

Electron energy-loss spectrometry on lithiated graphite

A. Hightower, C. C. Ahn,^{a)} and B. Fultz

Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125

P. Rez

Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287

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Transmission electron energy-loss spectrometry was used to investigate the electronic states of metallic Li and LiC₆, which is the Li-intercalated graphite used in Li-ion batteries. The Li *K* edges of metallic Li and LiC₆ were nearly identical, and the C *K* edges were only weakly affected by the presence of Li. These results suggest only a small charge transfer from Li to C in LiC₆, contrary to prior results from surface spectra obtained by x-ray photoelectron spectroscopy. Effects of radiation damage and sample oxidation in the transmission electron microscopy are also reported. © 2000 American Institute of Physics. [S0003-6951(00)04428-4]

Lithiated graphite is the standard anode material in Li-ion rechargeable batteries.¹ Highly crystallized graphite can intercalate Li atom to a maximum composition of LiC₆. This is equivalent to a specific charge of 372 Ah kg⁻¹,² although in practice graphite anodes have specific energies of 320–360 Ah kg⁻¹. Graphite anodes have high voltages of 3–4 V versus the cathode, but the difference in electrochemical potential between metallic Li and lithiated graphite is small, of order 0.01 V. The intercalation of Li into highly crystallized graphite changes the stacking sequence of the hexagonal planes from an ABABAB to AAAAAA.³ This change in stacking sequence and the high chemical potential of Li in graphite suggest that a better understanding of the interlayer states of LiC₆ may facilitate improvements to Li-ion electrochemical cells.

The results of numerous studies on the band structure of Li intercalated graphite demonstrate the difficulty in determining the degree of hybridization between Li atomic orbitals and graphite interlayer states. Early theoretical calculations of the LiC₆ band structure began with the notion of complete charge transfer of Li valence electrons to the graphite *p* bands.^{4,5} This evolved into an elegant theory of alkali-intercalated graphite interlayer states as interacting nonorthogonal hybrid states of Li *2s* and graphite interlayer states.^{6,7} This gives credence to x-ray photoelectron spectroscopy (XPS) results by Momose *et al.*⁸ and others⁹ claiming Li to be intercalated into graphite as ionic Li⁺. Early experimental work by Grunes *et al.*¹⁰ using electron energy-loss spectroscopy (EELS) demonstrated distortions of the graphite band structure upon intercalation of alkali metals. Hartwigsen *et al.*¹¹ used a density functional theory, local density approximation to determine the degree of charge transfer from Li to the intercalant host lattice to be 0.5e for LiC₆ and 0.4e for LiC₈. Further experiments using inelastic x-ray scattering spectroscopy by Schülke¹² were able to correlate features of LiC₆ spectra to band structure calculations by Holzwarth *et al.*¹³

The present letter reports transmission EELS measurements of the Li *K* edge in intercalated graphite and in me-

tallic Li. After showing oxidation tendencies of the transmission electron microscopy (TEM) samples and how this was controlled, we show that the Li *K* edge for Li in LiC₆ resembles the Li *K* edge of neutral metallic Li rather than of Li⁺. We believe that the name “Li-ion” battery is therefore misleading.

LiC₆ samples were prepared by electrochemical methods.¹⁴ Anodes were constructed from KS 44 graphite using 6 wt % poly(vinylidene fluoride) as a binder. A ternary mixture of alkyl carbonates, i.e., 1:1:1 of ethylene carbonate, diethylene carbonate, and dimethyl carbonate (DMC) with 1 M LiPF₆ was used as the electrolyte. Carbon half-cells were subjected to 40 electrochemical charge-discharge cycles. The carbon electrodes were left in a charged state before being washed in DMC and vacuum dried.

Thin samples of metallic Li and LiF were prepared by thermal evaporation onto amorphous holey carbon TEM grids. A glove bag filled with Ar gas was placed over the evaporator to minimize atmospheric exposure during transfers. The evaporating chamber was backfilled with Ar where the samples were immersed in Flourinert[®] FC-43, gettered with Li chips. The LiC₆ samples were crushed with a mortar and pestle in an Ar-filled glove box. The powdered anode material was placed onto holey carbon TEM grids. The TEM grids were immersed in Li-gettered Flourinert FC-43 before insertion into the microscope load lock, where the Flourinert evaporated. Transmission EELS spectra were acquired at room temperature using a Gatan 666 parallel detection magnetic prism spectrometer attached to a Philips EM 420 transmission electron microscope. Energy resolution of the spectrometer was about 1.2 eV with a dispersion of 0.2 eV per channel. Measurements were performed with 100 keV electrons at a collection angle of either 11 or 50 mrad. EELS spectra of the evaporated samples were acquired with image coupling. The LiC₆ spectra were acquired with diffraction coupling. The TEM beam current was approximately 7 nA.

X-ray diffractometry was performed with an Inel powder diffractometer using Mo *K_α* radiation ($\lambda = 0.07092$ nm). Anode materials were sealed under Ar with paraffin wax in Pyrex capillary tubes. X-ray diffraction patterns, as shown in Fig. 1, confirmed the presence of LiC₆ and LiC₁₂ phases in

^{a)}Electronic mail: cca@caltech.edu

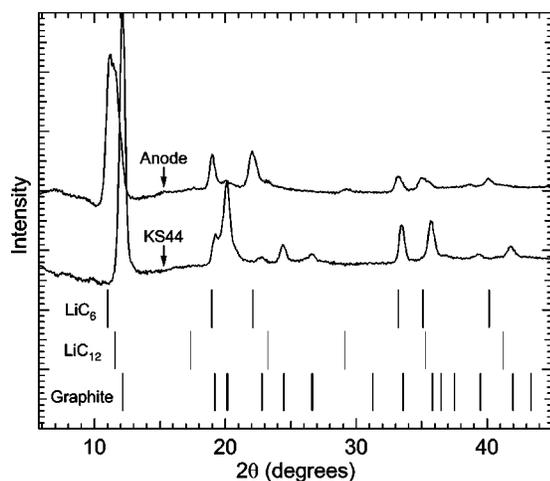


FIG. 1. X-ray diffraction patterns of KS 44 graphite and electrochemically lithiated graphite containing LiC_6 and LiC_{12} phases.

the graphite anode materials. These results were consistent with the color of lithiated graphite which depends on the predominance of LiC_6 (green/gold) or LiC_{12} (blue/black).¹⁵ The diffraction peaks were broader for LiC_6 than for the unlithiated KS 44 graphite samples.

The reactivity of reduced Li and its susceptibility to radiation damage under an electron beam present a formidable challenge to EELS analysis of LiC_6 . The majority of radiation damage is a result of the direct transfer of momentum from incident electrons to the Li nucleus, ejecting it from its lattice site. Average atomic displacement energies estimated from sublimation energies were found to be 6.1 eV for Li and 31.2 eV for C in graphite.¹⁶ Assuming elastic collisions, the knock-on damage, threshold energies for incident electrons are 19 keV for Li and 150 keV for C. Metallic Li samples appeared to “boil” during TEM observations at 200 keV. This was determined to be a consequence of knock-on damage since the calculated temperature rise was negligible, approximately 1 K.¹⁷ We chose a microscope voltage of 100 keV as a reasonable compromise between knock-on damage and instrument performance.

Beam damage of metallic Li was studied at 100 keV by concentrating the electron beam onto a thin area of the Li sample. Figure 2 presents a time sequence of EELS spectra for this exposed region. Over a few minutes, the spectral area of the low-loss region was reduced significantly, resulting in the suppression of Li plasmons at 7.5 and 15 eV. This is consistent with a thinning of the sample as Li atoms are ejected from the sample under the electron beam. In image mode, regions of the specimen were observed to shrink, especially under a focused incident beam.

Over a slightly longer time scale under a focused beam, the Li plasmons evolved into distinct profiles commonly associated with oxidized Li.¹⁸ During this time, as shown in Fig. 2, the broad profile of the Li *K* edge evolves into two sharp peaks at 59.5 and 64.5 eV, similar to peaks observed from samples exposed to atmosphere.¹⁸ Exposure to the intense electron beam stimulates Li reactions with moisture and oxygen present in the microscope, leading to the formation of LiOH and Li_2O .¹⁹ The Li *K* edge in our LiC_6 samples showed the same peaks at 59.5 and 64.5 eV after the samples were exposed to atmosphere.

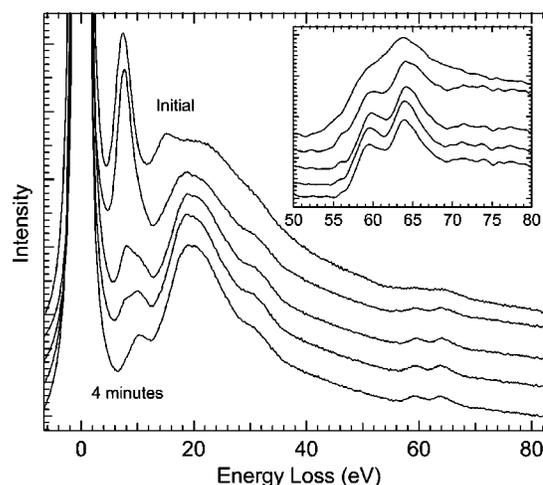


FIG. 2. EELS spectra of beam-damaged Li. Spectra were acquired at approximately equal intervals from nearly zero, to 4 min of electron beam exposure.

Figure 3 presents the C *K* edges of LiC_6 and KS 44 graphite. A peak at 301 eV is found in LiC_6 but not in the graphitic carbon. Disko²⁰ and others²¹ have demonstrated the sensitivity of the C *K* edge to the direction of the momentum transfer vector \mathbf{q} . We therefore do not expect the intensity of the $1s \rightarrow \pi^*$ peak to be reliable, since it is not an average over many crystal orientations. Nevertheless, the onset energy of the C *K* edge and the location of the $1s \rightarrow \pi^*$ peak are essentially the same for graphitic carbon and LiC_6 .

Figure 4 displays the Li *K* edge obtained from intercalated LiC_6 , LiF, and metallic Li. We identify the onset of the Li *K* edge in the metallic sample at 55 eV, consistent with results of Liu and Williams.¹⁸ The broad profile of the metallic Li *K* edge is consistent with the promotion of core electrons into a continuum of free electron states. The Li *K* edge onset of LiC_6 is shifted by only 0.2 eV from the *K* edge of metallic Li and has a similarly broad profile. Our observed Li *K* edge for LiC_6 lacks the peaks at 59 and 63 eV previously observed by Grunes *et al.*¹⁰ These peaks evidently originate from oxidized Li—they are found in samples exposed to atmosphere, or after long times in the microscope (Fig. 2). The Li *K* edge of LiF, similar to that reported by

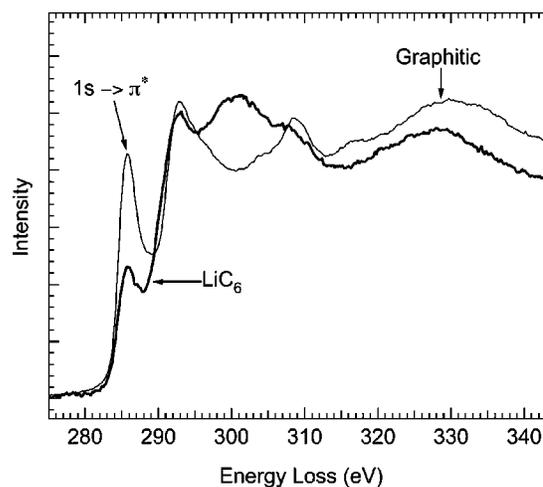


FIG. 3. C *K* edge for LiC_6 and KS 44 graphite, normalized by the area 50 eV after edge onset.

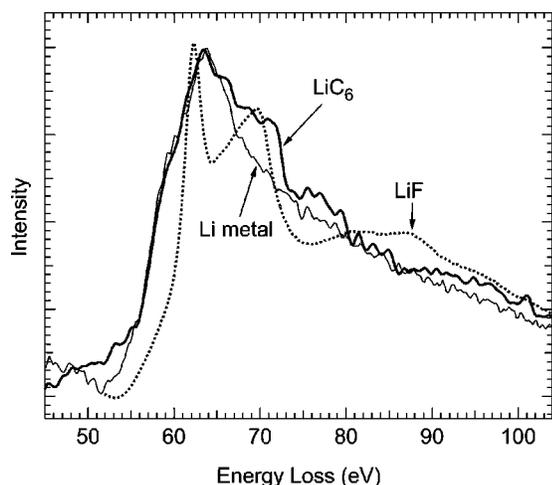


FIG. 4. Li *K* edge of metallic Li, LiC_6 , and LiF . The pre-edge background of the raw data was fit to an exponential and subtracted from the data.

Chen *et al.*,²² shows a strong chemical shift and sharp features of well-defined unoccupied states. Such large differences are expected with the large electron transfer from Li to F.

Our EELS spectra of the Li *K* edge indicate that Li in LiC_6 has a local electronic structure more similar to Li metal than Li^+ , contrary to previous XPS results. Extensive XPS results confirm a Li *K* edge chemical shift of about 3 eV in LiC_6 with respect to metallic Li,^{8,9} easily resolved from the 1.3 eV chemical shift of Li_2O .²³ The mean free path of photoelectrons measured by XPS is on the order of 1 nm. Thus, assuming that the surface Li remains unreacted, we expect XPS to be more sensitive to Li surface states.

The similarities of Li *K* edges in LiC_6 and metallic Li are consistent with observed electrochemical potentials. Measurements of electrochemical potentials in half cells show LiC_6 to be less than 0.01 V above Li metal.²⁴ The similar chemical potentials of Li in LiC_6 and metallic Li suggest similar environments for valence electrons. Electrochemical potentials and EELS Li *K* edge profiles both suggest limited charge transfer from Li to surrounding carbon. The observed EELS C *K* edge is little affected by intercalated Li, but effects should be diminished by the 6:1 ratio of C to Li, and could be diminished further if there were a loss of Li from the TEM sample. The shape of the Li *K* edge, on

the other hand, would be unaffected by any possible loss of Li, or perhaps would appear even more ionic, since the electrochemical potential of Li would be lowered.

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