

Fluorine-Doped Solid-State Electrolytes in Lithium-ion Batteries: Potential for a Cleaner Future

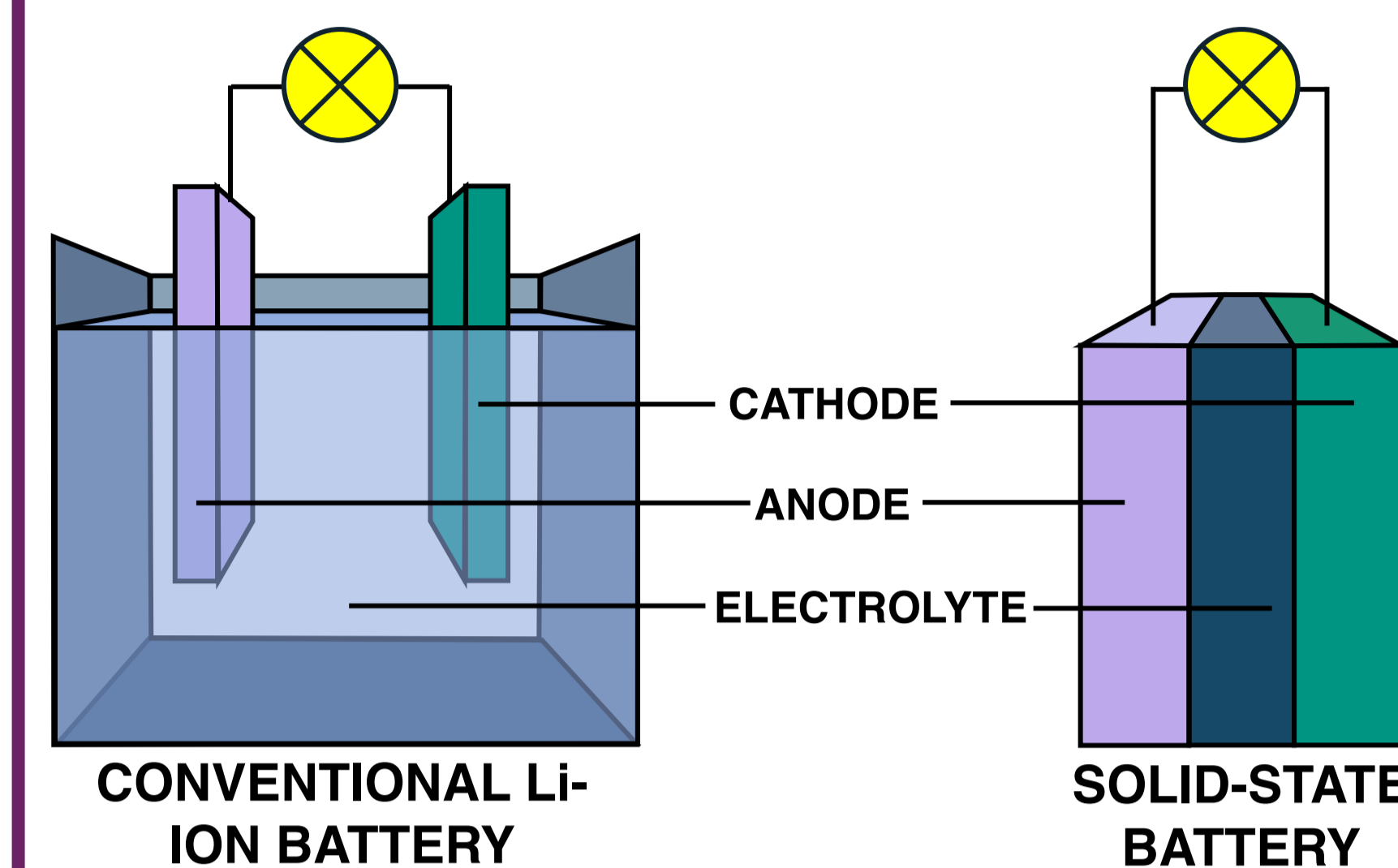
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1. BACKGROUND

- Batteries play a crucial role towards the electrification of technologies which progress to a low carbon-future.
- Rechargeable Lithium-ion batteries will improve renewable energy distribution globally – predicted to reduce global energy emissions by 30% by 2030.
- High volumetric energies, power densities, rechargeability and low electronic conductivities are challenging factors.
- Solid-state electrolytes (SSEs) now desirable relative to liquid electrolytes.



- Liquid electrolytes: short-circuits due to Li-build up, fires and explosions if hydrocarbon gases are not released (thermal runaway).
- SSEs: impervious to short circuiting due to their non-flammable nature, eliminating heat/fire failures.
- SSEs: non-toxic, faster charging times, longer lifetimes, higher energy densities.

Fig. 1 - Schematic representation of the components of a conventional Li-ion battery and solid-state battery

- Fluorine-doped Lithium-rich Anti-perovskites (LiRAPs) are a promising class of SSEs – exhibit structural flexibility.

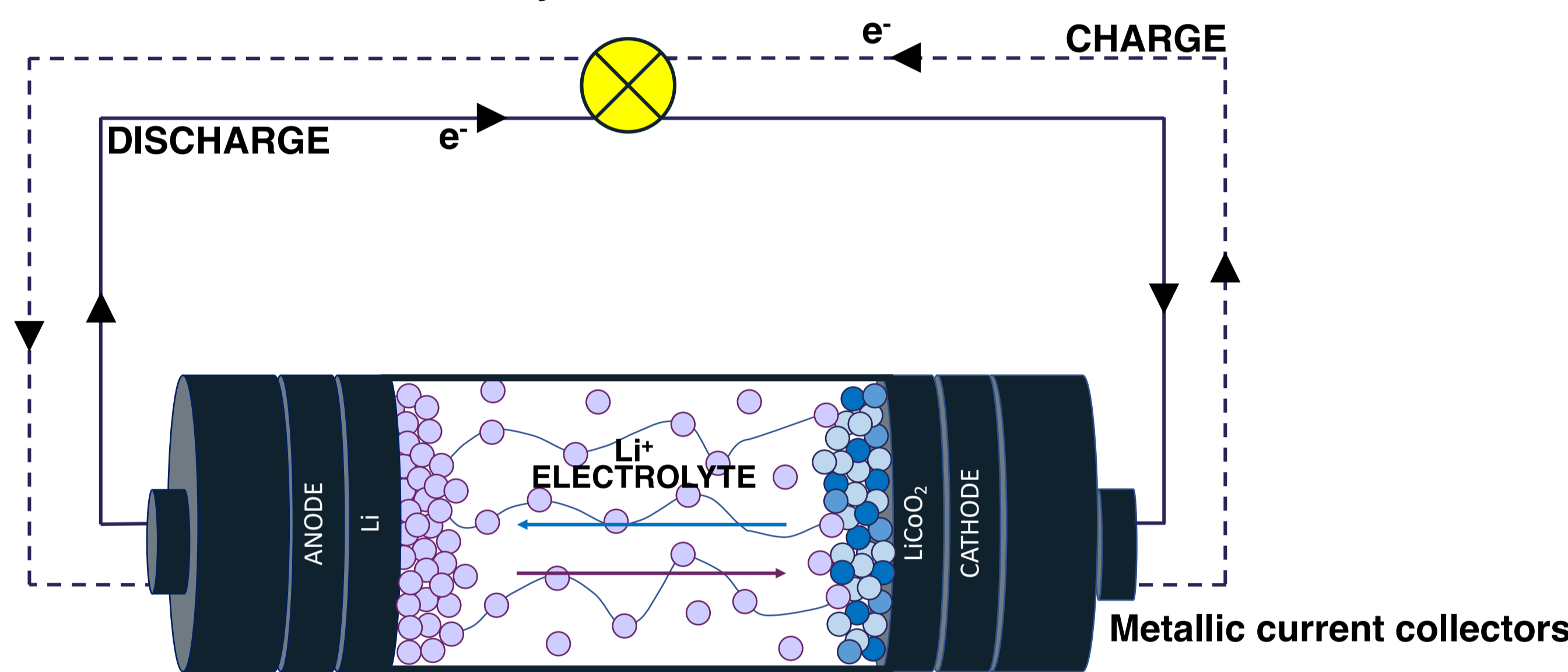
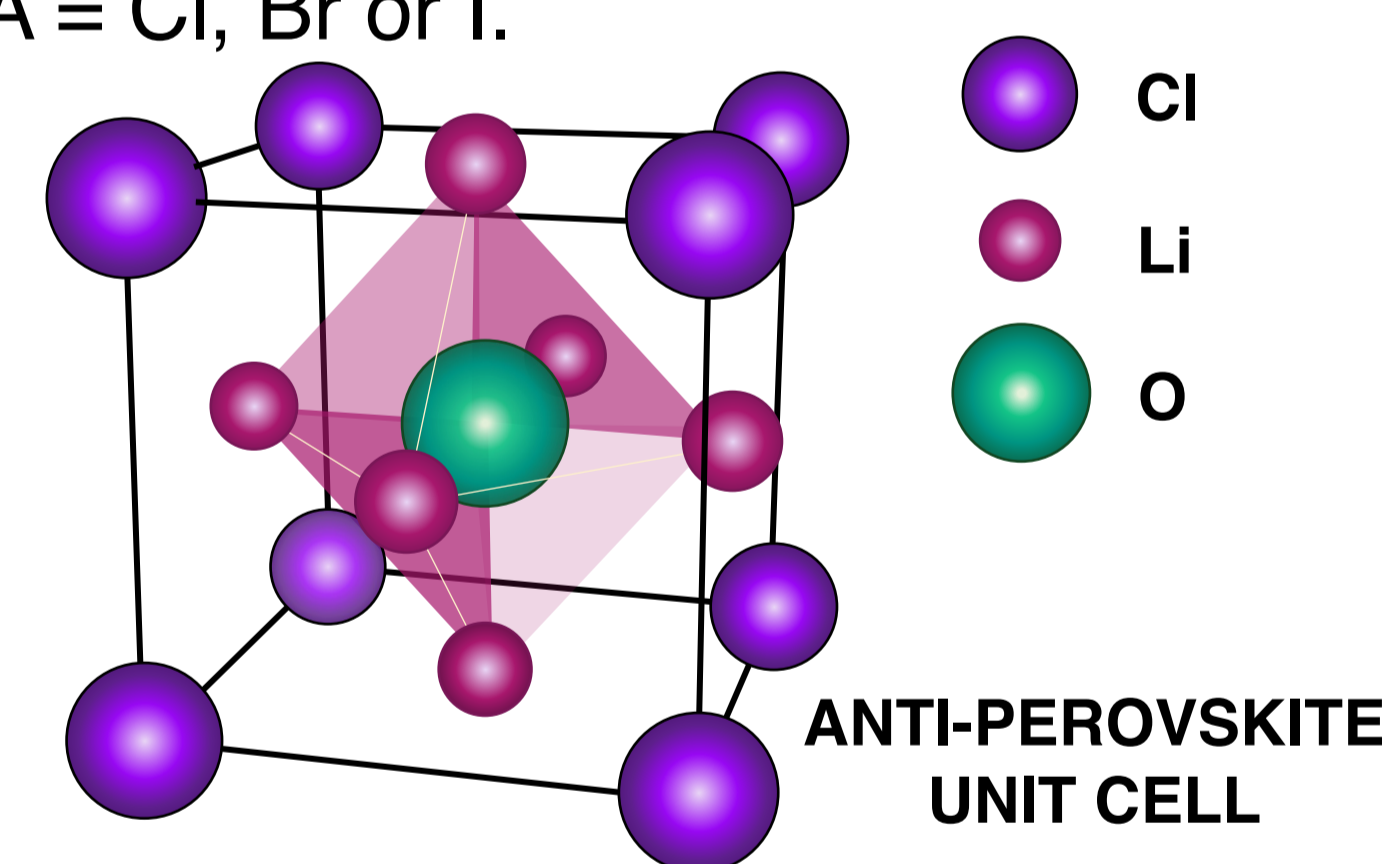


Fig. 2 - Schematic representation of a solid-state battery composed of two electrodes: Lithium Anode and LiCoO₂ cathode, separated by a Li-ion conducting electrolyte of an anti-perovskite structure

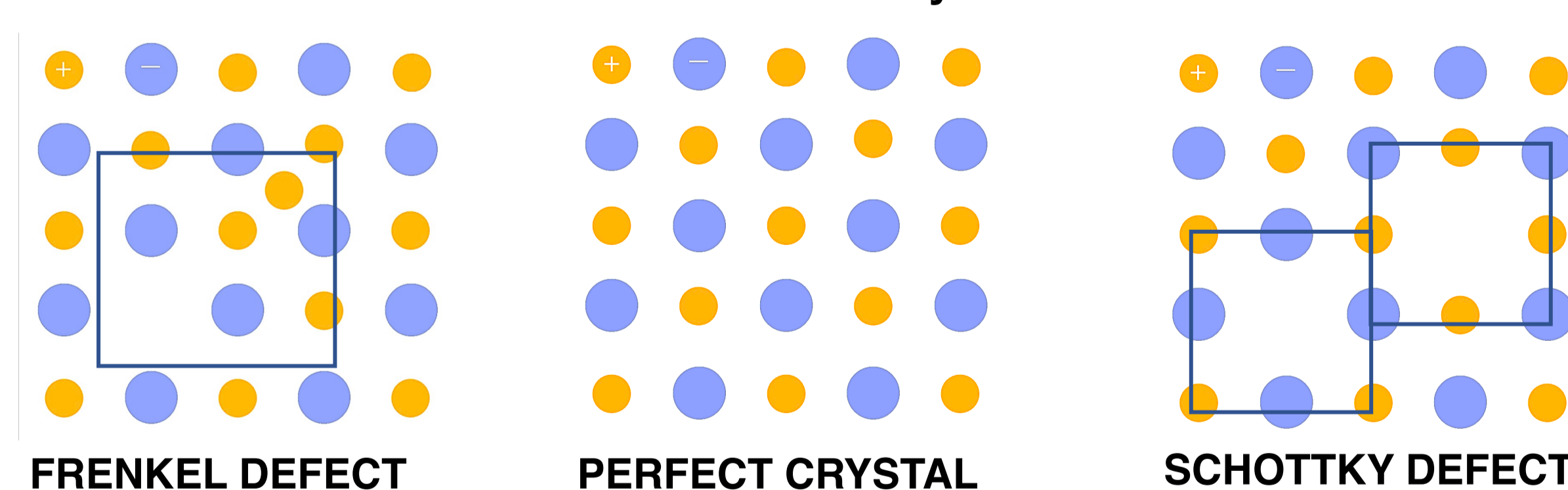
2. ANTI-PEROVSKITES HOPPING MECHANISM

- Anti-perovskites have the general formula $X_3^+B^{2-}A^-$ where X = electropositive element, B = divalent anion and A = monovalent anion.
- LiRAPs have general formula Li₃OA where A = Cl, Br or I.
- Anti-perovskites are lightweight, and electrochemically stable towards Li – possess promising ionic conductivity. Structurally flexible and tuneable.
- Most commonly studied systems include Li₃OCl and Li₂OHCl.



3. FRENKEL AND SCHOTTKY DEFECTS

- Structural defects aid Lithium ion mobility.



- Cation leaves original lattice site and occupies interstitial position on same crystal – density unchanged
- One vacancy and one interstitial defect

- Both cation and anion leave solid crystal – density decreases
- Two vacancies formed

REFERENCES

- J. Howard, Z. Hood, N. A. W. Holzwarth, *PhysRevsMaterials*, 2017, 1, 3-8.
- Li Y et al., *Angew Chem Int*, 2016, 55, 9965-9968.
- W. Xia et al., *Chemical reviews*, 2022, 122, 3766-3819.
- J. A. Dawson, T. Famprakis and K. E. Johnston, *J. Mater. Chem. A*, 2021, 9, 18746-18772
- Shuo Yan et al., *MDPI*, 2021, 7, 70-81
- A. Morscher, M. S. Dyer, B. Duff, G. Han, J. Gamon, L. M. Daniels, Y. Dang, T. W. Surta, et al., *Chem of Materials*, 2022, 33, 2206-2217.
- Y. Zhao and L. L. Daemen, *J. Am. Chem. Soc.*, 2012, 134, 15042-15047.
- M. J. Clarke, J. A. Dawson, T. J. Mays and M. S. Islam, *ACS Appl. Energy Mater.*, 2021, 4, 5094-5100.
- Z. Lu, J. Liu and F. Ciucci, *Energy Storage Mater.*, 2020, 28, 146-152.

4. FLUORINE DOPING

- Structural substitution of F onto the OH site results in phase change, increase ionic conductivity and lower activation energy.
- Orthorhombic Li₂OHCl → cubic structure at room temperature.
- Ionic conductivity due to hopping mechanism - Li⁺ ion diffuses into a vacancy, usually hindered by the coulombic repulsion and steric hindrance of the O-H-X hydrogen bond.

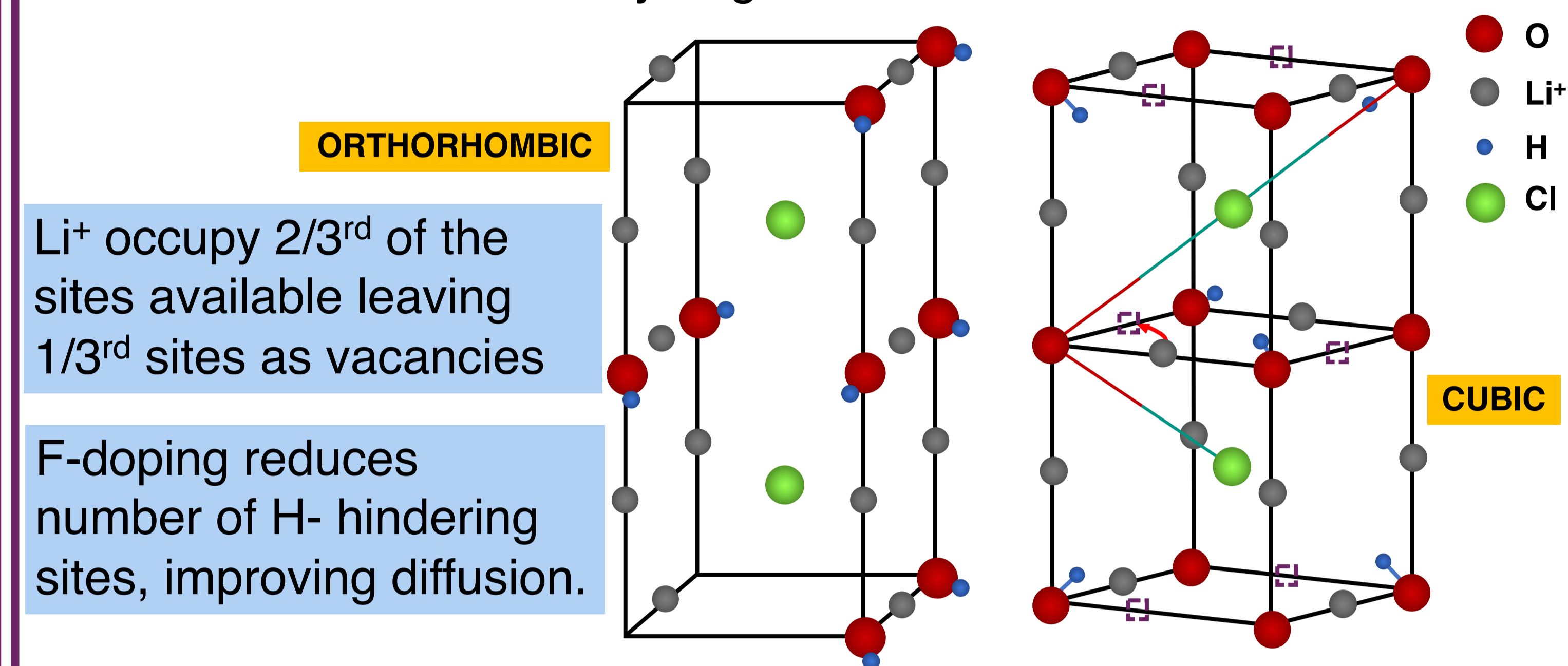
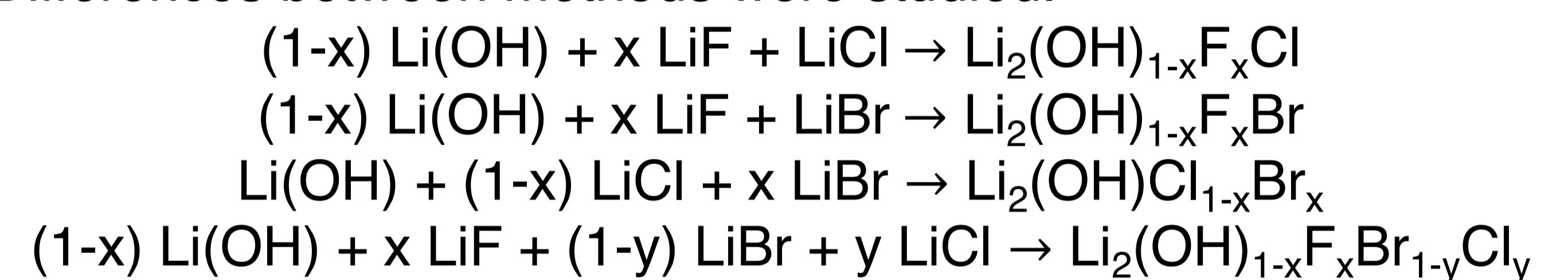


Fig. 3 – Orthorhombic and Cubic structures showing vacancies for the Lithium hopping Grotthuss' mechanism

5. LiRAPs SYNTHESIS and CHALLENGES

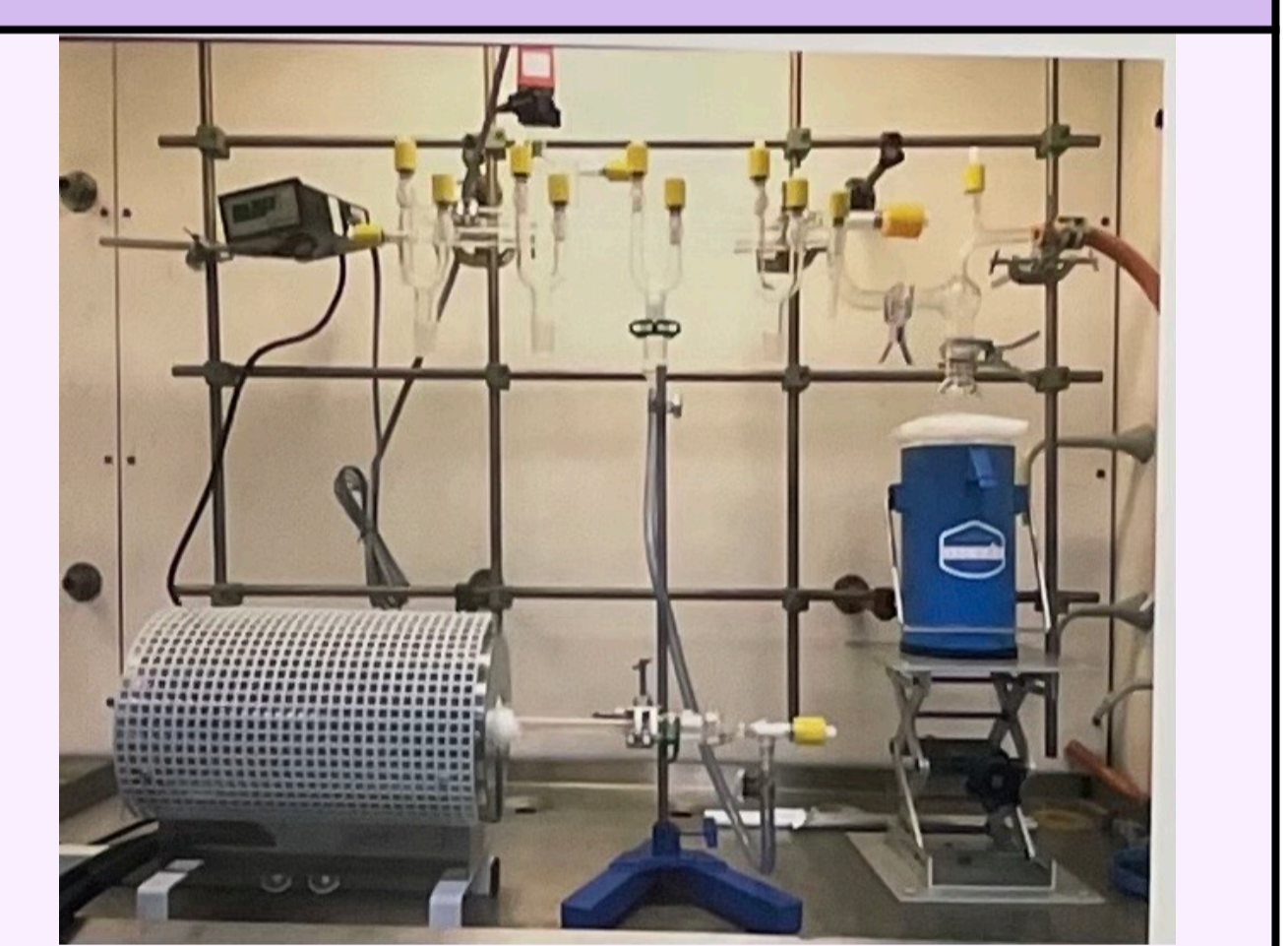
- LiRAPs are extremely air-sensitive (hygroscopic) and hydrophobic - samples prepared under inert conditions.
- Two solid-state methods used to produce four samples with compositions $0.0 \leq x \leq 1.0$
- Differences between methods were studied.



MUFFLE FURNACE in an Ar-filled Glovebox



SCHLENK LINE under Vacuum



6. RESULTS

- ⁷Li solid-state NMR studies used to monitor changes in the Li content and possible ion mobility.

Li₂(OH)_(1-x)F_xBr

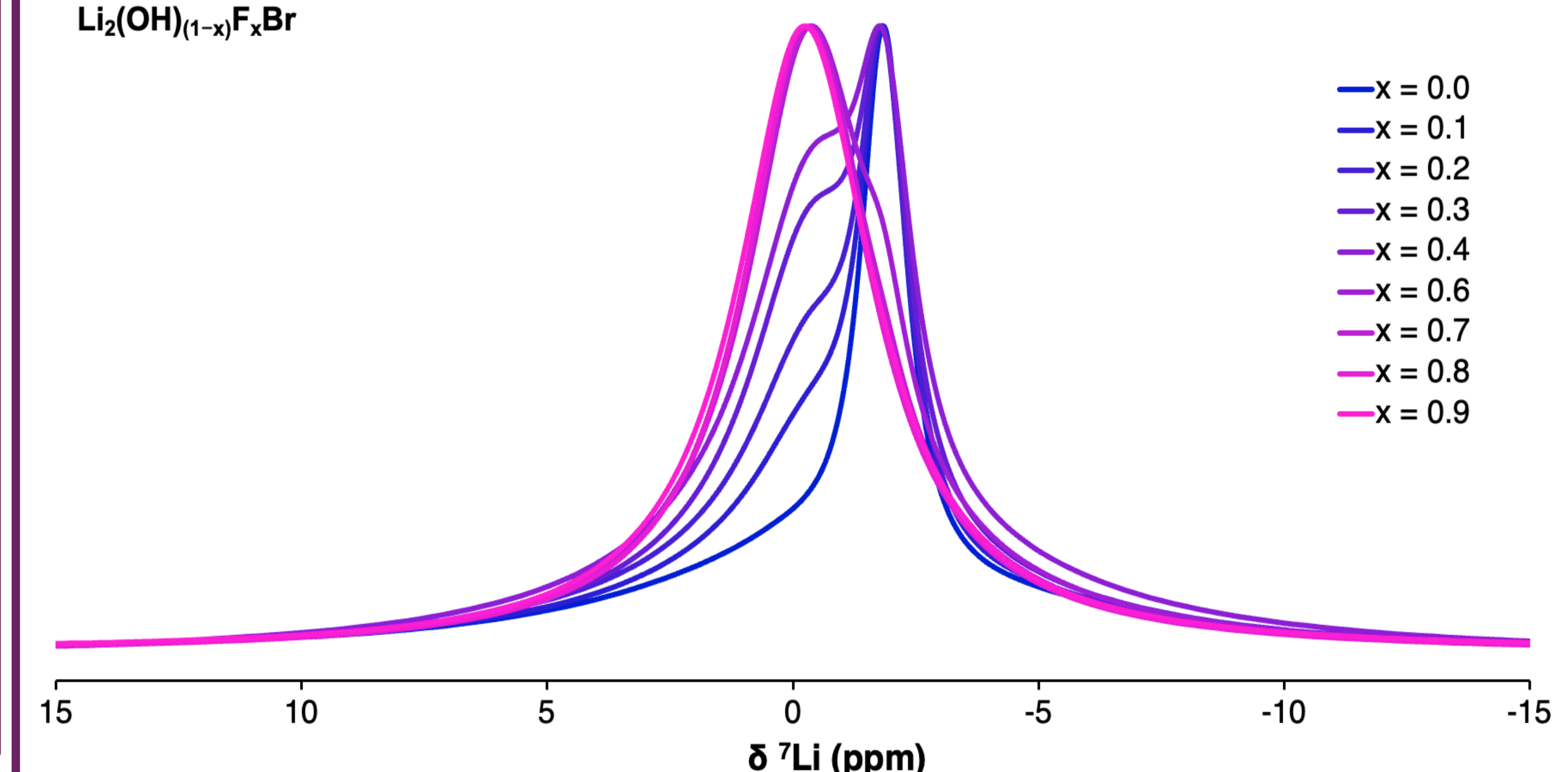


Fig. 4 – ⁷Li MAS NMR spectrum acquired for Li₂(OH)_(1-x)F_xBr

- Increased line broadening suggests OH⁻ ions can be replaced by F⁻ ions. However, after ~ x = 0.6 Fluorine, no doping taking place.

7. CONCLUSION

- A possible doping limit and structural phase transition are observed in Li₂(OH)_(1-x)F_xCl ($0.0 \leq x \leq 0.9$) which can be supported further using variable-temperature NMR (¹H, ⁷Li, ³⁵Cl) and XRD studies.
- Conductivity and neutron diffraction experiments could be used to characterise materials and observe improvements in electrochemical stability.
- New air-sensitive synthetic techniques are being employed and molecular dynamics simulations are underway to understand ion-mobility in LiRAPs.