Operando x-ray absorption spectroscopy on battery materials: a review of recent developments

Paolo Ghigna and Eliana Quartarone

1 Dipartimento di Chimica, Università di Pavia, V.le Taramelli 13, I27100 Pavia, Italy
2 Department of Chemistry and GISEL-INSTM, Via Taramelli 16, 287100 Pavia, Italy
* Author to whom any correspondence should be addressed.
E-mail: Paolo.ghigna@unipv.it

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Abstract
Although batteries represent a key tool for sustainable development, their working processes, in terms of reaction mechanisms, side reactions, ion transport and formation of a solid–electrolyte interface, are not yet fully understood. In this respect, operando experiments are of enormous importance for providing hints on the relevant chemical species that form while a battery is working. X-ray absorption spectroscopy (XAS) has for a long time been the standard in the investigation of local structures of materials. In this regard, applied operando can provide invaluable information on the working mechanisms of batteries. In this review, after introductory paragraphs concerning battery chemistry and the principles of XAS, some of the most important developments in operando XAS applied to battery science are considered. Emphasis is given to Li-metal, Na-ion, Li/sulfur and all solid-state batteries. Related and advanced techniques, such as resonant inelastic x-ray scattering and high-resolution fluorescence-detected x-ray absorption spectroscopy are discussed as well. Suggestions are offered for planning an XAS experiment at the synchrotron radiation source, and finally, some considerations concerning future developments are presented.

1. Introduction

Batteries are a key technology for drastically reducing greenhouse gas emissions from several sectors, such as light and heavy transport, power, stationary energy storage and industry [1–4]. To efficiently achieve satisfactory sustainability targets, batteries must have ultra-high performance capability, namely energy and power density approaching the theoretical values, outstanding lifetime and safety. To realize these aims, different chemistries have been explored to develop new materials for electrodes and electrolytes with better electrochemical properties in terms of high theoretical capacity, operating voltages, energy density, electron-transfer reactions, structural stability, higher safety and lower cost. The fact that these topics need to be urgently addressed is evidenced by the recent publication by a large-scale research initiative of its roadmap, which can be found at www.battery2030.eu (Inventing the sustainable batteries of the future, Battery 2030+ Roadmap).

Among several technologies proposed, Li-ion and the emerging post-Li batteries are still at the forefront for many applications, which are contributing to the growth of the electrochemical energy storage market and hold promise for the future society’s electrification and the mitigation of CO₂ emissions. The realization of this goal lies in the significant improvement achieved in device performance, due to the growing development of advanced electrode materials with high electrochemical potentiality [5].

Despite these impressive advances, the demand for even higher energy and power density is still the target for future batteries. The pursuit of these objectives requires an in-depth understanding of the structure-electrochemical property relationship and specifically, crucial problems, such as reaction mechanisms, degradation phenomena and structural evolution upon cycling and aging, ionic transport.
During operating conditions, parasitic processes and the formation of the solid–electrolyte interface (SEI) [6, 7].

During the last 30 years, battery science has witnessed an impressive flourish of synchrotron x-ray experiments, exploiting unique features, such as non-destructive experimental conditions, powerful light-source capability and compatibility to the operando measurement approach. The application of synchrotron radiation revealed valuable information under realistic battery operating conditions about electrode material kinetics of interfacial reactions at atomic and/or nanometric scale [8]. In this respect, in situ and operando techniques offer invaluable tools for the understanding of reaction mechanisms, SEI formation, side reactions, ion transport, etc [9, 10]. This topic has recently been the subject of excellent reviews, to which the reader is referred [11–17].

Synchrotron radiation methods embrace a wide portfolio of techniques exploiting scattering, spectroscopy and imaging. In particular, x-ray absorption spectroscopy (XAS) is well established as a powerful tool to evaluate electronic structure and chemical bonding, and changes thereof. Furthermore, it is the best probe to monitor the local environment and valence state during cycling. XAS can also provide useful structural information, including bond lengths and coordination numbers, and, unlike XRD, without the need of long-range order. This latter aspect is extremely important, especially in the case of materials undergoing crystalline-to-amorphous evolution upon cycling or aging [5].

While the application of different synchrotron radiation techniques to the understanding of battery chemistry has been the subject of recent excellent review papers [10, 12–17], a specific and comprehensive review of XAS and its recent developments is still lacking. In this work, therefore, we go through the more recent advances in the application of operando-XAS to battery materials and material functionality. Emphasis is given to four different categories of post-lithium batteries, namely Li-metal, Na-ion, Li/sulfur and all solid-state batteries. A very brief introduction to Li-based batteries is first provided to highlight the most critical challenges that are still open on these topics, followed by a short description of XAS, with highlights on advanced technical developments. The most representative studies of the operando XAS, within the last tenyears, are then described and some concluding remarks on future perspectives are finally discussed.

2. Battery and material design

A typical Li-ion cell consists of two electrodes inserting and de-inserting Li at the cathode at higher, and anode at lower redox potentials, respectively. Li ions migrate through the electrolyte, which can be a liquid absorbed into a porous separator, a solid (ceramic, polymer or hybrid) or gel. The electrodes are composite systems, made of proper amounts of electroactive materials, a carbonaceous additive and polymeric binder, mixed in order to ensure an optimal charge transfer at the interface [1–4].

This assembly can exploit hugely diverse chemistries. This has allowed over time the development of many different redox active systems, both for the anode and cathode, and various categories of electrolytes, leading to cells with modulable electrochemical performances in terms of capacity, energy and power density, lifetime and cycling behavior [18, 19].

From the first devices exploited by Sony in 1991, new-generation batteries have been developed in the case of Li-based chemistry, conventionally classified as gen 3 (advanced Li-ion), gen 4 (all-solid-state Li-ion or Li metal) and gen 5 (Li-air and Li-sulfur), and also of other chemistries, namely those which supercede Li or post–Lithium batteries (sodium-ion and multivalent ion) (Inventing the sustainable batteries of the future, Battery 2030+ Roadmap, March 2020, www.battery2030.eu).

Three main classes of redox materials have been deeply investigated as anodes and cathodes of Li and post-Li-ion batteries, differing in the reaction mechanism with alkali metal/ion: (a) high-capacity alloying and conversion electrode systems; (b) intercalation electrode systems; (c) alkali metal anodes [5].

In the first case, materials forming alloys or other compounds (e.g. oxides) with Li (or Na and other alkaline metals) are included, such as Si, P and $\text{M}_2\text{O}_3$ ($M = \text{Co, Ni, Cu, Sn, Zn, etc}$). The resultant storage capacity is very high, but they suffer huge volume expansion/contraction (even higher than 300%) upon cycling, which leads to significant issues, such as material pulverization, mechanical cracks and continuous SEI growth.

The second class of materials can intercalate or de-intercalate the ion into and from a crystal without causing structural collapse. These systems typically work as cathodes (e.g. Li-rich layered transition metal oxides or polyanionic compounds), offering higher capacity and energy density. The insertion/extraction of the guest ions is often accompanied by phase transition, as asymmetric or single solid solution transformations, two-phase reactions and order-disorder transitions, which significantly affect the cathode’s functional performance. Here, the critical challenges concern the near-surface structural and chemical instability during cycling and some complex reaction mechanisms occurring in the case of systems where the
anions contribute to the redox activity as for instance, oxygen in the case of oxides of semi-metals or second- or third-row transition metals (Ir, Ru, Sn).

Finally, alkali metal anodes, particularly in the case of Li, are, in principle, the best choice in terms of performance, due to the highest theoretical capacity with respect to the other systems. However, they suffer inhomogeneous electrodeposition upon cycling, causing dead Li-based dendrite growth and proliferation, leading to cell short circuits reducing the Coulombic efficiency to unacceptable levels [20].

It can be seen that all these issues relate to the structure of the materials, strongly evolving during cell operation, making the chemical, mechanical and electrochemical dynamics of these systems very complex. In this respect, the increasing application of synchrotron radiation techniques by the operando approach at multiple length scales both at macroscopic (electrode working in operating conditions) and microscopic levels (electronic configuration and crystal structure of the material) strongly contribute to the advancement of basic battery science. This is especially true for XAS, which has witnessed, during the past 20 years, an exponential growth in the reports on operando experiments (www.scopus.com).

3. XAS

Before discussing the basic principle of XAS, and for the sake of exact language, we distinguish here between the use of 'in situ' and 'operando' terminology. 'In situ' describes an experiment on a given system, undertaken while the phenomenon of interest is occurring, i.e. without altering the boundary conditions, which allows the phenomenon to occur. 'Operando' refers to 'in situ' experiments that are conducted under 'real working conditions' [21, 22]. For example, a spectroscopic probe may require a temperature as low as liquid He to operate, which is very far from real working conditions in the case of batteries, where real working conditions are achieved only if a true discharge/charge (or both) is allowed to take place simultaneously with the spectroscopic measurement. As anticipated in the above, x-ray absorption-based spectroscopies are progressively gaining ground as irreplaceable tools for operando experiments [8–10, 12–17]. Here, we present only an elementary explanation of the main phenomena that are at the basis of XAS, in order to assist the reader to appreciate the potentiality of operando XAS. Readers interested in the subject are referred to the excellent book by van Bokhoven and Lamberti [23].

The absorption of x-rays by matter causes bound core electrons to be excited to empty, high-energy lying states (see figure 1). When observed on the scale of tens or several tens of keV, the absorption spectrum of a certain compound is characterized by quite abrupt discontinuities called absorption edges. An absorption edge arises from the production of a photoelectron from a core level. The edge energy position is determined by the binding energy of the core level involved. Photoionization from levels with the principal quantum number \( n = 1, 2, 3 \) or 4, etc, gives rise to K, L, M, N, etc, edges. As for any electronic transition, the selection rules are \( \Delta S = 0, \Delta L = \pm 1 \) and \( \Delta J = \pm 1, 0, S, L \) and \( J \) being the spin, azimuthal and total angular momentum quantum number, respectively. As the energy of core levels is largely independent of the chemical state of an element, the energy of an absorption edge of a given atom is to a large extent constant, and this fact renders XAS an atomic selective probe.

On the scale of hundreds or tens of eV, the x-ray absorption spectrum is characterized by several structures, which are usually discussed after dividing the spectrum into two different regions. The energy region around the rising edge, which is conventionally defined as the region in the -20 < \( E_0 < +50 \) eV range, \( E_0 \) being the characteristic energy of the edge of interest, is called the x-ray absorption near edge structure (XANES). The energy region that extends from the edge up to the vanishing of the spectral structures (it may last for several hundreds or even thousands of eV) is called the extended x-ray absorption fine structure (EXAFS). EXAFS is caused by a single physical mechanism and is therefore more readily understood. The outgoing photoelectronic wave can be scattered by atoms in the surroundings and the scattered waves can then interfere with the outgoing wave. This interference gives rise to modulations in the absorption coefficient and these modulations are called EXAFS. For a given wavelength, the interference can be either constructive or destructive depending on the length traveled by the wave and this in turn depends on the radial distances at which the surrounding atoms lie, EXAFS turns out to be a probe for the two-body correlation (or radial distribution) function of the photoabsorber atom. In turn, a proper selection of the absorption edge selects the photoabsorber at will and therefore EXAFS is an invaluable tool for the investigation of the local order around selected atoms in matter.

The understanding of the XANES region is more complicated, due to the fact that two different phenomena are added in this energy region. These are (a) electronic transitions from the core level to 'bound' empty states and (b) multiple scattering processes by the surroundings of low kinetic energy (large wavelength) photoelectrons. Furthermore, the exact position of the absorption edge can be shifted in energy by a few eV. This is because the binding energy is determined by the Coulombic interaction between the core electron and the
nucleus and this interaction can be screened by outer (valence) electrons. The screening decreases with increasing oxidation state on the photoabsorber. As a result, the edge shifts to higher energies due to the increasing oxidation state of the photoabsorber and this effect is usually called the ‘XAS chemical shift’. In summary, XANES probes: (a) the local coordination geometry around the photoabsorber, as in the multiple scattering regime the scattering paths are determined by high-order (three- or four-body) correlation functions and (b) the local electronic structure around the photoabsorber, which is probed by the transitions to bound empty states or by determining the chemical shift. The local character of the electronic structure is due to the projection of the wavefunction of the final state onto the photoabsorber by the vanishing character of the wavefunction of the initial core state far away from the photoabsorber.

Outer electrons can fill the core hole produced after x-ray absorption. Energy conservation is obeyed by the emission of fluorescence x-rays or by the ejection of Auger electrons. Fluorescent x-rays can be detected to enhance the sensitivity in diluted or thick samples and Auger (and photoelectrons and secondary electrons) can be detected to enhance the sensitivity of XAS to the surface. Here, we note that all these processes cause the core hole to have a finite (and short) lifetime. Via the indetermination relation $\Delta t \Delta E \geq \hbar/2$, the effect of the finite lifetime is an overall broadening of the spectral structures. The high-energy-resolution fluorescence detection (HERFD) technique makes it possible to overcome this broadening. The technique consists of measuring the x-ray absorption spectrum via monitoring the intensity of a fluorescence line corresponding to a specific excited-state decay process and using a narrow energy resolution. HERFD-XAS is particularly important for measuring the K-edges of transition metals, where the 3d valence orbitals are reachable only via quadrupolar transitions giving rise to so-called pre-edge peaks. When both the incident and emitted energies are scanned, a 2D spectral map is generated, which is called a resonant inelastic x-ray scattering (RIXS) map or m-RIXS. RIXS provides an invaluable tool for probing valence shell excitations by element-selective, core-level spectroscopy. The interested reader is referred to pertinent literature [24].

In summary, the main characteristics of XAS are therefore: (a) it can be applied to every state of matter without any special requirement with respect to long-range order (in contrast to XRD); (b) it is a probe for the local order around the photoabsorber, being element selective, and it can detect phase transitions and/or the presence of metastable/instable phases and (c) it is an irreplaceable tool for the local electronic structure around the photoabsorber, and for oxidation states and changes thereof. It is readily apparent that all these features are of crucial importance to battery science. In addition, the penetration depth of x-rays with energies of the order of 10 keV may be of several hundreds of microns or of millimeters in most materials, and this makes the construction of an operando cell easy. In most cases, what is needed is just a window made of a material that sufficiently transmits in the x-ray spectral range. The cell is then readily inserted into a synchrotron radiation XAS beamline. We conclude this section with a brief comparison of XAS with other

Figure 1. Pictorial representation of a synchrotron, with a photograph of an operando battery cell for XAS installed at the XAFS beamline of the ELETTRA synchrotron radiation source (see section 5). Right panel represents schematically different phenomena taking place in XAS.
techniques that are used in battery chemistry, such as XPS, XRD and NMR. In short, XPS is a surface technique, which is quite difficult to apply to operando, and, in any case, would probe only a portion of the sample near the surface, which is a few nanometers thick in the best cases. XRD is sensitive to the long-range structure and can neither probe the local structure nor (directly) the electronic structure and changes thereof. NMR, NQR and MRI, which are related techniques, can obtain quite similar results to XAS in chemical speciation, detecting atomic connectivity, local symmetry and interatomic distances. However, NMR, although it is atomic specific, cannot be applied as universally as XAS to every element in the periodic table.

4. Review of operando studies on different batteries

4.1. Li-ion batteries (LIBs): cathode materials

Operando-hard XAS has been employed in the investigation of active materials for both cathodes and anodes in Li-based batteries for two main reasons: (a) high penetrability of hard x-rays and (b) XAS compatibility with the employed chemistry. LIB electrodes, in fact, commonly include multiple transition metals of the first row (3d TMs), whose K-edge energy lies between 4.5 and 10 keV, which fits very well the element-specific characteristic of XAS and may be easily measured using transmission mode set-ups. Consequently, a number of studies are available in the literature and collected in some recent reviews on the operando characterization of different electrochemical materials for cathodes and anodes (see for instance [5, 13]).

The very recent advances in operando XAS applied to LIBs have emphasized the great potentiality of this tool in revealing reaction intermediates, decoupling concomitant reactions and accurately tracking local structural evolution in a noninvasive manner, making it an essential technique for the study of electrochemical devices, such as batteries. The corresponding experiments typically provide a huge data set including hundreds of spectra, which need to be elaborated on within a reasonable time frame. To this end, an innovative approach has recently emerged to extract the entire information from these data, based on the use of chemometric tools, such as principal component analysis (PCA) and multivariate curve resolution (MCR). The first one is needed to determine the number of independent components required for a complete collection of spectra whereas MCR allows us to reconstruct the real spectral components without the use of any models or assumed information on the system [25].

With regard to the lithiation/delithiation mechanism of the positive electrode, olivines (LiMFePO₄), layered structures such as Li(NiₓCoₓMnₓ)O₂ and Ni-rich up to Co-free compositions have been primarily investigated.

Due to the XAS high spatial and time resolution, Ouvrard et al confirmed, for example, the two-phase reaction mechanism of LiFePO₄ delithiation to give FePO₄ [26]. A delay in the structural transformation of LiFePO₄ into FePO₄, also detected by XRD, was confirmed during a complete charge of 1 h (1C rate) in the Quick-XAS mode by observing the continuous evolution of the spectra. The presence of a biphasic structure of the system, excluding the formation of an amorphous phase, was demonstrated by the presence of isosbestic points. Fractions of these two phases were also quantified by a linear combination fit of the spectra collected between the two compositional extremes, LiFePO₄ and FePO₄. Furthermore, the same authors directly observed lithium content heterogeneity in the LiFePO₄-based cathode during cycling: some parts of the electrode were delayed, while other areas advanced, with respect to the mean state of charge (SOC), providing a map at different length scales of this heterogeneity. This heterogeneous behavior is likely due to the relationship between grain connectivity and ionic and electronic percolating networks, influenced by two main operative parameters, namely pressure and cycling rate, controlling the rate of electron supply to the active material.

Quantification of the d-metal charge state and local structure distortion was described by Operando-XAS for Mn-doped LiFePO₄ (LiFeₓMn₀.₅PO₄). Guda et al recently reported an Fe and Mn K-edges XAS study combined with Mossbauer spectroscopy. The authors observed a homogeneous Fe and Mn ion distribution in the structure, confirmed by the ion quadrupole splitting during the Mn²⁺/Mn³⁺ transition. This oxidative step is accompanied by a strong Jahn–Teller effect, which also influences the neighboring Fe atoms. The occurrence of two well-separated redox processes for Fe and Mn ion was further observed at the voltage plateau of 3.5 and 4.1 V, respectively, with the Fe K-edge position remaining unchanged at these voltages [27]. The Jahn–Teller effect in the LiFe₀.₇₅Mn₀.₂₅PO₄ system, occurring upon oxidation of the Mn center, was more precisely described by interpreting the XAS data collected from operando experiments at both the Fe and Mn K-edge system by using a chemometric approach. This kind of data analysis, in fact, allows the detailed reconstruction of the rather complicated reaction mechanism involving two different metal centers. The results proved that the Mn oxidation takes place through a Jahn–Teller octahedral distortion along with the rotation or tilt of the bridges between PO₄³⁻ groups that may be experimentally quantified [28].
Operando XAS experiments were also conducted during the lithium deintercalation from polyanionic systems as theavorite Li$_x$VPO$_4$F$_{1-y}$O$_y$, which are valuable active materials serving as positive electrodes in LIBs compared to the already commercialized LiFePO$_4$ for several reasons, such as the possibility of multielectron systems offered by these compositions and the interesting electrochemical properties conferred by vanadyl-type defects. In more detail, Croguennec et al studied the influence of these defects on the phase diagram and redox mechanism in the Li$_x$VPO$_4$F$_{1-y}$O$_y$ tavorite phase by combining operando-XAS and XRD. Operando XANES revealed for the first time the activation of the V$^{4+}$ = O/V$^{5+}$ = O redox couple during the first step of charging, followed by the activation at higher voltage of another redox couple, V$^{4+}$ /V$^{5+}$, for fluorine-rich environments, which is induced by further Li-ion extraction. This is made evident by the shift of the V K-edge towards higher energies, as illustrated in figure 2(a). The authors were able to reconstruct the spectra as the sum of three different components (figure 2(b)), the amount of which varies during lithiation, as shown in figure 2(c). This phenomenology leads to the formation of a mixed valence V$^{3+}$ /V$^{5+}$ phase at the end of the first vanadium oxidation step. This result, defined by the author as the redox paradox of vanadium in tavorite, although surprising, is in full agreement with the operating voltages of the end-member phases [29].

The Fourier transforms of EXAFS spectra and their corresponding fit were also used to gain insight into the local structure of this material to further support the proposed redox mechanism. The authors show that the local environments around vanadium, including the V$^{n+}$-X bonds along the propagation direction of the octahedra and all the V$^{n+}$-O bonds belonging to the square plane VO$_x$X$_2$, namely O = V$^{4+}$O$_2$=O, O = V$^{4+}$O$_2$=F, and X=V$^{3+}$O$_2$=X, characterized by different kinds of bond distances, evolves upon electrochemical Lithium extraction. In particular, the bond lengths along the propagation direction of the octahedral chains remain structurally immobilized at the local scale whereas a shortening of the V–O distances is in contrast observed. In very good agreement with XRD results, EXAFS also gives evidence of a competition between the ionicity of the V$^{n+}$ bonds and the covalency of V$^{n+}$ = O bonds, which constrains the system along the (001) direction with vanadyl distortion [29].

Operando XAS has shown great potentiality as a tool to obtain direct evidence of non-trivial oxygen participation in the redox process, taking into consideration that the probing of the oxygen electronic state may be seriously affected by the contamination of O-containing decomposition products deposited on the electrode surface. The anionic/cationic redox decoupling was recently described by Tarascon et al in an emerging class of materials, present in Li-rich metal oxide including metallic centers such as Ru and Ir, namely Li$_2$IrO$_3$ and Li$_2$RuO$_3$ (LRO) and related compositions. These active systems exhibit large capacity and long cyclability, thus being competitive with the NMC-based systems. The reason for such good performance lies in the reversible redox activity of oxygen (anionic redox) beyond what is merely expected from the transition metal cation. This additional redox activity has been interpreted in terms of cationic-anionic charge compensation and local structure evolution in LRO-based structure. This effect is quite difficult to isolate, due to the very complex mechanism of charge compensation from transition metals and O. Microstructural studies based on operando XPS and EPR were previously discussed in the literature, attempting to prove such a mechanism. However, the final quantification remains doubtful, due to the...
Figure 3. Spectroscopy-driven visualization of electrochemical reaction paths is demonstrated, enabling us to decouple the individual cationic-anionic dQ/dV contributions during cycling. Operando XAS characterization of the LRSO 5th cycle and chemometric analysis of the spectroscopic data. (a) Electrochemical sloped S-shape profile obtained in the operando cell, exhibiting hysteresis between charge and discharge. Bottom part shows the variation of relative concentrations of the three principal components, reconstructed by the MRC-ALS method, to fit all spectra measured during the selected charge/discharge cycle as a function of capacity over the charge and discharge paths. (b) Shift of the rising edge in the XANES region of the reconstructed Ru K-edge spectra comparing components I_5th and II_5th. (c) Comparison of components II_5th and III_5th, whose main change is at the pre-edge peak arising from the distortion of oxygen network (distorted RuO_6 coordination) as a consequence of anionic oxidation. (d) Methodology to successfully decouple the overlapping cationic-anionic redox reactions, individually tracked on the dQ/dV curve of the cationic and anionic processes. Reaction scheme is deduced from PCA, followed by MCR-ALS analysis. (e) Decoupled dQ/dV profiles and their resulting summation, which matches the overall as-measured dQ/dV profile from the operando cell. Reprinted with permission from [30]. Copyright (2017) American Chemical Society.
Figure 4. Chemical state of O in LiAl$_{x}$Ni$_{1-x}$O$_2$ ($x = 0.10$, LANO) probed by RIXS O K-edge mapping at different states of charge. Red arrow, white arrow and dashed line mark structural oxygen redox, TM-O hybridization and the elastic peak, respectively. Numbers in white refer to the potentials during charging (Ch) and discharging (Dch). Defined oxidized oxygen feature at the excitation and emission energy of 531.0 and 523.7 eV (red arrow), respectively, starts to emerge at 4.5 V during charging. Enhancement of this oxygen oxidation feature during charge and its reversible decrease during discharge clearly suggest the contribution of reversible structural oxygen redox in the LANO sample. Reprinted from [34], Copyright (2020), with permission from Elsevier.

Debye–Waller factor of Mn–O continuously increasing upon charging, in contrast to those of Co–O and Ni–O, which reveal only a slight change, indicating that the local structure induced by the electrochemical process mainly occurs around the Mn sites [33].

The redox activity of oxide ions in the crystal structure, charge compensation phenomena and lithium dynamics were investigated at high voltage in Ni-rich (LNO) [34–36]. In this kind of material, high-efficiency m-RIXS was particularly successful to differentiate TM-O hybridization from the oxygen oxidation state, as, in the RIXS map, they lie at different excitation and emission energy positions. Specifically, in the O K-edge RIXS, features of structural oxygen oxidation at 523.7 eV emission energy and 531 eV excitation are evident while the broad signal at 525 eV emission energy corresponds to the TM-O hybridization (figure 4). Mapping at different states of charge in the Al-doped Ni-rich cathode (LANO) well decoupled the two signals. In particular, the feature of oxidized oxygen becomes more pronounced upon charging, reaching its maximum intensity at 4.8 V, indicating a continuous oxidation of oxide ions in the structure during the charging process.

This phenomenon is promoted by Al doping, which also triggers oxygen release and surface Ni reduction when the doping level is in excess.

The coupling of a fine electrochemical test and operando XAS was also helpful in the understanding of the mechanism of capacity loss at high C rates in Li-rich 3$d$-transition metal layered oxides. This study revealed that the decrease in Li-ion diffusivity is strictly related to the disproportionate redox reaction occurring both on the surface and in the bulk and also to the slow kinetics of the O-redox process. The O-redox reaction at voltage higher than 4.5 V is responsible for the capacity reduction at higher C rates in the case of Li$_{1.15}$Mn$_{0.51}$Ni$_{0.17}$Co$_{0.17}$O$_2$ with a long-range cation-ordered arrangement, which has the 2TM-O-4Li configuration. In contrast, in Li$_{1.08}$Mn$_{0.55}$Ni$_{0.33}$Co$_{0.04}$O$_2$ (LNMR), where the configuration is a localized cation-disordered arrangement (3TM-O-3Li or 4TM-O-2Li), the TM-redox reaction is dominant because of a different redox mechanism due to the presence of 3TM (Mn, Ni and Co). The change in the chemical state and local coordination of each element during fast electrochemical cycling (3C), directly observed by fast-scanning XAS, proved that the LNMR superior rate performance is favored by a better diffusion and a reversible migration of Li ions, triggered by the redox behavior of Ni and Co. Electronically and structurally preferred atomic behavior is then shown when a redox reaction occurs between O and each TM during fast charging and discharging [37].
Chemiometric MCR-ALS analysis provides ‘pure’ spectral components which express, by their linear combination, the main modification of the XAS spectra. 104 XAS spectra collected during the first discharge at C/8 of the Ge electrode and reconstructed components from the analysis of the whole series: (a) XANES and (b) EXAFS regions of the experimental spectra (evolution of the spectra from the beginning (dark blue) to the end (green) of the discharge); (c) XANES and (d) EXAFS regions of the reconstructed components. (e) Evolution of the concentration of the MCR-ALS components during the lithiation of Ge: components 1 and 4 show pristine $\chi$-Ge and the final product after the first discharge; components 2 and 4 show maxima after 30 and 65 spectra from the beginning of the discharge, indicating 1 and 2 mol of Li per mol of Ge, respectively. Absorption edge shape of these four components suggest that the evolution of XANES spectra cannot be expressed as the simple linear combination of spectra for the pristine material and fully lithiated material. At least two new spectra are required, thus indicating that at least two additional phases are formed during the first discharge. Reprinted with permission from [43]. Copyright (2018) American Chemical Society.

Results obtained from Mn, Co and Ni XANES/EXAFS signals also provide evidence of the extraction of Li ion as Li$_2$O from the Li-rich layered oxide due to irreversible capacity loss during the first cycle, which seems to be dependent on the C rates. In particular, in the case of slow charge, Ni–O bond splitting is detected at about 4.2 V due to a Jahn–Teller distortion, which corresponds to an abrupt increase in the bond length observed in the EXAFS spectra of Mn–O and Co–O bonds [38].

In addition to Li-transition metal oxides, the corresponding fluorides were also investigated due to their potentially promising properties, as the high voltage related to fluorine electronegativity and high Li-ion conductivity [39], even if, on the other hand, the electron conductivity is still a limiting factor. Operando XANES at the Ni and Fe K-edges were collected in the case of LiNiFeF$_6$ in various states of charge and discharge. The reversibility of the electrochemical reaction during lithiation and delithiation was demonstrated, confirming that only Fe$^{3+}$ participates in the electrochemical process via reduction to Fe$^{2+}$, while Ni$^{2+}$ remains electrochemically inactive, as proved by the similarity of the spectra at the Ni K-edge in the pristine state and charged/discharged states with those of the NiF$_2$ [39].

4.2. LIBs: anode materials

In the field of electrochemically active materials for anodes in LIBs, XAS has been chiefly devoted to the study of the mechanism in Ge (and related alloys) and of conversion transition metal oxides, which usually deliver much higher specific capacity than the systems involving intercalation/deintercalation reactions.

Ge-based anodes are considered particularly promising for their high capacity, low voltage, fast Li-ion diffusivity and good transport properties. However, Ge undergoes huge volume expansion, similar to silicon, with consequent capacity loss, which is caused by electrode detachment from the current collector, pulverization and mechanical fracture. All these phenomena have been partially alleviated by forming nanostructured alloys between Ge and Si, Sn or by doping with atoms as Se, which favor easy strain accommodation and short diffusion pathways for electron and Li transport in these nanostructures [40–42].

The lithiation mechanisms of Ge during cycling were revealed by means of operando XAS, which is an ideal probe in the presence of amorphous phases. Monceau et al correlated the structural information coming from operando XRD, Raman spectroscopy, XAS and electrochemical tests to follow the lithiation mechanism of Ge at different C rates. In particular, the authors used the chemiometric approach to extract the maximum information from a whole set of more than 100 spectra during cycling, especially in the intermediate phases [43].

The results, reported in figure 5, suggest that the Li insertion mechanism in crystalline Ge (component 1) is strictly dependent on the C rate. Faster lithiation (high C rates) favors the growth of the crystalline Li$_{15}$Ge$_4$ compound (component 4) at the end of discharge, passing through the formation of fully amorphous or poorly crystallized intermediates, such as low-lithiated LiGe (component 2) and Li$_7$Ge$_3$ (component 3).
Slower lithiation (low C rates) leads to intermediate stages, but with the formation of Li$_2$Ge and amorphous Ge. Upon delithiation, only α-Ge is present, both at lower and higher C rates [43, 44].

If Ge is doped with Se to form Ge$_{0.9}$Se$_{0.1}$, the anodic electrochemical performance improves, likely due to enhanced material mechanical stability. This hypothesis has also been confirmed by combining operando XRD and XAS experiments. This structural study revealed the formation of a super-ionically conductive and amorphous Ge. Upon delithiation, only α-Ge is present, both at lower and higher C rates [43, 44].

Similar operando XAS studies were also conducted on Si$_x$Ge$_y$ (e.g. Si$_{0.5}$Ge$_{0.5}$), for which it was demonstrated that both elements are active upon cycling [46]. A reversible process of overlithiation was identified, leading to the formation of Li$_{15}$Si$_{5}$Ge$_{5}$, as a final compound, passing through an initial amorphization of Si$_{0.5}$Ge$_{0.5}$ at the beginning of the discharge and subsequent production of amorphous Li$_x$(Si/Ge) intermediates during discharging.

Operando XAS was also used to monitor the redox reactions involving transition metals such as Fe, Co, Mn and Ni, usually employed in oxide anodes based on the conversion process. This spectroscopic tool has been particularly helpful to elucidate the complex pathways of conversion reactions occurring during the lithiation and delithiation steps, whose mechanism, and the associated irreversible capacity losses, are not yet fully understood.

Recently, operando quick XAS was performed for the first time on pure spinel CoMnFeO$_4$ nanoparticles as anodes for LIBs [47]. A strong shift of both Fe and Mn K-edges to lower energy was clearly observed during Li uptake, in contrast to the Co K-edge, which remains almost unaltered (figure 6). Mn(III) is reduced first, giving a spectrum similar to that of MnO, followed by Fe(III)/Fe(II) reduction at a later stage. Besides the shift of the absorption edges, their shapes are also affected by lithiation. The pre-edge features, for instance, disappeared for all three metal cations when 2.5 Li per formula unit react, due to the fact that the spinel structure is transformed into a disordered rock-salt-type phase, leading to a slight increase in the TM-O distances. Along with this phase transition, Co (II), Mn (II) and Fe (II) are then further reduced to the metallic state in a one-step reaction at the end of the long plateau at 0.6 V, as proved by isosbestic points detectable at 6545 eV for Mn, 7123 eV for Fe and 7718 eV for Co in the spectra of all three metals. The metallic nanoparticles of Co, Fe and Mn appear embedded in an amorphous network of Li$_2$O, which is formed during the phase evolution of the spinel.

The charge process is reversible, as demonstrated by a strong shift of the Mn K-edge at higher energy, observed during the oxidation of Mn(0) and by the subsequent Fe(0) oxidation. In contrast, the Co(0)/Co(III) transition is only partially visible at the end of the charging process.

Similar mechanisms were also observed in the case of other nanoparticle-based conversion anodes such as CoFe$_2$O$_4$, both pure or in a composite with reduced graphite oxide [48, 49]. In these systems, however, less reversibility of the Co reduction/oxidation is evidenced, which is partially responsible for the capacity loss occurring during cycling.

The spinel/rock-salt structure transformation during the Li uptake, triggered by the ion movement from tetrahedral to octahedral neighboring vacant sites with the consequent formation of Li$_2$O, was also recently inferred by Passerini et al from operando Fe and Zn K-edge XAS, performed on carbon-coated spinel ZnFe$_2$O$_4$ nanoparticles [50].

Several intermediates are also usually observed during the conversion process of single transition metal oxides, such as Mn$_3$O$_4$, or even metal sulfides, such as FeS. In this case, operando XAS experimentally demonstrated that the oxide structure evolves upon lithiation through amorphous phases, in the sequence Mn$_3$O$_4$-LiMn$_2$O$_4$-MnO, which are obviously difficult to detect by XRD, before undergoing the final conversion step to the Mn metallic state. The sequence of these reactive steps is strictly dependent on the diffusion of several different ions within the intermediates, leading to an oxide, which is reduced and disordered enough to finally nucleate Mn nanoclusters [51].

In the case of Fe$_{1-x}$S-based anodes, Li et al showed by Fe K-edge XAS that the lithium storage mechanism takes place through several phase transitions from Fe$_{1-x}$S to Li$_2$Fe$_{1-x}$S$_2$ and finally to Fe(0) and Li$_2$S during the first lithiation step. Upon delithiation, conversely, the metallic iron and lithium sulfide are reconverted to the intermediate amorphous Li$_2$Fe$_{1-x}$S$_2$ with the simultaneous extraction of lithium ions from Li$_2$S to form Li$_{2-y}$S, which was observed for the first time in the literature for this kind of iron-deficient sulfide [52].

During the past two years, another promising family of anode materials for LIBs involving conversion reactions has emerged, based on high entropy oxides (HEOs), with rock-salt structure (see for instance [53]). Despite these interesting functional performances, the lithiation/delithiation mechanisms of these materials are very complex in terms of processes and for what concerns the structural stabilization effect of the configurational entropy, due to the final amorphous structure obtained during cycling. Very recently, Ghigna et al demonstrated how operando XAS can be used to assess the overall lithiation mechanism of the
Figure 6. (Left). Operando XANES spectra at Mn (top), Fe (middle) and Co K-edge (bottom) during uptake of the first 2.5 Li per f.u. (region I, blue lines), during uptake of more than 2.5 Li (region II, black lines), and during charge process (region III, red lines). Spectra of the pristine material show a pre-edge peak at Co, Mn and Fe K edges, which provide information on the local structure of each metal. (Right). Potential curve of the in situ cell (top) and K-edge position of Mn, Fe and Co (from top). In region I, the Co K-edge is only slightly affected by Li uptake, in contrast to Fe and Mn K-edge, showing a strong shift to lower energy. In region II, all the cations are reduced to the metallic state during the long plateau. At the end of region II, when the discharge is completed, the spectra of all three elements is similar to those obtained for metallic reference foils, suggesting that the metallic state is fully achieved for all the components (Co, Mn, Fe). Reprinted with permission from [47]. Copyright (2016) American Chemical Society.

Mg₀.₂Co₀.₂Ni₀.₂Cu₀.₂Zn₀.₄O TM-HEO anode with rock-salt structure [54]. The authors found that a multi-step process takes place, as apparent from the different behavior of the Co, Ni and Cu K-edges shown in the upper part of figures 7(a)–(c), respectively. The main steps are (a) the initial reduction of Cu²⁺ to Cu⁺ at the beginning of the lithiation process (figure 7(a), down); (b) conversion reaction by further reducing Cu⁺, Ni²⁺ and Co²⁺ to metals and by forming Li₂O. The reduction of Ni and Co leads to the collapse of the rock-salt crystal structure, with the consequent amorphization of the overall system, as proved by the strong reduction of the main peak (white line, WL) at the Co and Ni K-edges. The spectroscopy measurements also demonstrated the irreversibility of the oxide-to-metal conversion, leaving a mixture of metals and partially reduced oxide at the end of the first charge, which are not further re-converted during cycling. The anodic material is, then, highly non-homogeneous in chemical composition at the end of the lithiation process, resulting in a significant separation of all the metals. Other new XAS evidences were also discussed regarding...
the reduction of Zn\(^{2+}\) to Zn metal, still not reported in the literature for this kind of complex multi-element oxide (figure 7(b), down).

This conversion mechanism is also common in ternary intermetallic, such as TiSnSb. Stievano et al used operando XAS, complemented with chemiometric tools, at the Ti, Sn and Sb K-edges, to confirm that this system reacts with Li via a real conversion reaction in which the p-group metals, Sn and Sb, are electrochemically active whereas the transition metal Ti reversibly forms Ti metal nanoparticles. Ti binds back to the p-group metals in the delithiation process [55]. The fitting of the EXAFS spectra gives proof of the formation of Li\(_2\)Sn\(_2\) and Li\(_3\)Sb upon Li uptake, with consequent overall amorphization starting soon during the first cycle. Furthermore, PCA and MRC-ALS analyses suggest that the cycling reactions of Sn and Sb do not take place simultaneously, and that Sb is centered at higher potential than Sn.

In 2018, Villevieille et al used operando XAS on hybrid organic-inorganic materials as conversion anodes based on iron methylene diphosphonate (FeMeDP), which, as a negative electrode, provides a specific charge higher than that expected from a reaction solely based on the Fe(II)/Fe(0) redox couple [56]. The extra-charge hypothesis has been experimentally demonstrated only by means of operando P K-edge XAS experiments, carried out during lithiation/delithiation of FeMeDP. The XANES analysis proved that there is a contribution of anionic redox activity of phosphorus present in the disphosphazene ligand. Upon delithiation, the P oxidation takes place around 1 V, indicating a much larger specific charge with respect to the Fe oxidation observed via Fe K-edge XANES. This is illustrated by the XANES at the P K-edge shown in figures 8(a) and (c). EXAFS data (figure 8(b)) showed an elongation of P–O bonds and thereby a lower formal P oxidation state at the end of the second cycle.

More than for the importance of the active anode material itself, these results are remarkable for opening the possibility to demonstrate the P co-cycling of other systems containing phosphorus as an anion.
Figure 8. Operando XAS experiment on the FeMeDP material cycled between 0.1 and 3.0 V at 100 mA g$^{-1}$. (a) XANES spectra of the extreme points of the operando experiment with the H$_2$MeDP material as a reference. Change in the P electronic environment is observed when FeMeDP is reduced at 0.1 V (b) EXAFS Fourier transform spectra in the R-space of pristine FeMeDP compared to the in situ measurement of FeMeDP reduced to 0.1 V (not phase-corrected). In situ spectra highlight the change in the coordination environment, evidencing longer P–O bonds and lower formal P oxidation state. (c) Contour plot representation of the operando XANES measurement with the shift of the edge energy $E_0$ shown in the graph on the very right. Changes in the P K-edge XANES spectra are gradual, revealing the existence of two P environments. Reproduced from [56] with permission of The Royal Society of Chemistry.

Chemometric tools such as PCA and MRC-ALS were also recently used to interpret a large data set of XAS manganese K-edge spectra collected operando upon electrochemical oxidation of battery anode materials such as Li$_7$MnN$_4$. This approach enabled us to separate three independent environment spectra, which were ascribed to unusual Mn oxidation states in the redox process, which in turn were caused by the nitride chemistry at low potential, around 0.9–1.7 V versus Li$^+$/Li, namely the high-charge Mn$^{5+}$ ($3d^2$), Mn$^{6+}$ ($3d^1$), and Mn$^{7+}$ ($3d^0$). Consequently, the oxidation of Li$_7$MnN$_4$ was proved to take place through two successive biphasic domains into Li$_{6.1}$MnN$_4$ and subsequently to Li$_{5.7}$MnN$_4$, followed by a solid-solution-like structural evolution. This process seems to be reversible at both local and long-range scale [57].

4.3. Li–S batteries
Li–S batteries were first investigated by XANES at the S K-edge by Cusiner et al [58]. The authors used a carbon–sulfur composite electrode optimized for both the efficient transport of charge carriers and trapping of soluble polysulfides. They could explain the hysteresis in charge/discharge by showing that different mechanisms act in the two processes. In particular, during the reduction, $S^{2−}$ is formed, and, when its concentration increases enough to give rise to supersaturation, the sudden precipitation of Li$_2$S takes place. In contrast, during the charge, steady surface oxidation of Li$_2$S takes place and polysulfides such as $S_2^{2−}$ and $S_6^{2−}$ are formed. Polysulfides are well known as the main source of degradation in Li–S batteries due to the so-called polysulfide shuttle effect [59]. The same group [60] used the same experimental approach to show that radical $S_3^{−}$ can be formed in solvents, such as dimethoxyethane and 1,3-dioxolane, but it is not produced in electron pair donor solvents, such as dimethylacetamide.

The formation of polysulfide and polysulfide radicals was studied by several groups using operando XAS, also in combination with other probes, such as NMR and UV–vis spectroscopy, and XRD [61–67]. Several species could be detected, ranging from $S_8^{2−}$ to $S_2^{2−}$, and the rate of conversion of the polysulfide species...
into Li$_2$S could be measured [68]. One of the main problems in the speciation of the sulfur compounds with the XANES at the S K-edge is that the intensity of the main peak (white line, WL), which is in principle proportional to the number of empty p states, and therefore to the oxidation state of sulfur is affected in the fluorescence mode (vide infra) by self-absorption, and therefore is heavily distorted in the case of concentrated samples [61, 65, 69]. This problem can be minimized by means of RIXS. The resonant excitation condition significantly enhances the sensitivity of polysulfide detection while it strongly suppresses sulfate interference [69]. This approach has more recently been extended by the same group [70], who performed horizontal cuts in a K-L RIXS map of a Li$_2$S$_4$ standard solution, at an emission energy corresponding to the K$\alpha_1$ emission line (figure 9(a)). This allows us to obtain a HERFD-XAS spectrum, significantly enhancing the resolution in the absorption spectra, allowing a meaningful separation of the pre-edge peak from the WL (figure 9(b)), and a sensible extraction of intensities from the pre-edge peak.

Since the pre-edge intensity is correlated with the length of the S$_n^{2-}$ anion chain length, this approach could in principle give important information on the formation of different polysulfides at different values of the SOC of a battery.

The problem of polysulfide and different sulfur species distribution in the battery was addressed by Gorlin et al [71], who designed an operando cell allowing spatially resolved XAS experiments [65]. They were able to observe the intermediates that are produced at two locations of the cell, the Li$_2$S cathode and separator. In addition, they were able to rule out the formation of polysulfides during the first charge process while a constant concentration of polysulfides was detected during the second charge.

Operando XAS experiments [72] at the S K-edge also allowed us to rule out the formation of polysulfides and show the direct oxidation of Li$_2$S to S in a cathode consisting of carbon-coated Li$_2$S particles prepared by the carbothermal reduction of Li$_2$SO$_4$.

Sulfur K-edge operando experiments were used to understand the mechanism by means of which LiNO$_3$ suppresses the polysulfide shuttle effect in Li/S batteries [73]. The authors found that LiNO$_3$ can oxidize the shuttled polysulfides to Li$_2$SO$_3$ and Li$_2$SO$_4$ by reducing it to LiNO$_2$. The resulting compact lithium sulfate and sulfite layer on the anode effectively acts as a passivation layer, suppressing the reaction between polysulfides and lithium metal, in turn, hindering the polysulfide shuttle effect.

The shuttle effect and its suppression were more recently investigated by Jia et al, who successfully suppressed the shuttle effect by introducing an electrocatalytic layer of twinborn bismuth sulfide/bismuth oxide nanoclusters in a carbon matrix (BSOC). Operando S K-edge XAS experiments revealed the BSOC role in trapping polysulfides and catalyzing the conversion of sulfur species simultaneously [74].

4.4. All solid-state batteries (ASSBs)
Operando XAS on ASSBs is still at an initial stage, but it is intended to become a very powerful tool in the investigation of charge dynamics and related microscopic mechanism, even in the case of solid electrolytes. In terms of experimental approaches, SSBs offer a significant advantage because they are suitable to be studied by soft XAS, in contrast to those using liquid electrolytes, because there is no issue concerning
electrolyte evaporation into the vacuum chamber. This potentiality is highly attractive, allowing us to provide additional information about oxygen and transition metals.

Recently, operando soft XAS was used to study the charge/discharge mechanism of LiMn$_2$O$_4$ in the presence of a solid 180 $\mu$m thick Li-ion conductive glass ceramic electrolyte (NASICON-based). The analysis of the Mn L$_3$-edge spectra revealed an increase in the Mn$^{4+}$ component, compensating the charge during Li-ion extraction. Furthermore, no spectral feature changes are observed before and after the charge process. The results suggest that the electrochemical reaction proceeds preferentially at the cathode/ceramic electrolyte interface. In contrast, the Ti L-edge spectra show only a partial reduction from Ti$^{4+}$ to Ti$^{3+}$ with Li insertion at the anode side, thus evoking a more diffused Li concentration instead of a more localized collection specifically at the anode interface [75].

Operando soft XAS was also performed on solid-state batteries by screening two different types of cathodes, Li(Co$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$)O$_2$ and LiFePO$_4$, and a solid polymer electrolyte. The aim was to gain insight into the integrated dynamics of Li ion and electrons, due to the outstanding sensitivity of the probe to electronic states. Two mechanisms can be distinguished in NMC and LFP. In the first case, the electrochemical SOC is uniform across the electrode, in contrast to LFP, where strong relaxation and SOC gradient effects are observed. This is due to the phase transformation occurring in the olivine system, starting from the area close to the current collector. The electrode reaches uniform SOC distribution after hours of relaxation time. The contrast observed in charge dynamics in both electrodes is due to the combination of charge conductivity, phase transformation mechanism and morphology at the mesoscale level [76].

4.5. Na batteries

Most of the operando XAS investigations of Na batteries involve materials that are used as cathodes. The P2 phase Na$_{0.74}$CoO$_2$ cathode material for Na batteries was investigated by operando XANES and EXAFS at the Co K-edge [77]. The results showed that Na intercalation proceeds as a result of the Co$^{3+}$/Co$^{4+}$ redox couple, which is accompanied by a contraction of the $c$ axis of the hexagonal crystal structure.

The Na$_{0.83}$Li$_{0.17}$Ni$_{0.21}$Mn$_{0.64}$O$_2$ compound, which has the same hexagonal crystal structure, was studied at both the Ni and Mn K-edges [78]. The XANES results unequivocally showed that, while Mn remains in the Mn(IV) oxidation state, Ni(III) and Ni(IV) reversibly form during the charging process. In addition, the operando EXAFS data allowed us to assess the local structural distortions induced by the charging discharging process in both the local chemical environments of Mn and Ni.

Sottmann et al [79] investigated, by quasi-simultaneous XRD and XAS, the Prussian blue analog compound Na$_{1.32}$Mn[(Fe(CN)$_6$)$_{0.83}$]$\cdot$H$_2$O, where two different crystal structures (monoclinic and cubic) can be formed by varying the water content $z$. They were able, by working at the Mn and Fe K-edges, to correlate the different plateaus in the voltage versus capacity curves of both charging and discharging processes to different electrochemical processes involving the Mn$^{3+}$/Mn$^{4+}$ and Fe$^{2+}$/Fe$^{3+}$ redox couples.

Lin et al [80] examined the sodiation and lithiation processes of a TiS$_2$ cathode in a Na-ion battery. By working at both the Ti and S K-edge, they showed that redox processes in both Ti and S are involved in the sodiation process. By using the MCR-ALS analysis of XAS to analyze the sizable XANES data set, they could show that several phases participate in the reaction mechanisms, with at least one intermediate present in addition to the pristine TiS$_2$ and final NaTiS$_2$ materials. Analysis of the operando EXAFS data combined with ex situ XRD data allowed us to identify this intermediate with Na$_{0.55}$TiS$_2$.

Dixon et al [81] exploited the full potentiality of XAS by studying the different mechanisms of the working of SnO$_2$ as a conversion cathode for Li and Na batteries. By working at the Sn K-edge, and considering both the XANES and EXAFS regions, they were able to show that lithiation completely reduces SnO$_2$ to metallic Sn, which in turn forms a Li–Sn alloy. Conversely, the delithiation starts with Li de-alloying and successive oxidation of tin to SnO$_2$. In contrast, sodiation only partially converts SnO$_2$ to metallic Sn.

Incomplete reduction has been attributed to the formation of a dense Na$_x$Sb$_{1-x}$ phase resembling metallic Sb and then SnO$_2$. Using chemometric techniques to analyze the large set of experimental data, the authors were able to follow the concentration profiles of the different species, and link the principal features of the electrochemical process to specific reaction steps. This approach proved that the formation of sodiated phases is gradual and proceeds first by sodiating Sb and then Sn. The stepwise and steady increase in volume resulting from this regular process was found to be less damaging for the electrode than a sudden reduction, which occurs in the case of lithiation. Moreover, a cushion for volume expansion is provided by the large degree of amorphization. The same group used the same experimental approach to investigate the mechanism of the electrochemical
Figure 10. Two possible geometries of a battery with cylindrical symmetry with respect to an incident x-ray beam. Beam can lie on a plane that is longitudinal (left) or transverse (right) with respect to the principal symmetry axis of the battery.

reaction of Sb as a cathode for Na batteries [83]. They could again evidence the formation of Na$_3$Sb and detect the presence of amorphous Sb, which is reversibly sodiated/de-sodiated during the subsequent cycles. However, in this case, the presence of intermediate Na-Sb phases (for example, Na$_x$Sb$_y$) could not be revealed as their spectral signatures in the EXAFS and XANES regions are too similar to that of Na$_3$Sb and amorphous Sb. The investigation was then extended to the sodiation of BiSb by working simultaneously at the Bi L$_3$ and Sb K-edges [84]. By combining the operando EXAFS data with XRD, mechanisms for the charge and discharge processes were proposed, where the ternary Na$_3$Bi$_{0.5}$Sb$_{0.5}$ intermetallic corresponds to the fully discharged state. Zhou et al used operando XAS to study the redox reactions of the Na$_3$Bi$_{0.5}$Fe$_{0.5}$Ni$_{0.5}$O$_2$ and NaMn$_{1/3}$Fe$_{1/3}$Ni$_{1/3}$O$_2$ materials and found different redox behavior. The first compound has Ni$^{3+}$/Ni$^{4+}$ and Fe$^{3+}$/Fe$^{4+}$ couples that are active while Mn ions are inactive during the charge/discharge processes. The second compound undergoes deeper redox reactions from Ni$^{2+}$/Ni$^{3+}$/Ni$^{4+}$ and Fe$^{3+}$/Fe$^{4+}$, while the Mn ions are irreversibly oxidized to Mn$^{4+}$ in the first charge process [85].

The anodic part has been less investigated; Xu et al used XANES at the Ti K-edge to assess the mechanisms of the working of Na$_2$Ti$_3$O$_7$ as an ultra-low voltage anode material for Na batteries. They demonstrated that Ti$^{4+}$ is reduced to Ti$^{3+}$ upon Na$^+$ ion intercalation [86].

4.6. Other batteries
Quite a few types of different batteries were studied using operando XAS, ranging from Zn/air batteries [87, 88] and Mg anode batteries [89–93] to Mg/S batteries [94].

5. Experimental details: operando cells and beamlines

A comprehensive discussion of the instrumentation needed to perform operando XAS experiments on a battery is well beyond the scope of this paper. However, some general considerations are due in order to help the reader to plan possible investigations. It should be kept in mind that two main items are needed. An electrochemical cell and a synchrotron radiation XAS beamline, although operando investigations were also demonstrated to be feasible by means of laboratory XAS equipment [27].

With regard to the electrochemical cell, given a battery with cylindrical symmetry, two geometries are possible, longitudinal and transverse as illustrated in figure 10.

With this in mind, one has first to consider that operando studies on batteries are usually performed in fluorescence mode; characteristic fluorescence photons are collected, whose number is proportional to the absorption coefficient. In this case, the absorption coefficient $\mu$ is given by $\mu \approx I_f/I_0$, where $I_f$ and $I_0$ are the intensity of the fluorescence and impinging beam, respectively. The preference for the fluorescence geometry is because x-rays are strongly absorbed by matter. For example, the absorption length of x-rays having energy of 9 keV in graphite is less than 1 mm. It is apparent that, in these conditions, any meaningful experiment in transmission mode on a battery is very difficult, if not impossible. Absorption effects are made even worse in transverse geometry, which however allows spatially resolved experiments. As a final comment concerning
this point, we note that the probing depth in XAS depends on the energy of the impinging x-ray beam and the electron density of the sample. Typical values are in the micron or several tens of microns range for hard x-ray impinging on a 3d transition metal oxide, to less than 100 nm for soft x-ray impinging on a heavy metal sample.

We note that commercial coin cells can easily be adapted for fluorescence XAS with longitudinal symmetry. The CR2325 coin cell is usually used by drilling a hole at the side of the electrode of interest and fixing an airtight window made of a material sufficiently transparent to x-rays. Similar considerations also hold for pouch cells.

Swagelok cells were originally developed by Leriche et al [95] and then widely used by other groups. Swagelok cells are quite versatile, and their application to in situ and operando characterizations of batteries by x-ray tomography was recently discussed [96]. The reader should take into account that XAS experiments are usually simpler and therefore cells used in tomography can be readily adapted for XAS. It should also be noted that several manufacturers provide electrochemical cells designed for in situ or operando x-ray diffraction or reflection spectroscopy. These cells are also an excellent option for working with XAS in fluorescence mode.

The penetration depth of x-rays should be carefully taken into account for the choice of window material and cell assembly. Roughly speaking, far from the absorption edges, the absorption coefficient of x-rays in matter is a decreasing function of energy. This means that low-energy x-rays are strongly absorbed. It is useful here to make the distinction between ‘soft’, ‘tender’ and ‘hard’ x-rays. This classification is somewhat arbitrary and different authors may use different categorization. Here, we use the categorization of Northrup et al [97], according to which soft x-rays have energy lower than 1 keV, hard x-rays greater than 5 keV, and tender x-rays are in between.

Kapton has been widely used, with minimal adjustments, in a large part of the experimental studies on Li–S batteries. The S K-edge is at ca. 2470 eV, and operando experiments in the sub 5 keV range are made quite difficult by the low penetration depth of x-rays. Beryllium offers a larger penetration depth and therefore is often preferred. An example of an electrochemical cell that can work with liquid electrolytes in the tender x-ray region can be found in the work by Nakanishi et al [98]. In the sub 1 keV energy region, an illustration of an electrochemical cell for in situ XAS can be found in [99].

Other types of cells comprise the Argonne multipurpose in situ x-ray electrochemical cell [100], radially accessible tubular in situ x-ray cell [101], soft XAS cells [102] and capillary-type cells [103].

Another point that needs to be addressed in planning an operando XAS experiment is the possible damage that could be induced on the battery materials by the x-ray beam. Beam damaging is in general a stochastic process, which is not fully understood and involves different mechanisms, such as radical formation, bond-breaking, local heating, etc. Here, we note that beam damage induced by x-rays is more likely in soft materials, such as polymers, and therefore can possibly occur in polymeric electrolytes. In addition, x-ray beam damage can induce changes in the oxidation state of 3d metals.

Concerning the beamline, access to synchrotron radiation facilities is usually based on reviewed proposals. In table 1, we summarize the main instruments available at synchrotron radiation sources. We envisage that this list could help the reader in planning an operando XAS experiment, with the advice to discuss it in advance with the beamline staff. They are usually very keen on informing the potential user on what can and cannot be done.

6. Perspectives and concluding remarks

Detailed knowledge of the mechanisms of the working of a battery is a fundamental prerequisite for its engineering and performance improvement. Indeed, while thermodynamics, via the Nernst equation, gives instruments for determining the equilibrium potential of a given electrochemical reaction, electrochemical reactions that actually take place in a battery are outside equilibrium. A battery under load is not in equilibrium and therefore the measured voltage and battery capacity may differ significantly from the equilibrium values, and the further from equilibrium (i.e. the higher the charge or discharge currents), the larger the deviation between the battery voltage and capacity equilibrium and the realistic battery voltage may be. This is the origin of polarization. Polarization effects have a significant impact on battery operation, and factual reaction mechanisms, via the kinetics of electrochemical reaction(s) and mass transport inside the battery, are crucial in determining the polarization. Moreover, side reactions can occur that are different to the main oxidation and reduction reactions comprising a battery. Side reactions are a formidable source of detrimental effects on capacity and coulombic efficiency. XAS, with its unique ability of determining chemical and oxidation states of elements, coupled with elemental selectivity, is a unique tool for resolving these problems. We have also shown that operando XAS experiments are rather easy to perform; provided
Table 1. The list of synchrotron radiation beamlines used for performing the experiments reviewed in this work. For operational beamlines, the URL of the website is given. Non-operational beamlines are marked with asterisks; double asterisks mark beamlines not available at present for XAS experiments.

| Synchrotron radiation facility | Beamline/website | Energy range (keV) | References |
|-------------------------------|------------------|-------------------|------------|
| APS (USA)                     | X18A*            | 5–25              | [33, 77, 88] |
|                               | X19A*            | 2.1–17            | [62]       |
|                               | 8BM–TES          | 2–5               | [80]       |
|                               | www.bnl.gov/psbeamlines/beamline.php?r=8-BM 4–3 | 2.4–11 | [68] |
|                               | www.ssrslslac.stanford.edu/content/beam-lines/bH-3 14–3a | 2.1–5 | [71] |
| CHESS (USA)                   | F3*              | 6–30              | [51]       |
| ALS (USA)                     | 8.0.1            | 0.08–1.25         | [34, 66, 76, 91, 93, 99] |
|                               | 9.3.1**          | 2.3–6             | [63, 66]   |
|                               | 10.3.2           | 2.1–17            | [66]       |
|                               | 6.3.1*           | 0.25–2            | [66, 89]   |
|                               | www.als.lbl.gov/beamlines/6-3-1/ 5.3.1 | 0.6–2 | [66, 73, 74, 94] |
| SPRING–8 (Japan)              | 20BM             | 2.7–32.7          | [45, 78, 86, 92] |
|                               | 131DE            | 2.4–28            | [60]       |
|                               | www.aps.anl.gov/Beamlines/Directory/Details/beamline_id=32 | 0.17–3.3 | [90] |
|                               | 131DE            | 2.4–28            | [60]       |
|                               | www.aps.anl.gov/Beamlines/Directory/Details/beamline_id=62 | 0.17–3.3 | [90] |
|                               | BL27SU           | www.spring8.or.jp/wkg/BL27SU/instrument/lang-en/INS-000000287/instrument_summary_view | 5–37 | [35] |
|                               | BL39XU           | www.spring8.or.jp/wkg/BL39XU/instrument/lang-en/INS-000000312/instrument_summary_view | 5–37 | [35] |
| SR center Ritsumeikan University (Japan) | BL–10 | 1–4.5 | [98] |
|                               | www.ritsumei.ac.jp/acd/re/srcbeamline.html BL–11 www.ritsumei.ac.jp/acd/re/srcbeamline.html | 0.5–1.2 | [75] |

(Continued.)
| Synchrotron radiation facility | Beamline/website | Energy range (keV) | References |
|-------------------------------|------------------|--------------------|------------|
| PETRA III (Germany)           | P65              | 4–44               | [52]       |
|                               | https://photon-science.desy.de/facilities/petra_iii/beamlines/p65_applied_xafs/index_eng.html | | |
|                               | P64              | 4–45               | [84]       |
|                               | https://photon-science.desy.de/facilities/petra_iii/beamlines/p64_advanced_xafs/index_eng.html | | |
| ANKA (Germany)                | XAS              | 2.4–27             | [47]       |
|                               | www.anka.kit.edu/992.php | | |
| BESSY (Germany)               | mySpot           | 4–25               | [39]       |
|                               | www.helmholtz-berlin.de/pubbin/igama_output?modus=einzel&sprache=en&gid=1626&typoid=35512 | | |
|                               | KMC–2            | 4–15               | [48]       |
|                               | www.helmholtz-berlin.de/pubbin/igama_output?modus=einzel&sprache=en&gid=1615 | | |
| PAL (South Korea)             | BL10C            | 4–40               | [37]       |
|                               | https://pal.postech.ac.kr/paleng/bl10C/ | | |
| SLS (Switzerland)             | microXAS         | 3–23               | [36]       |
|                               | www.psi.ch/en/sls/microxas | | |
|                               | PHOENIX          | 0.3–8              | [56, 65]   |
|                               | www.psi.ch/en/sls/phoenix | | |
| Diamond (UK)                 | B18              | 2–35               | [38]       |
|                               | www.diamond.ac.uk/Instruments/Spectroscopy/B18.html | | |
|                               | I18              | 2.05–20.5          | [71]       |
|                               | www.diamond.ac.uk/Instruments/Spectroscopy/I18.html | | |

(Continued.)
| Synchrotron radiation facility | Beamline/website | Energy range (keV) | References |
|-------------------------------|-----------------|-------------------|------------|
| **ELETTRA (Italy)**           | XAFS            | 2.4–27            | [28, 54, 61, 64, 68, 72, 104] |
|                               | [28], [54], [61], [64], [68], [72], [104] |                   |            |
|                               | www.elettra.trieste.it/it/lightsources/elettra/elettra-beamlines/xafs/xafs.html |                   |            |
| **ESRF (EU)**                 | BM30B/FAME CRG  | 4.8–40            | [57]       |
|                               | www.esrf.eu/home/UsersAndScience/Experiments/CRG/BM30.html |                   |            |
|                               | BM23            | 5–75              | [50, 81]   |
|                               | www.esrf.eu/home/UsersAndScience/Experiments/MEx/BM23.html |                   |            |
|                               | BM26A/DUBBLE CRG| 5–45              | [55]       |
|                               | www.esrf.eu/UsersAndScience/Experiments/CRG/BM26 |                   |            |
|                               | BM01B/Swiss Norwegian CRG | 6–22 | [79]       |
|                               | www.esrf.eu/UsersAndScience/Experiments/CRG/BM01/bm01-a |                   |            |
|                               | ID26            | 2.4–27            | [69, 70]   |
|                               | www.esrf.eu/UsersAndScience/Experiments/EMD/ID26 |                   |            |
| **SOLEIL (France)**           | SAMBA           | 6–35              | [26, 31, 82, 83] |
|                               | www.synchrotron-soleil.fr/en/beamlines/samba |                   |            |
|                               | ODE             | 3.5–25            | [26]       |
|                               | www.synchrotron-soleil.fr/en/beamlines/ode |                   |            |
|                               | LUCIA           | 0.8–8             | [26]       |
|                               | www.synchrotron-soleil.fr/en/beamlines/lucia |                   |            |
|                               | ROCK            | 4.5–40            | [29, 30, 43, 46, 84] |
|                               | www.synchrotron-soleil.fr/en/beamlines/rock |                   |            |
| **SSRF (China)**              | BL14W1          | 4.5–40            | [87]       |
|                               | https://e-ssrf.sinap.cas.cn/beamlines/bl14w1/ |                   |            |
the experimental constraints (penetration depth, concentration of photo-absorber, etc) are met, the information that can be obtained is invaluable.

The potential development of operando XAS applied to batteries involves the attainment of finer details concerning the electronic structure and chemical state, which are, in principle, contained in a XANES spectrum. These details are attractive to obtain as they can be indicative of the reaction mechanisms. For example, the exact white-line intensity in the K-edge XANES spectrum of 3d transition metals is related to slight deformations and distortions of the local coordination polyhedron. However, the extraction of this information is a complex issue because of the intrinsic difficulty in simulating a XANES spectrum from first principles and for the fact that in an operando experiment, a variety of different chemical environments are unavoidably probed at the same time. While the first issue can in principle be solved by using model compounds, advanced calculation tools and/or a combination thereof, the second issue requires advanced experimental probes, such as nano-beams to map the spatial distribution of the different chemical environments.

HERFD-XAS and RIXS will play a crucial role in the detailed understanding of the battery chemistry. A review of the recent (updated to 2018) advances in the application of RIXS to the study of battery chemistry can be found in [105] while some more recent progress is discussed in [106] and [11].

In the soft x-ray regime, the applications of operando XAS (soft-XAS) are much more limited, mainly due to the low penetration depth of x-rays with energy lower than 1 keV and the severe vacuum limitations thereof. However, soft-XAS would provide invaluable information for a complete understanding of the mechanisms of phenomena taking place at material surfaces and interfaces, and would be of fundamental use in battery science. Indeed, light elements (O, N, C) have absorption edges in the sub 1 keV energy range, and the L_{2,3} edges of transition metals, where the 3d valence levels show up with strong dipole-allowed excitations, are in the same range. The development of operando cells for performing experiments in the soft x-ray regime is therefore highly desirable for a complete monitoring of all the valence levels of most of the battery materials [17, 76, 103].

A final remark concerns the experimental data treatment. Operando XAS experiments can produce large data sets that are difficult to handle. Chemometric techniques can be extremely useful in this case. In addition to the examples given above, the reader may be interested in further examples [81, 104].

Data availability statement

No new data were created or analyzed in this study.

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ORCID iDs

Paolo Ghigna  https://orcid.org/0000-0002-8680-7272
Eliana Quartarone  https://orcid.org/0000-0002-1192-7747

References

[1] Tian Y et al 2021 Promises and challenges of next-generation ‘beyond Li-ion’ batteries for electric vehicles and grid decarbonization Chem. Rev. 121 1623–69
[2] Kim T, Song W, Son D Y, Ono L K and Qi Y 2019 Lithium-ion batteries: outlook on present, future, and hybridized technologies J. Mater. Chem. A 7 2942–64
[3] Zhang J-G, Xu W and Henderson W A 2017 Lithium Metal Anodes and Rechargeable Lithium Metal Batteries (Springer Series in Materials Science vol 249) (Berlin: Springer) pp 1–194
[4] Julien C, Mauger A, Viji A and Zaghib K 2016 Lithium Batteries: Science and Technology (Berlin: Springer) pp 1–619
[5] Armand M et al 2020 Lithium-ion batteries—current state of the art and anticipated developments J. Power Sources 479 228708
[6] Zhao J, Cano M, Giner-Casares J J, Luque R and Xu G 2020 Electroanalytical methods and their hyphenated techniques for novel ion battery anode research Energy Environ. Sci. 9 2618–56
[7] Talai E, Bonnick P, Sun X, Pang Q, Liang X and Nazaar L F 2017 Methods and protocols for electrochemical energy storage materials research Chem. Mater. 29 90–105
[8] Gong Z and Yang Y 2018 The application of synchrotron X-ray techniques to the study of rechargeable batteries J. Energy Chem. 27 1566–83
[9] Boebinger M G, Lewis J A, Sandoval S E and McDowell M T 2020 Understanding transformations in battery materials using in situ and operando experiments: progress and outlook ACS Energy Lett. 5 335–45
[10] Liu D et al 2019 Review of recent development of in situ/operando characterization techniques for lithium battery research Adv. Mater. 31 1806620

[11] Roychoudhury S et al 2021 Deciphering the oxygen absorption pre-edge: a caveat on its application for probing oxygen redox reactions in batteries Energy Environ. Mater. accepted (https://doi.org/10.1002/eenm.212119)

[12] Li W, Lutz D M, Wang L, Takeuchi K J, Marschilok A C and Takeuchi E S 2020 Peering into batteries: electrochemical insight through in situ and operando methods over multiple length scales Joule 5 77–88

[13] Lin F et al 2017 Synchrotron x-ray analytical techniques for studying materials electrochemistry in rechargeable batteries Chem. Rev. 117 13123–86

[14] Shadliz, Zhao E, Zhou Y-N, Xu X, Yang Y, Hu E, Bak S, Gu L and Yang X-Q 2018 Advanced characterization techniques for sodium-ion battery studies Adv. Energy Mater. 8 1702588

[15] Tripathi A M, Su W N and Hwang B J 2018 In situ analytical techniques for battery interface analysis Chem. Soc. Rev. 47 736–51

[16] Hu E, Wang X, Yu X and Yang X-Q 2018 Probing the complexities of structural changes in layered oxide cathode materials for Li-ion batteries during fast charge—discharge cycling and heating Acc. Chem. Res. 51 290–8

[17] Bak S-M, Shadliz, Lin R, Yu X and Yang X-Q 2018 In situ/operando synchrotron-based x-ray techniques for lithium-ion battery research npg Asia Mater. 10 563–80

[18] Reddy M V, Subba Rao G V and Chowdari B V R 2013 Metal oxides and oxysalts as anodes for Li-ion batteries Chem. Rev. 113 5364–457

[19] Fergus J W 2010 Recent developments in cathode materials for lithium ion batteries J. Power Sources 195 939–54

[20] Cheng X B, Zhang R, Zhao C Z and Zhang Q 2017 Toward safe lithium metal anode in rechargeable batteries: a review Chem. Rev. 117 10403–73

[21] Bañares M A, Guerrero-Pérez O M, Luis J, Fierro G and Cortez G G 2002 Raman spectroscopy during catalytic operations with porous materials J. Mater. Chem. 12 3357–42

[22] Bañares M A 2007 Preface Catal. Today 15 1–2

[23] van Bokhoven J A and Lamberti C 2015 13X-Ray Absorption and X-Ray Emission Spectroscopy: Theory and Applications vol 1–2 (New York: Wiley)

[24] Bauer M 2014 HERFD-XAS and valence-to-core-XES: new tools to push the limits in research with hard x-rays! Phys. Chem. Chem. Phys. 16 13827–37

[25] Felse M, Iadecola A, Sougrati M T, Conti P, Giorgetti M and Steiviano L 2019 Applying chemometrics to study battery materials: towards the comprehensive analysis of complex operando datasets Energy Storage Mater. 18 328–37

[26] Ouvrard G, Zerrouki M, Soudan P, Lestriez B, Masquelier C, Morcrette M, Hamelet S, Belin S, Flank A M and Baudelet F 2013 Heterogeneous behaviour of the lithium battery composite electrode LiFePO4 J. Power Sources 226 19–21

[27] Shapovalov V V, Guda A A, Kosova N V, Kubrin S P, Podgornova O A, Abaroa A M, Lamberti C and Soldatov A V 2020 Laboratory operando Fe and Mn K-edges XANES and Mössbauer studies of the LiFePO4/Fe2O3 cathode material Radiat. Phys. Chem. 175 108065

[28] Iadecola A, Perea A, Aldon L, Aquilanti G and Steiviano L 2017 Li deinsertion mechanism and Jahn-Teller distortion in LiFePO4: an operando x-ray absorption spectroscopy investigation J. Phys. D: Appl. Phys. 50 144004

[29] Boivin E, Iadecola A, Fauth F, Chotard J N, Masquelier C and Croguennec L 2019 Redox paradox of vanadium inavorite LiVPO4F1−x−y, Chem. Mater. 31 7367–76

[30] Asat G, Iadecola A, Delacourt C, Dedryvère R and Tarascon J M 2017 Decoupling cationic-anionic redox processes in a model Li-rich cathode via operando x-ray absorption spectroscopy Chem. Mater. 29 9714–24

[31] Koga H, Crogueneuc L, Menétrier M, Mannessiez P, Weil F, Delmas C and Belin S 2020 Operando x-ray absorption study of the redox processes involved upon cycling of the Li-rich layered oxide Li1.20Mn0.15Co0.15Ni0.15O2 in Li ion batteries J. Phys. Chem. C. 118 5700–9

[32] Chen C H, Pan C J, Su W N, Rick J, Wang C J, Venkateswarlu M, Lee J F and Hwang B J 2015 Operando x-ray diffraction and x-ray absorption studies of the structural transformation upon cycling excess Li layered oxide LiLi1.42Co0.19Ni0.19Mn0.19O2 in Li ion batteries J. Mater. Chem. A 3 8613–26

[33] Yu X et al 2014 Understanding the rate capability of high-energy density Li-rich layered Li2.15Ni0.15Co0.15Mn0.15O2 cathode materials Adv. Energy Mater. 4 e1300950

[34] Li N, Sallis S, Papp J K, McCloskey B D, Yang W and Tong W 2020 Correlating the phase evolution and anodic redox in Co-free Ni-rich layered oxide cathodes Nano Energy 77 105365

[35] Nishimura Y F, Oka H, Nonaka T, Makimura Y and Dohmae K 2019 Hard x-ray spectroscopic methods using emitted x-ray to understand charge compensation in positive electrode materials for lithium-ion batteries J. Power Sources 434 226721

[36] Nowack I, Grolimund D, Samson V, Marone F and Wood V 2016 Rapid mapping of lithium dynamics in transition metal oxide particles with operando x-ray absorption spectroscopy Sci. Rep. 6 1–9

[37] Jin W, Myeong S, Hwang J, Jung H, Sung J, Yoo Y, Kim M G and Cho J 2020 Unraveling the rapid redox behavior of Li-excess 3d-transition metal oxides for high rate capability Adv. Energy Mater. 10 1904092

[38] Kim T, Song H, Lunt A J G, Cihen G, Dent A J, Lu I. and Korusumky A M 2016 In operando x-ray absorption spectroscopy study of charge rate effects on the atomic environment in graphene-coated Li-rich mixed oxide cathode Mater. Des. 15 231–42

[39] Schroeder M, Eames C, Tomsett D A, Lieser G and Islam M S 2013 Li,FeFx (x = 2, 3, 4) battery materials: structural, electronic and lithium diffusion properties Phys. Chem. Chem. Phys. 15 20473–9

[40] Chan C K, Peng H, Liu G, McInrath K, Zhang X F, Huggins R A and Cui Y 2008 High-performance lithium battery anodes using silicon nanowires Nat. Nanotechnol. 3 31–5

[41] Chou C-Y and Hwang G S 2014 On the origin of the significant difference in lithiation behavior between silicon and germanium J. Power Sources 263 252–8

[42] Huang J Y et al 2010 In situ observation of the electrochemical lithiation of a single SnO2 nanowire electrode Science 330 1510–20

[43] Louai A C, Louai N, Fraisse B, LAhoued A, Iadecola A, Johannson P, Steiviano L, Seznec V and Moncoutid I 2018 Electrochemical lithiation of Ge: new insights by operando spectroscopy and diffraction J. Phys. Chem. C 122 3709–18

[44] Silberstein K E, Lowe M A, Richards B, Gao J, Hanrath T and Abrunh H D 2015 Operando x-ray scattering and spectroscopic analysis of germanium nanowire anodes in lithium ion batteries Langmuir 17 2028–35

[45] Li T et al 2020 In situ and operando investigation of the dynamic morphological and phase changes of a selenium-doped germanium electrode during (de)lithiation processes J. Mater. Chem. A 8 750–9
[78] Karan N K, Slater M D, Dogan F, Kim D, Johnson C S and Balasubramanian M 2014 Operando structural characterization of the lithium-substituted layered sodium-ion cathode material P2-Na0.85Li0.15Ni0.12Mn0.66O2 by x-ray absorption spectroscopy J. Electrochem. Soc. 161 A1107

[79] Sottmann J, Bernal F L M, Yusenko K V, Herrmann M, Emerich H, Wragg D S and Margadonna S 2016 In operando synchrotron XRD/XAS investigation of sodium insertion into the prussian blue analogue cathode material Na0.52Mn[Fe(CN)6]0.68≈0.32H2O Electrochim. Acta 200 305–13

[80] Lin C-H et al 2020 Operando structural and chemical evolutions of TiS2 in Na-ion batteries J. Mater. Chem. A 8 12339–50

[81] Dixon D, Avila M, Ehrenberg H and Bhashkar A 2019 Difference in electrochemical mechanism of SnO2 conversion in lithium-ion and sodium-ion batteries: combined in operando and ex situ XAS investigations ACS Omega 4 9731–8

[82] Fehse M, Sougrati M T, Darwiche A, Gabaudan V, La Fontaine C, Monconduit L and Stievano L 2018 Elucidating the origin of superior electrochemical cycling performance: new insights on sodiation-desodiation mechanism of SnSb from: operando spectroscopy J. Mater. Chem. A 6 8724–34

[83] Darwiche A et al 2018 The electrochemical sodiation of Sb investigated by operando x-ray absorption and 121Sb mössbauer spectroscopy: what does one really learn? Batteries 4 25

[84] Darwiche A et al 2019 Operando x-ray absorption spectroscopy applied to battery materials at ICGM: the challenging case of Bi2Sb’s sodiation Energy Storage Mater. 21 1–15

[85] Zhou D, Wang J, Liu X, He X, Sun F, Murzin V, Schumacher G, Yao X, Winter M and Li J 2020 Operando x-ray absorption spectroscopy investigations on Na0.8Li0.2Fe1.9Mn0.1O2 positive electrode materials for sodium and sodium-ion batteries J. Power Sources 473 228557

[86] Xu J, Ma C, Balasubramanian M and Meng Y S 2014 Understanding Na0.5TiO2 as an ultra-low voltage anode material for a Na-ion battery Chem. Commun. 50 12564–7

[87] Liu X, Wang L, Yu P, Tian C, Sun F, Ma J, Li W and Fu H 2018 A stable bifunctional catalyst for rechargeable zinc–air batteries: iron–cobalt nanoparticles embedded in a nitrogen-doped 3D carbon matrix Angew. Chem., Int. Ed. 57 16166–70

[88] Park J, Park M, Nam G, Kim M G and Cho J 2017 Unveiling the catalytic origin of nanocrystalline yttrium ruthenate pyrochlore as a bifunctional electrocatalyst for Zn-Air batteries Nano Lett. 17 3974–81

[89] Arthur T S et al 2017 Interfacial insight from operando XAS/TEM for magnesium metal deposition with borohydride electrolytes Chem. Mater. 29 7183–8

[90] Hattori M et al 2018 Role of coordination structure of magnesium ions on charge and discharge behavior of magnesium alloy electrode J. Phys. Chem. C 122 25204–10

[91] Kao L C et al 2020 In-situ/operando x-ray absorption spectroscopic investigation of the electrode/electrolyte interface on the molecular scale Surf. Sci. 702 121720

[92] Bomnick P, Blanc L, Vajargah S H, Lee C-W, Sun X, Balasubramanian M and Nazar L F 2018 Insights into Mg2+ intercalation in a zero-strain material: thiospinel Mg2Zr2S4 Chem. Mater. 30 4683–93

[93] Wang H et al 2020 Reversible electrochemical interface of Mg metal and conventional electrolyte enabled by intermediate adsorption ACS Energy Lett. 5 200–6

[94] Xu Y et al 2019 In situ x-ray absorption spectroscopic investigation of the capacity degradation mechanism in Mg/S batteries Nano Lett. 19 2928–34

[95] Leriche J B et al 2010 An electrochemical cell for operando study of lithium batteries using synchrotron radiation J. Electrochem. Soc. 157 A606

[96] Tan C, Daemi S R, Taiwo O O, Heenan T M M, Brett D J L and Shearing P R 2018 Evolution of electrochemical cell designs for in-situ and operando 3D characterization Materials 11 2157

[97] Northrup P, Lerii A and Tapper R 2016 Applications of ‘Tender’ energy (1–5 keV) x-ray absorption spectroscopy to resonant inelastic scattering XAS data for the investigation of the lithiation mechanisms in high entropy oxides Surf. Sci. 659 1217–20

[98] Nakashima K, Kato D, Arai H, Tanida H, Mori T, Ohta T and Ogumi Z 2014 Novel spectro-electrochemical sources of BiSb’s sodiation Electrochim. Acta 106 294–300

[99] Vasconcelos F, Fracchia M, Pianta N, Ghigna P, Quartarone E and D’Angelo P 2020 Multivariate curve resolution analysis of operando XAS data for the investigation of the lithiation mechanisms in high entropy oxides Chem. Phys. Lett. 760 137968

[100] Yang W and Devereaux T P 2018 Anionic and cationic redox and interfaces in batteries: advances from soft x-ray absorption spectroscopy to resonant inelastic scattering J. Power Sources 389 188–97

[101] Dai K et al 2019 High reversibility of lattice oxygen redox quantified by direct bulk probes of both anionic and cationic redox reactions Joule 3 518–41