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QUEEN'S UNIVERSITY IONIC LIQUID LABORATORIES

QUILL

The electrochemistry of new borate anions

Haris Amir

Supervisors: Professor John D. Holbrey and Professor Małgorzata Swadźba-Kwaśny

CONFIDENTIAL - QUILL, 25th March 2024

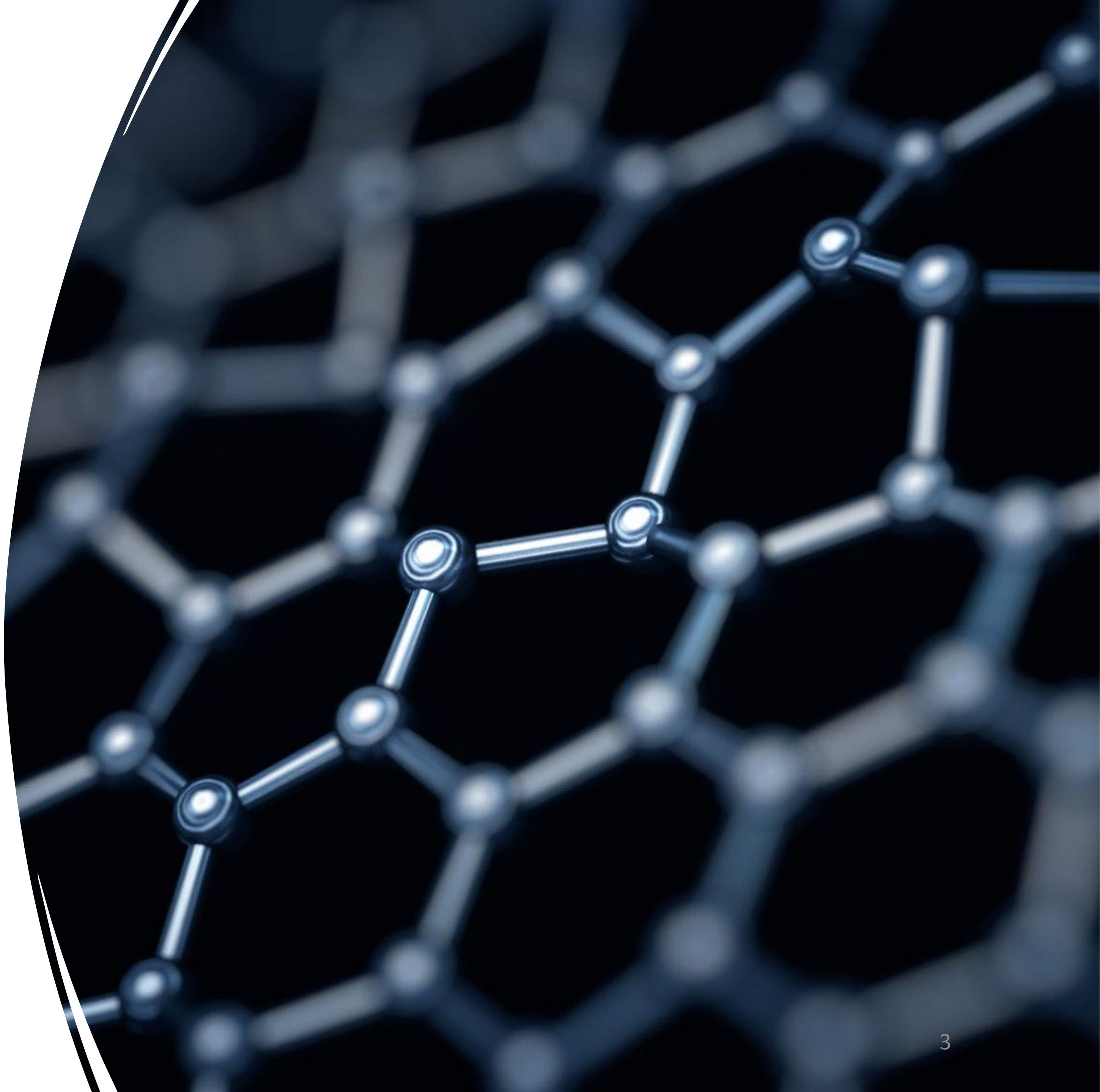
Abbreviations

- LIBs – Lithium ion batteries
- SIBs – Sodium ion batteries
- OIPCs – Organic ionic plastic crystals
- SEI – Solid electrolyte interphase
- DSC – Differential scanning calorimetry

J.-Y. Hwang, S.-T. Myung and Y.-K. Sun, *Chem Soc Rev*, 2017, **46**, 3529– 3614.

Overview

- The future of batteries
- Organic ionic plastic crystals
- Diffusion NMR spectroscopy
- Electrochemistry of Na borate salts



Lithium *vs.* sodium batteries

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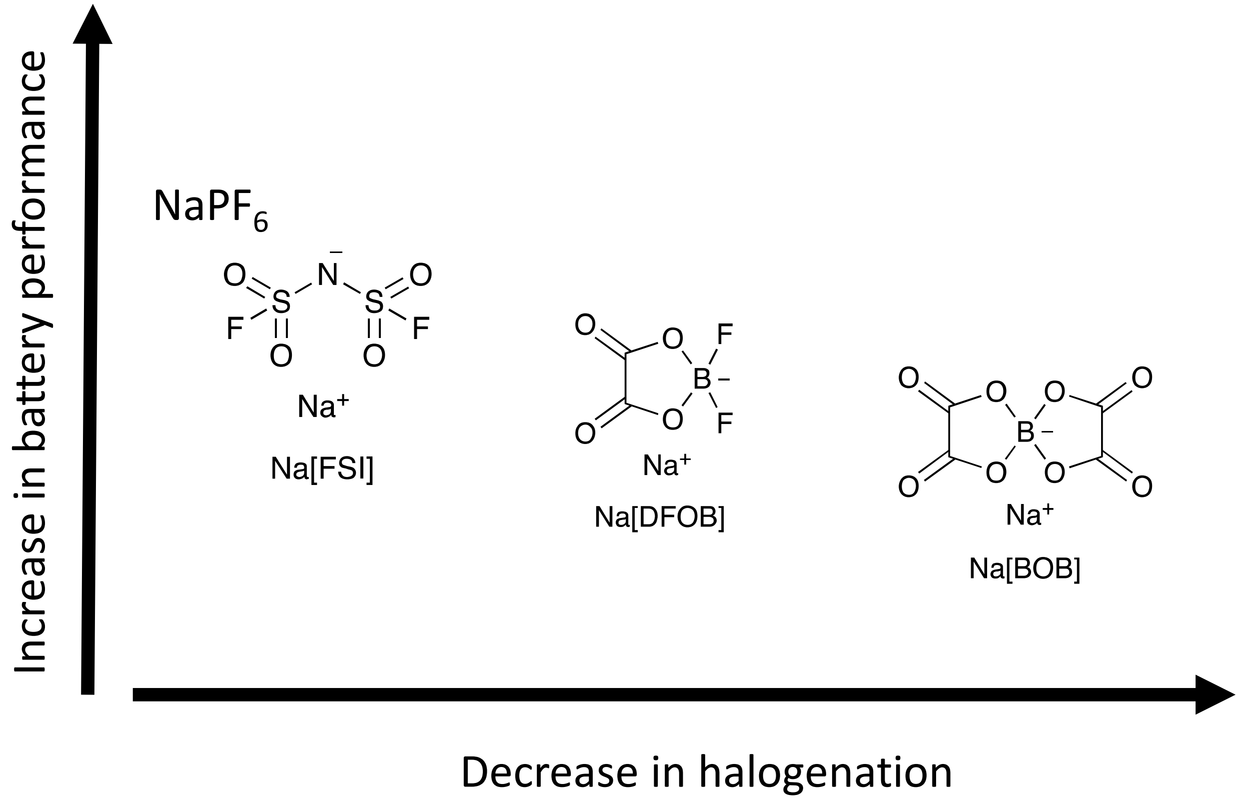
- Lithium ion battery (LIB) are used in most electronic devices/vehicles
- Limited lithium availability – price increase ($5000/tonne in 2010)
- Sodium ion battery (SIB) best candidate ($135 – 165/tonne)

J.-Y. Hwang, S.-T. Myung and Y.-K. Sun, *Chem Soc Rev*, 2017, **46**, 3529– 3614.

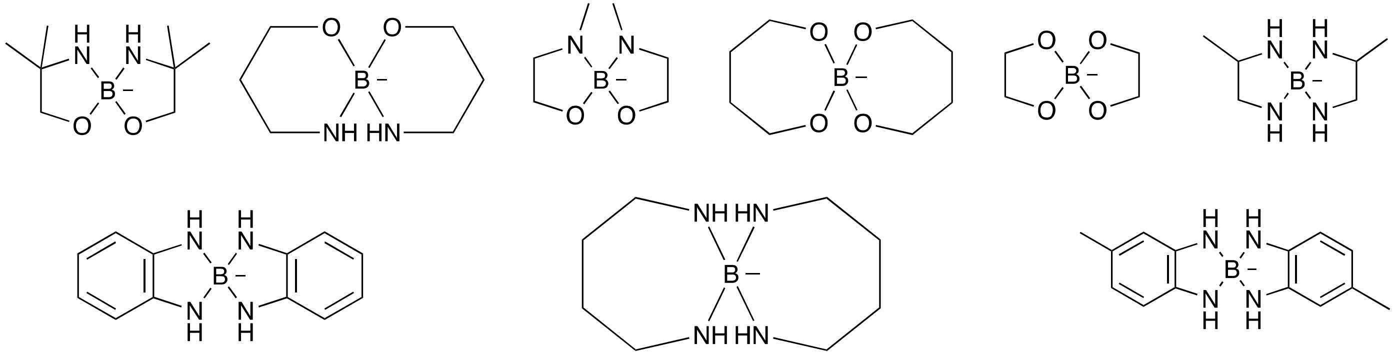
Electrolytes

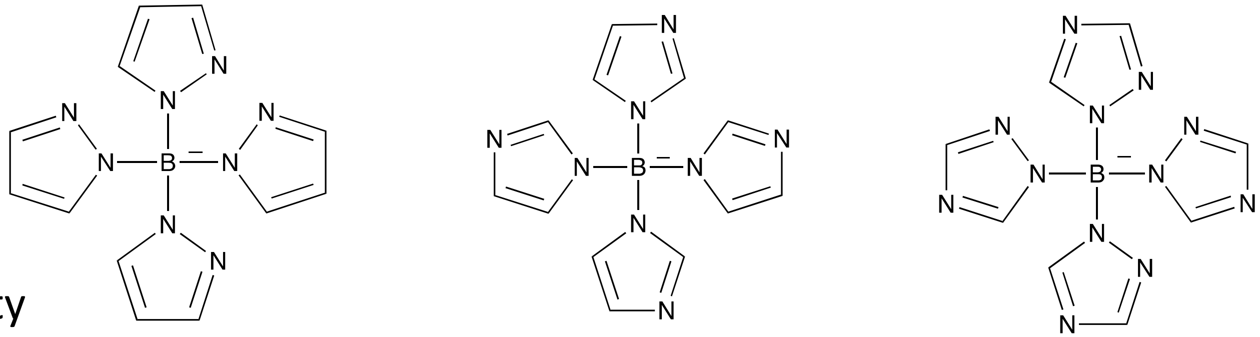
- Fluorinated sodium salts form promising solid electrolyte interphase
- Global movement to move away from using fluorinated industrially
- Sodium borates looked at as greener alternatives



A. Ponrouch, *et al., Energy Environ Sci*, 2012, **5**, 8572.
J. Chen, *et al., Chem Commu*, 2015, **51**, 9809–9812.

New borate anions





- B-N bonds improved water stability
- 5-membered cyclic borate anions are thermodynamically stable
- The B-N containing ILs have a higher thermal stability
- B-N bond length (1.45 Å) are shorter than B-O bonds (1.66 Å)
- Viscosity of $[B(NO)]^-$ was found to be lower than the common $[BScB]^-$ anion

Organic ionic plastic crystals (OIPCs)

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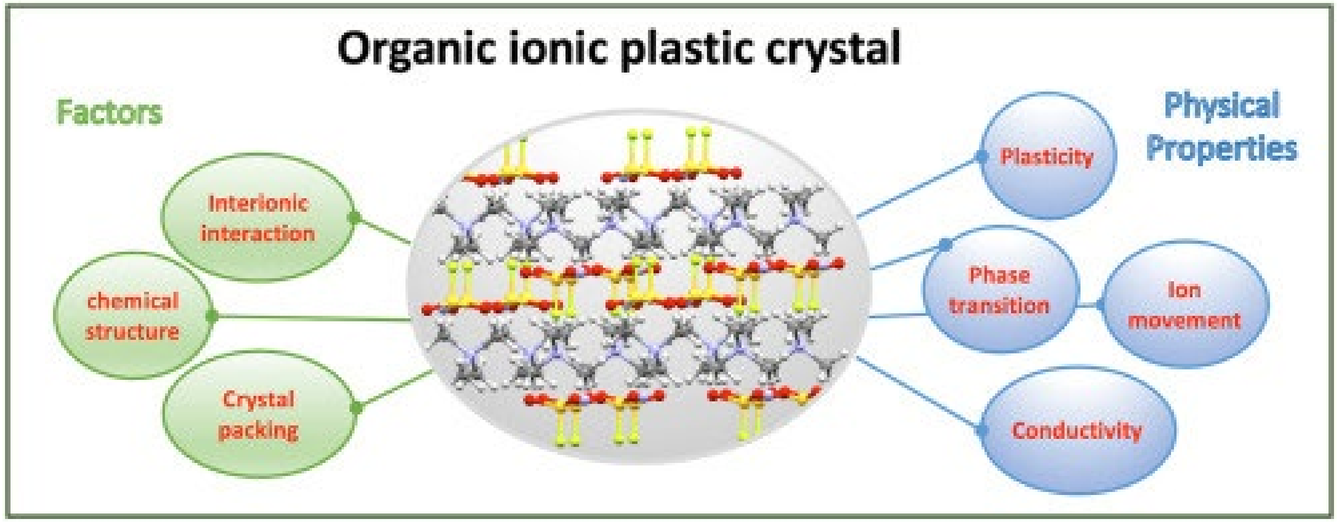
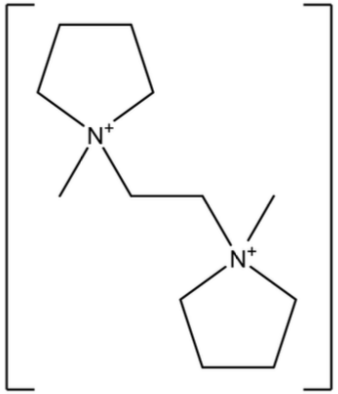
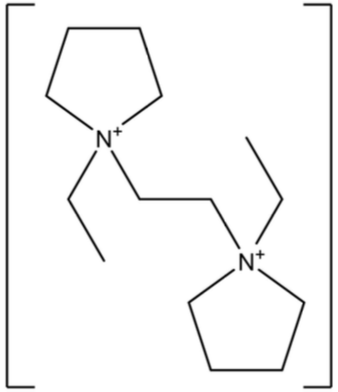
- They consist of long-range ordered crystalline lattice
- Go through one or more solid-solid phase transition
- Introduces crystallographic changes with short range disorder arises from rotational motions of the molecule
- Behaviour is found to be favoured when used as an electrolyte





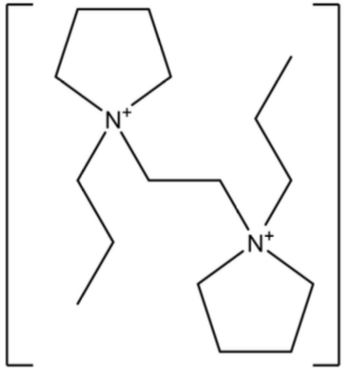
$[C_2\text{-Pyrr1}]^{2+}$

(a)



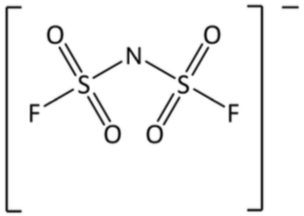
$[C_2\text{-Pyrr2}]^{2+}$

(b)



$[C_2\text{-Pyrr3}]^{2+}$

(c)

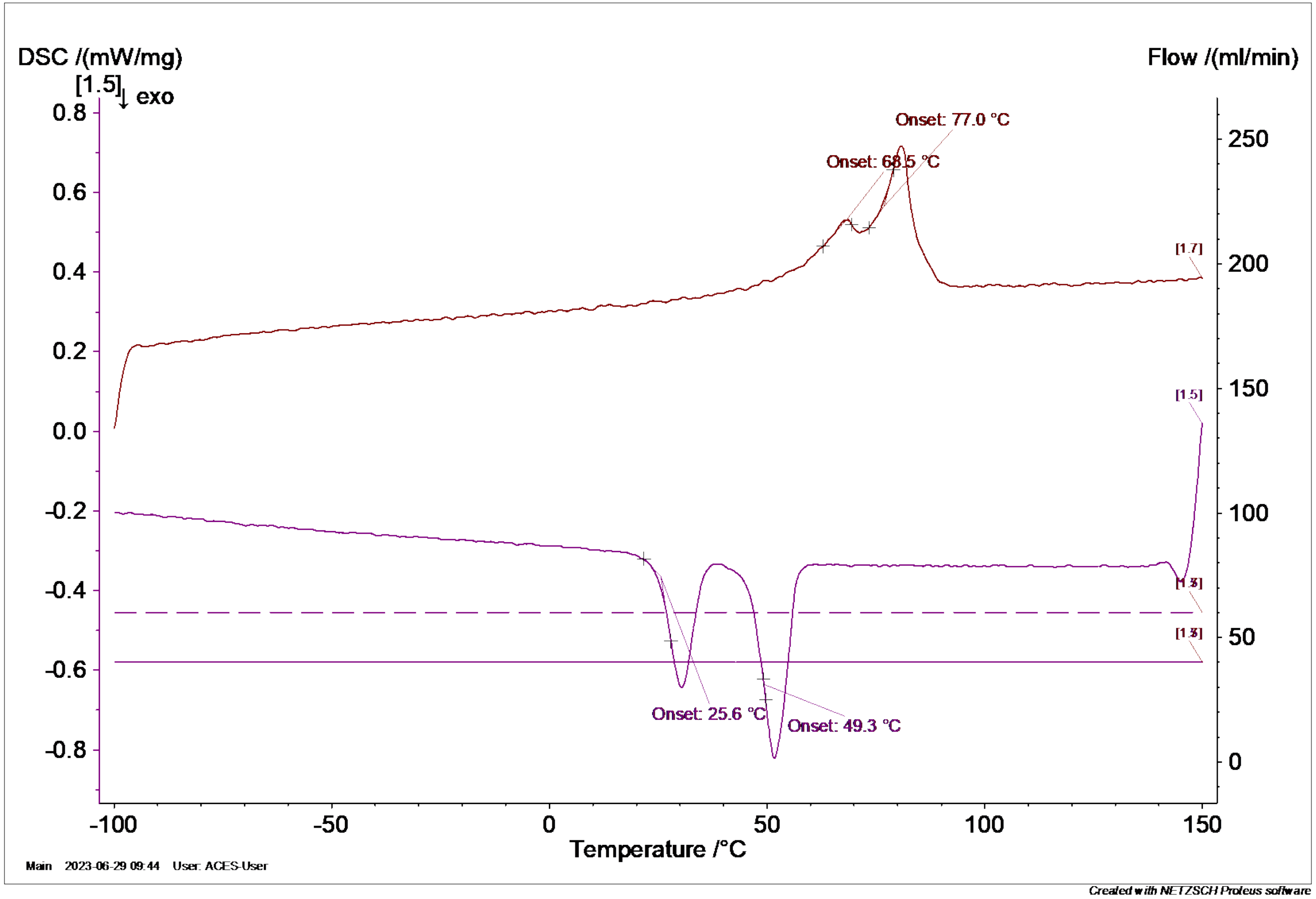


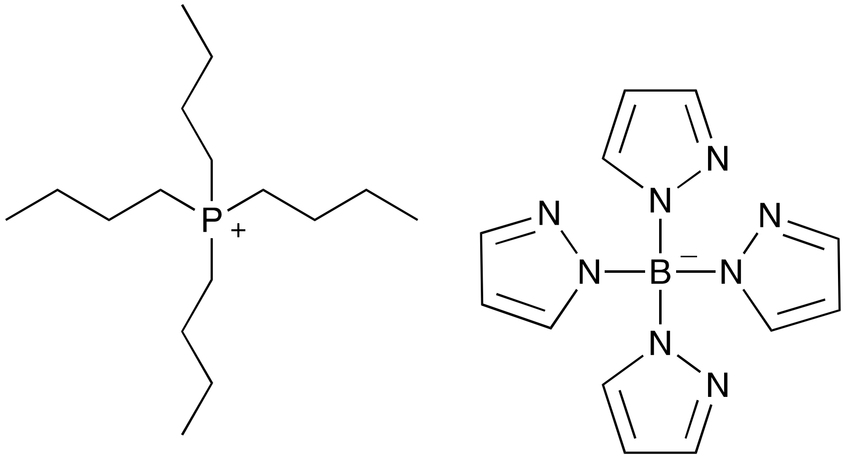
$[FSI]^-$

(d)

Abeysooriya., S., *et al., Phys. Chem. Chem. Phys.*, 2022, **24**, 4899
Sirigiri. N., *et al.*, Mater. Today Phys., 2022 **22,** 100603

DSC of $[P_{4444}][B(pyrazole)_4]$

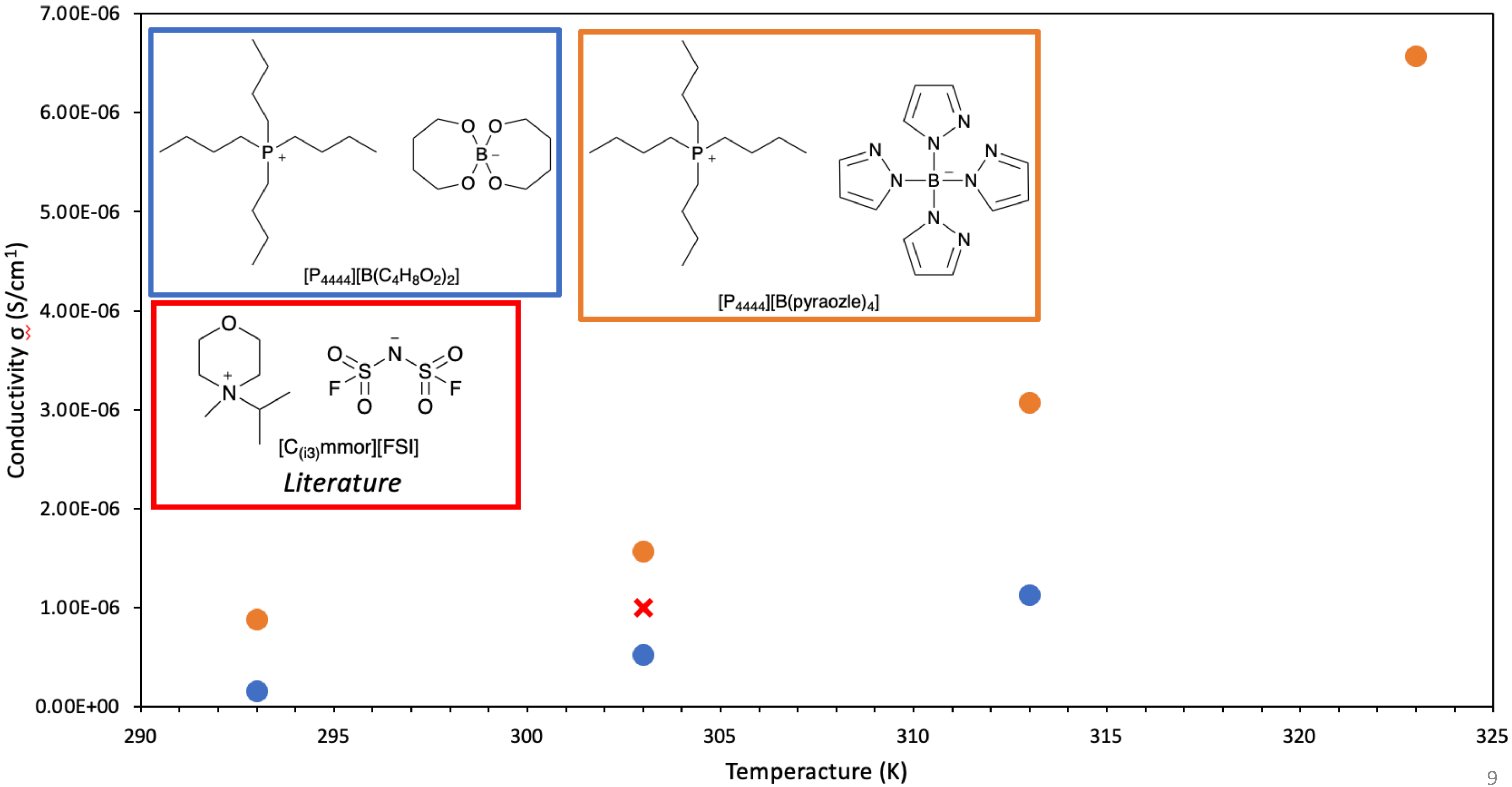




$[P_{4444}][B(pyraozle)_4]$

Phase II – phase I: ΔS = 3.17 J K^{-1} mol^{-1}

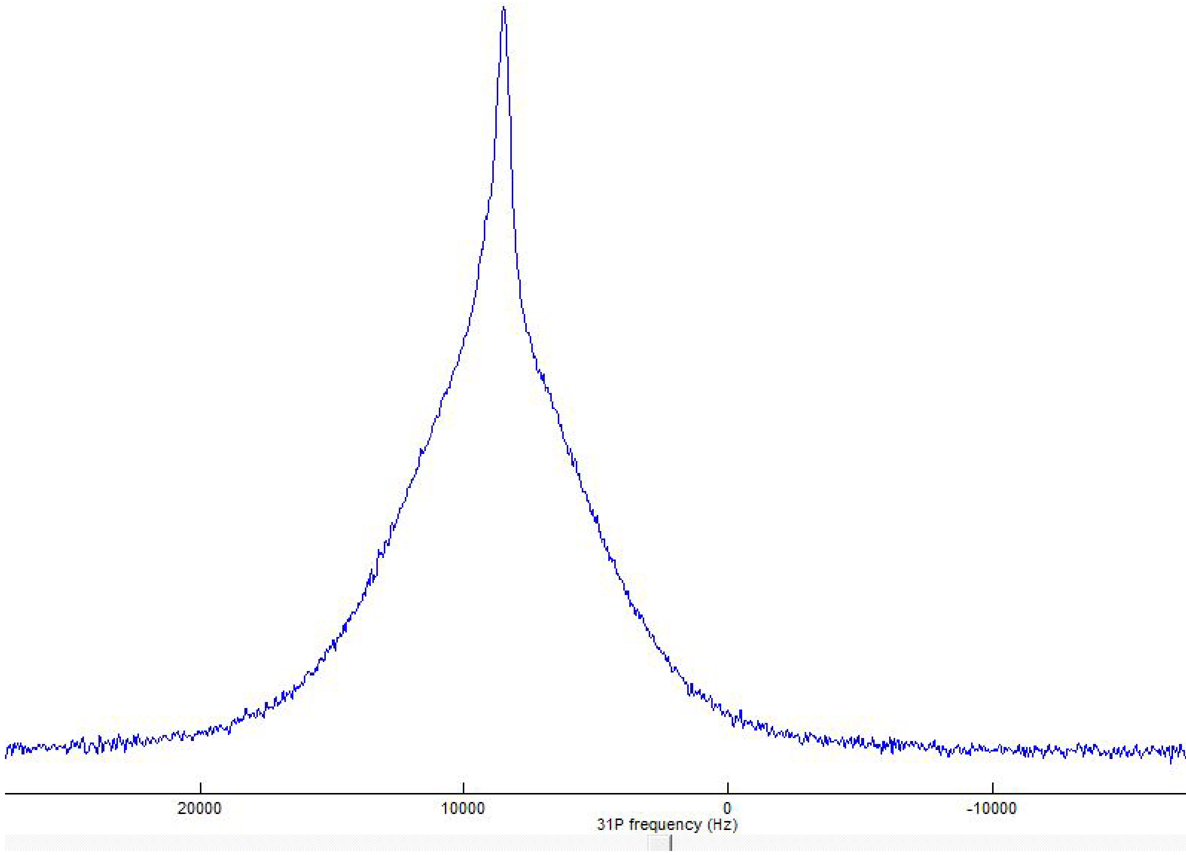
Conductivity of $[P_{4444}]^+$ based OIPCs



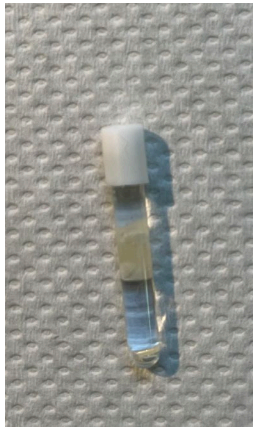
Sourjah A., *et al., Phys. Chem. Chem. Phys.*, 2023, **25**, 16469

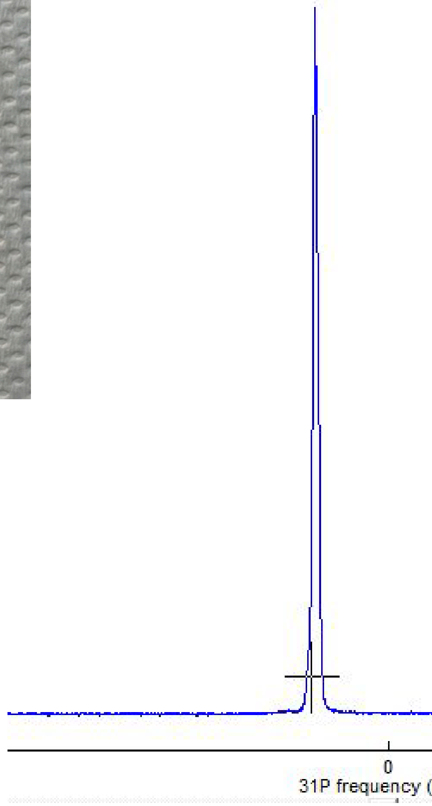
Solid state NMR spectroscopy

- Molecules have a fixed orientation relative to the magnetic field – the anisotropy of the various interactions needs to be considered.
- Gives information about the kinetics of the molecules – static or dynamic.

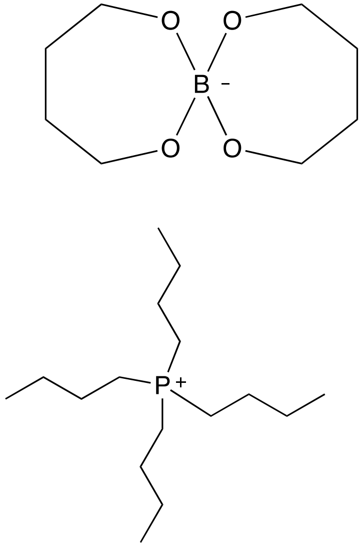


^{31}P NMR -30 ˚C

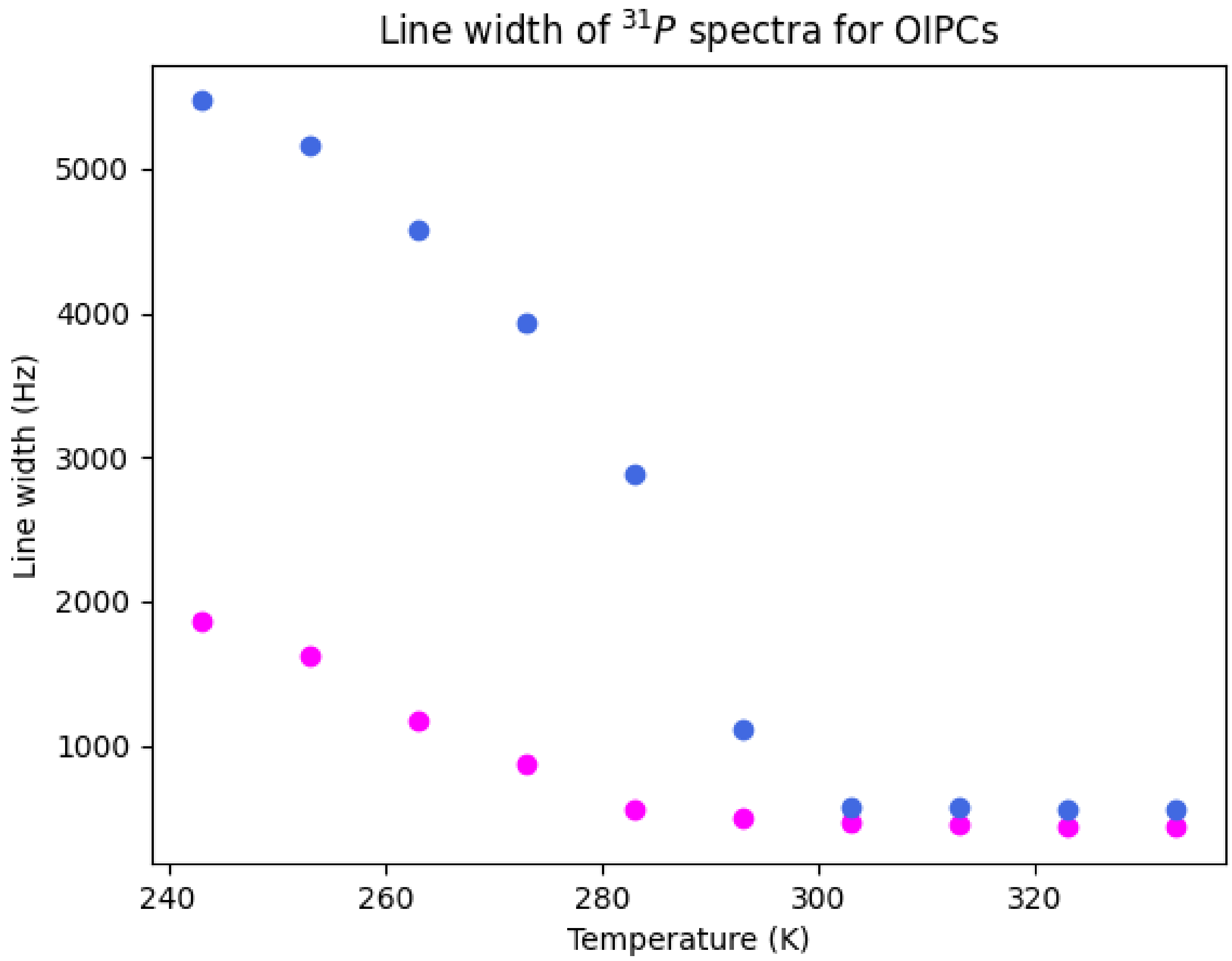


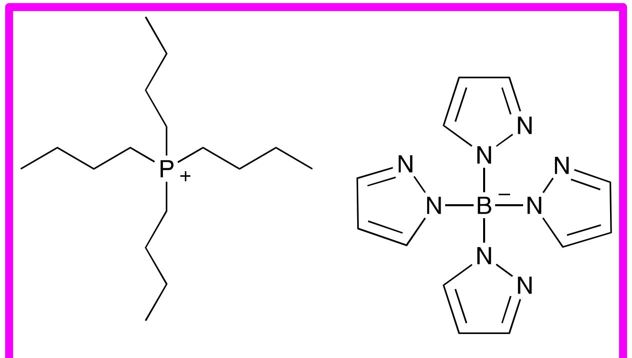


^{31}P NMR 60 ˚C

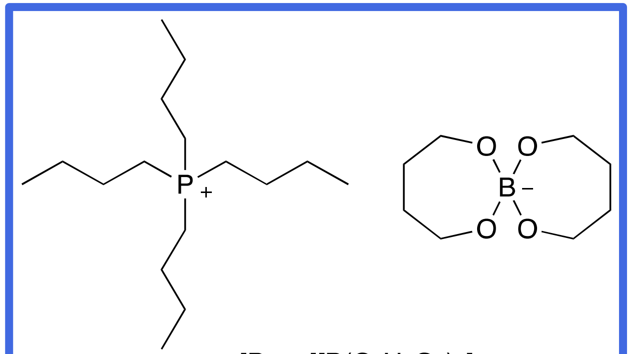


Dynamics of $[P_{4444}]^+$ based OIPCs



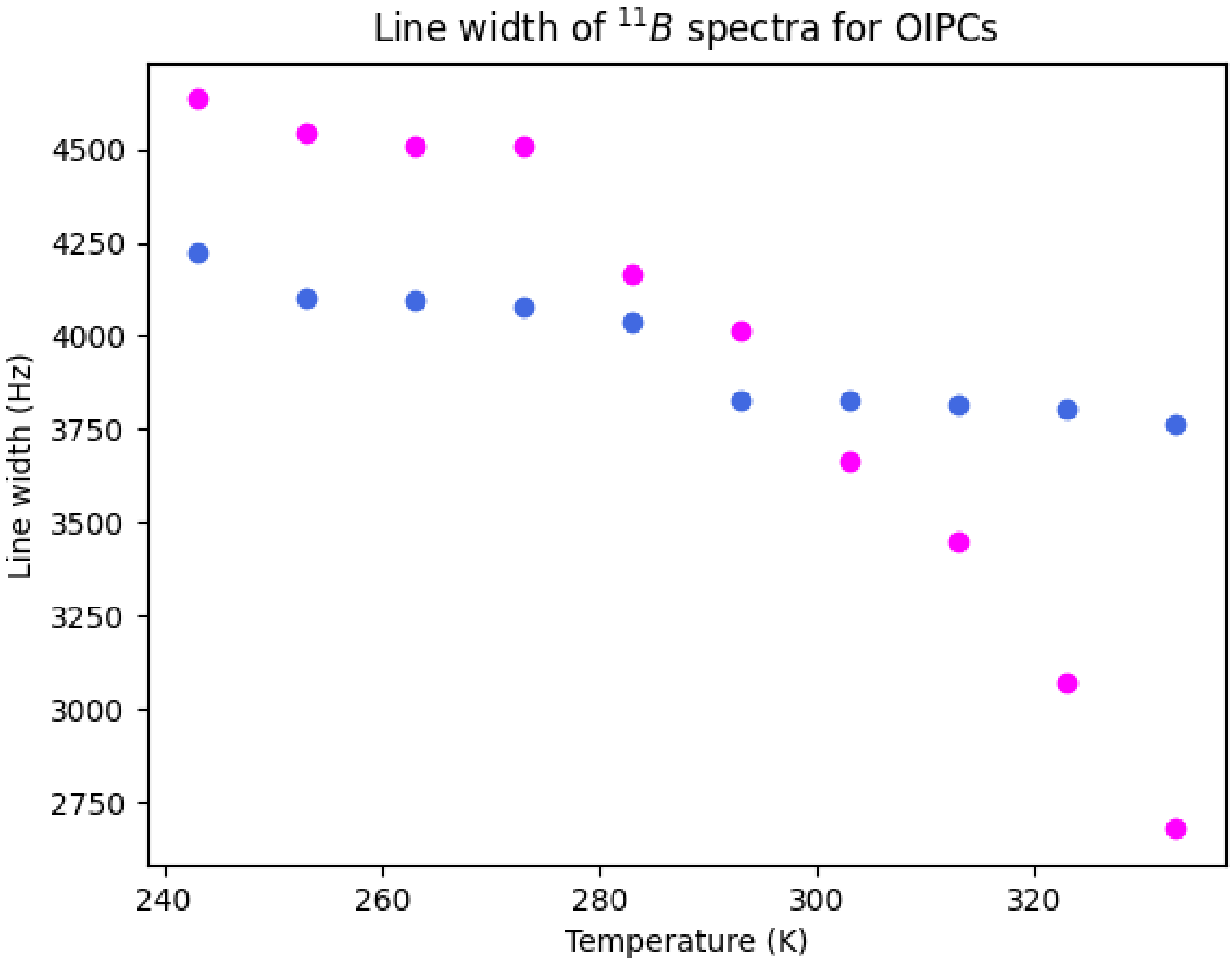


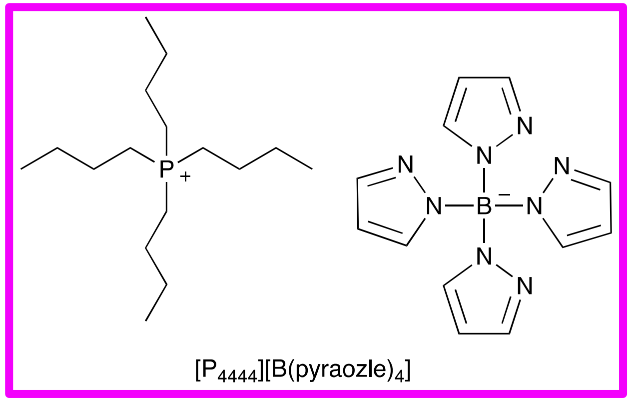
$[P_{4444}][B(pyraozle)_4]$

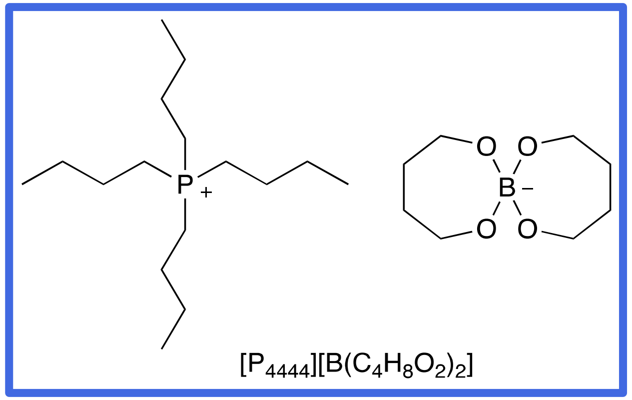


$[P_{4444}][B(C_4H_8O_2)_2]$

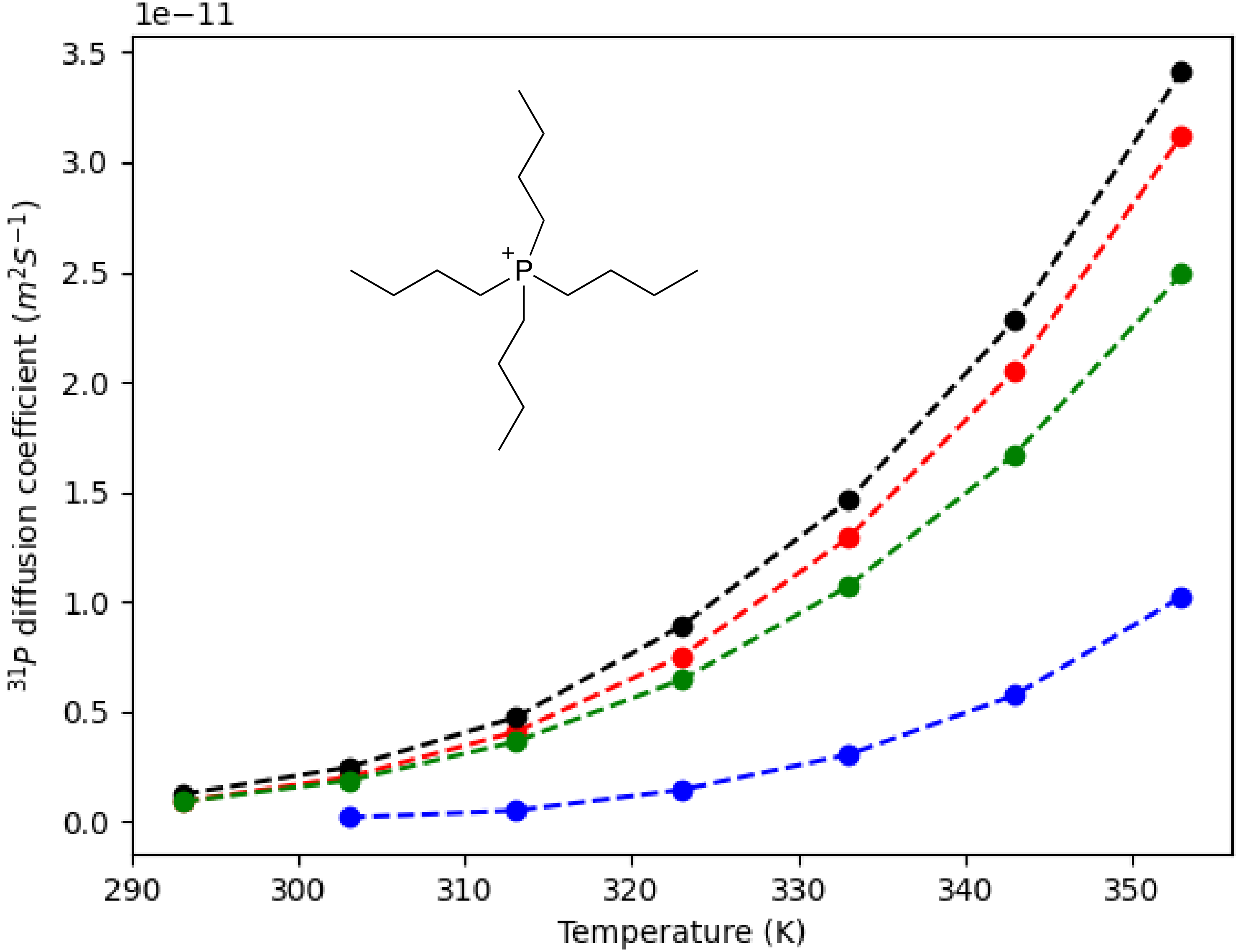
Dynamics of $[P_{4444}]^+$ based OIPCs

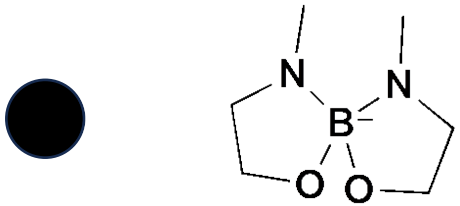


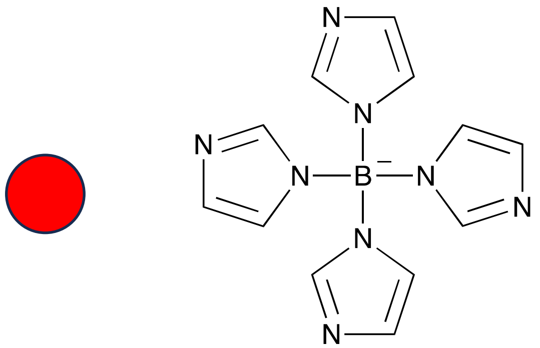


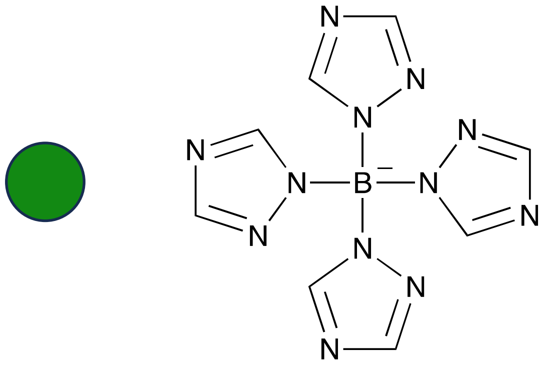


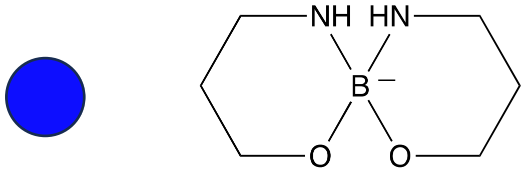
Diffusion coefficient of the phosphonium cation in $[P_{4444}]^+$ base ionic liquids



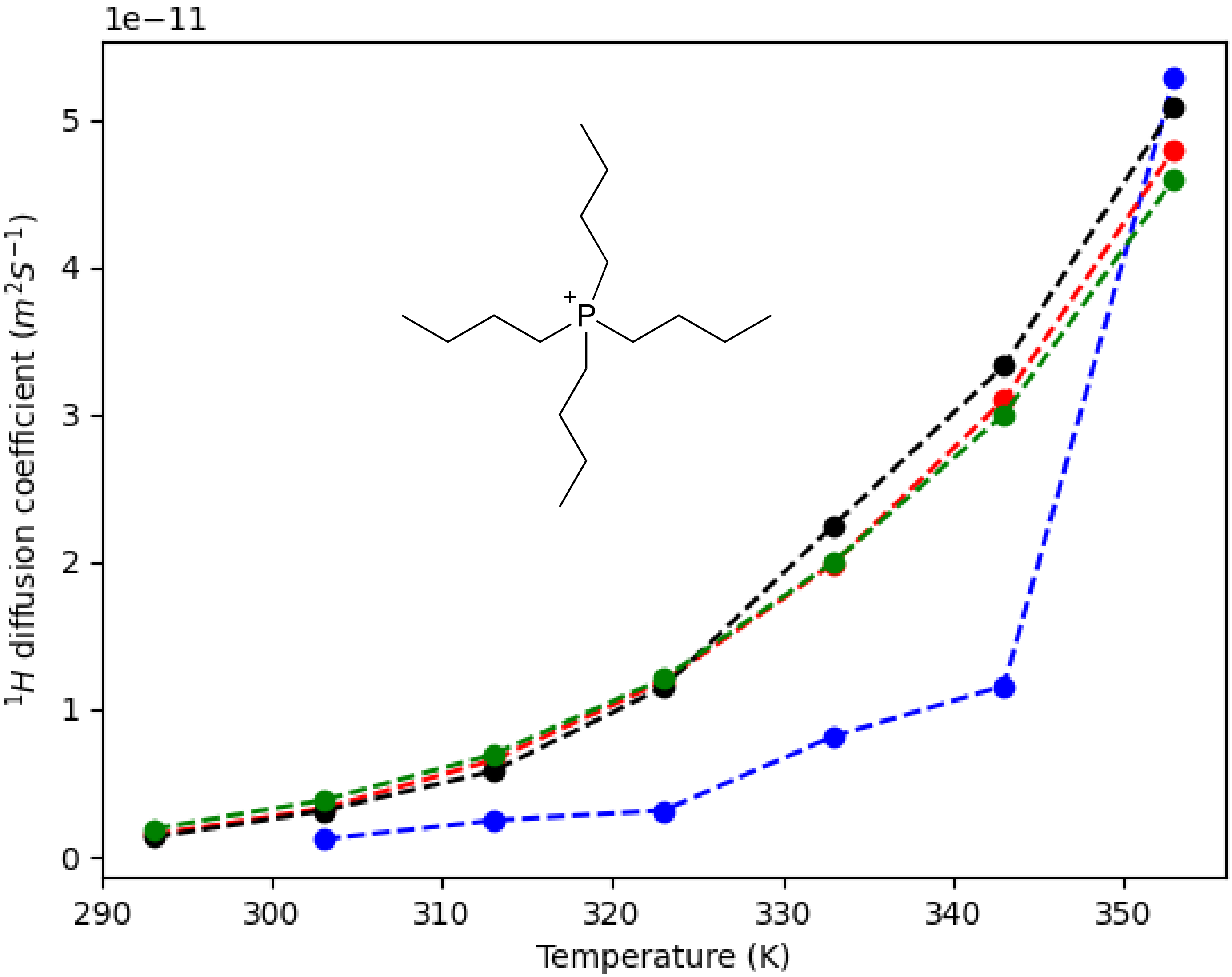


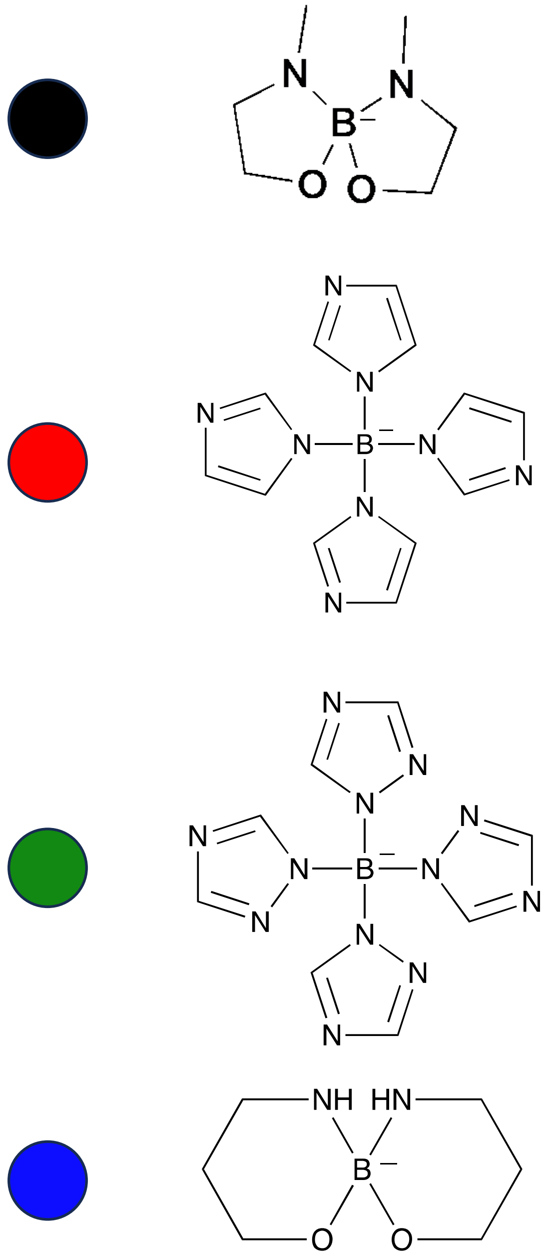






Diffusion coefficient of the phosphonium cation in $[P_{4444}]^+$ base ionic liquids





Electrochemistry studies

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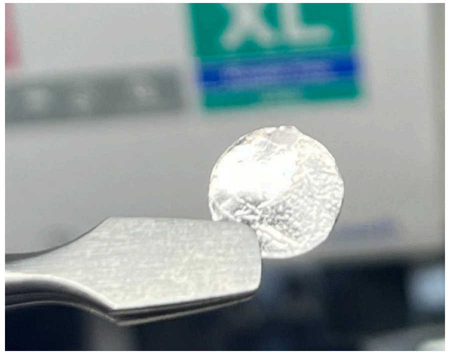

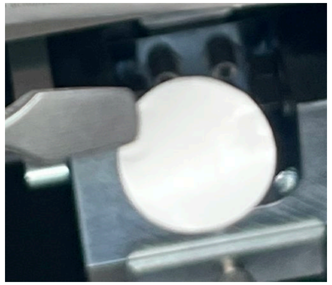

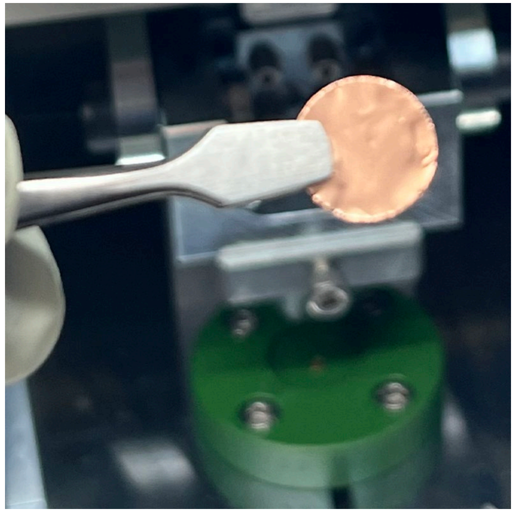

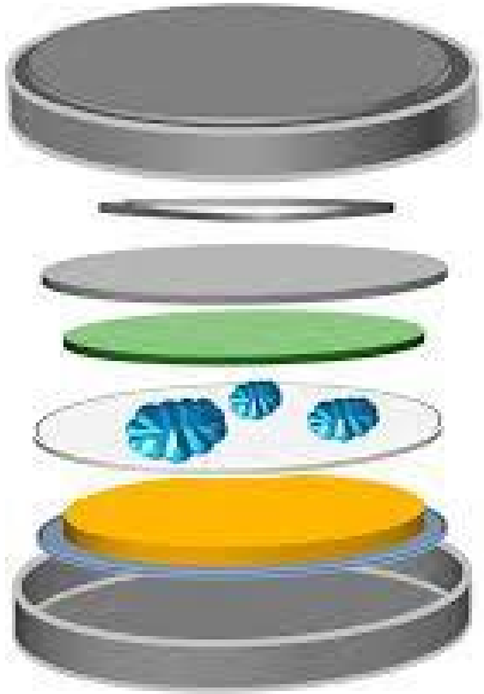

PEIS – resistance of a material
OCV – the rest potential can be recorded, commonly used as preconditioning time
CV – determine oxidative and reductive species
CA – measure the current response to an applied potential step, used to look at the surface area of the working electrode.

CV – Coin cell

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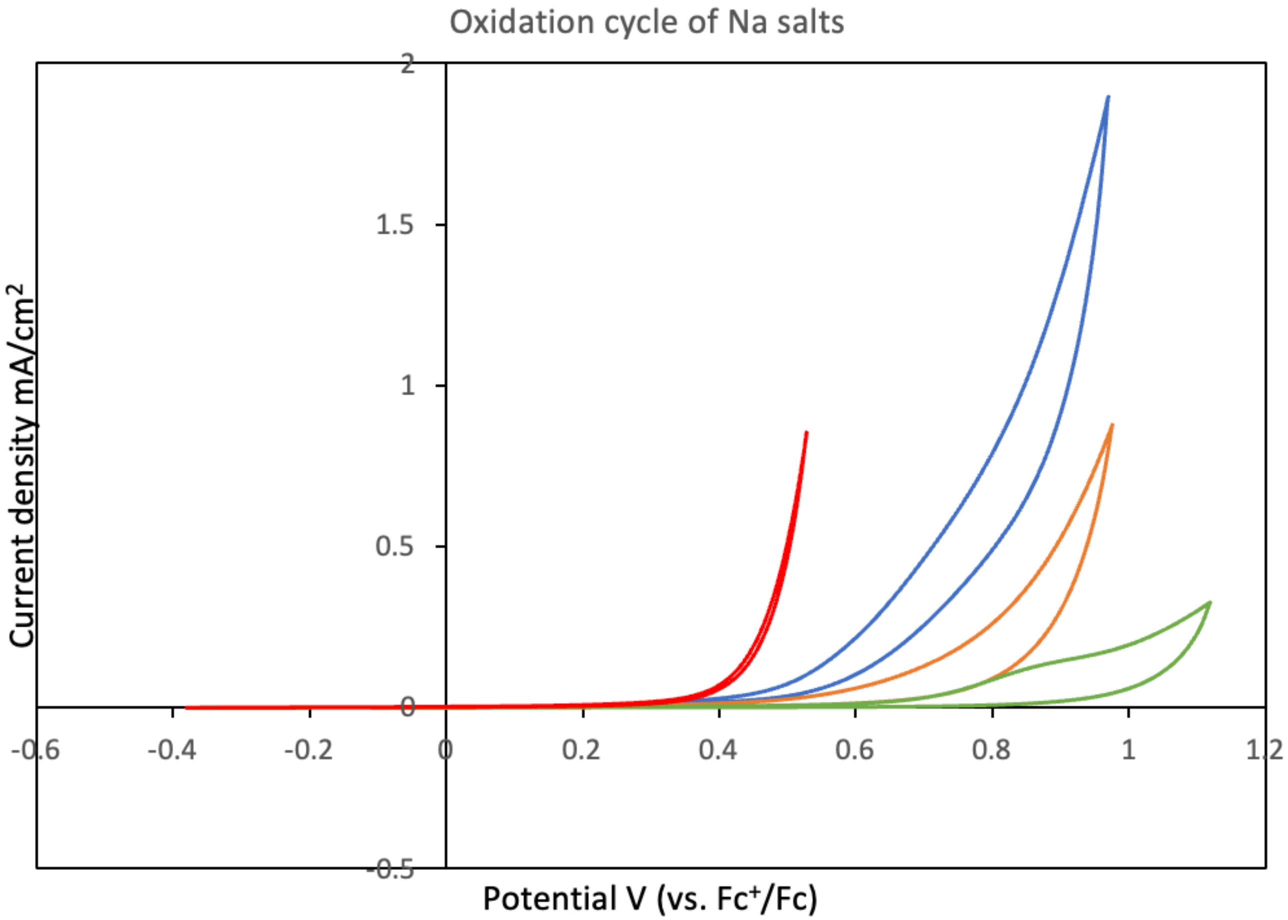

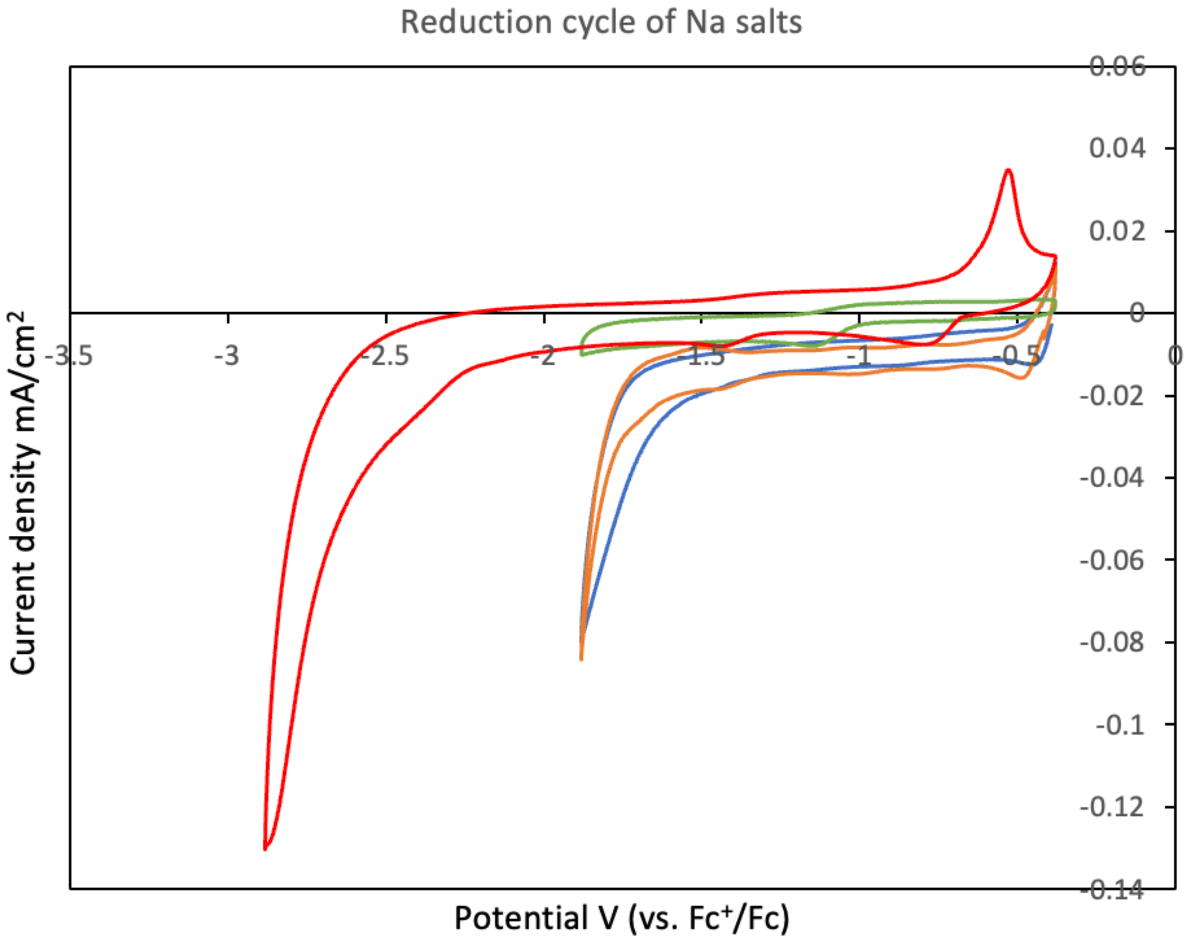

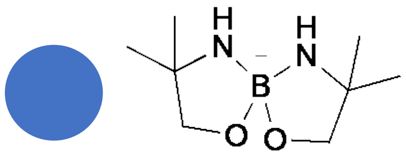

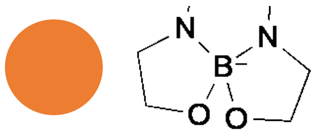

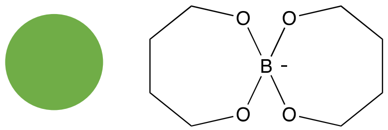

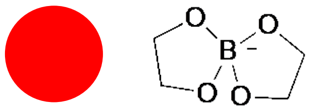

Significance of SEI

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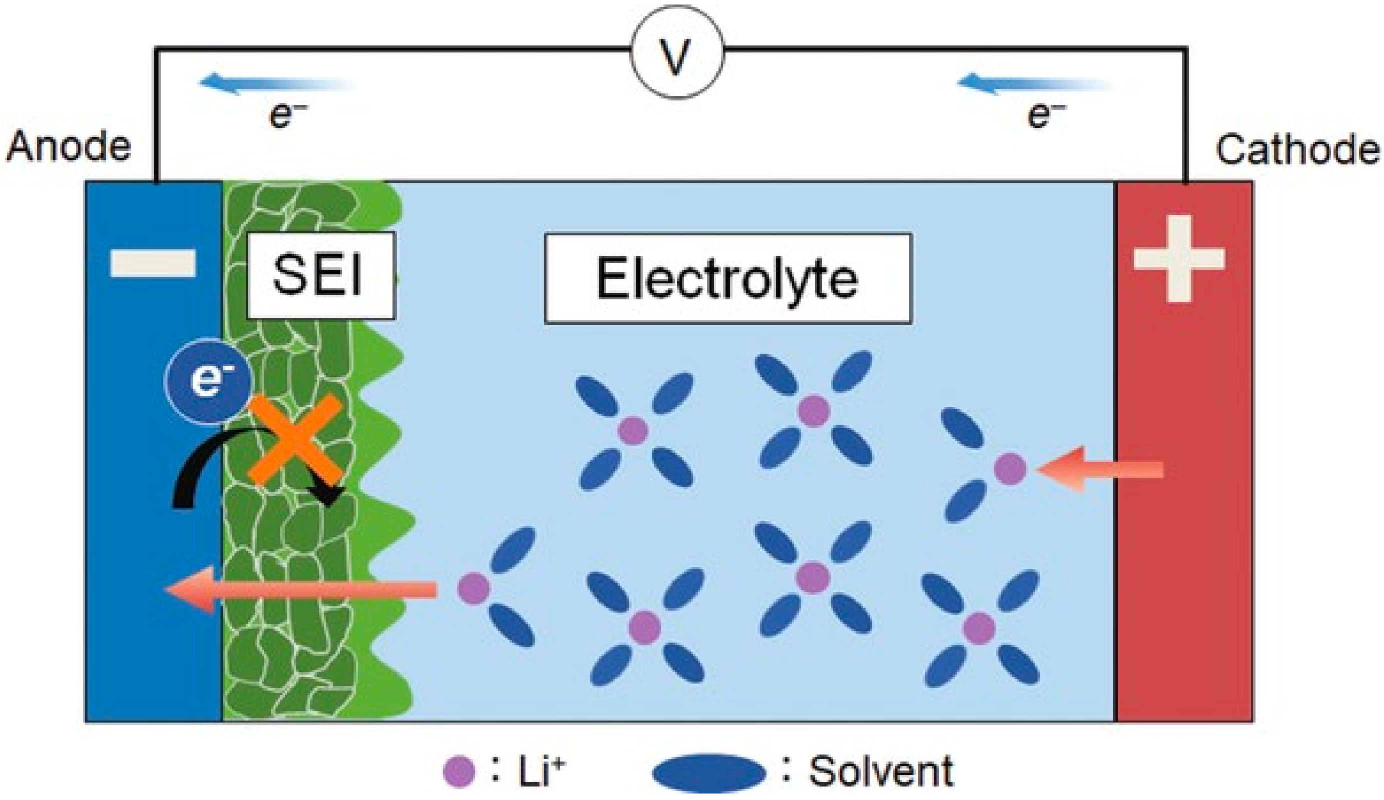
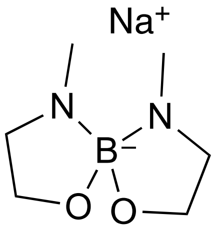
- SEI – Solid electrolyte interphase
- Ion conductive yet electron-insulating layer on electrodes
- Formed by the reductive decomposition of electrolytes during the initial charge
- SEI layer has a crucial role on the safety, power, and lifetime of batteries
- Typical compositions of an SEI layer in lithium-ion batteries is Li_2CO_3, LiF or $ROCO_2Li$ (R = alkyl groups)



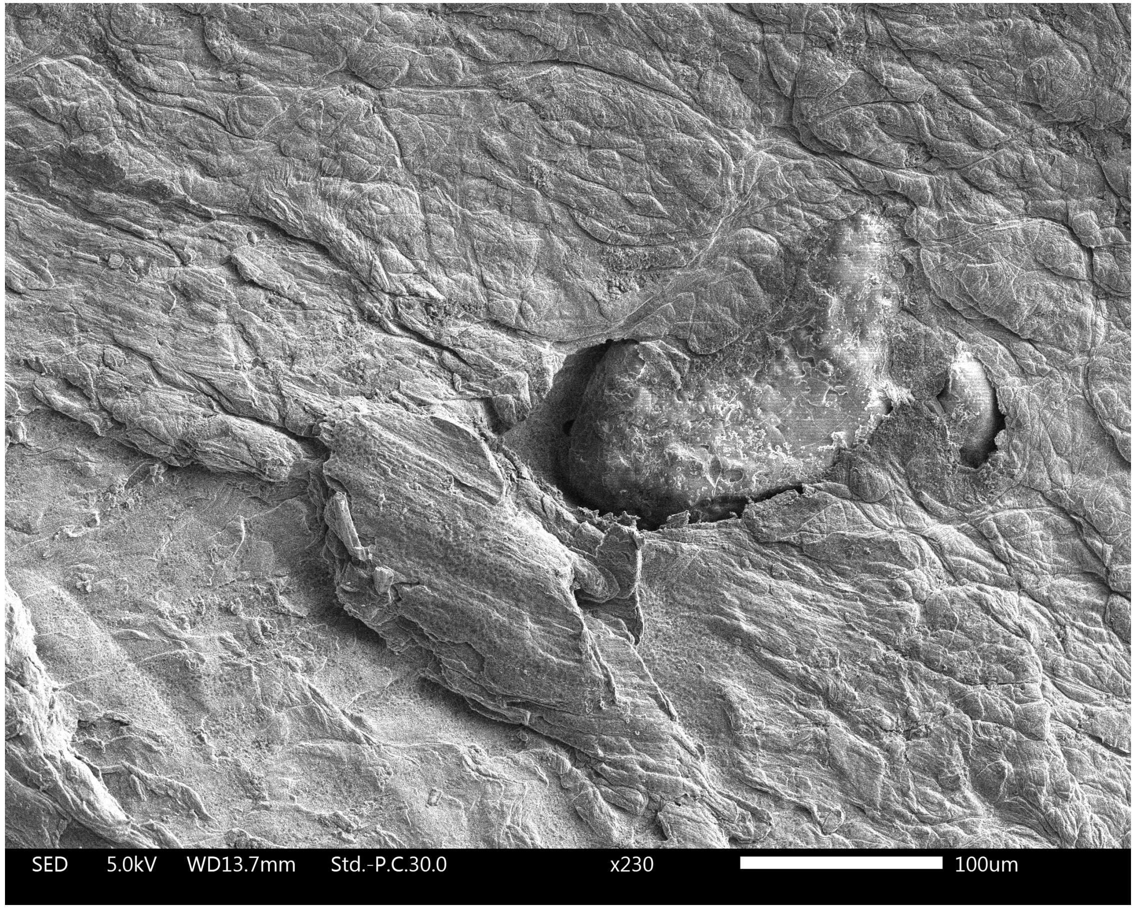
Takenaka, N., *et al.*, 2021, *Adv. Mater.*, ***33***(37).

SEM



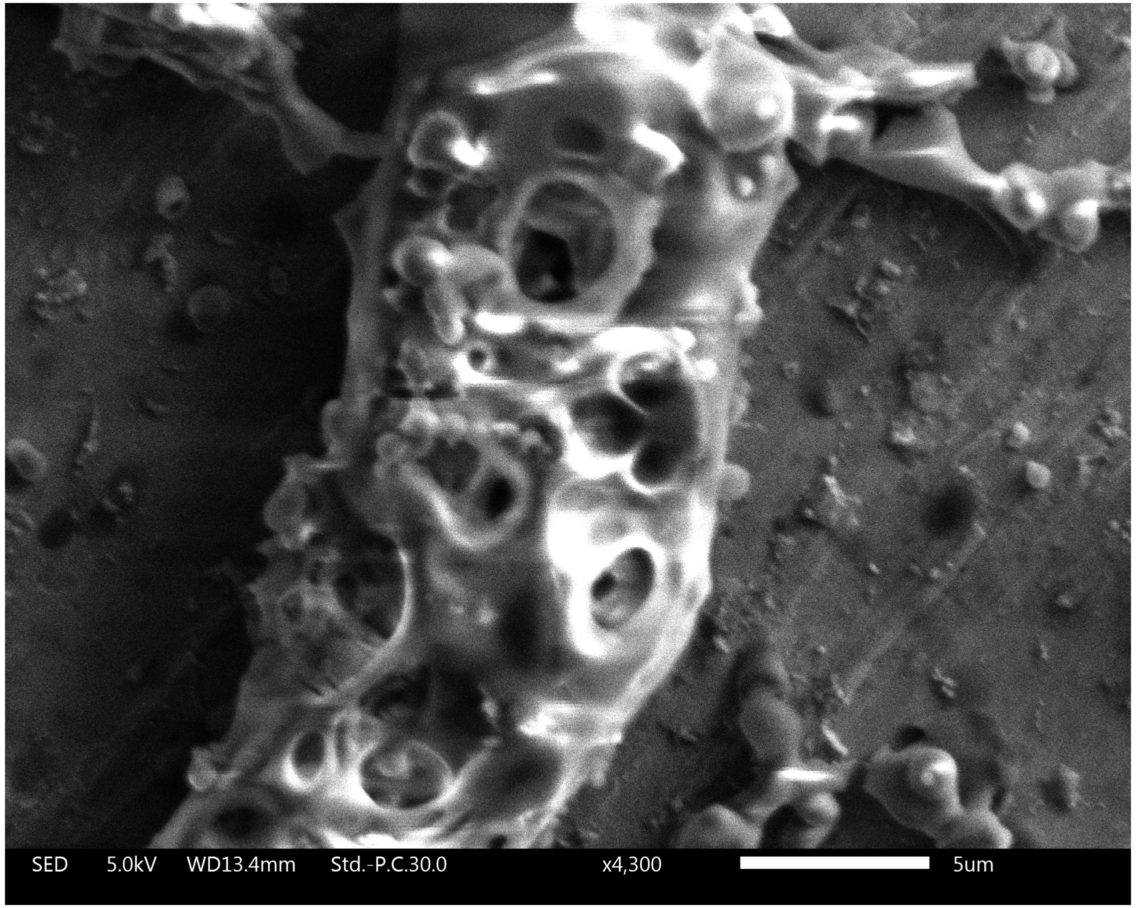
$Na[B(C_3H_7NO)_2]$

Na anode



Na electrode O 35 %, C 10 %, Na 55%

Cu cathode



Cu electrode N 7 %, O 18 %, C 8%, Na 9%, Cu 58%

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Summary

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- DSC confirms the presence of a solid-solid transition, $[P_{4444}]^+$ based OIPCs
- $[P_{4444}]^+$ OPICs show similar conductivity to known fluorinated OIPCs
- The phosphonium cation significantly more mobile
- H-bonding may be playing a role in the diffusion of $[P_{4444}]^+$ based ionic liquids
- SEM shows formation of SEI layer

Future work

- Investigate the performance of OIPCs as solid electrolyte
- Simulation modelling to investigate how the cation and anion interact
- Determine if the SEI formation helps improve the performance of Na batteries

Acknowledgements

- Professor John D. Holbrey
- Professor Małgorzata Swadźba-Kwaśny
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