

Fine structure and chemical shifts in nonresonant inelastic x-ray scattering from Li-intercalated graphite

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The authors report measurements of hard x-ray nonresonant inelastic x-ray scattering (IXS) from the Li and C 1s electrons of fully staged LiC₆ Li-intercalated graphite prepared by both chemical and electrochemical methods. They find that the Li 1s orbital shifts to higher energies relative to Li metal. Relative to graphite, the C 1s IXS for LiC₆ shows a shift for the σ -orbital threshold to lower energies, but no shift for the π^* resonance. The findings provide bulk-sensitive evidence for substantial charge transfer from the Li intercalant to the carbon host and establish important groundwork for future *in situ* electrochemical studies. © 2007 American Institute of Physics.

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A wide range of metals form intercalation compounds with sp^2 -bonded graphitic carbon. These compounds show many interesting phenomenon,^{1–3} including structural staging as the intercalant concentration increases and complex electronic properties due to the interplay of states between the graphene sheets and the interlayer regime. The recent discovery^{2,4} of superconductivity in CaC₆ and YbC₆ has renewed interest in metal intercalation of graphite, especially as regards the details of charge transfer from the metal intercalants. Li-intercalated graphite (LIG) is of particular interest both as the best studied, canonical member of this class of materials, but also due to its relevance for present day rechargeable battery technology.^{3,5} Commercial Li-ion batteries use carbonaceous materials for the negative electrode (anode). Among the various carbonaceous materials, graphite is the most attractive candidate due to its high theoretical intercalation capacity, natural abundance, durability under repeated electrochemical cycling, and low cost. The use of graphite also helps circumvent safety issues surrounding the use of a pure Li metal anode.

For these reasons, it is surprising that while the structure of LIG at different stages of intercalation is well settled,⁶ there is still often-contentious debate⁷ about the existence and details of the charge transfer between the Li intercalant and the graphite host. This situation is largely due to the extreme sensitivity of LIG to oxygen (and other contaminants) together with the surface sensitivity of many of the relevant spectroscopic techniques. Here, we overcome these problems through the use of hard x-ray nonresonant inelastic x-ray scattering (IXS), focusing on the contribution to IXS from the Li and C 1s initial states. This type of IXS is unique among the relevant core-shell spectroscopies in having in-

trinsic bulk sensitivity and easy compatibility with a wide range of sample environments. We report below measurements of the IXS from both electrochemically and chemically prepared LiC₆, together with several reference materials. Given that the industrially relevant phases of LIG are electrochemical, there is a pragmatic value in this study which goes beyond the obvious pedagogical merit; specifically, our study establishes much of the experimental groundwork for future *in situ* IXS studies of the lithiation/delithiation process in Li ion batteries.

IXS studies were performed using the multielement LERIX spectrometer at sector 20-ID (PNC/XOR) at the Advanced Photon Source. This instrument permits high-throughput measurements of IXS with ~ 1.3 eV energy resolution and ~ 0.1 eV accuracy in energy calibration.⁸ The incident x-ray flux was $\sim 5 \times 10^{12} \text{ s}^{-1}$ and typical incident photon energy is ~ 10 keV. The penetration length of ~ 10 keV x-rays in LiC₆ is well over 2 mm, ensuring a truly bulk-sensitive measurement. The valence Compton contribution to the total IXS signal has been removed through subtraction of a smooth background. Golden colored stage-1 LiC₆ samples were prepared by both chemical and electrochemical methods.⁹ Details of sample preparation, electrochemical and x-ray diffraction characterization can be found in Ref. 10.

In Fig. 1, we show the Li 1s contribution to the IXS cross section for Li metal, LiF (single crystal, Alpha Aesar), chemically prepared LiC₆ with \mathbf{q} approximately parallel to \hat{c} , chemically prepared LiC₆ with \mathbf{q} spanning 10° – 30° from the basal plane, the unwashed electrochemically lithiated LiC₆ sample, and the corresponding washed sample. Interspersed in Figs. 1(d) and 1(f) are *ab initio* calculations, as labeled. Specifically, those two curves show the result of real-space full multiple scattering calculations using a modification of FEF (Ref. 11) to allow for the nontrivial momentum transfer in IXS.¹² Due to the large mean-free path of the photoelec-

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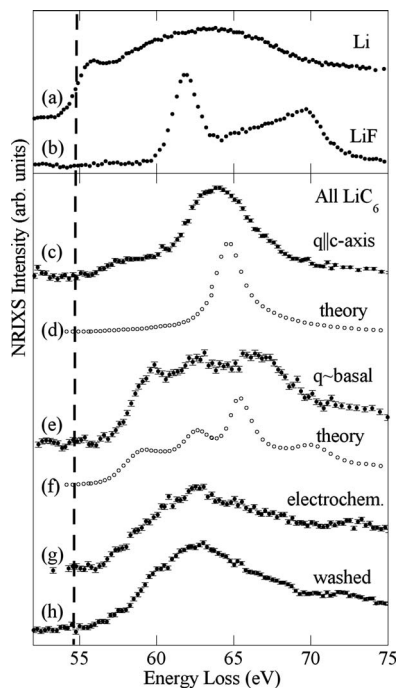


FIG. 1. Li 1s IXS intensity for several materials. (a) Li metal, with $q=0.8 \text{ \AA}^{-1}$. (b) LiF, with $q=0.8 \text{ \AA}^{-1}$. (c) Chemically prepared LiC_6 , with \mathbf{q} approximately parallel to \hat{c} and having $q=0.8 \text{ \AA}^{-1}$. (d) *Ab initio* calculation for the same conditions as in (c). (e) chemically prepared LiC_6 , with \mathbf{q} spanning 10° – 30° from the basal plane and having an average $q=9 \text{ \AA}^{-1}$. (f) *Ab initio* calculation for \bar{q} parallel to basal plane for $q=10.4 \text{ \AA}^{-1}$. (g) electrochemically prepared LiC_6 , with $q=0.8 \text{ \AA}^{-1}$. (h) Electrochemically prepared LiC_6 washed with dry acetonitrile and having $q=0.8 \text{ \AA}^{-1}$.

tron in low-Z materials, the calculation cluster size was expanded to 12 \AA and was extended in the c direction to include multiple graphene layers. The general agreement in near-edge shape and features is additional evidence in favor of the integrity of the samples; it is highly unlikely that phases formed by decomposition of the LiC_6 would show such agreement.

The dashed vertical line in Fig. 1 (54.8 eV) shows the position of the absorption edge of Li metal. Allowing for differences in experimental details, the Li metal results are in good agreement with the prior measurements of IXS,¹³ electron energy loss spectroscopy,^{14,15} and x-ray absorption fine structure (XAFS).¹⁶ However, the Li metal measurements are in disagreement with the EELS measurement of Hightower *et al.*,⁷ where the midpoint of the leading edge of the spectrum is shifted upward by $\sim 2 \text{ eV}$ with respect to the present results. Given the preponderance of evidence for a binding energy of $\sim 55 \text{ eV}$ for Li 1s, we infer that the Li metal results in the prior EELS study⁷ are in error. The results on the second reference material, LiF, are in good agreement with prior measurements by EELS (Ref. 7) and XAFS,¹⁷ although our results do demonstrate some radiation damage effects in the intensity of the second peak.¹⁷

The measurements for chemically prepared LiC_6 in both orientations [Figs. 1(c) and 1(e)] are in good agreement with a prior IXS experiment¹⁸ on a chemically prepared sample, including the 2 eV chemical shift with respect to Li metal for both sample orientations and also much of the fine structure once one allows for the much higher momentum transfer in Fig. 1(e) in the present study. The Li 1s IXS intensities for both the as-prepared and the washed electrochemically prepared samples [Fig. 1(g) and 1(h)] show a similar positive

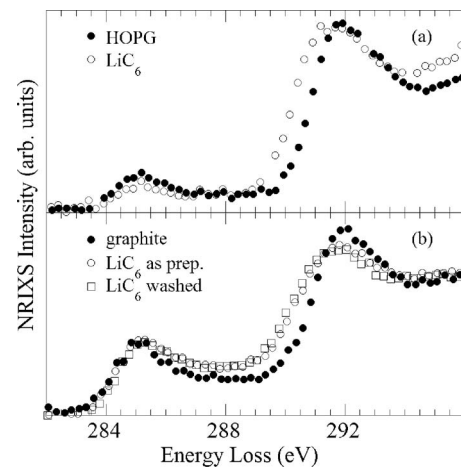


FIG. 2. (a) C 1s IXS intensity for HOPG (filled circles) and chemically lithiated LiC_6 (open circles) for \mathbf{q} at approximately 72° to \hat{c} with a magnitude of 9.8 \AA^{-1} . (b) The C 1s IXS intensity at $q=9.8 \text{ \AA}^{-1}$ for polycrystalline graphite (filled circles) and electrochemically prepared samples, both as prepared (open circles) and washed (open squares). Note the absence of any measurable chemical shift in the π^* resonance, but the negative shift of $0.6 \pm 0.1 \text{ eV}$ in the σ orbital threshold.

shift in edge position with respect to lithium metal. The relative absence of fine structure in the spectra is due to orientational averaging for these polycrystalline samples. The agreement between the spectra for the as-prepared and washed samples demonstrates that small amounts of residual Li-rich electrolyte are irrelevant for IXS studies: IXS is a truly bulk-sensitive measurement.

With the exception of the aforementioned EELS study,⁷ all prior measurements^{14,18,19} which are sensitive to the binding energy and near-edge excitations of the Li 1s initial states studied chemically prepared samples and all also found a chemical shift to higher binding energy of $\sim 2 \text{ eV}$. The discrepancy with respect to Hightower *et al.*,⁷ the only prior study on an electrochemically prepared sample (washed), is not due to the LiC_6 measurement in that study but is instead due to the incorrect reference Li spectrum, as mentioned above. The observation of a chemical shift of a few eV (Refs. 14, 18, and 19) in LiC_6 with respect to Li metal has been qualitatively interpreted as evidence for charge transfer from the Li 2s orbitals to states having lower (but not necessarily zero) overlap with the Li atom. The proposed transfer of electrons to graphenic π bands^{20–22} in LiC_6 is at least qualitatively consistent with the observed chemical shift.

In Fig. 2, we show superimposed the IXS spectra for the HOPG and chemically prepared LiC_6 data (top panel) and polycrystalline graphite and electrochemically prepared LiC_6 (bottom panel). The position of the π^* resonance at 284 eV is invariant, while the σ threshold of the lithiated samples shifts by $\sim 0.6 \text{ eV}$ to lower energies. This result is not dependent on the large momentum transfer for the data shown; the IXS from the electrochemically prepared samples at low q exhibits the same behavior.²³ Both the positions of these features and the relative shifts, however, are in disagreement with the early IXS measurements of the C 1s scattering in LiC_6 by Schulke *et al.*²⁴ Given the agreement between our HOPG spectra and standard XAFS spectra,²⁵ we are confident in the quality of the energy loss calibration of the present study. Recent soft x-ray absorption studies²⁰ also find that the energy of the π^* resonances does not change on

lithiation, but observe a larger downward shift of the σ threshold by ~ 1.3 eV. It is unclear if this discrepancy may be due to the higher surface sensitivity of the soft x-ray measurement.²⁶

Prior x-ray emission and XAFS studies of C 1s find evidence for charge transfer to the π bands of the graphitic sheets in LiC₆.^{20,22} This interpretation provides a useful framework in which to discuss our IXS result that a chemical shift is seen only for the σ threshold and not the π^* resonance when moving from graphite to LiC₆. We note that the absence of measurable chemical shift of the π^* -resonance has also been reported in EELS studies of alkali-metal intercalated single walled carbon nanotubes.²⁷ As discussed in that work, although there is a shift in the Fermi level and consequently a possible shift in the position of the π^* resonance due to charge transfer, the discrete and strongly excitonic nature of this feature makes the shift invisible. Still working under the hypothesis of charge transfer from the Li intercalant to the π band of the graphitic sheets, the shift in the σ threshold is most naturally explained as a simple consequence of the increased in-plane lattice constant. The C–C bond length of LiC₆ is ~ 0.15 Å longer than in graphite.¹ Density functional theory calculations have, in fact, explained the increased lattice constant as being due to charge transfer to the π band.²⁸ Molecular systems with C–C bonding show a clear trend for decrease in the σ threshold (and associated near-edge shape resonances) with increasing bond length.^{25,29} This is well understood as a consequence of multiple scattering of the photoelectron.²⁵

In summary, we find overwhelming evidence in favor of an ~ 2 eV chemical shift in the Li 1s edge position of LiC₆ with respect to Li metal, for both chemical and electrochemical sample preparations. The observed IXS from the C 1s initial state shows a modest decrease in the σ threshold but no change in the position of the π^* resonance in LiC₆ with respect to graphite. This behavior is understood as a consequence of charge transfer from the Li intercalant to the π bands of the graphitic sheets and the concomitant increase in the C–C distance. This study demonstrates the ready compatibility of IXS with electrochemically prepared materials, especially as regards the insensitivity of IXS to residual electrolyte. This is an important experimental proof of principal for future *in situ* IXS studies of the lithiation/delithiation process in Li-ion batteries.

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