

# Investigation of sodiation mechanisms of organic anode materials

Using a combination of solid-state NMR, powder XRD & pair distribution function techniques



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## Abstract

- Investigating the sodiation mechanism by which sodium ions intercalate into the Na<sub>2</sub>BDC structure, enabled increased understanding of how the process occurs, and will help to **discover other compatible materials**.
- Various characterisation techniques were used to analyse structural changes between the pristine and sodiated molecule.
- Pristine Na<sub>2</sub>BDC was also lithiated to allow a full comparison across the range of possible samples, and to analyse if the mechanism differed between lithium and sodium ion intercalation.

## Motivation

- Sodium-ion batteries look to be more sustainable alternatives to their lithium-ion counterparts, as they are **cheaper**, have significantly **higher natural abundance**, and are **more environmentally friendly**.<sup>1</sup>
- Hard carbon is the most readily used anode in sodium-ion batteries to enable successful sodium intercalation, but using hard carbon requires both **high temperatures** and **energy intensive synthesis conditions**.
- Organic anode materials such as sodium dicarboxylates are shown to be more sustainable anode substitutes to hard carbon, and within this project, **sodium benzene dicarboxylate** (Na<sub>2</sub>BDC) was used as the model structure.<sup>2</sup>

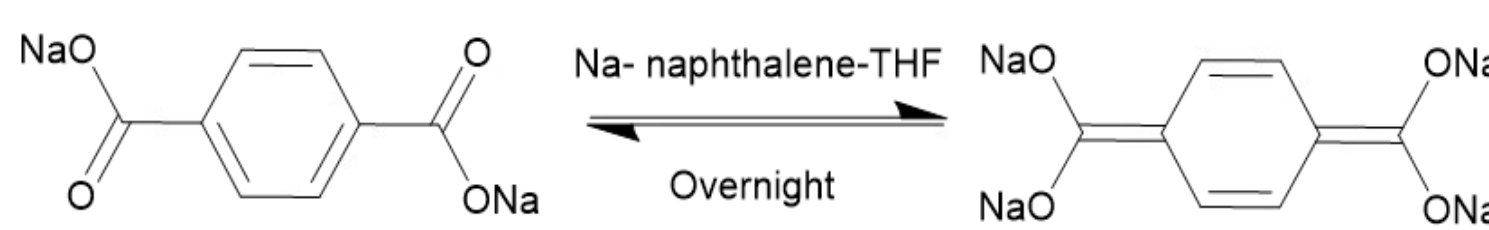


Figure 1. Proposed mechanism of the sodiation of pristine Na<sub>2</sub>BDC

## Methods

- Pristine synthesis**- Prepared by solvothermal reflux of NaOH and terephthalic acid for 2 hours.
- Soaking of pristine sample**- A 3M solution of Na-naphthalene-THF was prepared, using 1.154 g of naphthalene, 3 mL of THF solution, and 0.207 g of small chunks of sodium metal. 1.5 mL of solution was added to the pristine sample and left overnight to soak and a colour change was observed from a white powdered pristine to a dark-brown coloured powder after sodiation.
- PDF analysis and refinement**- Calculated the probability of a pair of atoms being found at specified distances apart. It produced a set of peaks, which each corresponded to a specific bond contribution. PDF extraction was performed using PDFgetX2, and PDF refinement was carried out using PDFgui.
- ssNMR**- Carried out on a Bruker Avance III HD 700 MHz NMR spectrum, using a combination of 2.5 mm and 3.2 mm rotors, to pack the pristine, sodiated and lithiated samples, with NMR analysis taking place on Topspin 3.5pl7 software.
- PXRD and Rietveld refinement**- Carried out on a Rigaku Smartlab Diffractometer containing a 9 kW Cu-source generator over a range of 5-65°. Rietveld refinement was undertaken using the GSAS II software.

## Section 1- Pristine phase characterisation

- PXRD was obtained of synthesised Na<sub>2</sub>BDC sample, and compared to simulated data, generated on Vesta, to **ensure sample purity**.
- There are no impurities present in the sample and the **peak positions are consistent**, although changes in peak intensity are visualised.

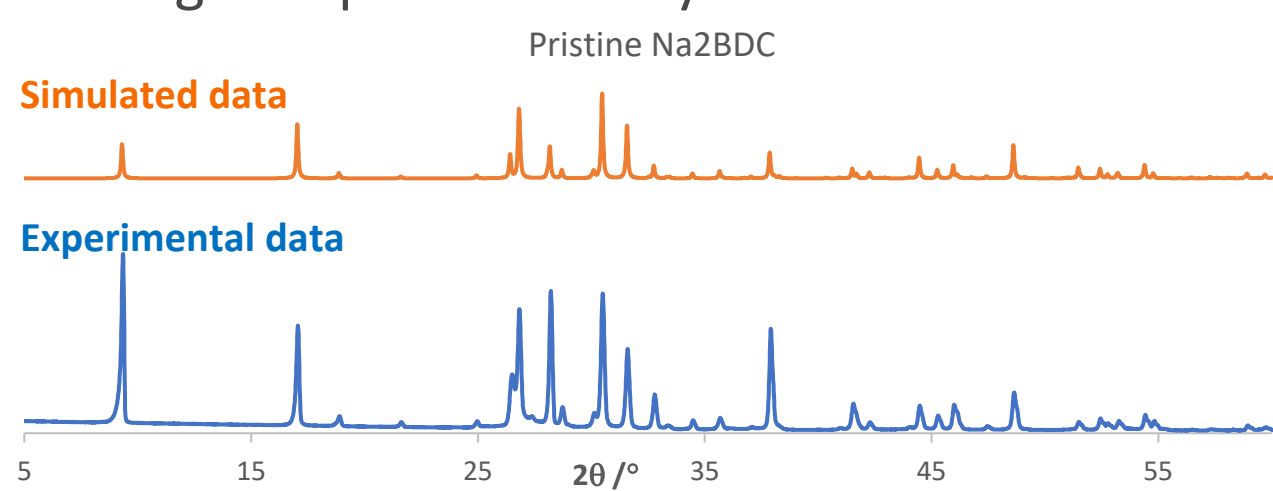


Figure 2. Overlay of simulated & experimental PXRD pristine Na<sub>2</sub>BDC

- PDF of the pristine Na<sub>2</sub>BDC sample was extracted, and individual simulations of specific bond contributions to the original spectrum were generated, enabling each **peak to be assigned to specific bonds**.

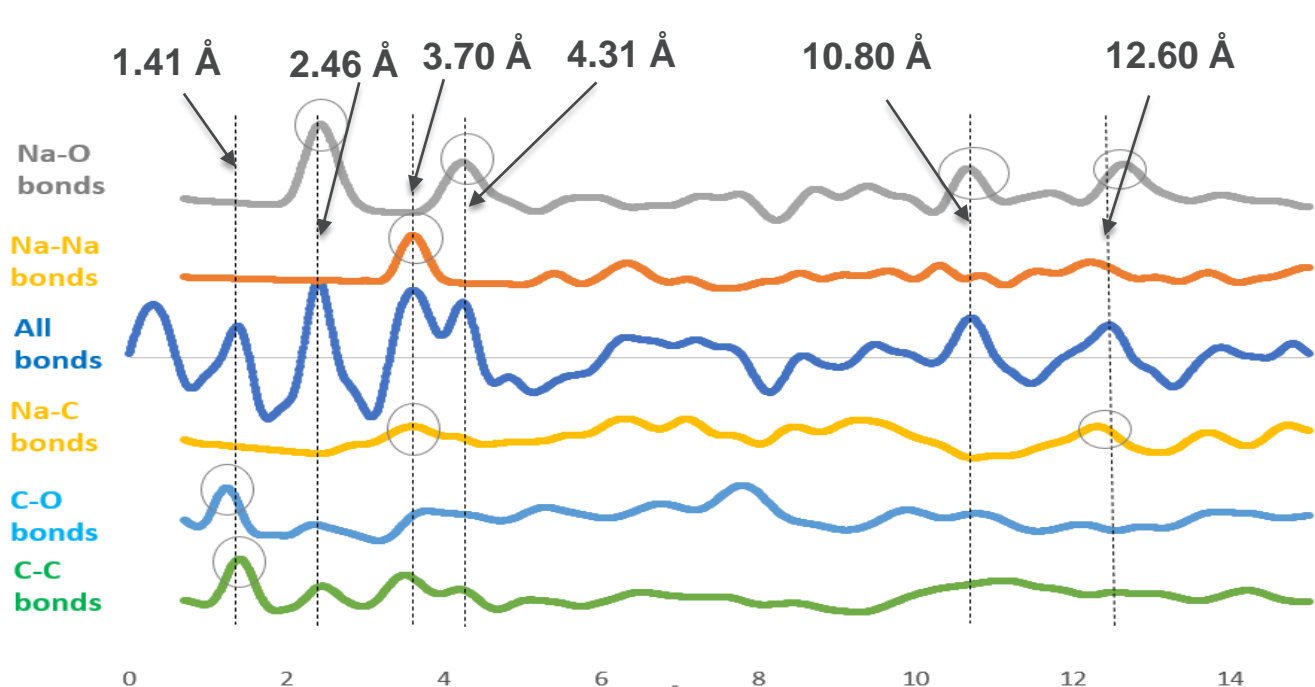


Figure 3. Visualisation of the various bond contributions to the peaks for the PDF spectrum of pristine Na<sub>2</sub>BDC

## Section 2- ssNMR analysis

- <sup>13</sup>C NMR spectral overlay highlights that there appears to be a **lower conversion rate** for the lithiated sample, due to more pristine peaks remaining than in the sodiated sample.
- Two additional peaks present in the two intercalated samples, and a **change in the chemical shift peak positions**, confirm a structural change.

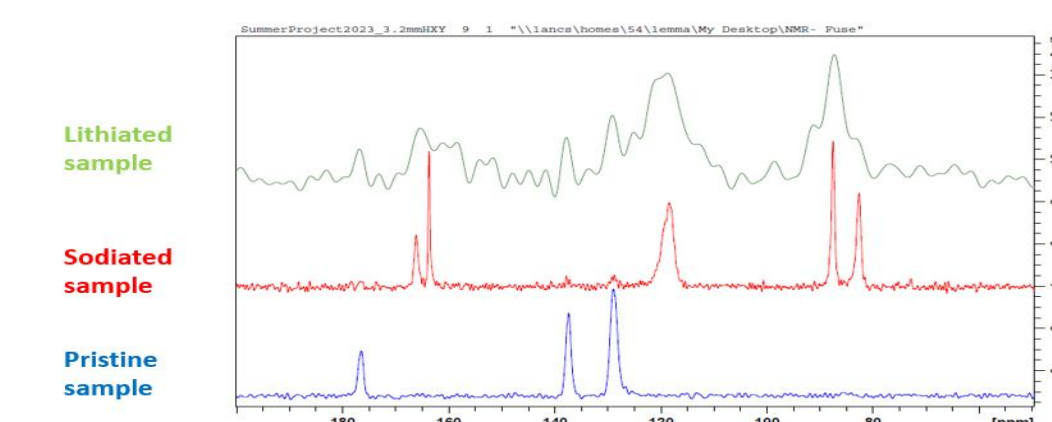


Figure 4. The <sup>13</sup>C overlay for the three Na<sub>2</sub>BDC samples

- <sup>23</sup>Na spectral overlay shows a **significant increase in the number of sodium sites** in the sodiated sample, and the MQMAS comparison provides further evidence for this.

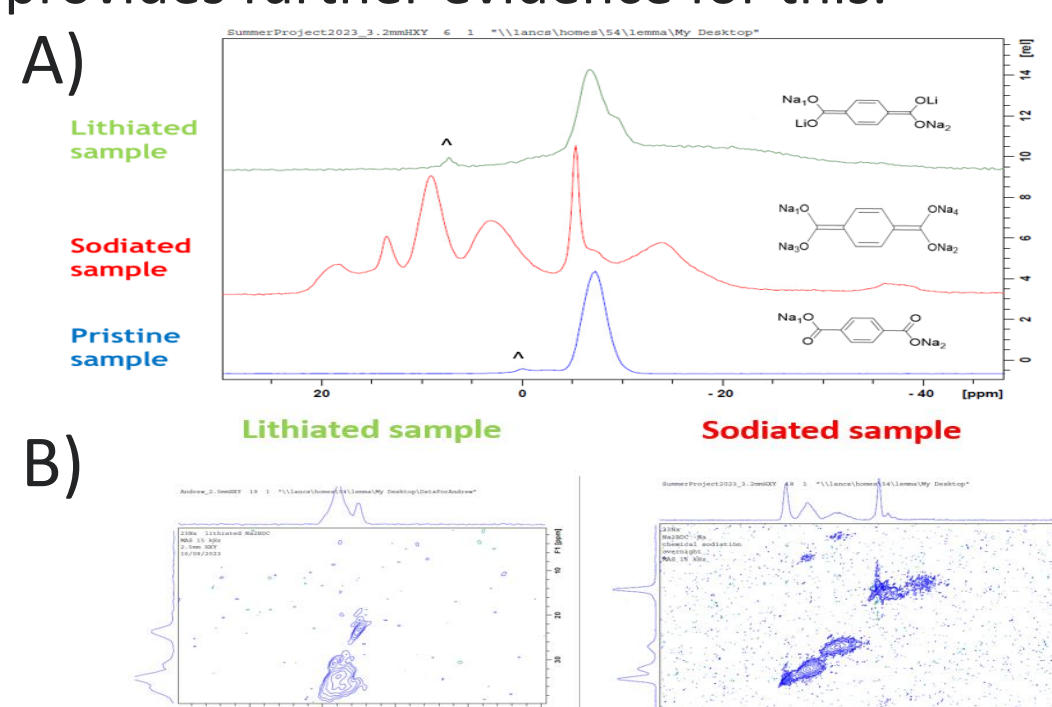


Figure 5. A) The <sup>23</sup>Na overlay for the three Na<sub>2</sub>BDC samples B) MQMAS spectra for the lithiated and sodiated samples respectively<sup>3</sup>

## Section 3- PDF analysis of the three Na<sub>2</sub>BDC samples

There are a multitude of variations in the PDF spectra between the three Na<sub>2</sub>BDC phases:

- The first major peak (C-C & C-O bonds) appears to have an **increased average distance** in the lithiated sample compared to the other two samples, which appears difficult to explain.
- After approximately 8 Å, both intercalated samples **flatten off**, showing minimal peaks, which contrasts to the pristine, whereby **strong peaks** are still shown up to 15 Å.
- Li-Li bonds in the lithiated sample are **difficult to observe**, which is not surprising, due to the ions being much lighter than sodium.

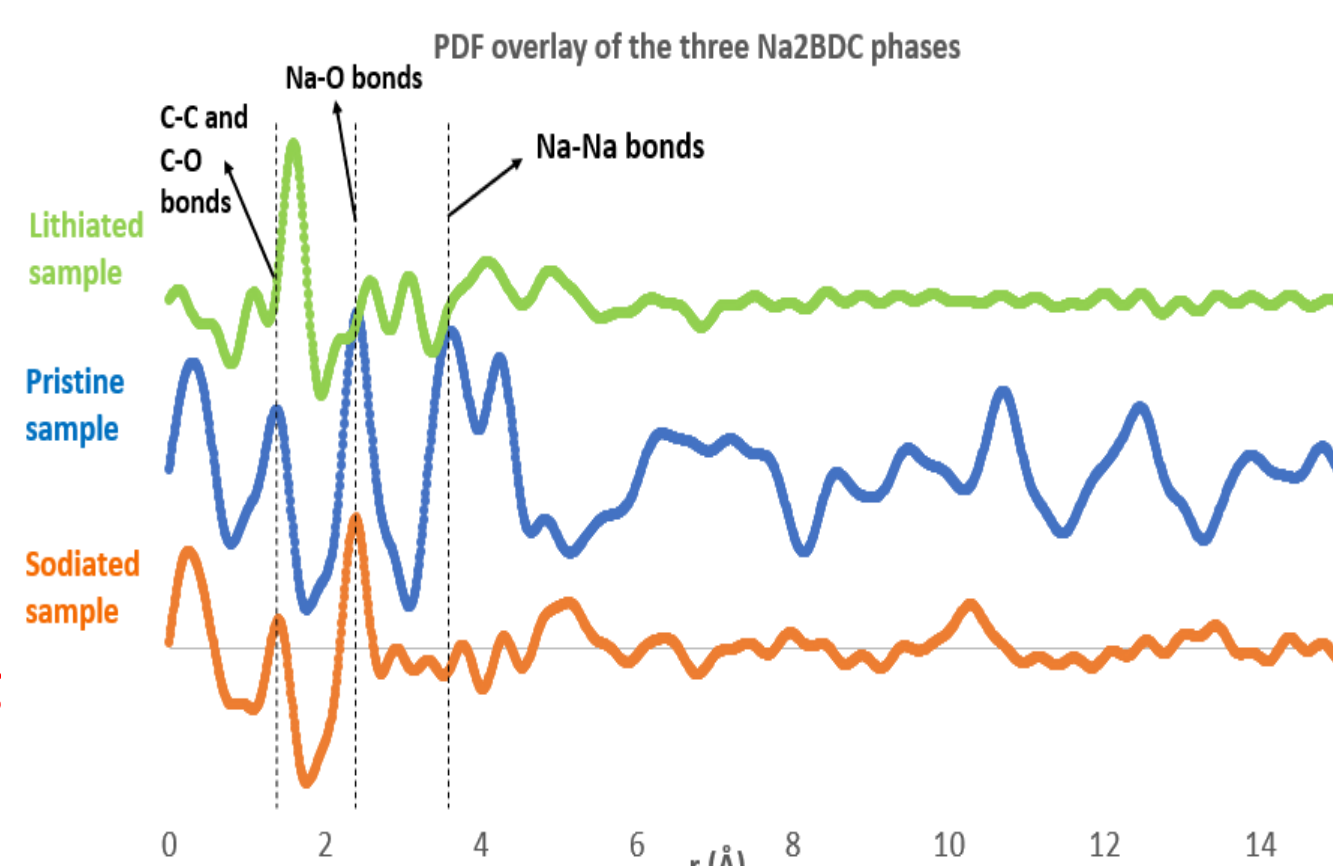


Figure 6. An overlay showing the key peaks for the PDF of the three Na<sub>2</sub>BDC samples

## Conclusions

- The data obtained from the project points heavily towards the intercalation of ions into the pristine Na<sub>2</sub>BDC, causing **significant alterations to the structure** of the molecule.
- The ssNMR <sup>13</sup>C data implies that **multiple phases** may exist within the sodiated sample, which causes the **increased number** of carbon environments, and explains the two sets of adjacent peaks.

## Impact / Next steps

- Utilising both PDF and NMR characterisation techniques to quantify the structure of molecules is an exciting and innovative field of research.
- Next steps may involve performing these techniques on a **wider range** of sodiated dicarboxylate molecules, such as Na<sub>2</sub>NDC and Li<sub>2</sub>BDC, to see if the **observed results vary** with the specific molecule used.

## Intern bio

Andrew is studying Chemistry at Lancaster University and is going into the fourth and final year of his integrated Master's degree. Andrew has always been interested in identifying the structure of molecules via NMR spectroscopy, and his main areas of interest involve both analytical and computational research. Andrew's next steps will involve securing a chemistry related graduate scheme.



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## References

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