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Synthesis and characterization of Na_3PS_4 and $\text{Na}_{2.85}\text{P}_{0.85}\text{W}_{0.15}\text{S}_4$ as solid electrolytes

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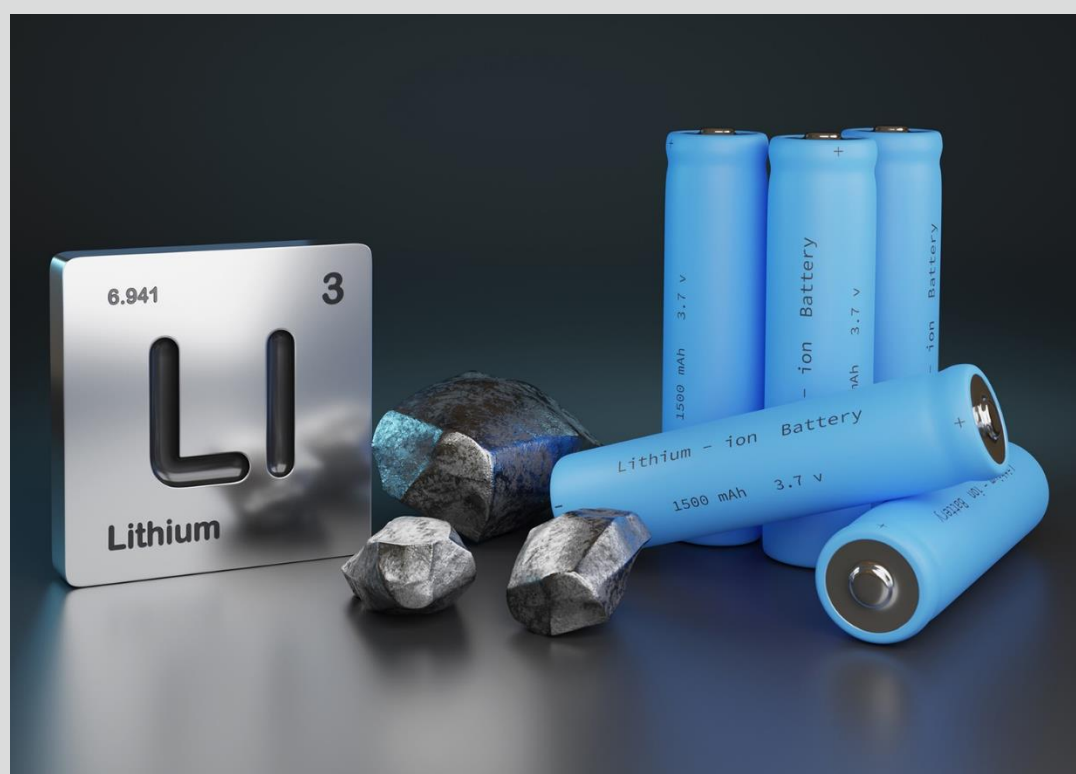
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INTRODUCTION

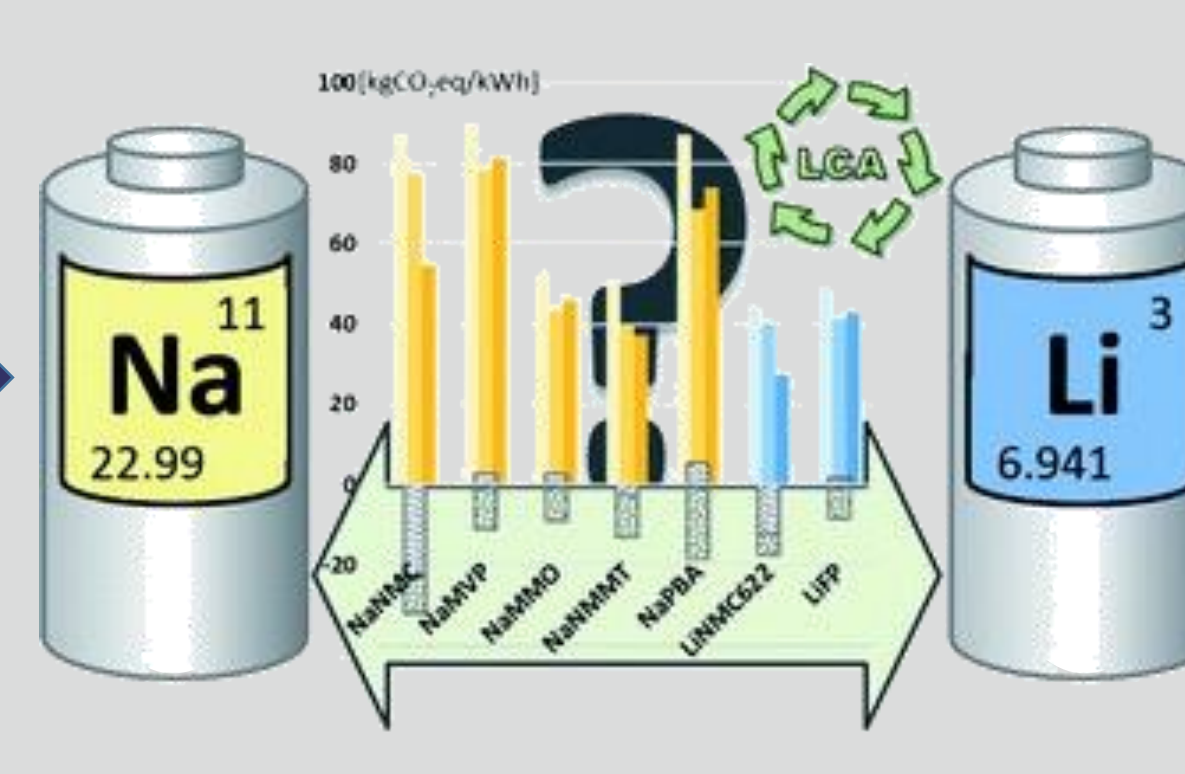
The next generations of post-lithium systems are already under development. These hold the promise of overcoming some of the remaining challenges associated with current lithium-ion battery technology related to safety, the need for scarce resources and their environmental impacts. Figures obtained from [1] and [2]



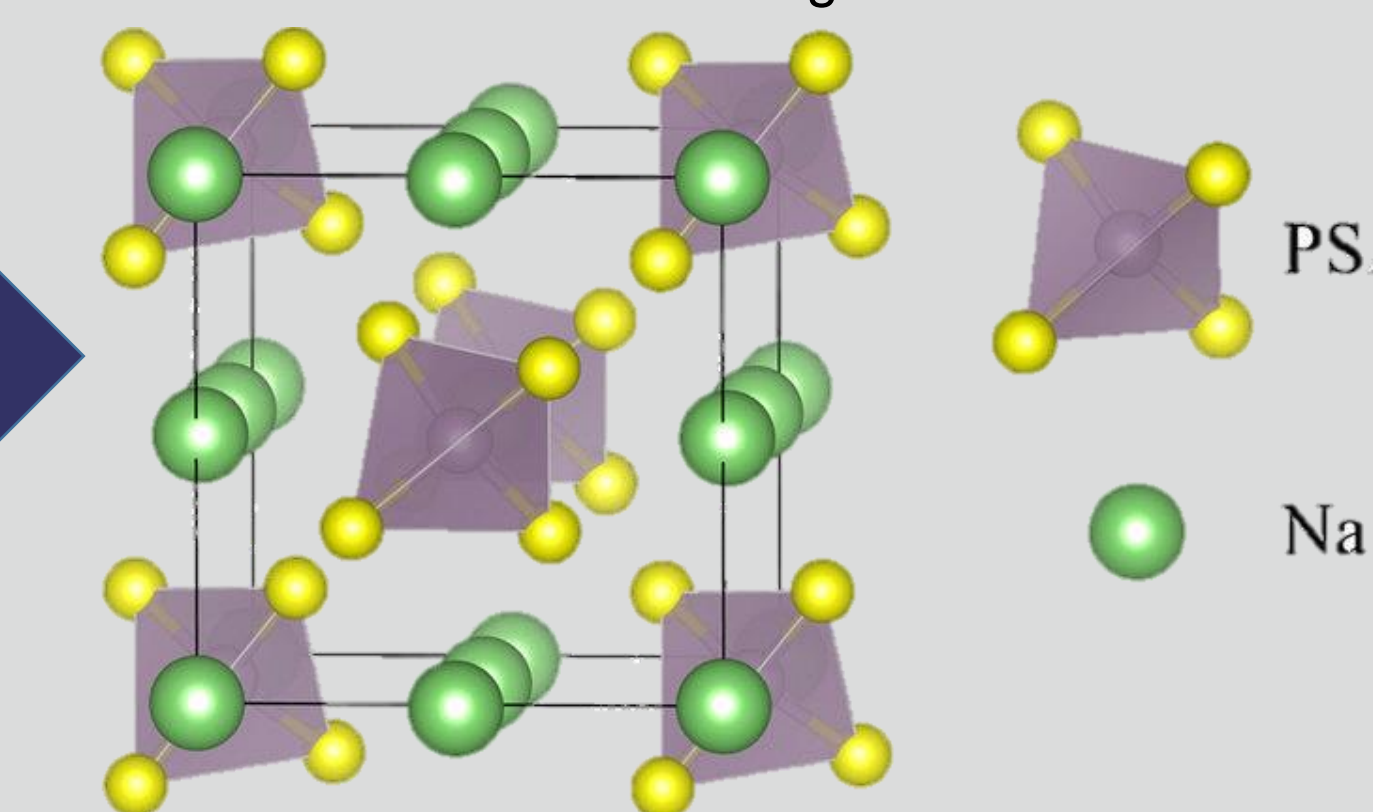
PROBLEM



Na as a solution?

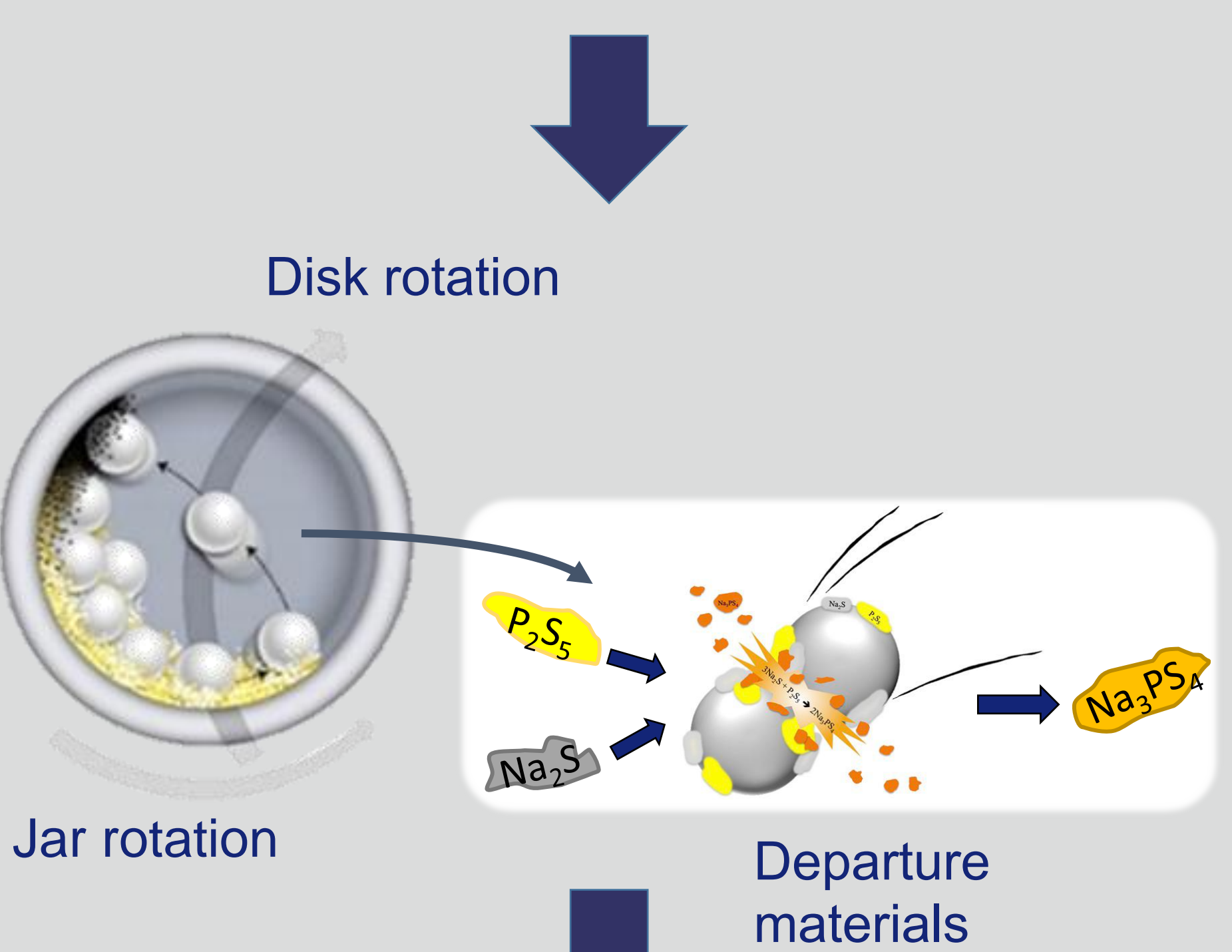


Na_3PS_4 (NPS) is a sodium superionic conductor that crystallizes in the $I-43m$ space group and reaches ionic conductivities in the range of the mS/cm



METHODOLOGY

Mechanochemical synthesis following procedure described in [3].



Heat treatment (HT) based on procedure described in [4].

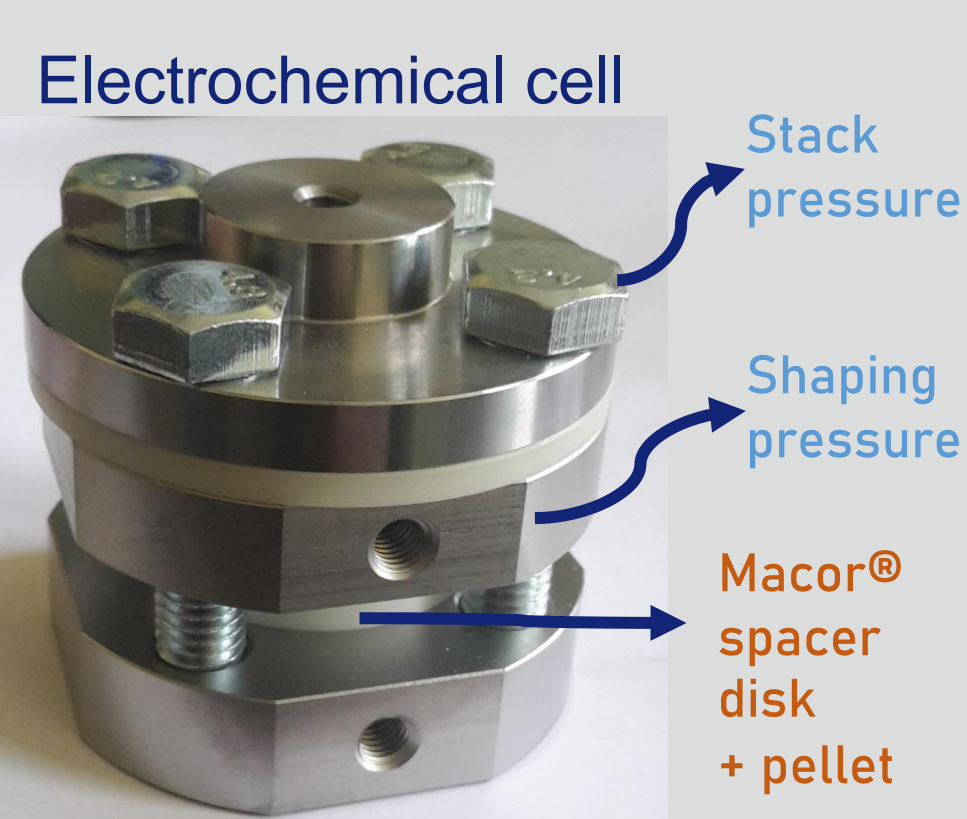
- Sample HT-1
- HT: 300°C, 16 h
 - Atmosphere: vacuum, pellet contained in Macor® spacer disk
- Sample HT-2 (NPS only)
- HT: 270°C, 1.5 h
 - Atmosphere: argon, pellet covered by Na₂S in alumina crucible

Synchrotron X-ray diffraction

- $\lambda = 0.1653 \text{ \AA}$
- Sealed capillaries

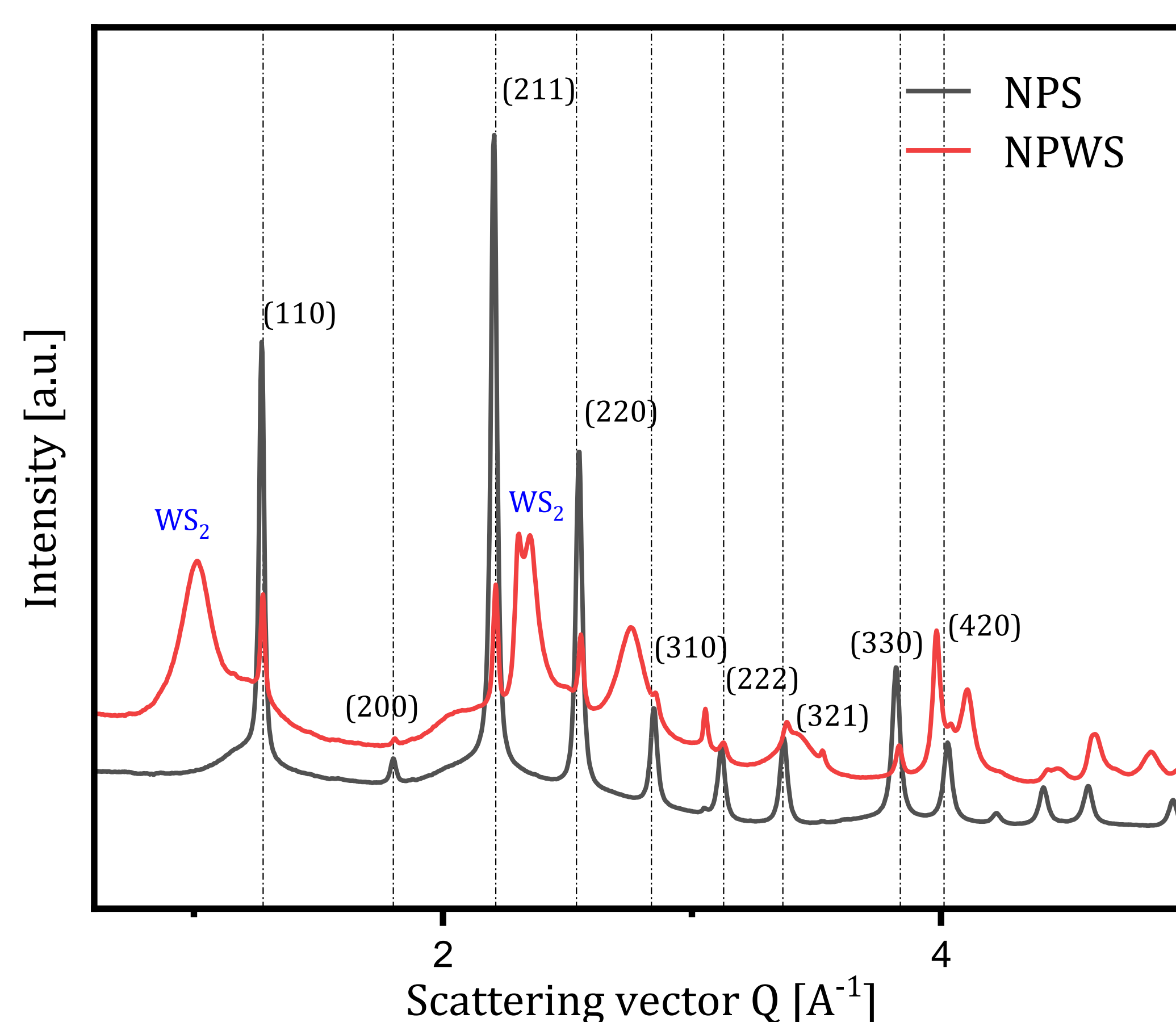


Impedance spectroscopy

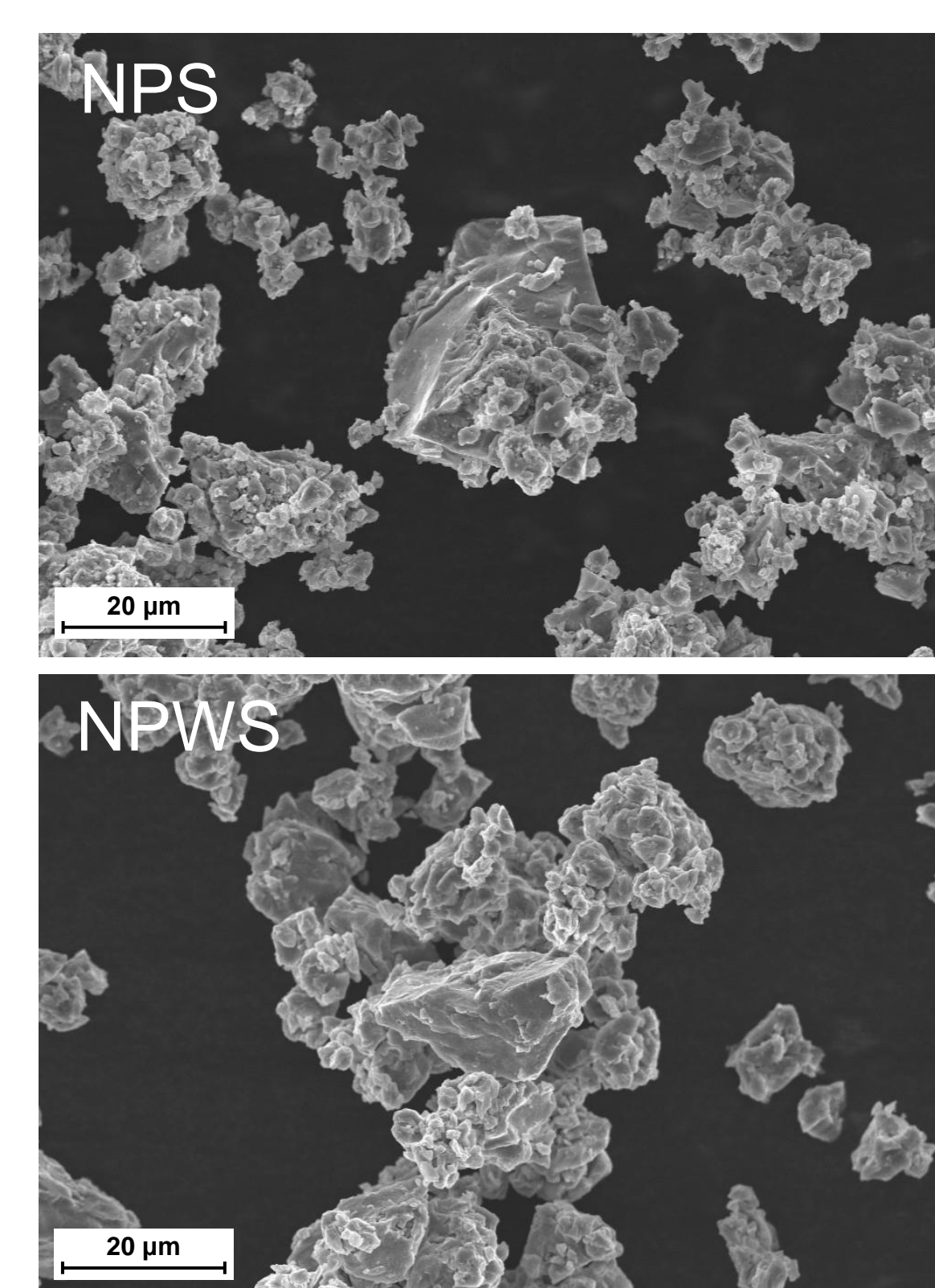


TECHNIQUES AND RESULTS

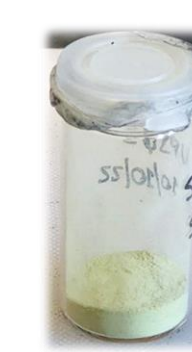
Material characterization - XRD



SEM



Crystalline Na_3PS_4 phase cubic $I-43m$ space group [3]



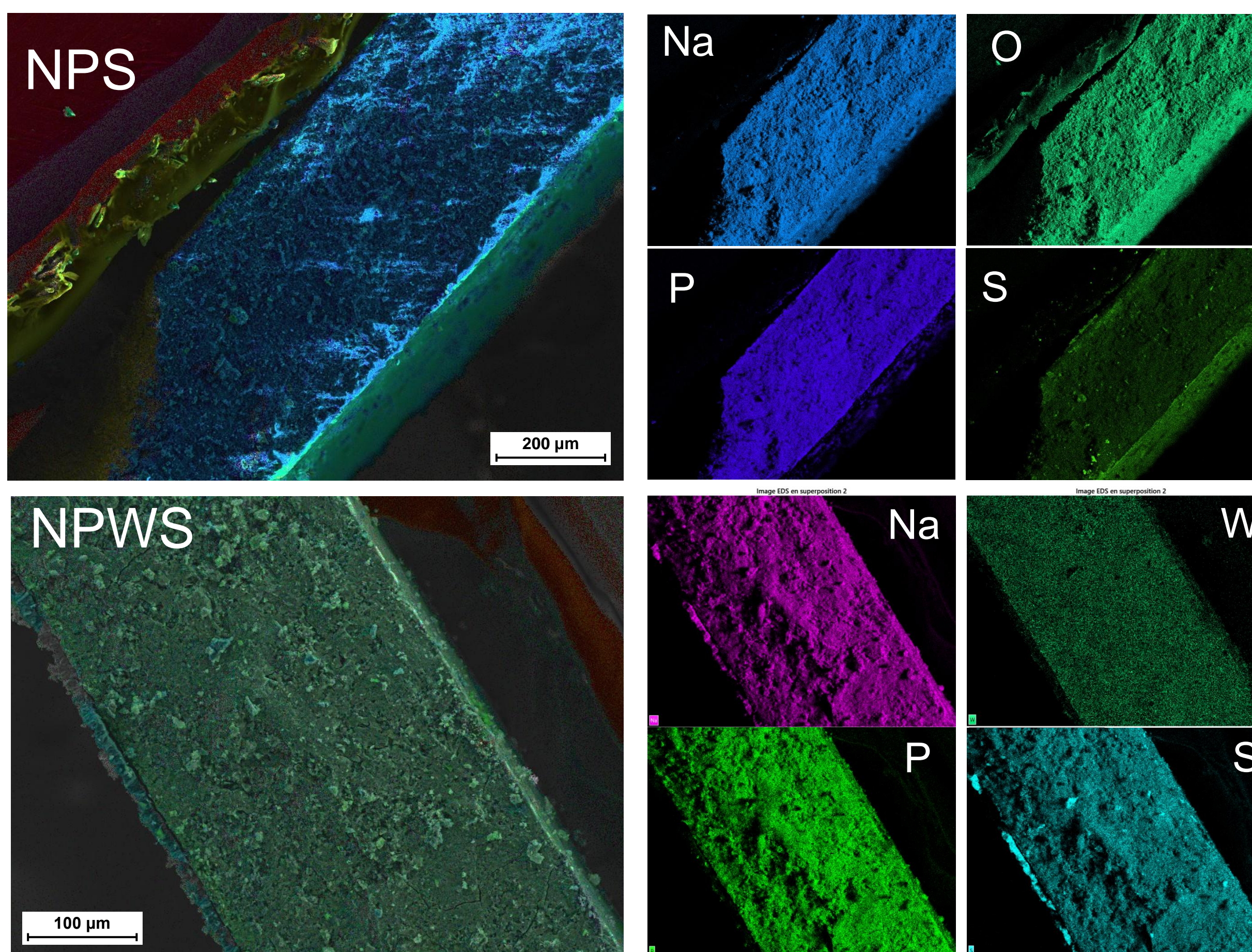
NPS

$\text{Na}_{2.85}\text{P}_{0.85}\text{W}_{0.15}\text{S}_4$
Two crystalline phases coexist, i.e., Na_3PS_4 and WS_2 [4]



NPWS

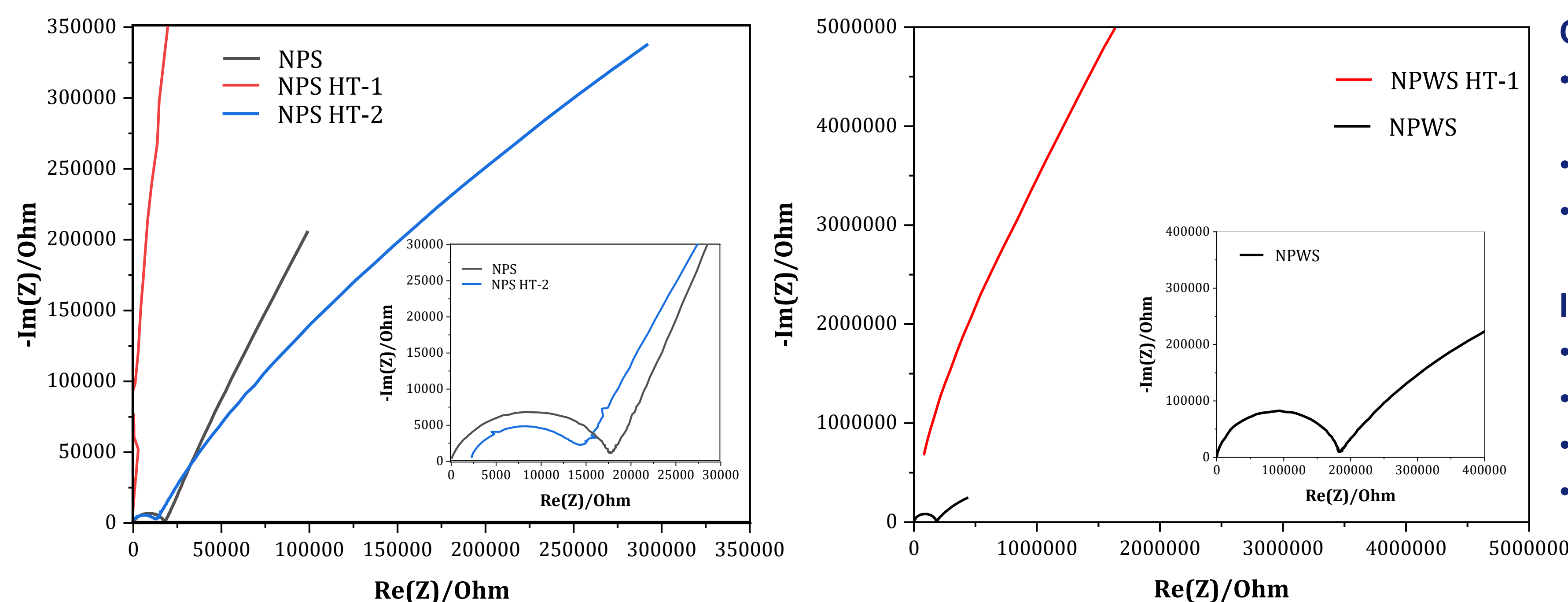
SEM - Energy Dispersive X-ray (EDX)



- Cross-section of the pellets (NPS and NPWS)
- Evidence of reaction with Macor® holder during with treatment due to the presence of O and Si in the samples.
- Presence of high porosity.

View of the contact surface between Macor® and electrolyte

Electrochemical characterization - EIS



Cell parameters

- Shaping Pressure: 382 MPa
- Stack P: 127.5 MPa
- Time: 15 min

Ionic conductivity

- NPS: 6.0 $\mu\text{S/cm}$
- NPS HT-2: 13 $\mu\text{S/cm}$
- NPWS: 0.54 $\mu\text{S/cm}$
- Both HT-1: insulants

References

- [1] J. F. Peters, M. Baumann, J. R. Binder, and M. Weil, "On the environmental competitiveness of sodium-ion batteries under a full life cycle perspective-a cell-chemistry specific modelling approach," *Sustain. Energy Fuels*, vol. 5, no. 24, pp. 6414–6429, 2021, doi: 10.1039/d1se01292d.
- [2] Chu, Iek-Heng; Kompella, Christopher S.; Nguyen, Han; Zhu, Zhuoying; Hy, Sunny; Deng, Zhi; Meng, Ying Shirley; Ong, Shyue Ping (2016). Room-Temperature All-solid-state Rechargeable Sodium-ion Batteries with a Cl-doped Na₃PS₄ Superionic Conductor. *Scientific Reports*, 6(), 33733–. doi:10.1038/srep33733
- [3] Nguyen, Han; Banerjee, Abhik; Wang, Xuefeng; Tan, Darren; Wu, Erik A.; Doux, Jean-Marie; Stephens, Ryan; Verbist, Guy; Meng, Ying Shirley (2019). Single-step synthesis of highly conductive Na₃PS₄ solid electrolyte for sodium all solid-state batteries. *Journal of Power Sources*, (), 126623–. doi:10.1016/j.jpowsour.2019.05.031
- [4] Fumika Tsuji; Akira Nasu; Atsushi Sakuda; Masahiro Tatsumisago; Akitoshi Hayashi; (2021). Mechanochemical synthesis and characterization of Na₃-P₁-W₄ S₄ solid electrolytes. *Journal of Power Sources* doi:10.1016/j.jpowsour.2021.230100

CONCLUSIONS

- X-ray diffractograms show a cubic crystalline phase of Na_3PS_4 and a mixture of Na_3PS_4 and WS_2 for the $\text{Na}_{2.85}\text{P}_{0.85}\text{W}_{0.15}\text{S}_4$ sample.
- SEM-EDX results confirmed that a reaction occurs between the sample holder (Macor®) and the solid electrolytes during the heat treatments.
- Electrochemical results show that a heat treatment under Ar slightly improves the ionic conductivity for the NPS sample, while the HTs in presence of Macor® spacer turn the materials into ionic insulants.