

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

Mark J. Henderson <sup>1</sup> and John W. White <sup>2</sup>

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

<sup>1</sup>mjh@rsc.anu.edu.au

<sup>2</sup>jww@rsc.anu.edu.au

**Abstract**— Stage I C<sub>6</sub>Li and stage II C<sub>12</sub>Li 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 C<sub>6</sub>Li and C<sub>12</sub>Li 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 LiBH<sub>4</sub> 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% H<sub>2</sub>, 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 H<sub>2</sub> 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 LiBH<sub>4</sub> 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 LiBH<sub>4</sub>-graphite mixture exhibits only a limited effect on the dehydrogenation of LiBH<sub>4</sub> confirming that confinement in the nanoporous host is crucial to altering the properties of this hydride. LiBH<sub>4</sub> 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 C<sub>6</sub>Li to 12.5 Å for the ternary compound. [15] It is this phenomenon that we exploit for the storage of THF-soluble LiBH<sub>4</sub> within the galleries of the ternary THF–Li–graphite compound.

TABLE I

INTERLAYER SPACINGS OF TERNARY ALAKLI-METAL  
INTERCALATION COMPOUNDS

Ternary alkali-metal intercalation compounds		
Composition	THF layer mode	Identity period / Å
$C_{12}Li(THF-d_8)_{2.13}$ <sup>[15]</sup>	double	12.45
$C_{12}Li(THF-d_8)_{2.13}$ <sup>[15]</sup>	double	10.63
$*C_{24}M(THF)_3$ <sup>[16]</sup>	single	8.95
$C_{24}K(THF)_2$ <sup>[16]</sup>	single	8.88
$C_{24}K(THF)_{2.5}$ <sup>[13]</sup>	single	8.9 <sup>[17]</sup>
$C_{24}K(THF)_1$ <sup>[16]</sup>	single	7.16
$C_{24}Cs(THF)_{1.3}$ <sup>[13]</sup>	single	7.06

\* 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  $C_6Li$  or stage II  $C_{12}Li$ . This low temperature approach not only avoids any complications arising from the formation of the lithium acetylide contaminant,  $Li_2C_2$ , 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  $[Li(THF)_x]^+$  tetrahedral complexes between the graphene planes resulting in a significant increase in the interlayer spacing ( $d$ ), e.g., for  $C_6Li$  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 ( $\mu_{THF} = 5.8 \cdot 10^{-30}$  Cm). [24]

We have studied the reaction of THF and  $C_6Li$  or  $C_{12}Li$  (prepared by a low temperature liquid lithium route) with the aim charging the ternary compound with a THF-soluble metal hydride such as  $LiBH_4$  or  $LiAlH_4$ . Alternatively where  $H_2$  is considered as the hydrogen source, Monte-Carlo simulations have shown that a Li-THF-GIC

ternary could adsorb up to 4 wt%  $H_2$  at 300 K but would require 10 MPa pressure of  $H_2$ . [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  $\sim 10^{-6}$  mm Hg to minimise adsorbed water on the graphene 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.  $LiBH_4$  (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  $C_6Li$  and stage II  $C_{12}Li$ . 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 1/100<sup>th</sup> mm) via a glass T-piece that was connected to the capillary and then closed with a screw rotaflow stopcock. THF-coordinated  $C_6Li$  or  $C_{12}Li$  was prepared by condensing freeze-thawed THF into a 2 mm diameter capillary containing powdered Li-GIC.

### C. Reaction between $C_6Li$ and $LiBH_4$

A 2 mol dm<sup>-3</sup> solution of  $LiBH_4$  (1.4 mL, 2.8 mmol) was added to  $C_6Li$  (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  $C_6Li$ .

### 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 ( $\lambda$ ) 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 ( $2\theta$ ).

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,  $\lambda$  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. $C_6Li$

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  $C_6Li$  having an interlayer spacing ( $d$ ) of 3.74 Å, in agreement with the literature value of 3.7 Å. [27] The small peak at 33.7° is attributed to a reflection of  $Li_2O$ . No reflection originating from liberated graphite was evident, indicating that the formation of  $Li_2O$  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  $C_{12}Li$  appears as a shoulder at 24.9°.

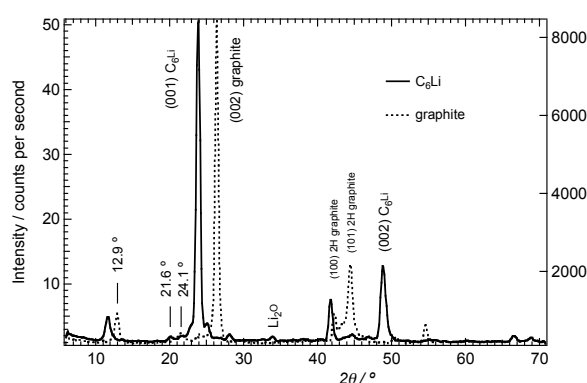


Fig.1 X-ray diffraction patterns displayed as  $I$  vs  $2\theta$  of (i) powdered  $C_6Li$  prepared using graphite outgassed at 280 °C at  $\sim 10^{-6}$  mm Hg for five days (full line) and (ii) outgassed graphite (dotted line).  $\lambda = 1.54$  Å.

A sample of  $C_6Li$  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  $C_6Li$  (not shown) displayed the (002) reflection of graphite  $2\theta = 26.4^\circ$  and the (111) reflection of  $Li_2O$  at  $2\theta = 33.5^\circ$  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  $C_6Li$  to liquid THF.

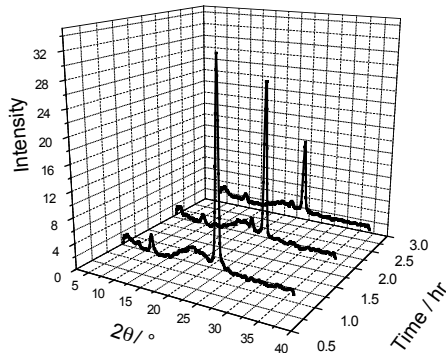


Fig. 2 Successive X-ray diffraction patterns of powdered  $C_6Li$  exposed to liquid THF. 1<sup>st</sup>–3<sup>rd</sup> hour, displayed as  $I$  vs  $2\theta$ .  $\lambda = 1.54 \text{ \AA}$ .

The data of Figure 3(a) is displayed as  $\log_{10}$  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)  $C_6Li$  reflection, the appearance of low intensity reflection at  $6.8^\circ$  ( $0.49 \text{ \AA}^{-1}$ ) and broad scattering between  $15^\circ$  and  $23^\circ$ . The coherence length ( $L_c$ ) of the planes responsible for the broad scattering was estimated from the Scherrer relation,  $L_c = (0.94\lambda) / B_{(002)} \cos\theta$ , where  $\lambda$  and  $\theta$  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  $25 \text{ \AA}$ . The low angle reflection at  $6.8^\circ$  is assigned the (001) reflection of 1<sup>st</sup> stage  $C_6Li(THF)$  ternary compound with  $d = 12.8 \text{ \AA}$ . This large spacing is slightly larger than the value of  $12.5 \text{ \AA}$  reported Beguin et al. [23], [11] who demonstrated that ternary lithium–GICs swell to this interlayer spacing regardless of the starting binary  $C_nLi$  (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  $55^\circ$  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 3<sup>rd</sup> hour after exposure to THF. The reflections at  $1.175 \text{ \AA}^{-1}$ ,  $1.245 \text{ \AA}^{-1}$ ,  $1.315 \text{ \AA}^{-1}$  and  $1.455 \text{ \AA}^{-1}$  are equally spaced in  $q$  by  $0.07 \text{ \AA}^{-1}$  indicating that a  $\sim 90 \text{ \AA}$  periodicity also exists in this ternary system. The experiment was repeated. The XRD pattern obtained from this

new experiment at four days after mixing  $C_6Li$  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  $0.13 \text{ \AA}^{-1}$  but with greater coherence length of  $\sim 55 \text{ \AA}$ . In addition, another set of broad reflections clustered at the sub-multiple value of  $0.65 \text{ \AA}^{-1}$  ( $d = 9.7 \text{ \AA}$ ) was evident.

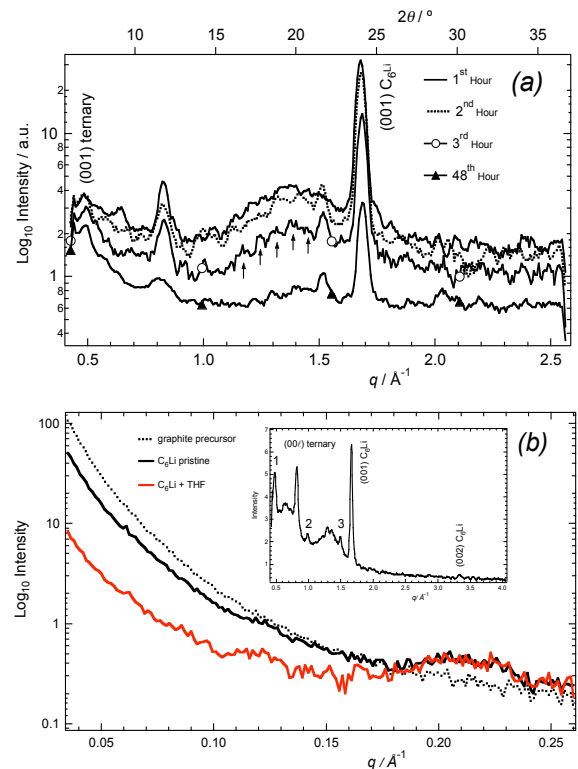


Fig. 3 (a) Successive X-ray diffraction patterns of powdered  $C_6Li$  exposed to liquid THF, 1<sup>st</sup>–48<sup>th</sup> hour, displayed as  $\log_{10} I$  vs  $q$ . Data from Figure 2. Small angle X-ray scattering measurements displayed as  $\log_{10} I$  vs  $q$  of (i) graphite precursor (dotted line); (ii) pristine  $C_6Li$  (solid line) and (iii)  $C_6Li$  exposed to liquid tetrahydrofuran after two days (red line). Insert shows XRD pattern denoting (00 $\ell$ ) of the ternary THF–Li–graphite compound after four days.  $\lambda = 1.54 \text{ \AA}$ .

The inset to Figure 3(b) also shows clearly the first three (00 $\ell$ ) reflections of the 1<sup>st</sup> stage ternary compound. As the (001) and (002) reflections of the pristine  $C_6Li$  are still evident in the pattern after four days, complete conversion of the binary  $C_6Li$  into the ternary compound had not been achieved. The SAXS pattern of the mixture is shown in Figure 3(b) together with that of out-gassed graphite and pristine  $C_6Li$ . The pattern shows two weak scattering maxima centred at  $0.12 \text{ \AA}^{-1}$  and  $0.21 \text{ \AA}^{-1}$ . 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

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.

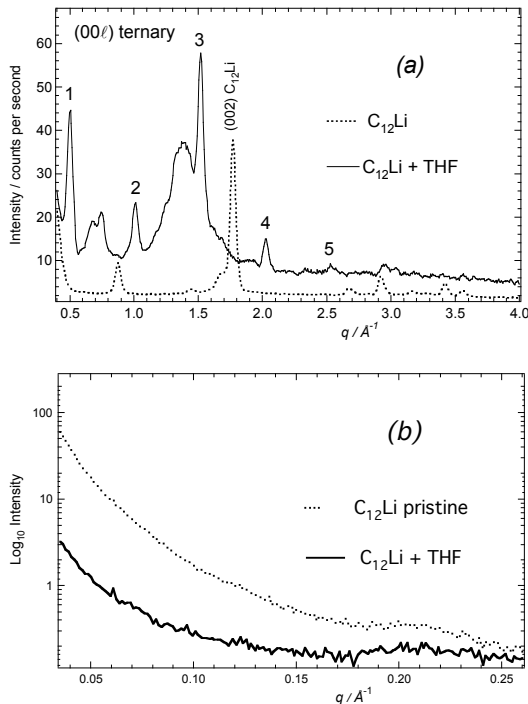


Fig. 4 (a) X-ray diffraction patterns displayed as  $I$  vs  $q$  of (i) powdered  $C_{12}Li$  (dotted line) and (ii) powdered  $C_{12}Li$  exposed to liquid THF after two days, displayed as  $I$  vs  $q$ .  $\lambda = 1.54 \text{ \AA}$ . (b) Small angle X-ray scattering measurements of powdered  $C_{12}Li$  (dotted line) and (ii) powdered  $C_{12}Li$  exposed to liquid THF after two days displayed as  $\log_{10} I$  vs  $q$ .  $\lambda = 1.54 \text{ \AA}$ .

Pristine  $C_{12}Li$ , Figure 4(a) displays the (002) reflection corresponding to an interlayer spacing of  $7.1 \text{ \AA}$ , in good agreement with the literature value of  $7.065 \text{ \AA}$ . [18] After 48 hours exposure of  $C_{12}Li$  to liquid THF, a series of strong reflections at  $0.50 \text{ \AA}^{-1}$  ( $7.1^\circ$ );  $1.0 \text{ \AA}^{-1}$  ( $14.3^\circ$ );  $1.5 \text{ \AA}^{-1}$  ( $21.5^\circ$ );  $2.0 \text{ \AA}^{-1}$  ( $28.9^\circ$ ) and  $2.5 \text{ \AA}^{-1}$  ( $36.2^\circ$ ) 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  $12.5 \text{ \AA}$ . 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<sup>st</sup> 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 H  rold. 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  $0.7 \text{ \AA}^{-1}$  and  $1.4 \text{ \AA}^{-1}$ , 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  $C_6Li$  exposed to THF forms a ternary THF-Li-graphite compound having a rational formula  $C_6Li(THF)_{1.4}$ . [23] Using the most dilute case where  $LiBH_4(THF)_3$  is entrapped within the crowded graphene planes, a  $LiBH_4:C_6Li:THF$  mole ratio approximately 1:2:3 provides a first guide to stoichiometry. As the reaction between  $C_6Li$  and THF is slow, the hydride- $C_6Li$ -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  $C_6Li$ .

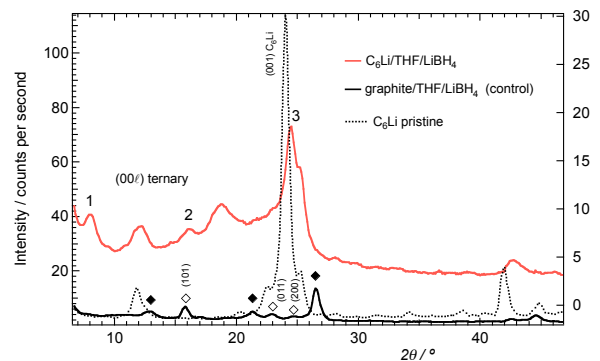


Fig. 5 X-ray diffraction patterns displayed as  $I$  vs  $2\theta$  of (i) powdered product of  $C_6Li + LiBH_4$  after reflux in THF (red line); (ii) a control obtained from graphite +  $LiBH_4$  after reflux in THF (black line) and (iii)  $C_6Li$  precursor (dotted line). The reflections from graphite and its impurities are indicated by  $\blacklozenge$ . The reflections from  $LiBH_4$  are indicated by  $\blacklozenge$ .  $\lambda = 1.54 \text{ \AA}$ .

## 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  $40^\circ$  and  $65^\circ$   $2\theta$  using  $\text{CuK}\alpha$  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  $3.44 \text{ \AA}$ – $4.89 \text{ \AA}$  but are centred near  $3.5 \text{ \AA}$ , and  $4.5 \text{ \AA}$ , [34]. A reflection at  $6.607 \text{ \AA}$  has also been reported for a carbon crystal obtained from marble [35].

The small reflections between  $3.9 \text{ \AA}$ – $4.4 \text{ \AA}$  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  $\text{C}_6\text{Li}$  and  $\text{C}_{12}\text{Li}$  precursors show reflections that cluster near  $0.7 \text{ \AA}^{-1}$  and  $1.3 \text{ \AA}^{-1}$ . We can conclude from the absence of lower order reflections from the SAXS study that the spacings represented by these clusters are 1<sup>st</sup> and 2<sup>nd</sup> order reflections and represent distances near  $9 \text{ \AA}$ . 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  $[\text{Li}(\text{THF})_2]^+$  complexes. Finally, a super lattice of about  $90 \text{ \AA}$  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  $12.4 \text{ \AA}$ , 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  $q = 0.21 \text{ \AA}^{-1}$ , similar to that observed for pristine  $\text{C}_6\text{Li}$ . It is tempting to posit the formation of a higher stage in the Li–C system, Stage VIII  $\text{C}_{72}\text{Li}$  which is reported to form at low pressures and has an interlayer spacing of  $27.05 \text{ \AA}$  [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  $\text{C}_6\text{Li}$  and  $\text{C}_{12}\text{Li}$  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  $\text{C}_8\text{M}$  ( $\text{M} = \text{K}, \text{Rb}$  and  $\text{Cs}$ ) that can display average unfaulted stacking domains in the  $c$ -axis direction of 6–10 layers. [37] However, structural faults separated by  $30 \text{ \AA}$ , 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  $\text{FeCl}_3$ -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  $\text{C}_6\text{Li}$  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  $\text{C}_6\text{Li}$  [39] which showed that surfaces of this binary material consist of island-like structures  $20 \text{ \AA}$ – $30 \text{ \AA}$  in depth as well as  $>100\text{nm}$  terraces separated by steps.



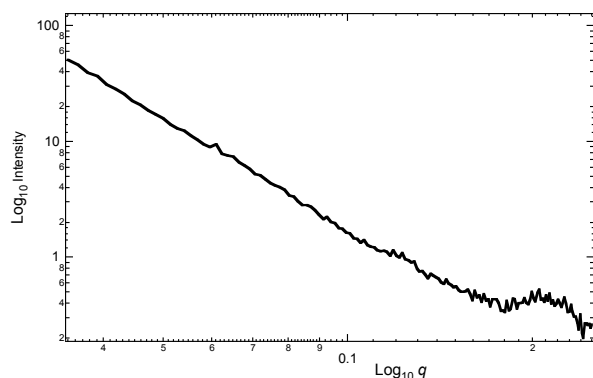


Fig. 6 Small angle X-ray scattering measurements of pristine  $C_6Li$  expressed as  $\log I$  vs  $\log q$ .  $\lambda = 1.54 \text{ \AA}$ .

The THF–Li–graphite compound was not destroyed by the action of  $LiBH_4$  during the refluxing conditions of the experiment as shown by the first three  $(00\ell)$  reflections of a ternary compound of Figure 5. Compared with the pattern obtained from the  $C_6Li$  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,  $(00\ell)$  reflections and the broad scattering typical of the ternary compound but has an interlayer spacing of  $11 \text{ \AA}$ , 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  $C_6Li$ . Unfortunately, a conclusion of the crystallinity of  $LiBH_4$  remains ambiguous because the scattering from the solid ternary THF–Li–graphite masks any reflections from  $LiBH_4$ .

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  $C_{12}Li$  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  $C_6Li$  or  $C_{12}Li$  prepared using this graphite was exposed to liquid tetrahydrofuran. Stage I  $C_6Li$  was converted to a ternary compound in the presence of  $LiBH_4$  solution without decomposition to graphite.

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