An X-ray Diffraction and Small Angle X-ray Scattering Study of Solvated Li-Graphite Intercalation Compounds

Mark J. Henderson ¹ and John W. White ²

Research School of Chemistry, Australian National University,
Canberra ACT 0200, Australia

¹mjh@rsc.anu.edu.au
²jww@rsc.anu.edu.au

Abstract — Stage I C₆Li and stage II C₁₂Li were prepared using a low temperature liquid lithium route. Small angle X-ray scattering measurements of both pristine binary compounds indicated that the surfaces are highly dissected. As a result using a mixed layered graphite precursor containing pre-graphitic, chemically distinct lamellar domains, both C₆Li and C₁₂Li produced an additional suite of ternary structures after successive intercalation with Li and THF. The use of a THF–Li–graphite ternary compound to entrap LiBH₄ for hydride storage is explored.

Keywords — X-ray diffraction, X-ray scattering, intercalation, lithium.

I. INTRODUCTION

Lithium insertion compounds based on graphite anode are attractive anodes for reversible Li storage in the anode material in high energy density batteries in terms of safety and cycle life compared with lithium metal. [1] For other energy-based applications, e.g., hydrogen storage, the phase instability of the hydrogenated compounds presents significant challenges for a rechargeable system. [2], [3] At liquid nitrogen temperature, Li-doped carbons are reported to physisorb only 2-3 wt% H₂, less than that demonstrated by the carbon used to prepare the intercalation compound. Furthermore a requirement of both approaches is the use of 1-2 MPa H₂ pressures. [4]

Alternative hydrogen storage media are the light metal hydrides. [5] However, despite their many advantages for hydrogen storage, in general, they suffer from poor hydrogen absorption/desorption thermodynamics and kinetics. A recent approach to improve dehydrogenation and thereby promote safe and efficient hydrogen storage has involved confinement of LiBH₄ in nanoporous hosts including highly ordered nanoporous carbon, [6], mesoporous carbon, [7] carbon aerogel, [8] activated carbon [9] and carbon nanotubes. [10] Confinement exerts an influence on the microstructure of the occluded hydride thereby altering its properties, e.g., melting and decomposition points. It is noteworthy that the use of a LiBH₄-graphite mixture exhibits only a limited effect on the dehydrogenation of LiBH₄ confirming that confinement in the nanoporous host is crucial to altering the properties of this hydride. LiBH₄ can be confined in porous carbons using melt infiltration [6], [8] or by chemical impregnation technique using an ether solution of the hydride. [7], [9], [10] It is the latter method we envisage for the incorporation of metal hydride into lithiated graphite where the galleries are expanded by solvent. The direct reaction of polar solvents, e.g., THF on binary alkali-metal graphite intercalation compounds leads to ternary compounds for which the alkali ions Li, [11] K, [12], Cs [13] and Rb [14] are coordinated by the 2p electrons of the THF molecules. Table I presents the interplanar spacings of some alkali-metal intercalated graphites.

As a consequence of solvent intercalation, the interlayer spacing of the graphite sheets can swell significantly, e.g., from 3.7 Å for C₆Li to 12.5 Å for the ternary compound. [15] It is this phenomenon that we exploit for the storage of THF-soluble LiBH₄ within the galleries of the ternary THF–Li–graphite compound.
ternary could adsorb up to 4 wt% H₂ at 300 K but would require 10 MPa pressure of H₂. [25] Storage of a metal hydride at ambient conditions of temperature and pressure necessarily required a preliminary study in order to select the best Li–GIC host for the salt. In this article we present an X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) study of two THF–Li–graphite candidates. We show that the surfaces of pristine binary materials are not smooth. We also reveal that the short-range lamellar impurities within the graphite precursor could also be intercalated by lithium and subsequently by THF. As the disordered phases are chemically and physically distinct from the principal graphitic material, their ternary compounds remains chemically distinct from that derived from graphite.

II. EXPERIMENTAL DETAILS

A. Materials

Graphite powder (Ceylon graphite, sieved and Soxhlet extracted with toluene, particle size 53 mm-90 mm) was heated to 280 °C at a vacuum line at ~10⁻⁶ mm Hg to minimise adsorbed water on the graphite surfaces. However, we note that complete removal of water requires outgassing at 1500 °C. [26] Lithium (Analytical reagent, BDH) was rinsed in HPLC-grade hexane to remove the protective liquid paraffin, dried and then stored in a glove box (VAC DRI-LAB) under an argon atmosphere containing less than 10 ppm oxygen. Prior to use surface oxides were removed from the lithium with a scalpel. Tetrahydrofuran was distilled from Na/benzophenone under nitrogen and freeze-thawed thrice under argon prior to use. LiBH₄ (Aldrich, 2 mol dm⁻³ in THF) was used without further purification.

B. Li and THF intercalation into graphite

A liquid lithium route just above the melting point of lithium was used to prepare the binary stage I C₆Li and stage II C₁₂Li. For X-ray diffraction analysis, an aliquot of the free-flowing gold or dark purple powder was loaded into a glass capillary (1.5 mm diameter, 80 mm long, wall thickness 1/00⁻⁴ mm) via a glass T-piece that was connected to the capillary and then closed with a screw rotaflow stopcock. THF-coordinated C₆Li or C₁₂Li was prepared by condensing freeze-thawed THF into a 2 mm diameter capillary containing powdered Li-GIC.

| TABLE I |
| INTERLAYER SPACINGS OF TERNARY ALKALI-METAL INTERCALATION COMPOUNDS |

<table>
<thead>
<tr>
<th>Ternary alkali-metal intercalation compounds</th>
<th>THF layer mode</th>
<th>Identity period / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂Li(THF-d₈)₂·Li</td>
<td>double</td>
<td>12.45</td>
</tr>
<tr>
<td>C₁₂Li(THF-d₈)₂·Li</td>
<td>double</td>
<td>10.63</td>
</tr>
<tr>
<td>*C₂M(THF)₃</td>
<td>single</td>
<td>8.95</td>
</tr>
<tr>
<td>C₂₄K(THF)₂</td>
<td>single</td>
<td>8.88</td>
</tr>
<tr>
<td>C₂₄K(THF)₂·Li</td>
<td>single</td>
<td>8.9 [¹⁷]</td>
</tr>
<tr>
<td>C₂₄Cs(THF)₃</td>
<td>single</td>
<td>7.16</td>
</tr>
<tr>
<td>C₂₄Cs(THF)₃</td>
<td>single</td>
<td>7.06</td>
</tr>
</tbody>
</table>

* M = K, Rb and Cs

The methods for the preparation of Li–GICs include: the reaction of graphite with lithium vapour; lithium liquid; solutions of lithium in organic solvent [18], [19]; in ammonia [20]; in hexamethylphosphoramide [21]; or by ion exchange using K-GICs and Li salts. [22] In this study, a liquid lithium route just above the melting point of lithium, 180.6 °C is used to prepare stage I C₆Li or stage II C₁₂Li. This low temperature approach not only avoids any complications arising from the formation of the lithium acetylhydride contaminant, Li₂C₂, but can produce gram quantities of relatively pure binary compounds rapidly and quantitatively. As noted above, exposure of the binary compounds to THF forms ternary compounds containing [Li(THF)₆]⁺ tetrahedral complexes between the graphene planes resulting in a significant increase in the interlayer spacing (d), e.g., for C₁₀Li from 3.7 Å to 12.5 Å. [11], [15], [23]. These ternary THF–Li–graphite compounds form as a consequence of the polar nature of this ether to solvate Li⁺ ions via ion-dipole interaction (μTHF = 5.8 10⁻¹⁸ Cm). [24]

We have studied the reaction of THF and C₆Li or C₁₂Li (prepared by a low temperature liquid lithium route) with the aim charging the ternary compound with a THF-soluble metal hydride such as LiBH₄ or LiAlH₄. Alternatively where H₂ is considered as the hydrogen source, Monte-Carlo simulations have shown that a Li–THF–GIC
C. Reaction between C₆Li and LiBH₆

A 2 mol dm³ solution of LiBH₆ (1.4 mL, 2.8 mmol) was added to C₆Li (0.48g, 6.1 mmol) in a 50mL round bottom flask. Dry THF (10mL) was added and the mixture stirred under an argon atmosphere for 3 days. The flask was then equipped with a condenser that had been evacuated and backfilled with argon, and the mixture refluxed for four hours under argon. Excess THF was removed by primary pumping for 30 minutes to yield a black powder. A graphite control was prepared using graphite instead of C₆Li.

D. Characterisation

1) X-ray diffraction: X-ray diffraction (XRD) measurements were recorded on an X-ray powder diffractometer based on a Huber 422 2-circle horizontal turntable goniometer, requiring the sample to be vertical. The diffractometer was equipped with a Philips generator operating at 40 kV and 20 mA and using a wavelength (λ) of 1.54 Å. The capillaries were mounted vertically into the diffractometer in transmission geometry. The data were recorded as intensity (I) or q as a function of angle (2θ). Interlayer spacings (d) were obtained from, \( d = \frac{2\pi}{q} \) where q the scattering vector, is defined as \( q = \frac{4\pi\sin\theta}{\lambda} \).

2) Small angle X-ray scattering: Small angle X-ray scattering (SAXS) measurements were recorded using a 1.638m Huxley-Holmes camera with an Elliott type GX-13 rotating anode X-ray generator operating at 34kV and 35 mA, λ of 1.54 Å.

3) Microanalyses: Lithium content was obtained inductively couple plasma-optical emission spectroscopy (ICP-OES) using an argon plasma. Carbon, hydrogen and nitrogen contents were obtained by combustion using the Carlo Erba method.

III. RESULTS

A. C₆Li

Figure 1 shows X-ray diffraction patterns of the lithiated graphite and that of the out-gassed graphite precursor. In addition to the (002) reflection at 26.4°, the graphite precursor displayed small broad reflections at 12.9°, 21.6° and 24.1° indicating that the material is not pure AB stacked graphite. The measurements of the graphite after intercalation by Li show a shift of the (002) reflection to 23.8° and 48.7° but we note that the peaks from the impurities also show a shift to higher spacings. The strongest peaks are indexed as the (001) and (002) reflections of the stage I intercalate compound C₆Li having an interlayer spacing (d) of 3.7 Å, in agreement with the literature value of 3.7 Å. [27] The small peak at 33.7° is attributed to a reflection of Li₂O. No reflection originating from liberated graphite was evident, indicating that the formation of Li₂O is a result of the oxidation of unintercalated Li from the inert gas atmosphere of the glove box of < 10 ppm oxygen. [28] The (002) reflection of contaminant stage II C₁₂Li appears as a shoulder at 24.9°.

![Fig.1 X-ray diffraction patterns displayed as I vs 2θ of (i) powdered C₆Li prepared using graphite outgassed at 280 °C at ~10⁻⁶ mm Hg for five days (full line) and (ii) outgassed graphite (dotted line). λ = 1.54 Å.](image)

A sample of C₆Li was chemically analysed after exposure to air. In air, the colour changed rapidly from gold to black. The X-ray diffraction pattern of an oxidised sample derived from C₆Li (not shown) displayed the (002) reflection of graphite 2θ = 26.4° and the (111) reflection of Li₂O at 2θ = 33.5° suggesting that lithium was completely de-intercalated from graphite after this treatment. Found C, 87.9 %; Li, 7.05%; H, 0.4%; N, 0.0% (Required C, 91.2%; Li, 8.8%; H, 0.0%; N, 0.0%). The results show near quantitative amounts of lithium and graphite.

B. THF sorption

Figures 2 and 3(a) show successive X-ray diffraction patterns obtained after exposure of C₆Li to liquid THF.
new experiment at four days after mixing C₆Li and THF is shown in the insert to Figure 3(b). The pattern shows similar features to that of Figure 3(a) with the broad scattering centred at 0.13 Å⁻¹ but with greater coherence length of ~55 Å. In addition, another set of broad reflections clustered at the sub-multiple value of 0.65 Å⁻¹ (d = 9.7 Å) was evident.

The inset to Figure 3(b) also shows clearly the first three (00l) reflections of the 1st stage ternary compound. As the (001) and (002) reflections of the pristine C₆Li are still evident in the pattern after four days, complete conversion of the binary C₆Li into the ternary compound had not been achieved. The SAXS pattern of the mixture is shown in Figure 3(b) together with that of outgassed graphite and pristine C₆Li. The pattern shows two weak scattering maxima centred at 0.12 Å⁻¹ and 0.21 Å⁻¹. As similar scattering is evident in the SAXS pattern obtained from the pristine binary but not evident in that obtained from graphite precursor, we can conclude that the small angle

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Fig. 2 Successive X-ray diffraction patterns of powdered C₆Li exposed to liquid THF. 1st-3rd hour, displayed as I vs 2θ. λ = 1.54 Å.

The data of Figure 3(a) is displayed as log₁₀ intensity, I, versus scattering vector, q to enable a comparison with a small angle X-ray scattering pattern presented later where we explore the scattering from large length scales. The diffraction patterns reveal diminishing intensity of the (001) C₆Li reflection, the appearance of low intensity reflection at 6.8º (0.49 Å⁻¹) and broad scattering between 15º and 23º. The coherence length (Lc) of the planes responsible for the broad scattering was estimated from the Scherrer relation, Lc = (0.94λ) / B(002)-cosθ, where λ and θ are the wavelength of the incident beam and the diffraction angle, respectively and B(002) is a measure of the line broadening to have a coherence length of 25 Å.

The low angle reflection at 6.8º is assigned the (001) reflection of 1st stage C₆Li(THF) ternary compound with d = 12.8 Å. This large spacing is slightly larger than the value of 12.5 Å reported Beguin et al. [23], [11] who demonstrated that ternary lithium–GICs swell to this interlayer spacing regardless of the starting binary C₆Li (where n = 6, 12, 18). The stage I ternary compound exists as graphite intercalated with double layers of Li and THF; the latter having a mean 55º tilt with respect to the axis normal to the graphene planes. [15]

Arrowed in Figure 3(a) is a suite of reflections superimposed on the broad scattering for the pattern collected at the 3rd hour after exposure to THF. The reflections at 1.175 Å⁻¹, 1.245 Å⁻¹, 1.315 Å⁻¹ and 1.455 Å⁻¹ are equally spaced in q by 0.07Å⁻¹ indicating that a ~90 Å periodicity also exists in this ternary system. The experiment was repeated. The XRD pattern obtained from this
scattering does not originate from the intercalation of solvent but from the intercalation of lithium.

C. C_{12}Li

The X-ray diffraction and X-ray scattering behaviour for C_{12}Li is summarised in Figure 4.

![Graph showing X-ray diffraction patterns and small angle X-ray scattering measurements.](image)

Fig. 4 (a) X-ray diffraction patterns displayed as $I$ vs $q$ of (i) powdered C_{12}Li (dotted line) and (ii) powdered C_{12}Li exposed to liquid THF after two days, displayed as $I$ vs $q$. $\lambda = 1.54$ Å. (b) Small angle X-ray scattering measurements of powdered C_{12}Li (dotted line) and (ii) powdered C_{12}Li exposed to liquid THF after two days displayed as $log I$ vs $q$. $\lambda = 1.54$ Å.

Pristine C_{12}Li, Figure 4(a) displays the (002) reflection corresponding to an interlayer spacing of 7.1 Å, in good agreement with the literature value of 7.065 Å. [18] After 48 hours exposure of C_{12}Li to liquid THF, a series of strong reflections at 0.50 Å⁻¹ (7.1°); 1.0 Å⁻¹ (14.3°); 1.5 Å⁻¹ (21.5°); 2.0 Å⁻¹ (28.9°) and 2.5 Å⁻¹ (36.2°) appear in the pattern. These reflections are indexed as the first five (00$\ell$) reflections of the ternary compound having the known interlayer spacing of 12.5 Å. As the (002) reflection of the pristine C_{12}Li vanished after treatment with THF, full conversion of the binary C_{12}Li into the ternary compound was achieved within two days. The presence of the 1$^{st}$ stage ternary compound regardless of whether or not C_6Li or C_{12}Li was the precursor material supports the Staging Domain or Pleated Layer model [29] proposed by Daumas and Hérold. According to this model the intercalant in an $n$-stage compound covers a fraction of $1/n$ of the area of each graphene sheet, rather than the intercalant being present only in one of every $n$ sheets. In addition to the reflections of stage I THF–Li–graphite Figure 4 also shows broad peaks centred at 0.7 Å⁻¹ and 1.4 Å⁻¹, similar to those found when C_6Li was exposed to THF.

D. Reaction of a Li-GIC and LiBH$_4$

The stoichiometry required for a LiBH$_4$/ THF–Li–graphite composite can be estimated because the precise nature of the precursors are known. LiBH$_4$ forms three THF adducts, LiBH$_4$(THF), LiBH$_4$(THF)$_2$ and LiBH$_4$(THF)$_3$. [30] Beguin et al., have shown that C_{6}Li exposed to THF forms a ternary THF–Li–graphite compound having a rational formula C$_6$Li(THF)$_4$. [23] Using the most dilute case where LiBH$_4$(THF)$_4$ is entrapped within the crowded graphene planes, a LiBH$_4$:C$_6$Li:THF mole ratio approximately 1:2:3 provides a first guide to stoichiometry. As the reaction between C_{6}Li and THF is slow, the hydride–C_{6}Li–THF mixture was refluxed for several hours under an inert atmosphere. The X-ray diffraction pattern of the black powder obtained after primary pumping for 30 minutes is shown in Figure 5 superimposed on pattern obtained from a control for which the graphite precursor replaced binary C$_6$Li.

![Graph showing X-ray diffraction patterns.](image)

Fig. 5 X-ray diffraction patterns displayed as $I$ vs $2\theta$ of (i) powdered product of C$_6$Li + LiBH$_4$ after reflux in THF (red line); (ii) a control obtained from graphite + LiBH$_4$ after reflux in THF (black line) and (iii) C$_6$Li precursor (dotted line). The reflections from graphite and its impurities are indicated by ●. The reflections from LiBH$_4$ are indicated by ◊. The reflections from C$_6$Li are indicated by ●. $\lambda = 1.54$ Å.
IV. DISCUSSION

Natural graphite is a structurally complex material. Highly orientated graphite can show line broadening due to rotational or twist defects between otherwise perfect substacks. [31] Most graphites also show intermixing of hexagonal (2H) and rhombohedral (3R) polytypes [32], [33] for which reflections between 40° and 65° 2θ using CuKα wavelength show significant differences as a result of the changes of space group symmetry. Mixed layering in disordered Ceylon graphite comprises carbon-rich, pre-graphitic C–(H,O,N) sheet [34] where the interplanar spacings derived from the (002) reflections of the impure or pre-graphitic phases show a range of spacings from 3.44 Å–4.89 Å but are centred near 3.5 Å, and 4.5 Å, [34]. A reflection at 6.607 Å has also been reported for a carbon crystal obtained from marble [35].

The small reflections between 3.9 Å–4.4 Å near the graphite (002) peak, of Figure 1 probably originate from these disordered phases common in terrestrial carbons. The observation that these peaks shift to higher interplanar spacing after treatment with lithium demonstrate that these mixed phases can be intercalated by alkali-metal, are of carbonaceous not siliceous origin, and contain aromatic structures. The relatively short coherence length of 55 angstroms obtained after 96 hours exposure highlights the short-range stacking of these phases. It is noteworthy that solvated C₆Li and C₁₂Li precursors show reflections that cluster near 0.7 Å⁻¹ and 1.3 Å⁻¹. We can conclude from the absence of lower order reflections from the SAXS study that the spacings represented by these clusters are 1st and 2nd order reflections and represent distances near 9 Å. However, the nature of the ternary system cannot be known without considering additional information. As it is the THF molecules that dictate layer thicknesses, a comparison of distances with those of related solvated alkali-metal graphites, Table 1, suggests that the short-range lamellae might contain single layers of lithium ions and THF molecules containing [Li(THF)]⁺ complexes. Finally, a super lattice of about 90 Å is present in the pre-graphitic ternary system. This distance may reflect the periodicity of the thick pre-graphitic sheets that exist in the layered sequence of individual sheets as revealed by high resolution tunnelling electron microscopy, [34] in our case expanded by lithium and solvent intercalation. It is therefore possible that the constraints imposed by the thicker carbonaceous boundaries prevent the formation of a ternary THF–Li–graphite compound fully gorged with THF and having the maximum interlayer spacing of 12.4 Å, a constraint not imposed where pure graphite is the precursor.

With the exception of an overall decrease in scattering intensity, the SAXS pattern of the ternary THF–Li–graphite was similar to that of the pristine sample, Figure 4(b), displaying a broad peak centred at q = 0.21 Å⁻¹, similar to that observed for pristine C₆Li. It is tempting to posit the formation of a higher stage in the Li-C system, Stage VIII C₇₂Li which is reported to form at low pressures and has an interlayer spacing of 27.05 Å [18], [36], however, in the presence of THF the reflection of the binary compound would have reduced in intensity or even vanished as demonstrated by C₆Li and C₁₂Li when intercalated by THF. As the scattering is not evident in the out-gassed graphite precursor, another explanation for the small angle scattering is the formation of defects introduced into the graphite host during the intercalation processes or during cooling after reaction, e.g. intercalant migration from one domain to another. This effect is illustrated by stage I C₆M (M = K, Rb and Cs) that can display average unfaul ted stacking domains in the c-axis direction of 6-10 layers. [37] However, structural faults separated by 30 Å, unlike staging which is a long range phenomenon, would not provide the coherence length necessary to explain the small angle scattering shown in Figures 3(b) and 4(b).

The possibility of inhomogeneities from distribution of intercalant molecules then arises. Small angle X-ray scattering has been used to characterise the in-plane structure of FeCl₃-graphite compounds [38] that show structure due to ellipsoid shaped voids and/or intercalant islands. Figure 6 presents the SAXS pattern obtained from a pristine C₆Li sample expressed as log I vs log q and corrected for background scatter. The slope of the linear region of the plot was found to be -3.3 indicating a highly dissected surface in agreement with a scanning tunnelling microscopic study of C₆Li [39] which showed that surfaces of this binary material consist of island-like structures 20 Å-30 Å in depth as well as >100 nm terraces separated by steps.
Fig. 6 Small angle X-ray scattering measurements of pristine C₆Li expressed as log I vs log q, λ = 1.54 Å.

The THF–Li–graphite compound was not destroyed by the action of LiBH₄ during the refluxing conditions of the experiment as shown by the first three (00l) reflections of a ternary compound of Figure 5. Compared with the pattern obtained from the C₆Li precursor, the intensity of the principal reflection displays reduced intensity, a result of either increased disorder of the lamellar structure and/or reduced contrast from occluded boron. Second, (00l) reflections and the broad scattering typical of the ternary compound but has an interlayer spacing of 11 Å, slightly less than that for the ternary formed in the presence of liquid THF, a result of the removal of some THF by primary pumping on the sample. We note here that primary pumping of the black powder for prolonged periods, e.g., 20 hours resulted in the destruction of the ternary compound and the liberation of graphite but not the formation of gold-coloured C₆Li. Unfortunately, a conclusion of the crystallinity of LiBH₄ remains ambiguous because the scattering from the solid ternary THF–Li–graphite masks any reflections from LiBH₄.

Isav et al. have shown that ion-exchange reactions are more facile for stage II compounds compared to stage I compounds because less compaction between the graphene sheets promotes vacancies via metal deintercalation. [22] Work on the formation of composite Li-GICs-hydrides using stage II C₁₂Li is currently in progress in addition to hydrogen desorption experiments.

V. CONCLUSIONS

Mixed-layered carbons within a natural graphite precursor produced chemically distinct ternary compounds compared to known ternaries when either binary C₆Li or C₁₂Li prepared using this graphite was exposed to liquid tetrahydrofuran. Stage I C₆Li was converted to a ternary compound in the presence of LiBH₄ solution without decomposition to graphite.

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REFERENCES


