**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-ions) to macroscopic migrations through and across particles (macro-ions).
- Using a commercially relevant argyrodite (Li1.33PS2.33Cl1.33) 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 °C (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 (T1, maxima) and macroscopic ion (PF-G-NMR) mobility.
- Above this temperature, the PF-G-NMR determined diffusion coefficient decreases due to degradation of the Li1.33PS2.33Cl1.33.

**Microscopic Diffusion - ²Li T1-contrast MRI**

- Hot pressing increases the spin lattice relaxation (T1) within the electrolyte. An increase in T1 is indicative of improved microscopic ion mobility.
- A more homogenous spread of T1 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.

**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 °C.
- Small amounts (~2 %) of LiCl and LiS are present in all the electrolytes, including the cold pressed and are therefore not caused by hot-pressing.

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**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 °C 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.

**Methods – Sample Preparation**

- Hot pressing is a potentially commercially scalable methodology for densifying SSBs.
- Li1.33PS2.33Cl1.33 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.

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**Methods – Measuring Dynamics over Varying Length Scales**

- Measuring Dynamics over Varying Length Scales (2, 3, 5)
- Magnetic Resonance Imaging (MRI)
- Nuclear Magnetic Resonance (NMR)
- Positron Emission Tomography (PET)
- X-ray Diffraction (XRD)
- Pulsed Field Gradient NMR (PF-G-NMR)

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**References**


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**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.