, L. M.; Hu, Y. S.; Chuang, Y. D.; Shu, G. J.; Chou, F. C.; Weng, T. C.; Nordlund, D.; Sokaras, D.; Wang, Y. J.; Lin, H.; Barbiellini, B.; Bansil, A.; Song, X. Y.; Liu, Z.; Yan, S. S.; Liu, G.; Qiao, S.; Richardson, T. J.; Prendergast, D.; Hussain, Z.; de Groot, F. M. F.; Yang, W. L. Phase transformation and lithiation effect on electronic structure of LixFePO$_4$: an In-depth study by soft X-ray and simulations. *J. Am. Chem. Soc.* **2012**, 134, 13708–13715.

(5)   Devereaux, T. P.; Hackl, R. Inelastic light scattering from correlated electrons. *Rev. Mod. Phys.* **2007**, 79, 175–233.

(6)   Firouzi, A.; Qiao, R. M.; Motallebi, S.; Valencia, C. W.; Israel, H. S.; Fujimoto, M.; Wray, L. A.; Chuang, Y. D.; Yang, W. L.; Wessells, C. D. Monovalent manganese based anodes and co-solvent electrolyte for stable low-cost high-rate sodium-ion batteries. *Nat. Commun.* **2018**, 9, 861.

(7)   Zhuo, Z. Q.; Das Pemmaraju, C.; Vinson, J.; Jia, C. J.; Moritz, B.; Lee, I.; Sallies, S.; Li, Q. H.; Wu, J. P.; Dai, K. H.; Chuang, Y. D.; Hussain, Z.; Pan, F.; Devereaux, T. P.; Yang, W. L. Spectroscopic signature of oxidized oxygen states in peroxides. *J. Phys. Chem. Lett.* **2018**, 9, 6378–6384.

(8)   Zhuo, Z. Q.; Olalde-Velasco, P.; Chin, T.; Battaglia, V.; Harris, S. J.; Pan, F.; Yang, W. L. Effect of excess lithium in LiMn$_2$O$_4$ and Li$_{1.15}$Mn$_{1.85}$O$_4$ electrodes revealed by quantitative analysis of soft X-ray absorption spectroscopy. *Appl. Phys. Lett.* **2017**, 110, 093902.

(9)   Zhuo, Z. Q.; Hu, J. T.; Duan, Y. D.; Yang, W. L.; Pan, F. Transition metal redox and Mn disproportional reaction in LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ electrodes cycled with aqueous electrolyte. *Appl. Phys. Lett.* **2016**, 109, 023901.

(10)   Li, Q. H.; Qiao, R. M.; Wray, L. A.; Chen, J.; Zhuo, Z. Q.; Chen, Y. X.; Yan, S. S.; Pan, F.; Hussain, Z.; Yang, W. L. Quantitative probe of the transition metal redox in battery electrodes through soft X-ray absorption spectroscopy. *J. Phys. D Appl. Phys.* **2016**, 49, 413003.

(11)   Wu, J. P.; Song, J.; Dai, K. H.; Zhuo, Z. Q.; Wray, L. A.; Liu, G.; Shen, Z. X.; Zeng, R.; Lu, Y. H.; Yang, W. L. Modification of transition-metal redox by interstitial water in hexacyanometallate electrodes for sodium-ion batteries. *J. Am. Chem. Soc.* **2017**, 139, 18358–18364.

(12)   Olalde-Velasco, P.; Jiménez-Mier, J.; Denlinger, J. D.; Hussain, Z.; Yang, W. L. Direct probe of Mott-Hubbard to charge-transfer insulator transition and electronic structure evolution in transition-metal systems. *Phys. Rev. B* **2011**, 83, 241102.

(13)   Seo, D. H.; Lee, J.; Urban, A.; Malik, R.; Kang, S.; Ceder, G. The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials. *Nat. Chem.* **2016**, 8, 692–697.

(14)   McCalla, E.; Abakumov, A. M.; Saubanere, M.; Foix, D.; Berg, E. J.; Rousse, G.; Doublet, M. L.; Gonbeau, D.; Novak, P.; Van Tendeloo, G.; Dominko, R.; Tarascon, J. M. Visualization of O–O peroxo-like dimers in high-capacity layered oxides for Li-ion batteries. *Science* **2015**, 350, 1516–1521.

(15)   Luo, K.; Roberts, M. R.; Hao, R.; Guerrini, N.; Pickup, D. M.; Liu, Y. S.; Edström, K.; Guo, J. H.; Chadwick, A. V.; Duda, L. C.; Bruce, P. G. Charge-compensation in 3*d*-transition-metal-oxide intercalation cathodes through the generation of localized electron holes on oxygen. *Nat. Chem.* **2016**, 8, 684–691.

(16)   Xu, J.; Sun, M. L.; Qiao, R. M.; Renfrew, S. E.; Ma, L.; Wu, T. P.; Hwang, S.; Nordlund, D.; Su, D.; Amine, K.; Lu, J.; McCloskey, B. D.; Yang, W. L.; Tong, W. Elucidating anionic oxygen activity in lithium-rich layered oxides. *Nat. Commun.* **2018**, 9, 947.

(17)   Lebens-Higgins, Z. W.; Vinckeviciute, J.; Wu, J. P.; Faenza, N. V.; Li, Y. X.; Sallis, S.; Pereira, N.; Meng, Y. S.; Amatucci, G. G.; Der Ven, A. V.; Yang, W. L.; Piper, L. F. J. Distinction between intrinsic and X-ray-induced oxidized oxygen states in Li-rich 3*d* layered oxides and LiAlO$_2$. *J. Phys. Chem. C* **2019**, 123, 13201–13207.