

## Chemical Lithiation Reveals the Structures of Conjugated Tetralithium Dicarboxylates

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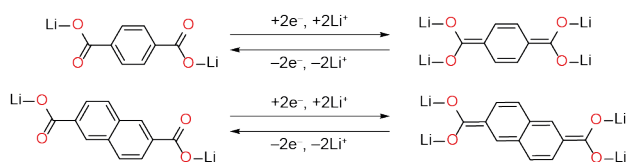
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**Conjugated metal dicarboxylates show promising properties as rechargeable battery anode materials, however, the structures of reduced (discharged) phases remain elusive. Here, we use chemical lithiation to solve the crystal structures of two tetralithium dicarboxylates for the first time. The structures are identical to those formed by electrochemical lithiation in coin cells. Solid-state NMR and DFT calculations show there is complete mixing of Li cations upon intercalation into the structure.**

The prevalence of rechargeable batteries in consumer devices is driving increasing interest in the development of sustainable battery chemistries. One family of materials that receiving significant interest is conjugated lithium dicarboxylates (Li<sub>2</sub>DCs), which show considerable promise as anode materials in lithium-ion batteries.<sup>1–3</sup> Li<sub>2</sub>DCs display high gravimetric capacities together with wide chemical diversity which allows their properties to be tuned and optimised. Additionally, they can be derived from green and sustainable sources, such as waste plastic.<sup>4,5</sup> However, organic anode materials tend to exhibit lower rate capabilities and cycle lives than more established anode materials such as graphite.

In 2009, Armand *et al.* showed that lithium benzenedicarboxylate (Li<sub>2</sub>BDC) can undergo reversible electrochemical lithiation to incorporate two further Li<sup>+</sup> ions per formula unit, to form Li<sub>4</sub>BDC.<sup>6</sup> This reaction occurred at 0.8 V vs Li<sup>+</sup>/Li<sup>0</sup> with a reversible capacity of 234 mA h g<sup>−1</sup> after 50 cycles. Lithium intercalation is proposed to occur *via* reduction of the BDC ligand with rearrangement of the  $\pi$  electron distribution as shown in Scheme 1. Increasing the degree of conjugation can improve cycling stability; this has been attributed to increased electronic conductivity,<sup>7–9</sup> although structural factors may also

be relevant. This effect can be seen when comparing Li<sub>2</sub>BDC with lithium naphthalenedicarboxylate (Li<sub>2</sub>NDC) which also undergoes reduction *via* a similar mechanism and displays higher rate capability.<sup>7,10</sup> However, despite the advances that have been made, there remains no clear consensus on the precise crystal structures of lithiated Li<sub>2</sub>DC phases. Knowledge of the locations of inserted Li ions, as well as any other structural rearrangements that take place upon reduction, will help to separate crystal structure and electronic structure effects, to further optimise these materials.



**Scheme 1.** Reaction scheme for the reversible reductive lithiation of Li<sub>2</sub>BDC and Li<sub>2</sub>NDC.

To gain insight into reduction mechanisms and the resulting structures, we prepared Li<sub>2</sub>BDC and Li<sub>2</sub>NDC as model dicarboxylate phases. Figs. 1a,b show galvanostatic charge-discharge curves for Li<sub>2+x</sub>DC/Li(s) coin cells cycled at a rate of C/20 between 0.7 and 3.0 V. The first discharges for Li<sub>2</sub>BDC and Li<sub>2</sub>NDC reach 425 mA h g<sup>−1</sup> and 520 mA h g<sup>−1</sup> respectively. These are higher than the theoretical capacities (Li<sub>2</sub>BDC – 255.1 mA h g<sup>−1</sup>; Li<sub>2</sub>NDC – 235.0 mA h g<sup>−1</sup>); however, additional capacity is expected due to contributions from carbon black,<sup>11,12</sup> as well as irreversible solid-electrolyte interphase (SEI) formation on the first discharge. For Li<sub>2</sub>BDC, a discharge capacity of 194 mA h g<sup>−1</sup> is achieved on the second cycle and the accessible capacity continues to decrease to 163.6 mA h g<sup>−1</sup> on the 5<sup>th</sup> cycle which is lower than the previously reported value;<sup>6</sup> this may be due to the unoptimised free-standing electrode used, as well as non-uniform particle size of Li<sub>2</sub>BDC crystallites (Fig. S1, 0.6 – 25.0  $\mu$ m), where larger crystallites do not fully lithiate due to the low

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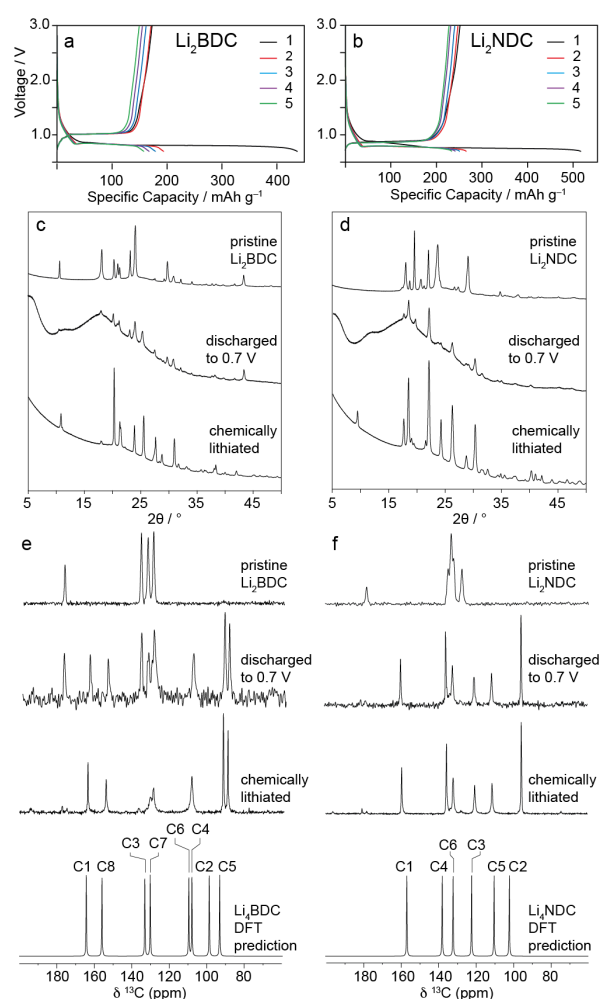
electronic conductivity. For  $\text{Li}_2\text{NDC}$ , a capacity of  $233.0 \text{ mAh g}^{-1}$  is reached on the 5<sup>th</sup> discharge, which is comparable to the theoretical capacity,<sup>7</sup> although it is possible the carbon additive and SEI could still contribute to the observed capacity at this point. The  $\text{Li}_2\text{NDC}$  sample used had a smaller average and range of crystallite sizes (Fig. S1,  $0.9 - 9.0 \mu\text{m}$ ) and also has higher intrinsic electronic conductivity.<sup>7</sup>

PXRD patterns of the as-made electrodes (Figs. 1c,d) are characteristic of the pristine  $\text{Li}_2\text{DC}$  phases. However, a broad background between  $19 - 25^\circ$  and discrete reflection at  $17^\circ$  are attributed to the carbon black additive and PTFE binder, respectively (Fig. S2). PXRD patterns for the discharged samples show an increased background due to the Kapton<sup>TM</sup> tape used to avoid air exposure (Fig. S2). For the discharged  $\text{Li}_2\text{BDC}$  anode, reflections of the pristine  $\text{Li}_2\text{BDC}$  phase are still evident; however, additional reflections are observed at  $25^\circ$  and  $27^\circ$ . For discharged  $\text{Li}_2\text{NDC}$ , pristine phase reflections are eliminated, and new reflections are observed between  $24^\circ$  and  $31^\circ$ . This indicates full conversion to a new phase, which is consistent with the capacity observed for this material. However, due to the low relative intensities it was not possible to resolve or index the phase(s) present for either discharged sample.

The  $^{13}\text{C}$  CPMAS NMR spectrum of the discharged  $\text{Li}_2\text{BDC}$  anode (Fig. 1e) shows residual resonances corresponding to the pristine phase, which is consistent with the lower-than-theoretical capacity. The appearance of new resonances between  $90.1$  and  $164.2 \text{ ppm}$  indicate a new phase has formed upon lithiation, which is consistent with the new PXRD reflections. No significant intensity is observed corresponding to SEI components or carbon additive; this is likely due to the relatively low mass fraction of SEI, and the absence of  $^1\text{H}$  in the carbon additive which precludes magnetisation transfer in the CPMAS experiment. The  $^{13}\text{C}$  CPMAS NMR spectrum of the discharged  $\text{Li}_2\text{NDC}$  anode (Fig. 1f) shows the pristine structure is no longer detected and instead six new resonances are observed between  $95.4$  and  $159.4 \text{ ppm}$ . This suggests that the close-to-theoretical capacity observed for this material reflects a higher level of conversion to the lithiated phase. For both materials, charging to  $3.0 \text{ V}$  results in complete reversion to the pristine phase (Fig. S3) for at least the first five cycles.

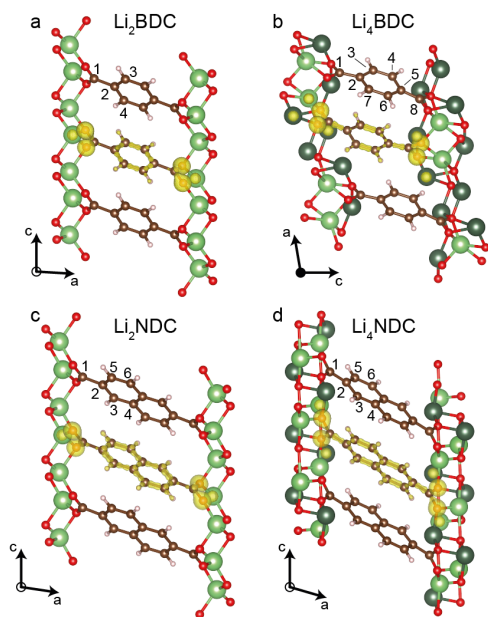
The PXRD and  $^{13}\text{C}$  CPMAS NMR data show electrochemical lithiation and delithiation drive reversible conversion between the pristine and reduced phases. However, from these results it is not possible to determine the structures of the reduced phases. An alternative approach for preparing reduced phases without the additional electrode components is chemical lithiation. This involves adding the solid  $\text{Li}_2\text{DC}$  to a solution containing lithium ions and a redox mediator. Naphthalene has a reduction potential of  $0.5 \text{ V vs. Li}^+/\text{Li}^0$ , which is below the observed plateaus at  $0.8 \text{ V}$  for  $\text{Li}_2\text{BDC}$  and  $\text{Li}_2\text{NDC}$ . Therefore, in a suitable solvent, naphthalene should oxidise  $\text{Li}$  metal to form  $\text{Li}^+$  and simultaneously drive reduction and lithiation of  $\text{Li}_2\text{DCs}$ .

$\text{Li}$  metal and naphthalene were dissolved in THF under argon to make a solution of  $3 \text{ M}$  concentration. The  $\text{Li}_2\text{DC}$  powders were soaked the ethereal solution for  $72$  hours before being washed in fresh THF and dried.  $^{13}\text{C}$  CPMAS NMR spectra of the recovered powders reveal almost complete conversion to



**Figure 1.** (a, b) Charge-discharge profiles of  $\text{Li}_2\text{DC}$  electrodes cycled at  $C/20$ . (c, d) PXRD patterns of pristine, electrochemically discharged, and chemically lithiated  $\text{Li}_2\text{DCs}$ . (e, f)  $^{13}\text{C}$  CPMAS NMR spectra of pristine, electrochemically discharged, chemically lithiated  $\text{Li}_2\text{DCs}$ , and DFT-predicted spectra for SCXRD  $\text{Li}_4\text{DC}$  structures.

reduced phases with the same chemical shifts as the electrochemically lithiated samples (Fig. 1e). Spectra of samples lithiated for shorter times show that the lithiation proceeds *via* a two-phase mechanism in both materials, with progressive loss of pristine phase resonances and simultaneous growth of the lithiated phase resonances (Fig. S4). Interestingly, chemical lithiation of  $\text{Li}_2\text{BDC}$  appears to proceed more slowly, requiring  $72$  hours for complete conversion compared to  $24$  hours for  $\text{Li}_2\text{NDC}$ . This mirrors the more sluggish electrochemical lithiation kinetics of  $\text{Li}_2\text{BDC}$  observed in this work and other studies.<sup>7</sup> EPR spectra of the lithiated samples show absorbances centred at  $g = 2.003$  for  $\text{Li}_4\text{BDC}$  and  $g = 2.004$  for  $\text{Li}_4\text{NDC}$  (Fig. S5). These results agree with previous data indicating the formation of carbon-centred radicals.<sup>6,13</sup> The radical concentration is low enough to permit the acquisition of undistorted NMR spectra; however, the  $^7\text{Li}$   $T_1$  values for the pristine  $\text{Li}_2\text{DCs}$  ( $\text{Li}_2\text{BDC}$   $191 \text{ s}$ ;  $\text{Li}_2\text{NDC}$   $264 \text{ s}$ ) decrease significantly after chemical lithiation ( $\text{Li}_4\text{BDC}$   $13 \text{ s}$ ;  $\text{Li}_4\text{NDC}$   $4 \text{ s}$ ). PXRD analysis of the chemically lithiated  $\text{Li}_2\text{DCs}$  also confirms phase purity (Figs. 1c,d) and retention of crystallinity.



**Figure 2.** Crystal structures of (a)  $\text{Li}_2\text{BDC}$ , (b)  $\text{Li}_4\text{BDC}$ , (c)  $\text{Li}_2\text{NDC}$  and (d)  $\text{Li}_4\text{NDC}$ . Three- and four-coordinate  $\text{Li}^+$  are shown in light and dark green, respectively. H, O and C atoms are shown in white, red and brown, respectively. DFT charge densities are superimposed in yellow.

The retention of crystallinity and identification of single lithiated phases for  $\text{Li}_2\text{BDC}$  and  $\text{Li}_2\text{NDC}$  prompted us to investigate single crystals. Crystals of the pristine phases were grown from vapour diffusion of acetone into aqueous solutions of the  $\text{Li}_2\text{DCs}$ . The structures were solved *via* single-crystal X-ray diffraction (SCXRD) analysis and the unit cell dimensions and structures agree well with literature structures (Tables S2, S3; CCDC 664607 ( $\text{Li}_2\text{BDC}$ ); 722281 ( $\text{Li}_2\text{NDC}$ )). Crystals were then soaked for 72 hours in the  $\text{Li}^+$ /naphthalene solution. This resulted in block-shaped crystals with a dark-red hue (Fig. S8). These were mounted in oil to prevent air exposure and SCXRD measurements were performed at 100 K. This gave two new structures with compositions  $\text{Li}_4\text{BDC}$  and  $\text{Li}_4\text{NDC}$  (Fig. 2); to our knowledge, these are the first experimental crystal structures reported for reduced forms of conjugated dicarboxylate materials. Crystallographic and structure refinement details are given in Tables S4, S5. Unit cell parameters for both SCXRD structures agree well with Le Bail extracted unit cell parameters of the PXRD samples (Table S1).

$\text{Li}_4\text{BDC}$  exhibits the monoclinic space group  $P2_1/n$ . Li sites  $\text{Li}1$ ,  $\text{Li}3$ , and  $\text{Li}4$  all have tri-planar coordination geometry, whereas  $\text{Li}2$  retains the tetrahedral coordination geometry observed in the pristine phase (Fig. S9). The carbon-carbon bond lengths C1-C2, C3-C4, C6-C7, and C5-C8 are contracted by between 2.2 – 8.6% when compared to pristine  $\text{Li}_2\text{BDC}$  (Table S6). Each reduced BDC ligand has identical coordination geometry to surrounding  $\text{Li}^+$ , and the  $\text{Li}_4\text{O}_4$  dicarboxylate layers are separated by diagonally oriented reduced BDC linkers (Fig. S9), with a herringbone-like stacking of the BDC linkers as seen in the pristine structure. However, due to differing chelation to  $\text{Li}^+$  at either end of the ligands, the structural symmetry is lowered and each carbon atom within each ligand is crystallographically distinct. Furthermore, each reduced ligand

is bent out of plane with an angle of  $7.4^\circ$  between C2-C5-C8. Alternation in the bending direction between adjacent layers leads to an approximate doubling of the unit cell  $c$  axis (Fig. S9).

$\text{Li}_4\text{NDC}$  exhibits the monoclinic space group  $P2_1/c$ . There are two distinct  $\text{Li}^+$  environments,  $\text{Li}1$  which has a highly distorted tri-planar coordination geometry, and  $\text{Li}2$  which has a distorted four-coordinate planar geometry (Fig. S10). Carbon-carbon bond lengths C1-C2, C3-C4, and C5-C6 are also contracted by 0.7 – 7.4% compared to  $\text{Li}_2\text{NDC}$  (Table S7). The NDC ligands also display a herringbone-like stacking arrangement as seen in the pristine phase; however, in contrast to  $\text{Li}_4\text{BDC}$  the symmetry of the ligand is retained.

To rationalise the experimental  $^{13}\text{C}$  chemical shifts, periodic DFT calculations were performed on geometry-optimised crystal structures of the reduced phases (Figs. 1e, f, Fig. S11, Tables S8, S9). For  $\text{Li}_4\text{BDC}$ , the calculated shifts are in good agreement with experiment, although the C4 and C6 resonances are unresolved in the experimental spectrum. For  $\text{Li}_4\text{NDC}$ , the calculated shifts also show good agreement with experiment. DFT charge density plots (Fig. 2) also support the proposed reduction mechanism. In the pristine phases, electronic charge is distributed approximately evenly around the rings within the ligand, and lower charge densities are observed on the carbonyl-quaternary C-C bonds. In the reduced phases, charge density is concentrated between the CH-CH bonds, and on the carbonyl-quaternary C-C bonds, reflecting the change in conjugation and loss of aromaticity of the rings.

The presented crystal structures of  $\text{Li}_4\text{BDC}$  and  $\text{Li}_4\text{NDC}$  unequivocally show that two  $\text{Li}^+$  cations intercalate per formula unit, and that the ligands are reduced in a two-electron process. The  $^{13}\text{C}$  CPMAS NMR data show that both chemical lithiation and electrochemical lithiation form the same structures, albeit with an incomplete reaction in the electrochemical method for  $\text{Li}_2\text{BDC}$ . Within the lithiated structures, the herringbone-like ligand arrangements are retained from the  $\text{Li}_2\text{DC}$  precursors. In a previous study of  $\text{Li}_2\text{NDC}$ , it was proposed on the basis of a PXRD refinement and DFT optimisations that the coordination environment and geometry of the  $\text{Li}_2\text{O}_4$  dicarboxylate layer is completely retained, but additional Li cations intercalate in two locations between the NDC layers.<sup>8</sup> However, the SCXRD structure determined here unambiguously shows only two  $\text{Li}^+$  cation environments, both of which are within the Li-O layer, and one of which has a tri-planar coordination geometry. DFT calculations show that the two previously proposed structures correspond to local energy minima, but our SCXRD structure is more stable than both of these by 0.07 and 0.20 eV per formula unit (Table S10). For  $\text{Li}_4\text{BDC}$  there is a more substantial rearrangement of the Li-O layer, with only a single site retaining tetrahedral coordination and the more complex coordination mode and bent geometry of the reduced BDC ligand.

Static  $^7\text{Li}$  NMR spectra for the pristine phases (Fig. 3) show intense  $^7\text{Li}$  central transitions surrounded by quadrupolar-broadened satellite transition powder patterns. The reduced phases show broader satellite transition powder patterns; this is consistent with DFT calculations that predict increased  $^7\text{Li}$   $Q_{\text{Li}}$  values for the lithiated structures (Table S11). For  $\text{Li}_4\text{BDC}$ , DFT overestimates the powder pattern line width by approximately

25%. This may suggest partial averaging of the quadrupolar interaction due to Li dynamics within the structure.

Given the substantial changes in Li ordering within the Li-O layers in both materials, it is natural to question on which crystallographic locations the inserted Li ions reside. It is important to note that for the reduced phases, each observed powder pattern comprises the superposition of individual powder patterns from the four ( $\text{Li}_4\text{BDC}$ ) or two ( $\text{Li}_4\text{NDC}$ ) different crystallographic Li environments in each structure. Therefore, inserted  $\text{Li}^+$  can be potentially distinguished from those remaining from the pristine phase using  $^7\text{Li}$  isotope tracking and exploiting the large difference in natural abundance of  $^6\text{Li}$  (7.8%) and  $^7\text{Li}$  (92.2%). To test this, natural abundance pristine samples were chemically lithiated with isotopically enriched solutions containing 95%  $^6\text{Li}^+$ . In addition,  $^6\text{Li}$ -enriched (95%) pristine samples were lithiated using natural abundance solutions. In this approach, if inserted  $\text{Li}^+$  ions preferentially reside on particular crystallographic sites, the relative intensities of the  $^7\text{Li}$  line shape components corresponding to these sites should be reduced in natural-abundance samples lithiated with  $^6\text{Li}$ -enriched lithium, and enhanced in  $^6\text{Li}$ -enriched samples lithiated with natural-abundance lithium. However, as shown in Fig. 3, the line shapes for all samples are identical, showing that  $^7\text{Li}$  ions are in fact distributed with equal probability across all sites within each structure. Therefore, there must be complete mixing of  $\text{Li}^+$  within the structure during lithiation. In addition, quantitative  $^7\text{Li}$  NMR measurements show that the  $^7\text{Li}$  population within the lithiated phase is always weighted towards the  $^7\text{Li}$  content of the ethereal solution and does not follow the  $^7\text{Li}$  content of the pristine phase (Tables S11–S12, Fig. S12). This indicates that during insertion of Li ions into the structure, there is a global ion exchange between the solid structure and the solution.

Herein we have shown that chemical lithiation of model organic battery anode materials can enable full structure solution of lithiated phases. The combination of SCXRD and solid-state NMR unequivocally shows that chemical and electrochemical lithiation produce the same structures. Furthermore,  $^7\text{Li}$  NMR and DFT shows there is complete rearrangement of  $\text{Li}^+$  within the  $\text{Li}_4\text{O}_4$  layer. Previously, the improved cycling efficiency of  $\text{Li}_2\text{NDC}$  over  $\text{Li}_2\text{BDC}$  has been attributed to only increased electronic conductivity of the former; however, the highlighted differences in the lithiated structures and complete rearrangement of the Li layers may allow for a re-examination of structure-property relationships in organic anode materials.

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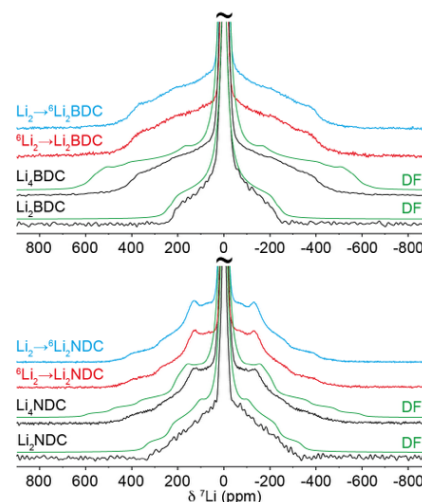
## Data availability

Crystallographic data has been deposited (2450774-7) at the CCDC and can be obtained from <https://www.ccdc.cam.ac.uk>. Additional

details are available in the corresponding ESI, and raw data underpinning this work is available at [link].

## Conflicts of interest

There are no conflicts of interest to declare



**Figure 3.** Experimental and calculated static  $^7\text{Li}$  NMR spectra of  $\text{Li}_2\text{DCs}$  and  $\text{Li}_4\text{DCs}$ . Calculated line shapes include 5 kHz line broadening.  $^6\text{Li}$ -enriched  $\text{Li}_2\text{DCs}$  lithiated with natural abundance solution are denoted  $\text{Li}_2 \rightarrow ^6\text{Li}_2\text{DC}$ ; natural abundance  $\text{Li}_2\text{DCs}$  lithiated with  $^6\text{Li}$ -enriched solution are denoted  $^6\text{Li}_2 \rightarrow \text{Li}_2\text{DC}$ .

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