Boron Nitride Modulates Polymer Electrolyte Conductivity

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The case for safer sodium-ion electrolytes

- Sodium is 100x less expensive than lithium
- Current electrolytes are flammable and risk thermal runaway
- Safer electrolytes are important for grid-scale energy storage

Thermal runaway is a major battery safety issue

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Usiskin et al. (2021), Gebert et al. (2021), Scutum London (2023)

Composite polymer electrolytes are promising

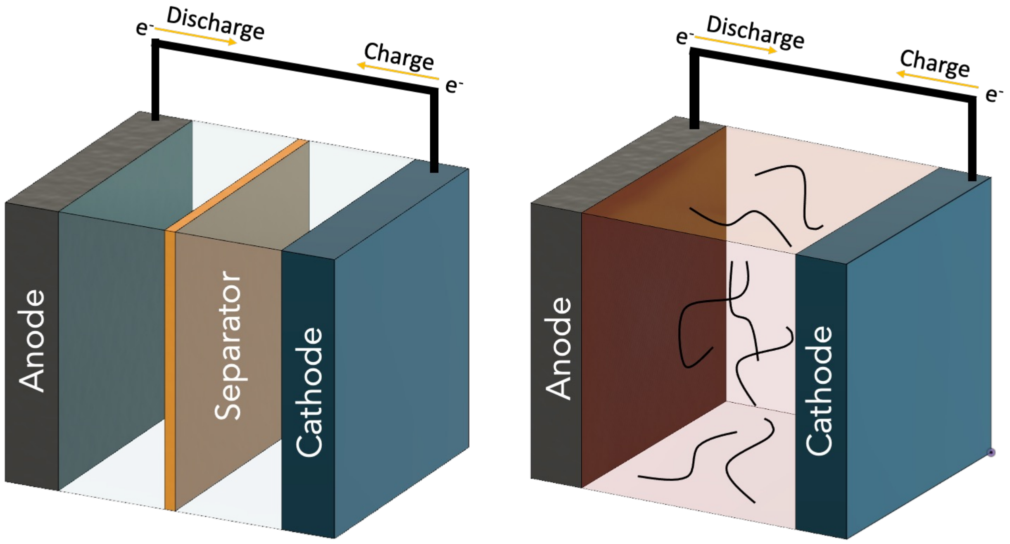


Fig. 1. Liquid (left) vs. polymer (right) electrolyte

Amorphous Crystalline

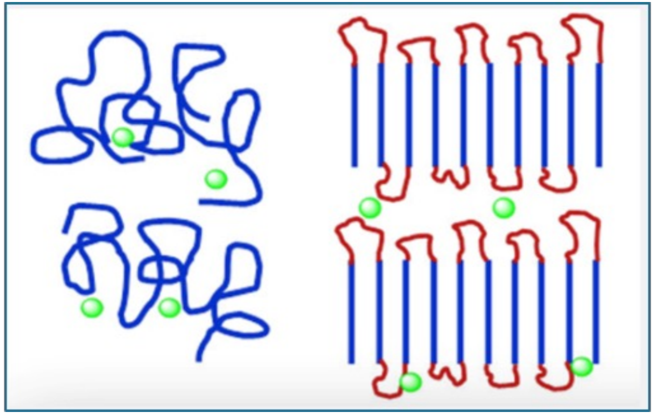
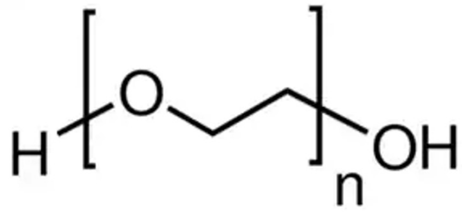


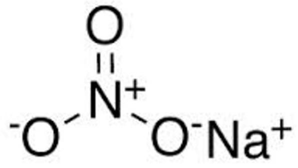
Fig. 2. (adapted from Cheng et al., 2014). Ions can only move through amorphous domains

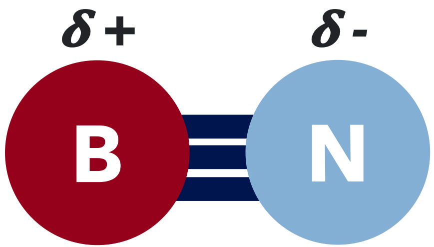
Model designed in Autodesk Fusion 360

Boron nitride is an interesting CPE filler

- Hexagonal boron nitride (BN) may interact with Na+ and NO3- ions
- BN increases the transference number of PEO–LiTFSI electrolytes
    - Li^{+}–BN binding energy: -157.6 kJ/mol
    - $TFSI^{-}$–BN binding energy: -166.51 kJ/mol





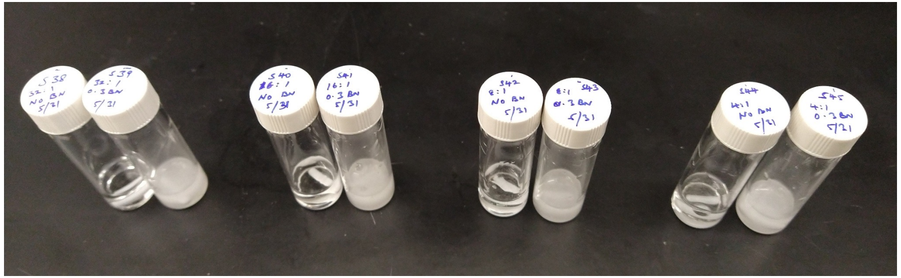


Sigma Aldrich (2023)

Methods

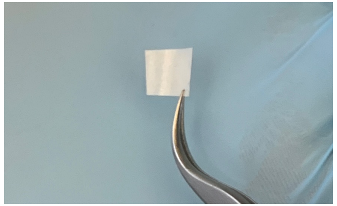
Phase 1: Prepare and cast solutions

- PEO, $NaNO_3$, and h-BN mixed in water
- 0.3 wt.% and 3 wt% h-BN, 4:1 and 24:1 ether O:Na^+ ratios, and controls (9 samples)
- Solutions cast on 1 in^2 glass slides (381 μm-thick)

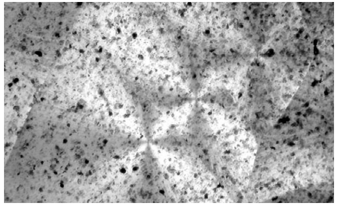


Phase 2: Dry in vacuum oven

- Hot plate at 120°C for 1h
- Vacuum oven at 120°C for 16h
- Vacuum chamber at 25°C for 1h



PEO Film, 25 mm^2



PEO crystal with 3% BN, 1.5 mm^2

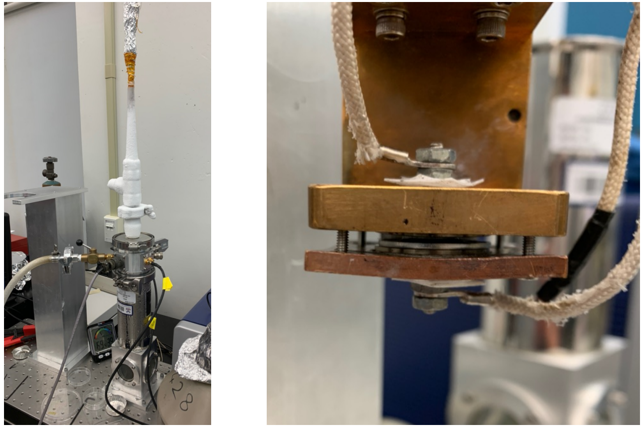
Phase 3: Characterize Samples

Structural Characterization

- Differential Scanning Calorimetry (DSC)
- X-Ray Diffraction (XRD)
- Fourier Transform Infrared Spectroscopy (FTIR)

Electrochemical Characterization

- Electrochemical Impedance Spectroscopy (EIS)

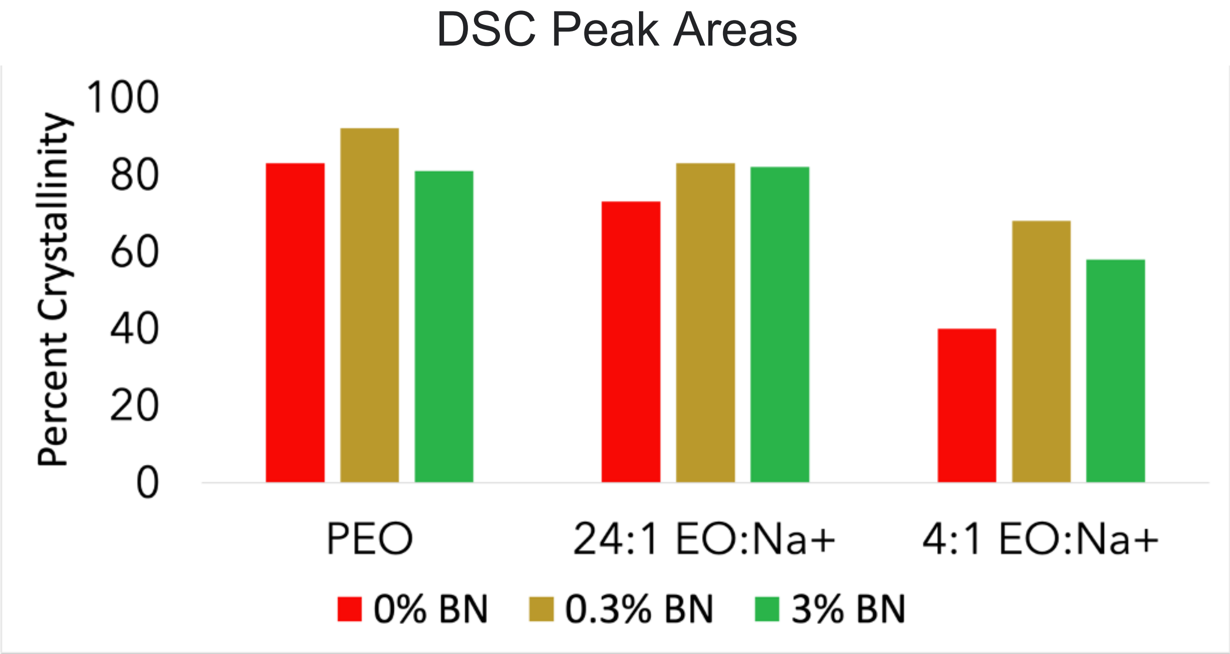


Cryostat (EIS)

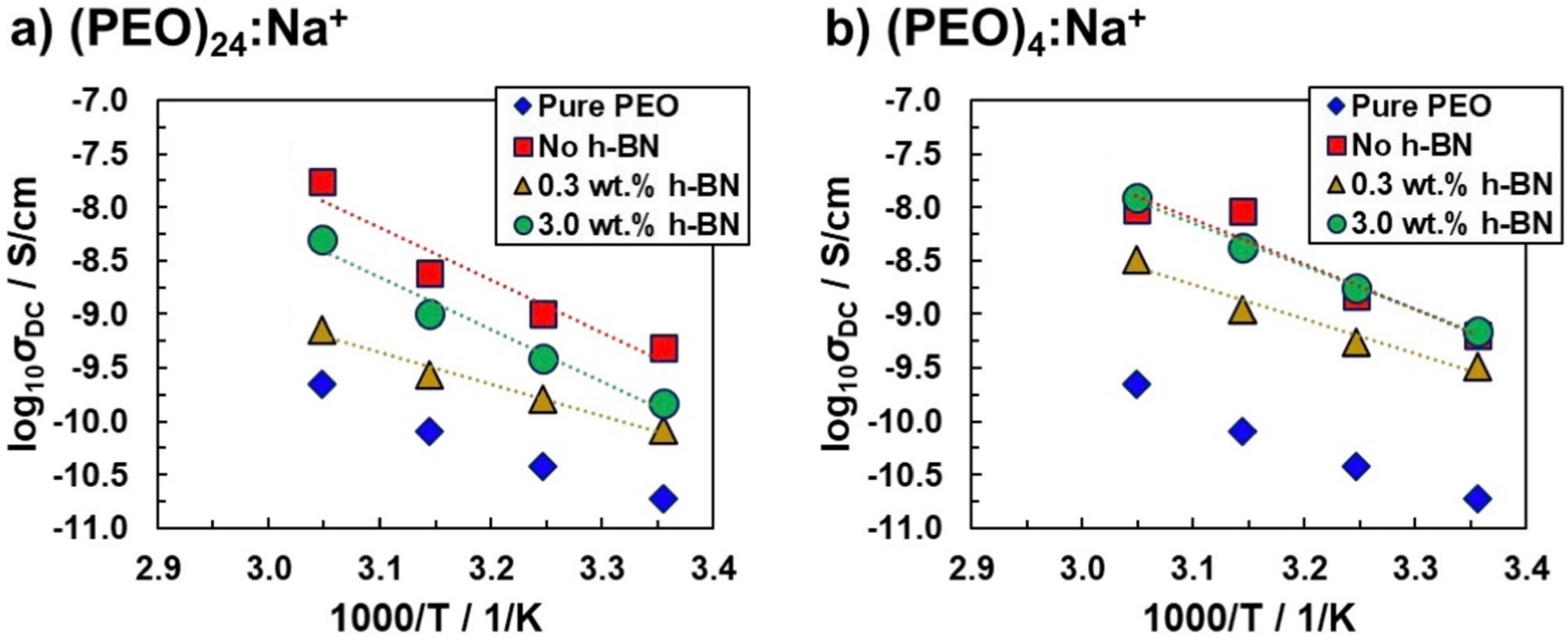
Results

Adding BN affects PEO crystallinity

- **Differential Scanning Calorimetry** shows heat of melting
- Increasing BN to 0.3% increases crystallinity
- Crystallinity decreases at 3%
- Overall increased crystallinity could hinder ion mobility



Crystallinity affects ionic conductivity

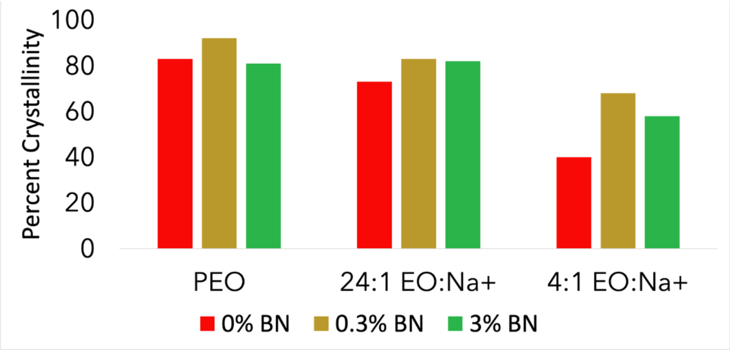


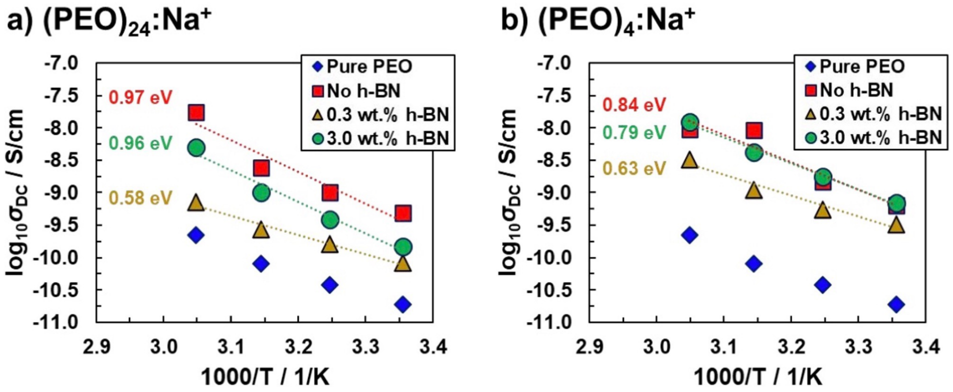
Ionic conductivity is highest for BN-free samples, showing the effect of increased crystallinity

Conclusions

- Adding BN can increase PEO crystallinity via enhanced nucleation
- The effect of increased crystallinity dominates, decreasing ionic conductivity
- Sodium CPE properties may be tailored by changing the geometry of filler materials

DSC Peak Areas





Acknowledgements

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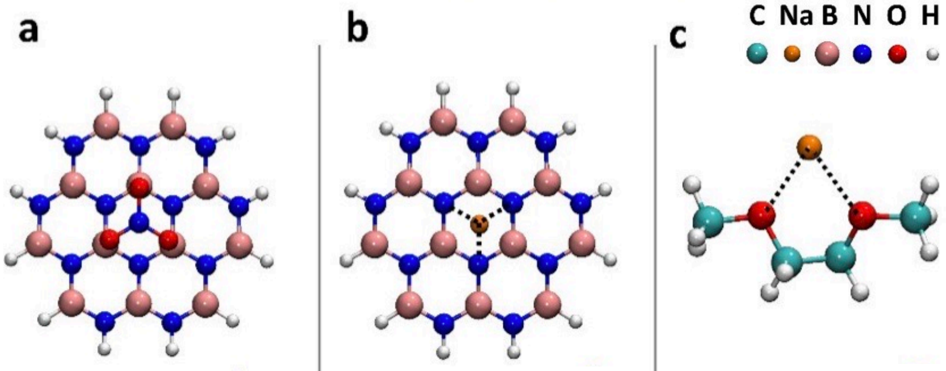
Supplementary Information

Phase 4: Compare to DFT Calculations

- Significant BN-salt binding energies
- Trends differ from lithium-ion literature

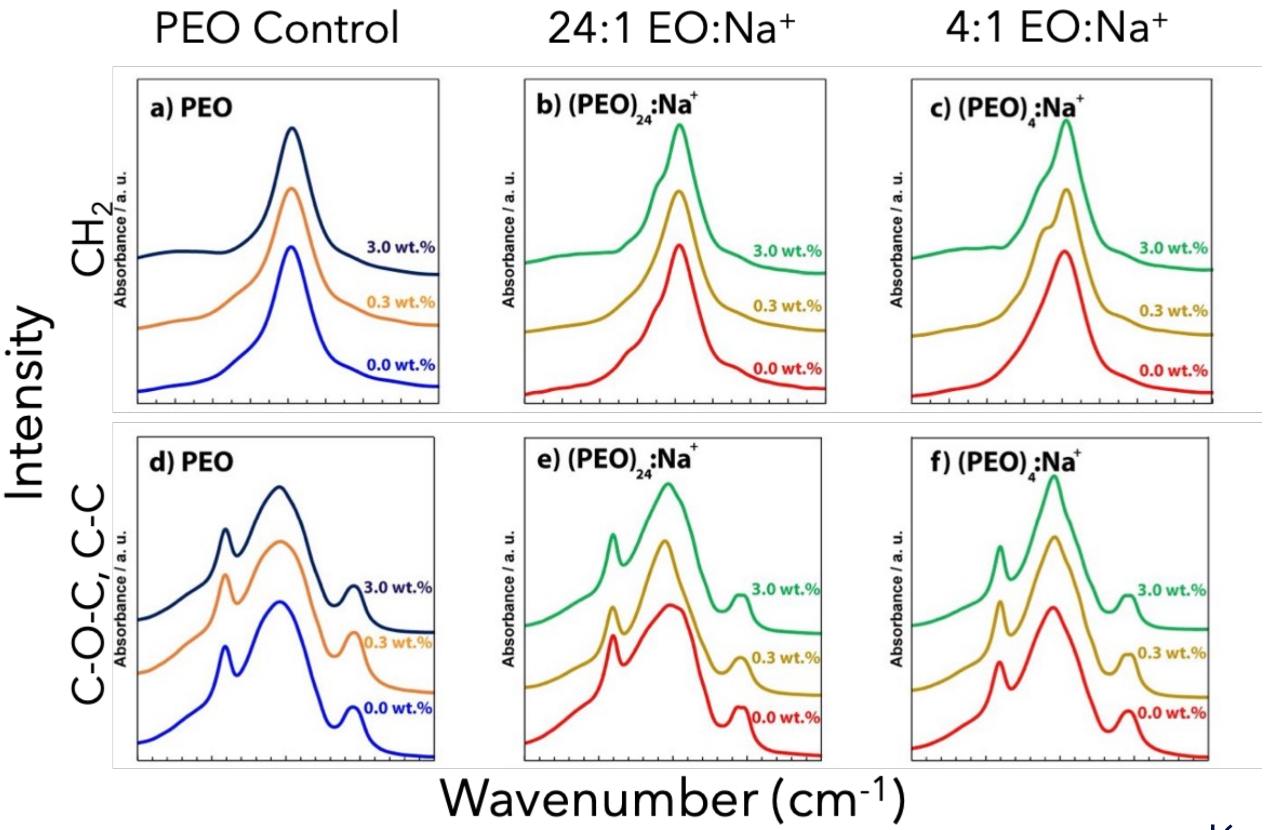
Complexation Energy (kcal/mol)



$BN\text{-}NO_3^-$	$BN\text{-}Na^+$	$PEO\text{-}Na^+$
-13.4	-29.3	-44.1

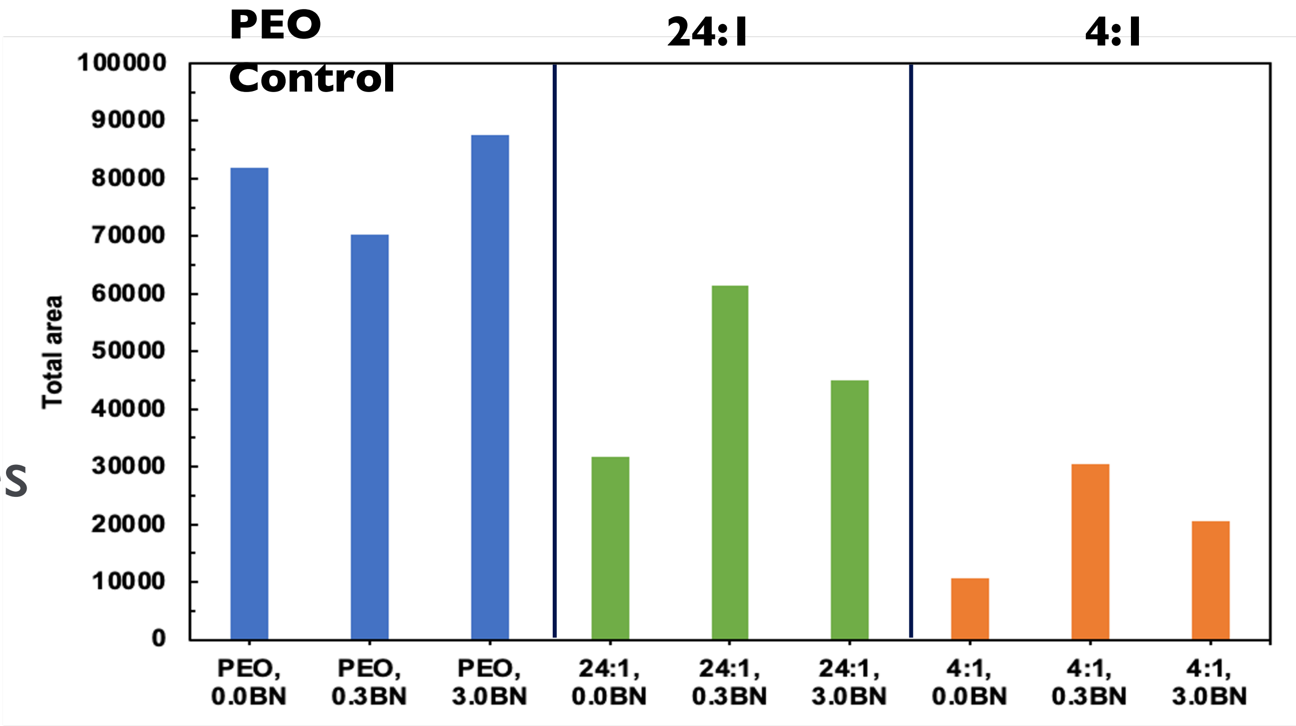
BN decreases PEO-$NaNO_3$ complexation

- PEO complexes with Na^+, decreasing crystallinity
- FTIR peaks (840 and 1100 cm^{-1}) broaden with salt
- Peaks narrow when BN is added



XRD peak area varies with h-BN loading

For salt-doped samples, total peak area (crystallinity) increases with 0.3% h-BN then decreases with 3% h-BN



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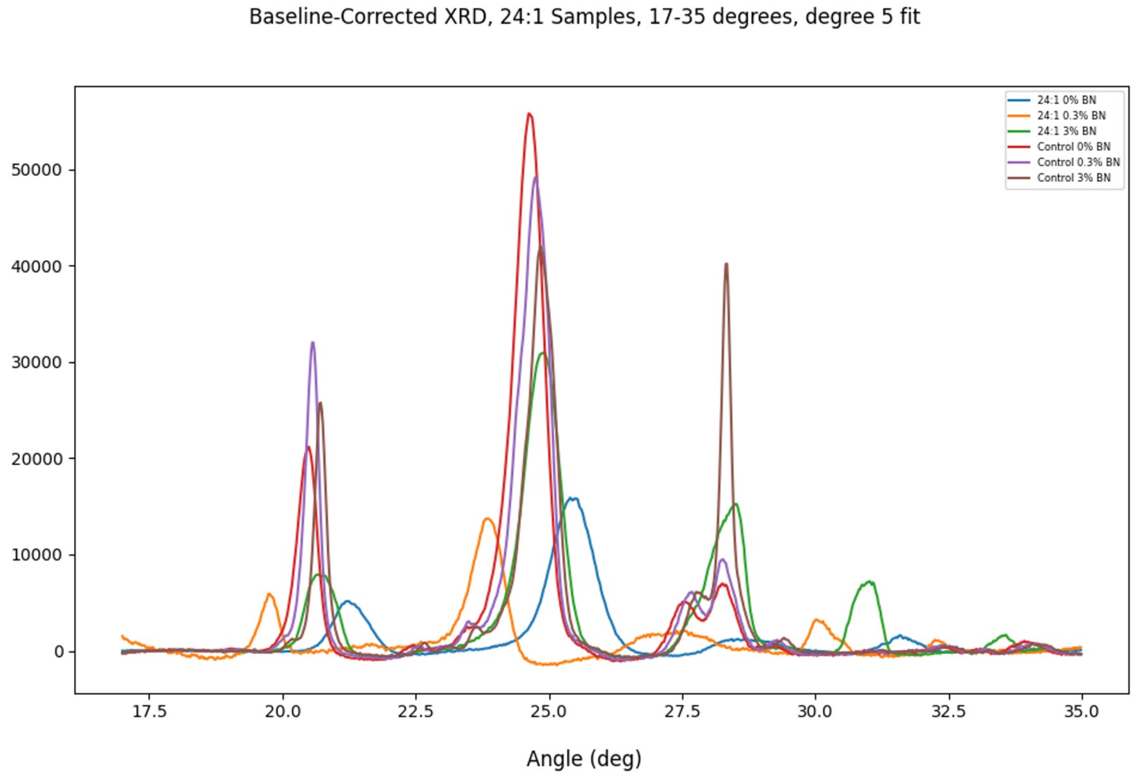
Additional XRD from Trial 2

No significant NaNO3 peaks appear in the 24:1 XRD traces



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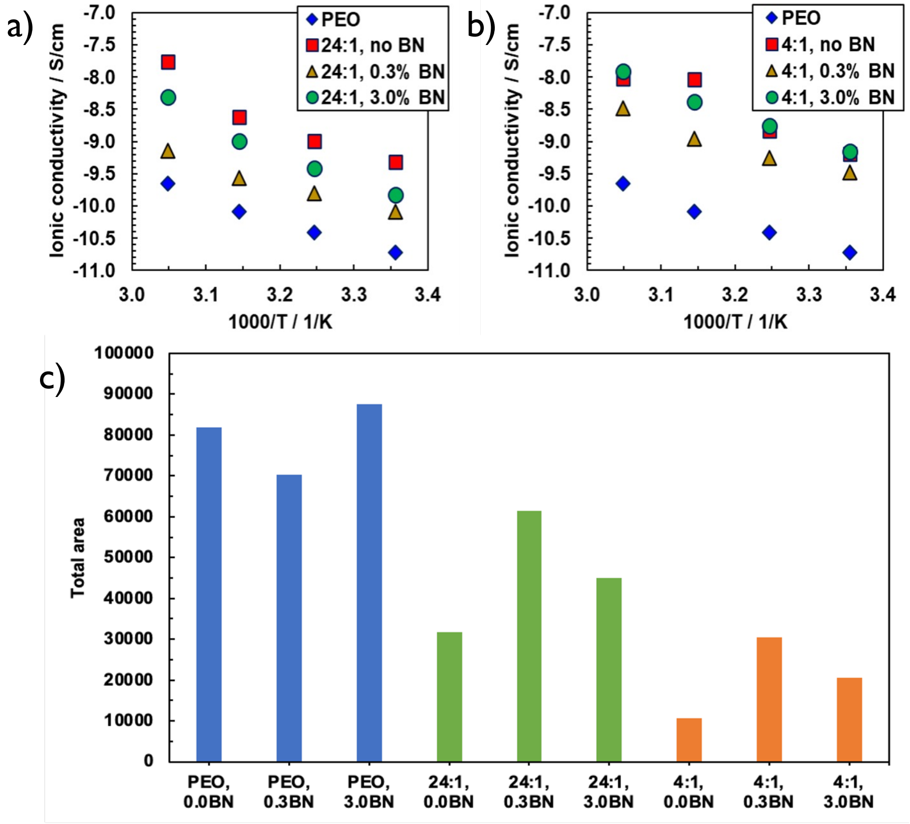
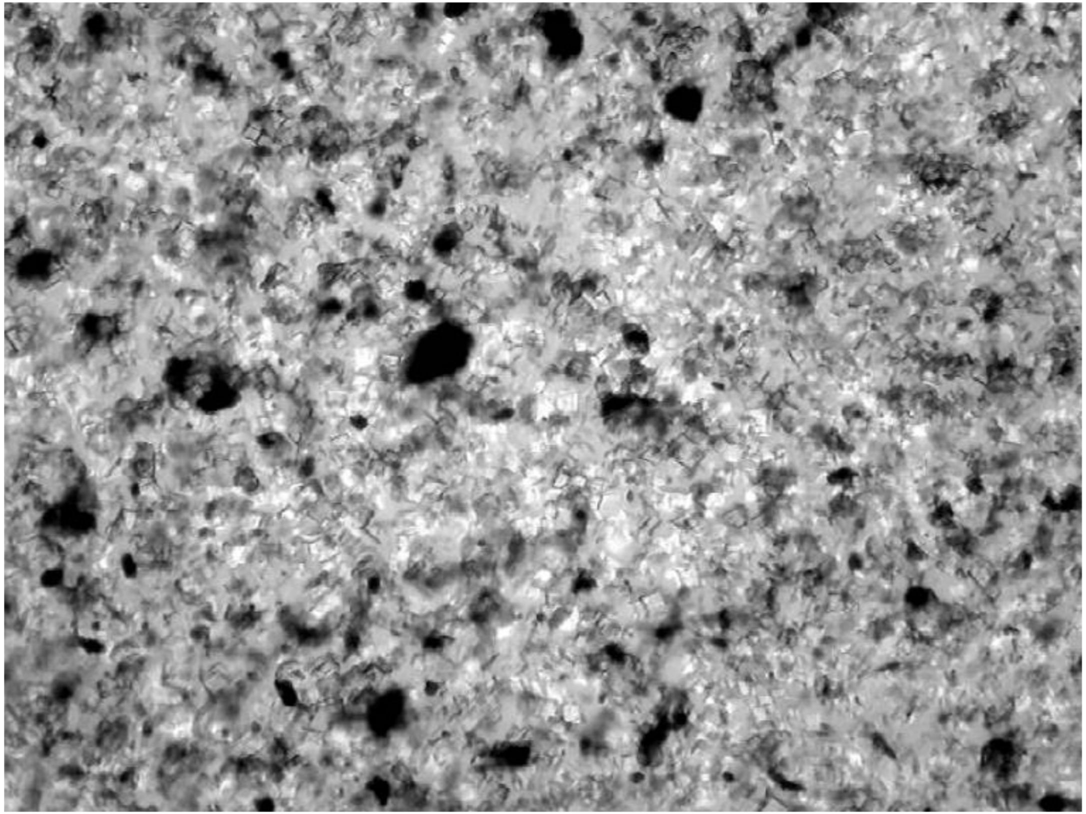
Ionic Conductivity and XRD Peak Area

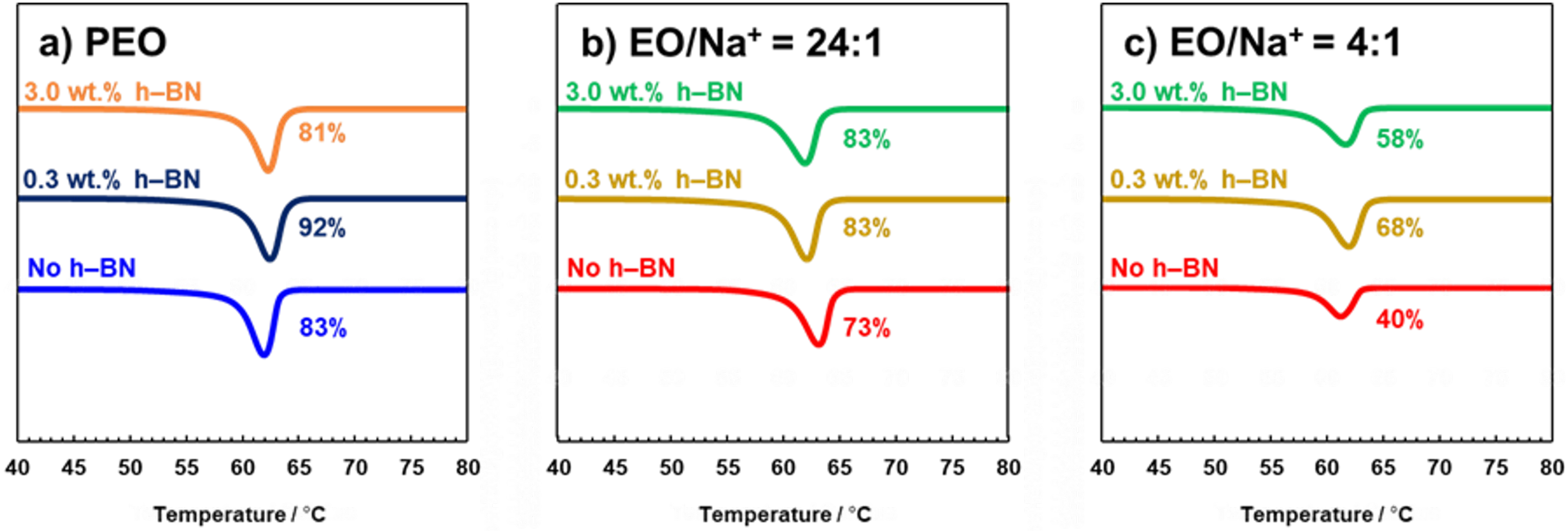
- Ionic conductivity follows the trend $IC_{No\ h\text{-}BN} > IC_{3.0\%} > IC_{0.3\%}$
- Interestingly, crystallinity follows the inverse trend $X_{No\ h\text{-}BN} < X_{3.0\%} < X_{0.3\%}$



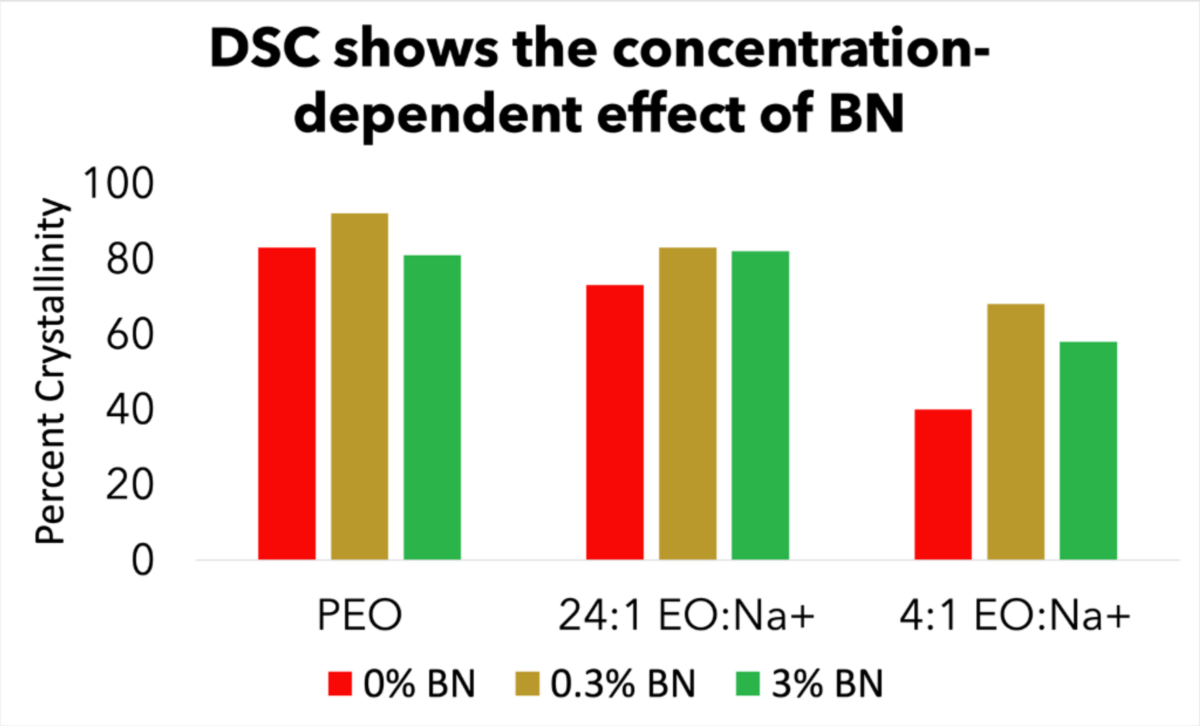
Salt Crystal image (4:1 $NaNO_3$, 3% BN)



DSC on polymer electrolytes



DSC shows the concentration-dependent effect of BN



PEO-$NaNO_3$ system is soluble in H_2O