Mapping Lithium Ion Mobility in All-Solid-State Batteries

How does hot pressing affect lithium diffusion in argyrodite electrolytes?

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Abstract

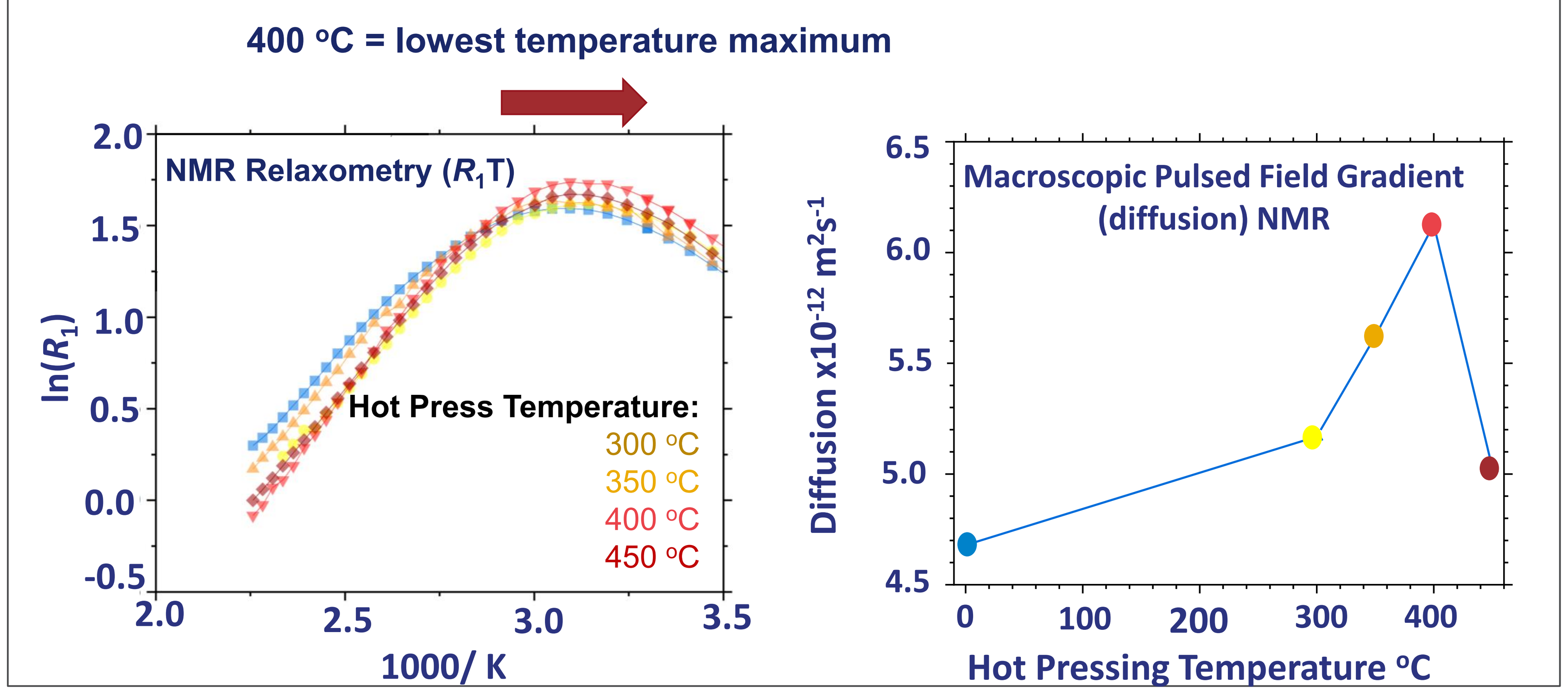
- Solid State Batteries (SSBs) have higher energy densities and are inherently safer than conventional lithium-ion Batteries (LiBs).
- However, commercialisation of SSBs is hindered due to low ion mobility.
- This is further complicated by the inability to measure lithium ion dynamics over a range of length scales, from one bond hops (nano-ionics) to macroscopic migrations through and across particles (macro-ionics).
- Using a commercially relevant argyrodite ($Li_{5.5}PS_{4.5}Cl_{1.5}$) we have explored a magnetic resonance probe to determine ionic conductivity and adding spatial resolution by MRI.
- Using this combined magnetic resonance approach the optimum hot-pressing temperature was found to be 400 ^oC (673.1 K), as above this temperature the material degrades.

Motivation

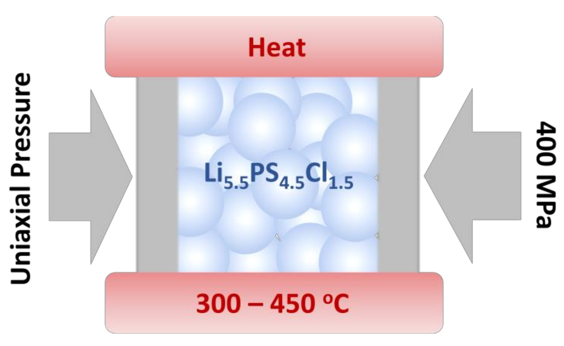
- There is a dearth of analytical techniques capable of measuring ionic conductivity over different length scales.
- Developing varying length scale diffusion NMR & MRI methods allows us to identify diffusion bottlenecks in SSBs.

Diffusion NMR

- Hot pressing to 400 °C increases both the *microscopic (T_1 maxima)* and *macroscopic ion* (PFG-NMR) *mobility*.
- Above this temperature, the PFG-NMR determined diffusion coefficient decreases due to degradation of the $Li_{5.5}PS_{4.5}Cl_{1.5}$.

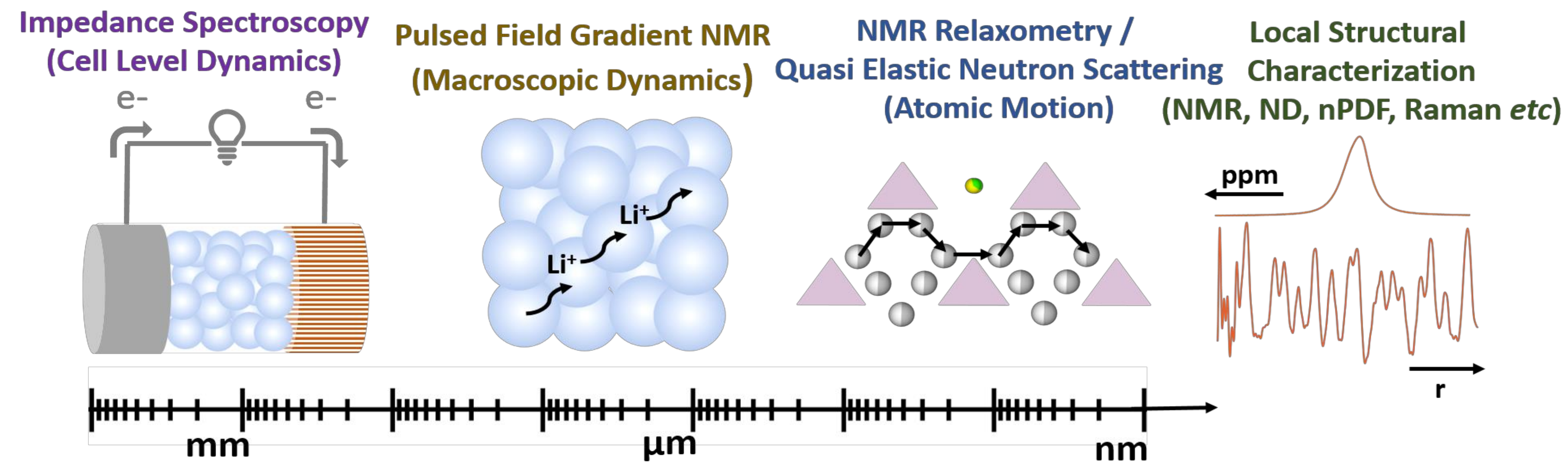


Methods – Sample Preparation

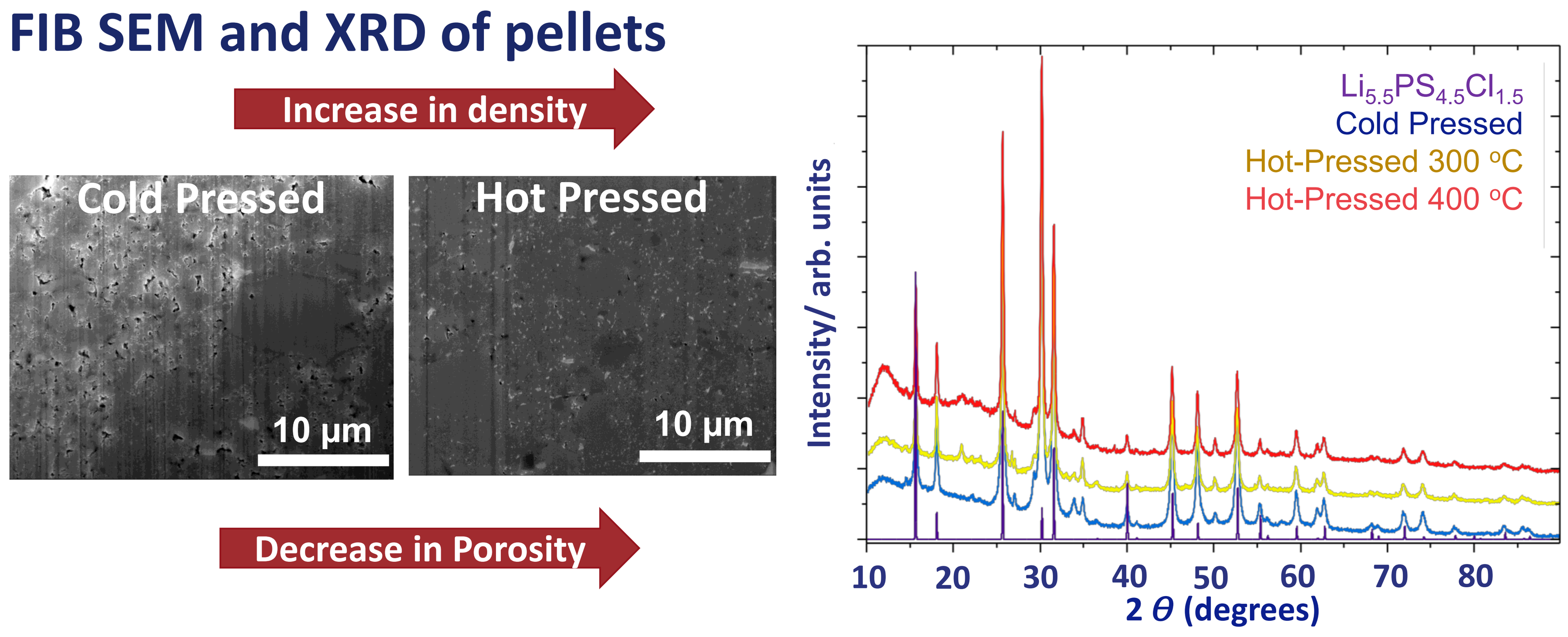


- Hot pressing is a potentially commercially scalable methodology for densifying SSBs.
- $Li_{5.5}PS_{4.5}Cl_{1.5}$ argyrodite powders were pressed uniaxially at 400 MPa.
- Whilst under pressure the 3 mm pellets were heated to various temperatures (300-450 °C) forming densified pellets.

Methods – Measuring Dynamics over Varying Length Scales[2,3]



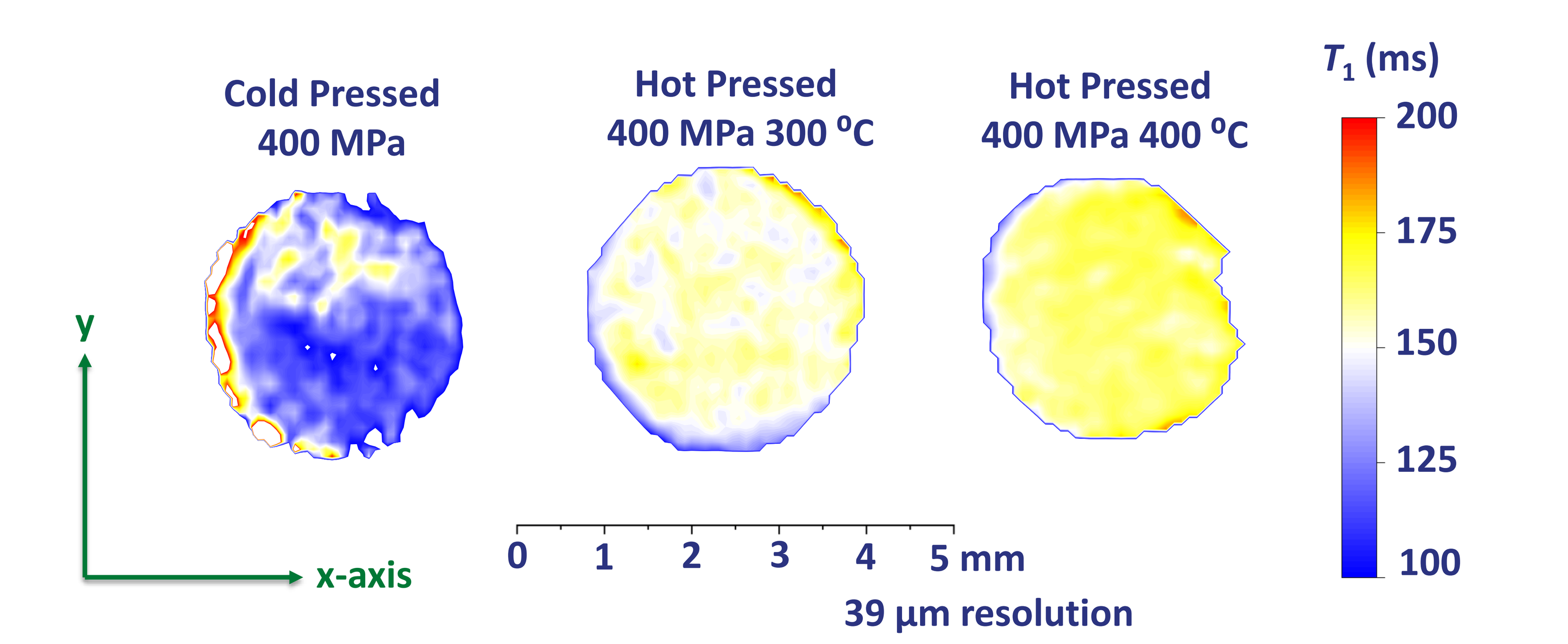
FIB SEM and XRD of pellets



- Focused ion beam-scanning electron microscope (FIB-SEM) demonstrates that hot pressing increases the density of the argyrodite.
- Powder X-ray diffraction (XRD) suggests that the chemical structure of the pellet is not being compromised by hot pressing up to 400 ^oC.
- Small amounts (~2 %) of LiCl and Li_2S are present in all the electrolytes, including the cold pressed and are therefore not caused by hot-pressing.

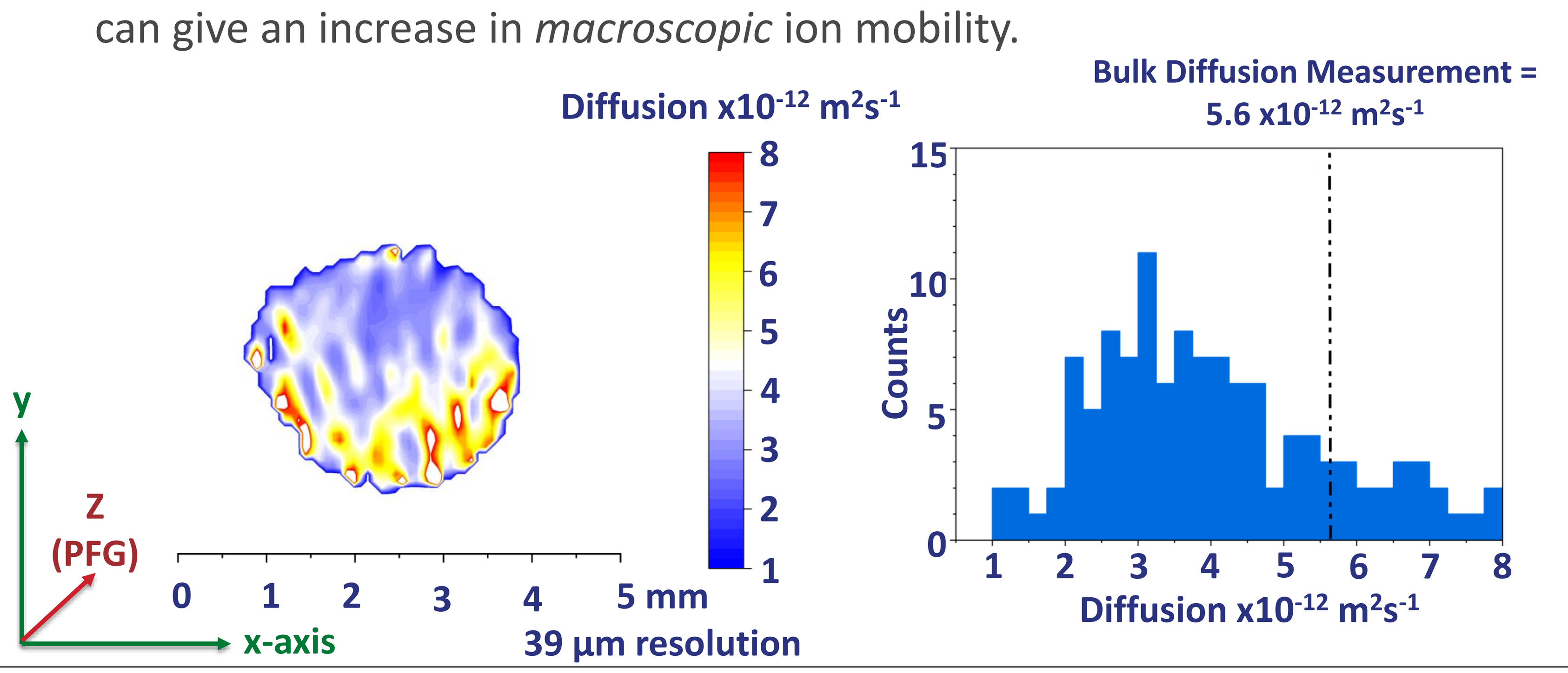
Microscopic Diffusion - ^{7}Li T_1-contrast MRI

- Hot pressing increases the spin lattice relaxation (T_1) within the electrolyte. An increase in T_1 is indicative of improved *microscopic* ion mobility.
- A more homogenous spread of T_1 relaxation times when hot pressing. This shows that not only increased microscopic lithium ion mobility when hot-pressed to 400 °C but also more evenly distributed mobility.



Macroscopic Diffusion - ^{7}Li diffusion-contrast MRI

- For the first time, diffusion-contrast MRI was used to give spatial information and *macroscopic* ion mobility.
- The hot-pressed pellet (350 °C) shows there is a range of macroscopic diffusion coefficients.
- The maximum diffusion ($8x10^{-12}$ m^2s^{-1}) is x2.5 greater than the average diffusion coefficient ($3x10^{-12}$ m^2s^{-1}). This suggests that further densification can give an increase in *macroscopic* ion mobility.



Impact / Next steps

- Novel diffusion-contrast MRI experiments were completed on solid state materials.
- This is a viable technique for gaining spatial diffusion information with macroscopic diffusion contrast.
- The results showed that hot pressing samples increases ion mobility at both microscopic and macroscopic length scales.
- Hot pressing at 400 ^oC gives the maximum increase in ion mobility without changing the microstructure or chemical structure.
- Future work will include optimization of diffusion-contrast MRI, the hot-pressing procedure, and testing full cell performance.

References

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2. M. Uitz, V. Epp, P. Bottke and M. Wilkening, *J Electroceram*, 2017, **38**, 142–156.
3. K. S. Han, J. D. Bazak, Y. Chen, T. R. Graham, N. M. Washton, J. Z. Hu, V. Murugesan and K. T. Mueller, *Chemistry of Materials*, 2021, 33, 8562–8590.

Intern Bio

Alice is a third year MSci student at Imperial College, London studying Chemistry. After graduating she hopes to pursue a DPhil in battery research and development.

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