CHARACTERISING ANTI-PEROVSKITE SOLID ELECTROLYTES
Using AFM to explore the properties of Li$_2$OHX systems

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INTRODUCTION
With the increased demand for renewable energy sources, solid state lithium metal batteries (SSLMBs) could pave the way for the future of energy storage. They offer several advantages over liquid electrolyte batteries, primarily:
- Safety
- Higher energy density
- Longer life cycle
- Wider operating temperature range

Lithium hydroxyhalide anti-perovskites (Li$_2$OHX, X = Cl, Br) are good candidates for the solid electrolytes required in these batteries due to their ionic conductivity, chemical inactivity when in contact with lithium and their low melting points (~300°C) which allows for dense samples to be produced in a single step, with the grain size controlled through the cooling rate. This is important as porosity and grain boundaries can lead to inhomogeneous lithium deposition$^2$.

Atomic force microscopy (AFM) was used to image these solids, capable of mapping the topography and mechanical properties simultaneously.

MOTIVATION
- Characterising the microstructure and properties of Li$_2$OHX and Li$_2$OHBr helps to understand the phase diagrams, guiding future synthesis
- This could help in the design of future batteries using these solid electrolytes

METHODS
- Pellets of each bromide and chloride, synthesised with a slight excess of LiOH (1:1.07, LiX:LiOH, due to seeing large impurities in the XRD for 1:1)$^2$, were set in an epoxy resin and polished using grinding papers in an argon filled glovebox
- The samples were then imaged using an optical microscope
- The AFM was calibrated to give the tip radius, deflection sensitivity and spring constant of the cantilever enabling accurate force determination during imaging
- PeakForce Quantitative Nanomechanical Mapping (PF-QNM) was employed to measure very fast force-displacement curves at every pixel, with the retrace curves used to calculate the elastic modulus of each sample (using the same imaging conditions) whilst the height was simultaneously mapped. Further information about AFM can be found here.

REFERENCE

OPTICAL MICROSCOPE IMAGES

CHLORIDE
- The polishing process revealed a dendritic microstructure with eutectic regions
- From the phase diagram, the secondary phase is expected to be LiOH
- The phase diagram is more complex and not fully understood, the reaction doesn’t pass through a eutectic point and so eutectic growth is not expected.

BROMIDE
- There is no evidence for impurity phases
- The only surface features are porosity and scratches (from the polishing)

 PF-QNM IMAGES: HEIGHT AND MODULUS MAPPING

CHLORIDE
- Height map
- Elastic Modulus

BROMIDE
- Height map
- Elastic Modulus

CONCLUSIONS
- A two phase eutectic region is shown in both the height map and modulus of the chloride sample, which is further evidenced by the modulus distribution plot showing two peaks for the chloride (one for each phase)
- The bromide sample appears to be a single phase in this region as shown by the single peak in the plot
- The chloride sample has a higher modulus in the anti-perovskite phase (the peak at about 70 GPa) compared to the bromide (peak at 35 GPa)

IMPACT / NEXT STEPS
- The difficulty of the synthesis of these pure solid electrolytes is often overlooked, and for the chloride there are multiple eutectic regions with impurities of LiOH (which will have impacts on the ionic conductivity and performance of the battery)
- The reactions during the synthesis of the bromide are complicated so further work should be done to identify the composition and elucidate the phase diagram
- A consideration of the mechanical properties of these solid electrolytes is important in the design of SSLMBs
- Further synthesis pathways should be explored to minimize the impurities, which will be crucial if these solid electrolytes are to be used in the future of SSLMBs

REFERENCES

INTERN BIO
Alex is a 4th year Chemistry Undergraduate studying at the University of Oxford. He completed his Faraday FUSE Internship in the Pasta Group at the University of Oxford.

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