

Short communication

Lithium K(1s) synchrotron NEXAFS spectra of lithium-ion battery cathode, anode and electrolyte materials

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Abstract

The lithium(1s) K-edge X-ray absorption spectra of lithium-ion battery relevant materials (Li metal, Li₃N, LiPF₆, LiC₆, and LiMn_{1.90}Ni_{0.10}O₄) are presented. The Li and LiC₆ spectra are discussed and compared with literature data. The Li in lithium-intercalated carbon LiC₆, typically used as anode battery electrode material, could be clearly identified in the spectrum, and a presumed purely metallic character of the Li can be ruled out based on the chemical shift observed. The Li in corresponding cathode electrode materials, LiMn_{1.90}Ni_{0.10}O₄, could be detected with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, but the strong (self-) absorption of the spinel lattice provides an obstacle for quantitative analysis. Owing to its ionic bonding, the spectrum of the electrolyte salt LiPF₆ contains a sharp π -resonance at 61.8 eV, suggesting a distinct charge transfer between Li and the hexafluorophosphate anion. In addition, LiPF₆ resembles many spectral features of LiF, making it difficult to discriminate both from each other.

Residual electrolyte on anodes or cathodes poses a problem for the spectroscopic analysis of the electrodes, because its Li spectrum overshadows the spectral features of the Li in the anode or cathode. The electrolyte must be removed from electrodes prior to spectroscopic analysis.

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1. Introduction

X-ray absorption spectroscopy has been widely used for the characterization of battery electrode materials. Particularly the cathodes of lithium-ion intercalation batteries have been the subject of such studies, i.e. lithium 3d-metal oxides, with Ni, Co, Mn, Cr, and Fe being the most pertinent 3d metals for these applications [1].

Study of the X-ray absorption of 3d metals in the cathodes proved rewarding, in particular in connection with in situ studies and X-ray diffraction [2]. A wealth of information on structural changes in the oxide lattices as a result of charging and discharging has been obtained. Carbon, a typical electrode material, has also been extensively studied with synchrotron techniques [3,4].

Lithium, the main player in this game, has been very elusive so far [4]. “Where does the Li go?”, as Claye and Fischer have put it recently [5], remains a key question in lithium-ion battery research. There exist few publications on the Li K-edge absorption of lithium [6–23] and some lithium compounds, and few only with explicit reference to battery applications [9–12]. The reasons for this discrepancy are manifold.

The near-edge X-ray absorption fine structure (NEXAFS) spectroscopy experiments require typically synchrotron

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radiation. The X-ray absorption K-edge of Li is around 55 eV, a very low energy compared to K-edges and L-edges of the 3d metals. The design of the majority of synchrotrons favors hard X-ray studies. In addition, soft X-ray studies are particularly surface sensitive and require sometimes additional instrumentation. While hard X-ray studies are relatively straightforward, meaningful detection of the Li K-edge can require pushing the limits.

Due to the difficulties associated with obtaining direct Li X-ray absorption data from lithium compounds, researchers tried to obtain information on the bonding state of Li via the bonding state of its neighbors, such as F, C, or O. The position of an absorption peak of an element in a spectrum can aid in the assignment of its functionalities, such as with C(1s) NEXAFS spectroscopy for carbon functional groups.

One recent study in Ref. [24] suggests formation of LiF on $\text{Li}_{1+x}\text{V}_3\text{O}_8$ after electrochemical cycling, based on F(1s) NEXAFS. The authors of that study compared pristine electrodes and cycled electrodes, but did not disclose whether the pristine electrode was ever exposed to electrolyte such as LiPF_6 . A similar approach is found in Ref. [25], where the authors studied the K-edges of oxygen and fluorine of the cathodes and suspected LiF on the cycled electrodes, although no lithium spectra were recorded. Comparison of pristine and cycled electrodes must be done with caution, and it could be a premature conclusion that LiF is formed, when it is only based on the spectra of fluorine, which may be present in the polymer binder and electrolyte.

More examples of how constituents in the battery system can obscure data are available in Refs. [26,4,27]. We have recently shown how the oxidation state of Mn at the LiMn_2O_4 surface can be affected by just preparing the electrode, i.e. mixing of oxides with carbon black, without any further steps such as cycling. Thereafter, the spectra of the manganese indicated a reduction of the Mn at the particle surface [26]. In Ref. [4], dimethyl carbonate (DMC) was used as electrolyte solvent. A sharp resonance at 292 eV in the C(1s) spectra was believed to be indicative of Li_2CO_3 , although it is only evidence for a carbonate species per se [28], which simply could be from the DMC in the electrolyte. The authors did not disclose whether they removed the electrolyte prior to the NEXAFS studies. In Ref. [27], C(1s) and O(1s) spectra were used to imply formation of Li_2CO_3 as a surface intermediate on a $\text{Li}_x\text{Ni}_{1-x}\text{O}$ catalyst. Here, too, no lithium spectra were recorded.

NEXAFS data per se are not always sufficient to make conclusions about the presence of specific phases in a material or on its surface, in particular if electrode materials were exposed to electrolyte that can be mistaken for newly formed species. It would be somewhat stretched, therefore, to conclude from carbonate in a C(1s) spectrum that lithium would be a corresponding cation, for instance, such as in Li_2CO_3 , or from a F(1s) spectrum, that LiF or LiPF_6 is formed, when the electrolyte was not completely removed.

Early X-ray absorption and emission studies on lithium were carried out by Sonntag [7] and Krisch et al. [8], for instance. More recent X-ray absorption studies were done by

Tsuji et al. [9–12]. They measured Li halides and found a sharp peak at 60 eV, and a broad peak at higher energies. Supported by molecular orbital calculations, they assigned these peaks to the Li(1s) valence band free orbital transitions [9].

We present here Li K-edge data on a set of cathode, anode, and electrolyte materials. Lithium metal has been used in the past as the anode material in lithium-ion batteries, and was later replaced by Li-containing materials such as Li-intercalated carbon and lithium-graphite for safety reasons. Lithium-nitride was suggested as electrode material already more than 20 years ago [29]. LiPF_6 is often used as electrolyte for lithium batteries. Finally, LiMn_2O_4 and other lithium/transition metal-oxides have been studied extensively by X-ray absorption with respect to the transition metal K-edges. For these materials we have recorded Li K-edge spectra.

2. Experimental equipment and procedures

2.1. Sample preparation

For the lithium metal spectrum, a 3 mm × 3 mm, 100 μm thick piece of Johnson Matthey battery grade lithium foil was mounted on a sample holder in an Argon-filled glove box and then transferred to the NEXAFS beamline in an Argon-filled load lock tube, which then was connected to UHV and evacuated. The lithium foil had a shiny surface right before acquisition of the spectra, and showed no visible signs of contamination or oxidation.

Li_3N fine powder was dispersed over carbon tape and mounted on one sample holder. Battery electrolyte (Merck, LiPF_6 crystals dissolved in ethylene carbonate and di-methyl carbonate) was deposited on a different sample holder; after evaporation of the solvent, a stain of dried LiPF_6 salt remained on the sample holder.

For cathode materials, $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ ($x=0.10, 0.08,$ and 0.05) spinel powders were synthesized by Li_2CO_3 , MnO_2 , and NiO (CMD IC#5, Japan Metals and Chemical) in the stoichiometric amounts and heating it in a muffle furnace with air at 1123 K and subsequent cooling to ambient temperature [2,26].

LiC_6 battery anodes were prepared electrochemically in a swagelok cell as follows [30–32]: the active material was natural graphite (SL20, Superior Graphite Co.). The anodes consisted of graphite (90%), polyvinylidene fluoride (PVDF) binder (10%, Kureha 9130) and Cu foil current collector (thickness 25 μm). Slurries for electrode casting were prepared from a mixture of graphite and PVDF dissolved in 1-methyl-2-pyrrolidinone (NMP). They were spread onto 25 μm thick Cu foil and dried under vacuum at 120 °C for 12 h. After drying, the electrodes were compressed by a roll press. All cells were assembled for testing in an Argon-filled glove box.

A 100 μm thick lithium foil was used as counter electrode and lithium source. A cell was assembled with a porous polypropylene film (Celgard 2500) separator and Merck LiPF_6 electrolyte in a swagelok cell, showing an open circuit potential of around 3 V (versus Li/Li^+). A typical voltamogram is shown in Fig. 1. The graphite electrode was lithiated by discharging with respect

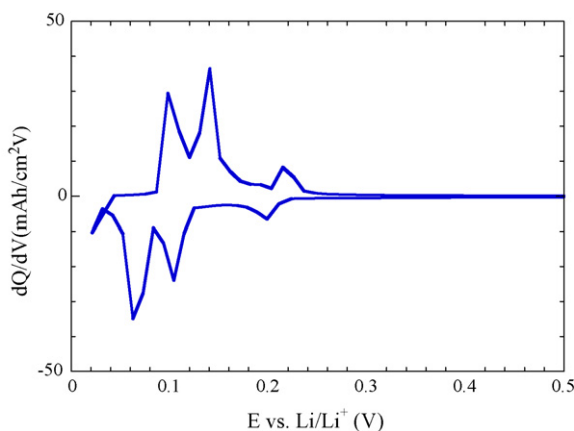


Fig. 1. Cyclic voltamogram for lithium intercalation in natural graphite.

to the Li counter electrode to 0.01 V. Five charge–discharge cycles were run by an Arbin battery cycler before the lithiated graphite electrode was removed at 0.01 V in the Argon-filled glove box. This lithiated graphite electrode had the well known yellowish golden surface, representative of Stage I LiC_6 . Before analysis, the lithiated graphite electrode was fully rinsed with DMC to remove the residue of electrolyte and soluble species, and then dried in the glove box.

Lithium intercalates into graphite and can form a compound with a stoichiometry of up to LiC_6 . The LiC_6 electrode is safer for cell operation than a metal lithium electrode, and has a cell potential only 5% lower than a cell with a lithium electrode [33]. Electrochemical lithiation of graphite is a relatively well studied multi stage process, although some fundamental questions remain open [34]. The Li content, i.e. chemical composition is a discontinuous function of the applied potential. By discharge of the carbon electrode to 0.01 V (versus Li metal) from OCV (around 3 V) or about 0.7–0.8 V (after 1 cycle), most of the lithium can be inserted between graphite layers. It is converted from LiC_{72} through LiC_{36} (around 0.2 V) and LiC_2 (around 0.1 V) to LiC_6 .

2.2. NEXAFS experiment

NEXAFS spectra were recorded at beamline 4.0.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory, with the storage ring operated at 1.5 GeV (Li, Li_3N , LiPF_6) or 1.3 GeV electron energy, respectively. Absorption was detected in the sample current mode (“target current spectroscopy”) in steps of 0.1 eV, with an energy resolution of 0.05 eV. Three scans of every sample were averaged. An aluminium mesh was used to monitor the incident intensity during recording of spectra for background subtraction. Its strong absorption by the L_2 $2p_{1/2}$ and L_3 $2p_{3/2}$ edges at 72.95 and 72.55 eV served for energy calibration. The residual pressure in the UHV system was typically 10^{-10} mbar.

Our spectra presented here were acquired by the more bulk sensitive target current detection technique. They are compared with energy loss and inelastic X-ray scattering data. Minor shifts on the energy axis calibration cannot be ruled out.

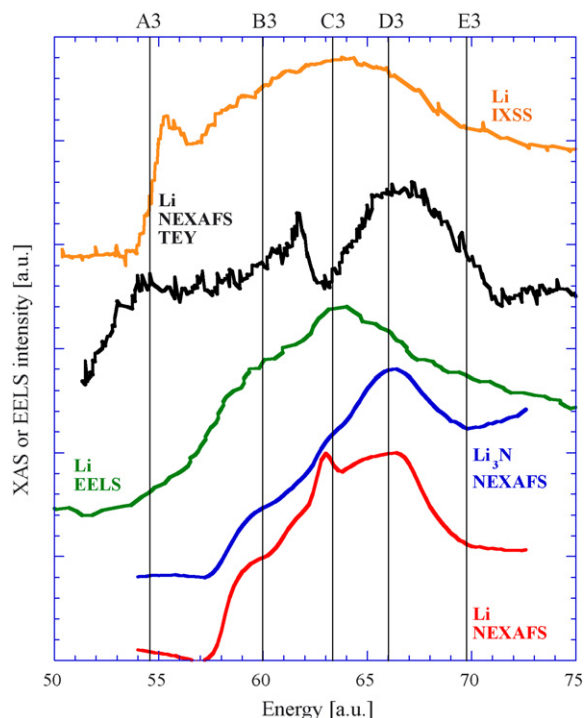


Fig. 2. Bottom to top: our NEXAFS $\text{Li}(1s)$ spectra of Li metal and Li_3N ; EELS spectrum of Li by Hightower et al. [18], Li NEXAFS of Tsuji et al. [9], IXSS of Li by Schülke et al. [14].

3. Results and discussion

3.1. Lithium metal

Our NEXAFS spectrum of the lithium metal is shown in Fig. 2, along with spectra obtained by other groups. The expected absorption edge at 55 eV [14,15] is resolved, but with very low intensity only. Fine structures are observed at around 59, 63, and 65 eV. Our experimental spectrum is in fair quantitative agreement with the NEXAFS for lithium metal experimentally found, calculated and discussed recently by Tsuji et al. [10], and EELS structures as observed by Grunes et al. [17], and Hightower et al. [18]. Our peak assignment and labeling in Fig. 2 follows the notation in [10], where the authors state that their Li spectra obtained with electron yield differ from the spectra obtained by Skinner and Johnston [16] and Haensel et al. [20], possibly due to surface contamination of their sample and the enhanced surface sensitivity of the electron yield detection technique. On the other hand, Hightower et al. [18] claim that their EELS spectra represent the bulk state of lithium. All aforementioned spectra, including our own NEXAFS spectra, show no significant spectral differences, as far as peak positions are concerned.

Under ambient conditions, lithium metal will slowly react with nitrogen, water and carbon dioxide. Depending on the ambient conditions, in particular on the extent of humidity, either Li_3N (black) or $\text{LiOH}\cdot\text{H}_2\text{O}$ (white) or Li_2CO_3 (white) will form. Included in Fig. 2 is the spectrum of Li_3N . The peaks of the metal are more pronounced, but they are at the same positions as those for Li_3N . Particularly B3, C3, and D3 are well reproduced.

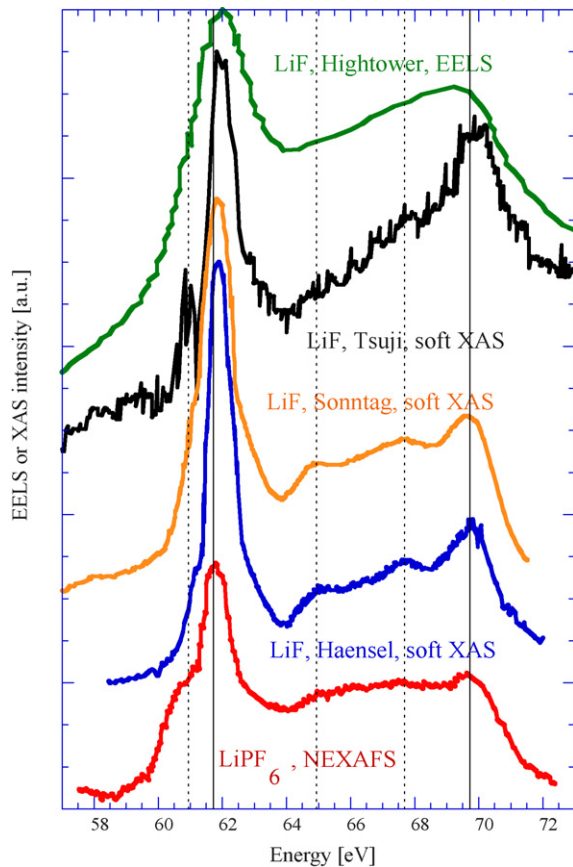


Fig. 3. Bottom to top: our NEXAFS Li(1s) spectrum of LiPF₆ electrolyte, and EELS and XAS spectra from LiF [7,9,18,20].

3.2. Electrolyte

As an electrolyte, typically an ion-conducting salt is used, such as LiPF₆, dissolved in an organic solvent. The spectrum of LiPF₆ is plotted in Fig. 3 along with a number of LiF spectra from other groups, and looks entirely different from Li and Li₃N. In particular it does contain a sharp π -resonance at 61.8 eV, suggesting a distinct charge transfer between Li and the hexafluorophosphate complexion. Another interesting feature is the pronounced bump at 69.5–70 eV, which is not observed for Li or Li₃N. In addition, the entire spectrum displays a significant chemical shift towards higher energies, compared to Li and Li₃N, confirming the strong ionic character of the bonding.

The spectrum of LiPF₆ thus shows some strong similarities with the spectrum of LiF in Refs. [18] and in [9], which has two strong absorption peaks at around 63 and 70 eV and a chemical shift of about 2 eV. The chemical shift of LiF versus Li is about 2.74 eV [19,20]. Chemical intuition suggests that LiF provides a stronger ionic bond and thus a larger electron shell polarization than LiPF₆, in line with the spectral observation. The earlier observed systematic chemical shift of the white line of lithium halides by Haensel et al. supports this view [20]. The pronounced bump at 70 eV is possibly from a polaron, which is frequently observed in lithium halides [21,22] by excitation of a Li(1s) electron and simultaneous emission of a longitudinal optical exciton [7].

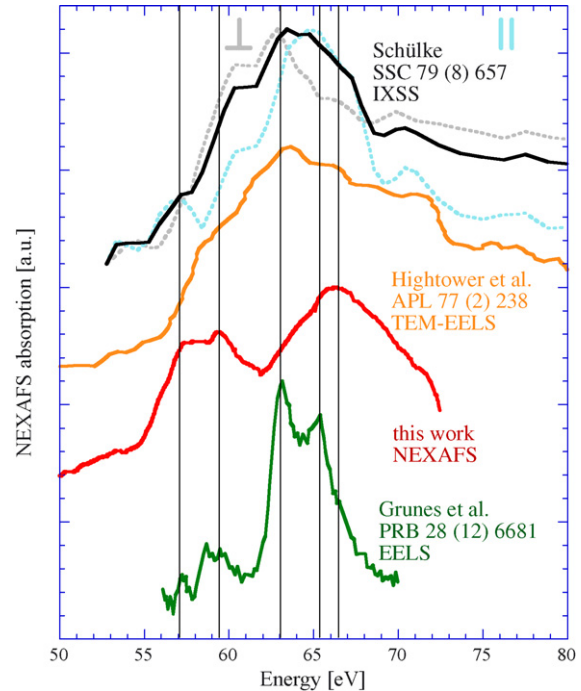


Fig. 4. Li(1s) spectra of LiC₆ [13,17,18]. Schülke's spectrum is given for perpendicular and parallel direction of the q -vector vs. the graphite c -axis (dashed curves), and for the computed convolution of both (solid, top). The second spectrum from the bottom is from our own NEXAFS studies. Grunes' spectrum [17] was obtained by subtraction of a power law background.

3.3. LiC₆

Our NEXAFS spectrum of LiC₆ sample in Fig. 4 shows two major, broad absorption structures at about 58 and 66 eV. Closer inspection reveals two resonances at 57 and 59 eV, a resonance at 66 eV, and a slight shoulder at 63 eV, in fair agreement with EELS data [17,18,23]. Grunes et al. [17] find with EELS the Li(1s) absorption peaks in LiC₆ at 57.1, 58.7, 63.0 and 65.2 eV. The two latter peaks are assigned to Li 2p symmetry due to orientation dependency by crystal field splitting.

Interaction and bonding state of Li in carbon, in particular when intercalated in graphite, have been under scrutiny for several decades. Grunes et al. believed it is possible that the C(1s) spectra of LiC₆ are influenced by the Li intercalation, though to a limited extent [17]; their weak peak at 57.2 eV (Li(1s) \rightarrow E_f dipole transitions) corresponds to our peak at 57 eV, in line with theory by Holzwarth et al. [35]. The peak at 59 eV results from Li(1s) \rightarrow unoccupied conduction band transitions, in line with the works of Grunes and Holzwarth. The features at 63 and 65 eV in our spectra are assigned by Grunes et al. [17] to dipole-allowed transitions from the Li(1s) core to the Li(2p)-derived states. Schülke et al. [13] come to similar conclusions by using inelastic X-ray scattering spectroscopy, as well as Fauster et al. [36] by angle resolved inverse photoelectron spectroscopy.

Holzwarth et al. [37] and Posternak et al. [38] go as far to claim that the supposed Li-band is native to graphite and independent of the presence of any Li in the graphite, implying there is no causal relationship between this band and lithium.

According to LDA calculations [39], charge transfer from lithium to the graphene sheets is expected, but Hightower et al. [18] believe that this charge transfer is small only, primarily because their EELS spectra of Li and LiC₆ do show fewer differences than Li metal and ionic LiF. The comparable cell potential between Li and LiC₆ [33] supports the suggestion of a small charge transfer. On the other hand, EELS performed with a TEM can be a very invasive technique and alter samples significantly [40].

Early ARPES data [41] indicate however (i) that lithium in LiC₆ is essentially Li⁺ and (ii) a distinct electron transfer from Li to C. Two independent surface sensitive XPS studies have shown that LiC₆ contains fewer spectral features than LiC₂ or lithium metal. Even a gradual evolution of spectral features with decreasing degree of intercalation of graphite with lithium was observed [42,43].

The apparent anomalous behaviour of lithium when intercalated into graphite is reflected by calculations on hyperlithiated hydrocarbon molecules [44], which, in violation of the octet rule, show that all Li atoms are bonded to the carbon central atom. However, the charges transferred from Li to carbon do not appreciably increase when lithium atoms are added into the molecule. Instead, the extra Li electrons contribute to the Li–Li bonding, forming a metallic cage around the central atom.

Given that the *extra* electrons [44] in hyperlithiated hydrocarbons, contribute more to the Li–Li bonding than to the bonding between Li and the host material, it could be possible that in LiC₆, only part of the Li atoms are indicative to the Li–C bonding, while other Li atoms exhibit more metallic bonding. The spectrum would be a superposition of a Li metal spectrum and a spectrum from a less lithiated sample, such as LiC₂, for instance. The two aforementioned XPS studies [42,43] support this view. Therefore, the less lithiated sample would differ more from a pure lithium spectrum, than a Stage I lithiated LiC₆, for instance. Our LiC₆ spectrum differs from the metal Li spectrum in as it has a large peak between 55 and 60 eV. We believe this peak could be indicative of Li–C bonding, while the broad structure at about 66 eV could possibly be from the metal-cage like Li–Li bonding [44].

3.4. Cathode materials

There are virtually no Li(1s) NEXAFS data available on Li ceramic compounds. Fig. 5 shows the Li metal spectrum, and also three spectra of LiMn_{2-x}Ni_xO₄, $x=0.10, 0.08, \text{ and } 0.05$. Spectral features are more pronounced in the Li metal than in the ceramic material. We believe that the strong absorption of Mn and Ni present a substantial barrier for the detection of the lithium. Generally, the M₂ 3p_{1/2} and M₃ 3p_{3/2} states of nickel at 68.0 and 66.2 eV could add a nickel specific absorption signature, which overlaps with the absorption of the lithium. However, the absorption by the M shell is a negligible effect, when the concentrations of Ni are small compared to the overall 3d metal content in the cathode. Our study on LiMn_{2-x}Ni_xO₄ at the Li K-edge did not reveal a systematic increase of Ni specific absorption at the M-edges as a function of Ni concentration, other than a slightly larger overall absorption.

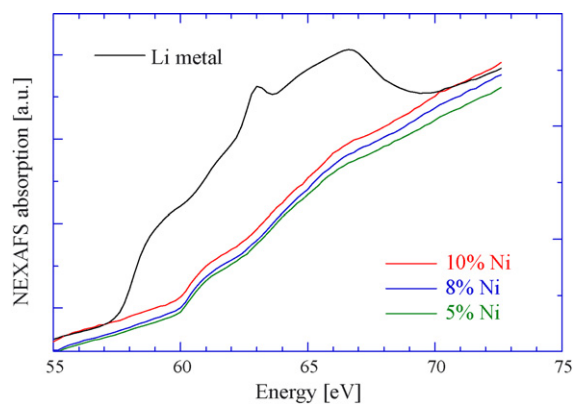


Fig. 5. Spectra of lithium metal (upper spectrum) and LiMn_{2-x}Ni_xO₄, $x=0.10, 0.08, \text{ and } 0.05$ (bottom spectrum).

While the onset of strong absorption for the Li metal is found at 57.5 eV, the onset for the LiMn_{1.90}Ni_{0.10}O₄ is found at 60 eV, suggesting a chemical shift of more than 2 eV. The next significant feature is at 66.5 eV and partially overlaps with a broad peak of the Li metal at the same energy. This feature is also observed for Li₃N. We believe that a quantitative analysis of Li(1s) spectra from such cathode materials requires spectra with very good statistical quality, which can be obtained by sufficiently long data acquisition time and subsequent averaging of spectra.

4. Conclusions

We have presented and discussed the Li(1s) NEXAFS spectra of battery relevant materials. For studies on actual battery materials, particularly electrodes that were in contact with electrolyte and operated, utmost caution with sample preparation is necessary. For instance, it is necessary to rinse the anodes or cathodes thoroughly in order to remove electrolytes, such as LiPF₆, in order to be able to assign the Li spectrum to the Li in LiC₆ anode, or Li manganate oxide cathode. Since Li(1s) NEXAFS can be a distinct surface sensitive technique, residual electrolyte on the surface will overshadow the signals from anodes and cathodes, in particular since electrodes are typically porous, and electrolyte can enter pores. One must bear this in mind in particular for studies of the solid electrolyte interface (SEI) formation on electrodes.

We believe that Li(1s) NEXAFS spectroscopy has the potential to resolve relevant issues in Li ion battery research, possibly including SEI formation, and the fate of lithium during cycling and battery degradation. We have shown that Li(1s) spectra of battery materials can be recorded and analyzed, and that significant spectral differences can be made out among different Li containing compounds. Spectral features could then aid in assignment of particular phases in a similar way as NEXAFS is used in other research disciplines.

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