

Stepwise reaction and degradation in solution synthesis of $\text{Li}_6\text{PS}_5\text{Br}$ from P_4S_{10}



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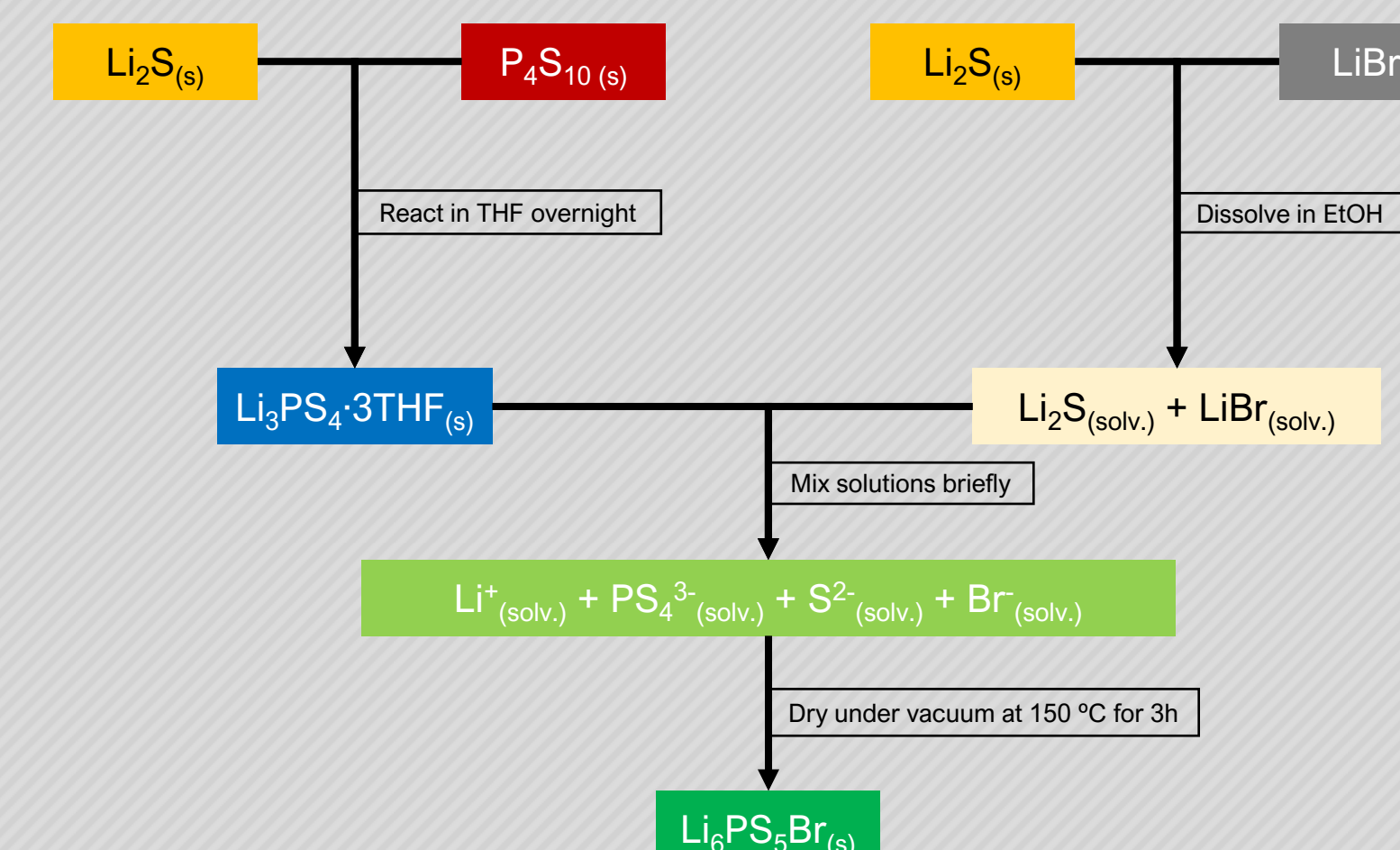
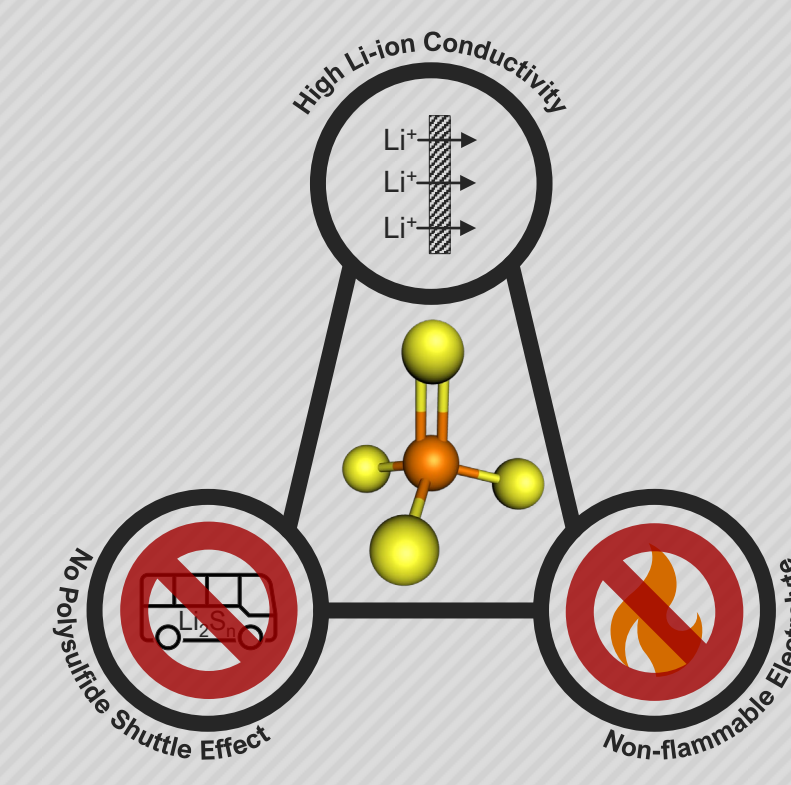
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Keywords: sulfide solid-state electrolytes, lithium thiophosphate, lithium argyrodite, solution synthesis

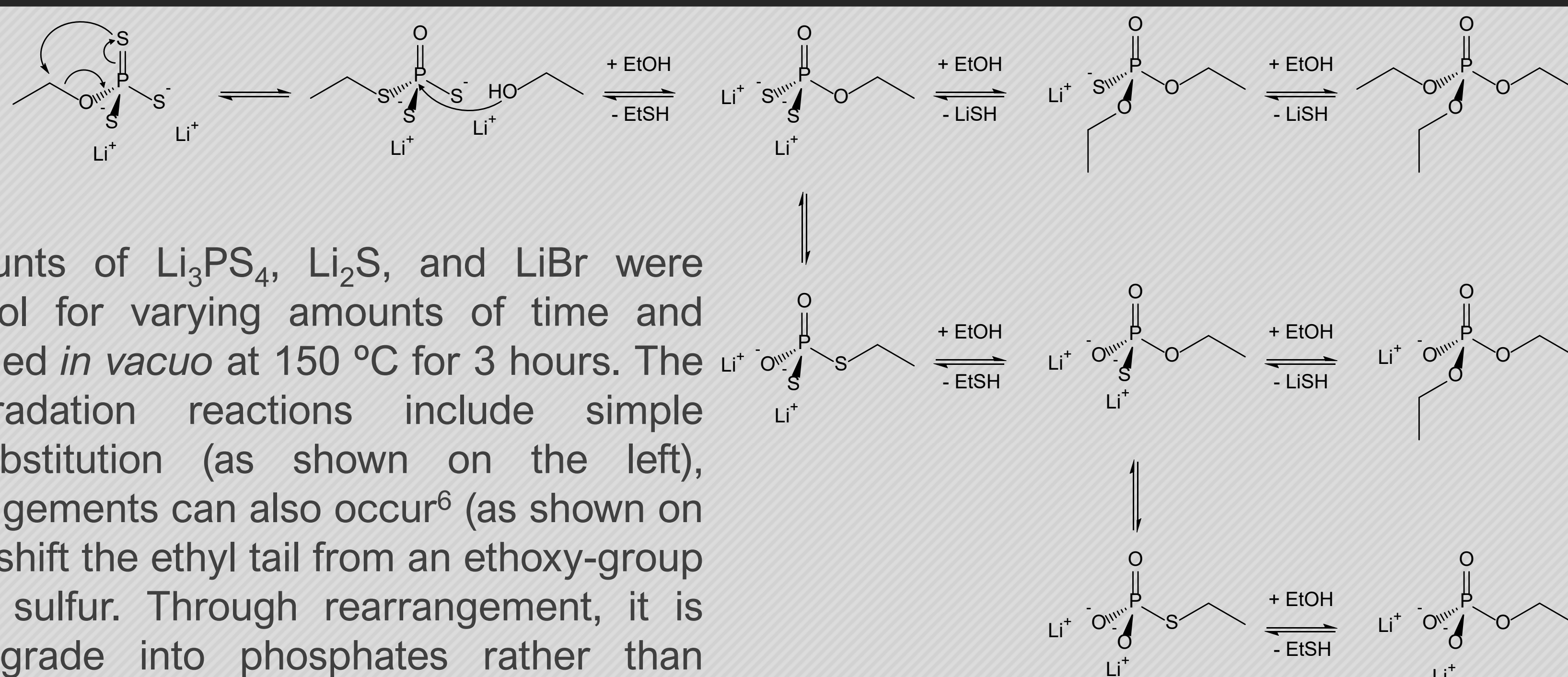
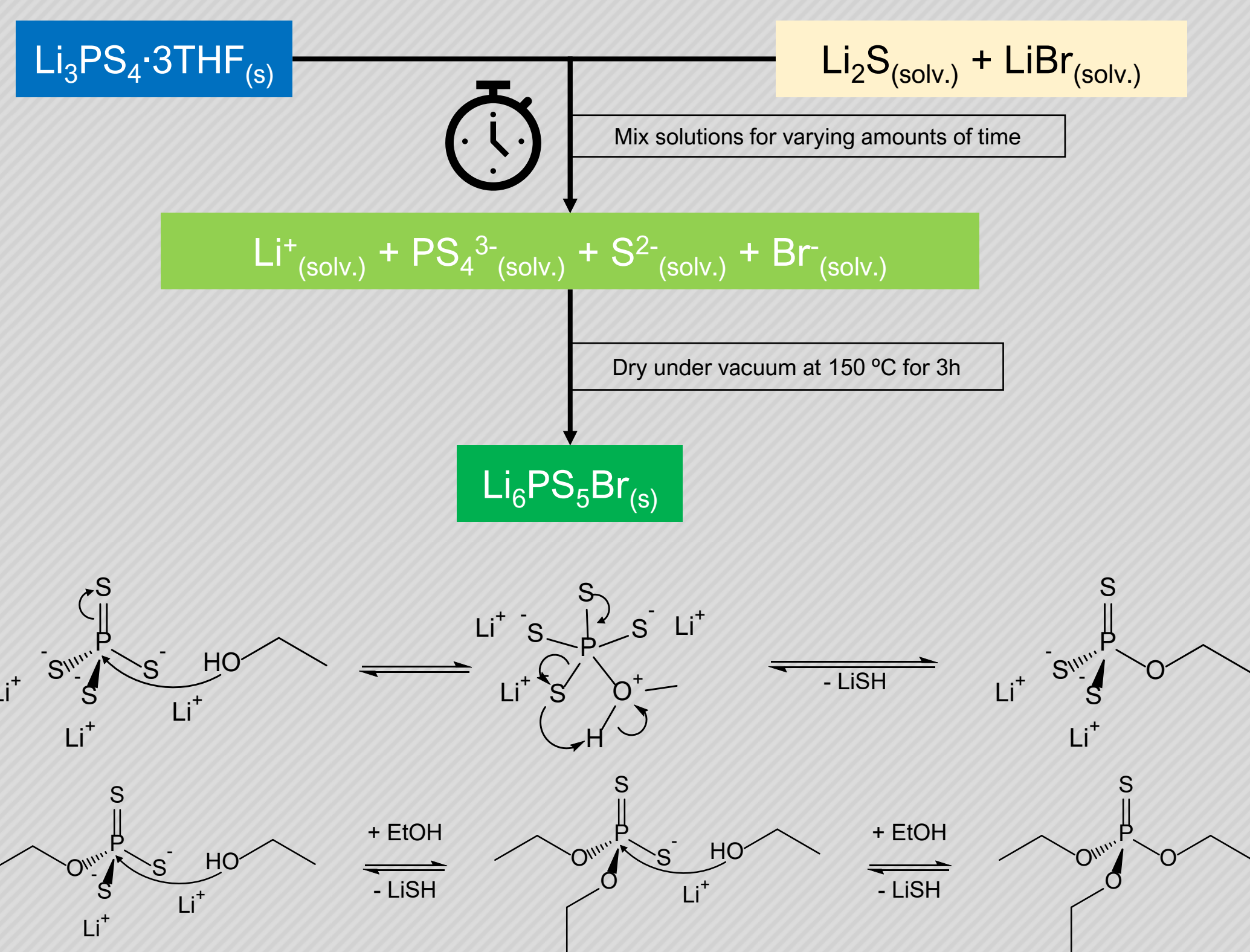
INTRODUCTION

Over half of all CO_2 from transport comes from normal passenger cars. Can we improve electric cars to tackle this?



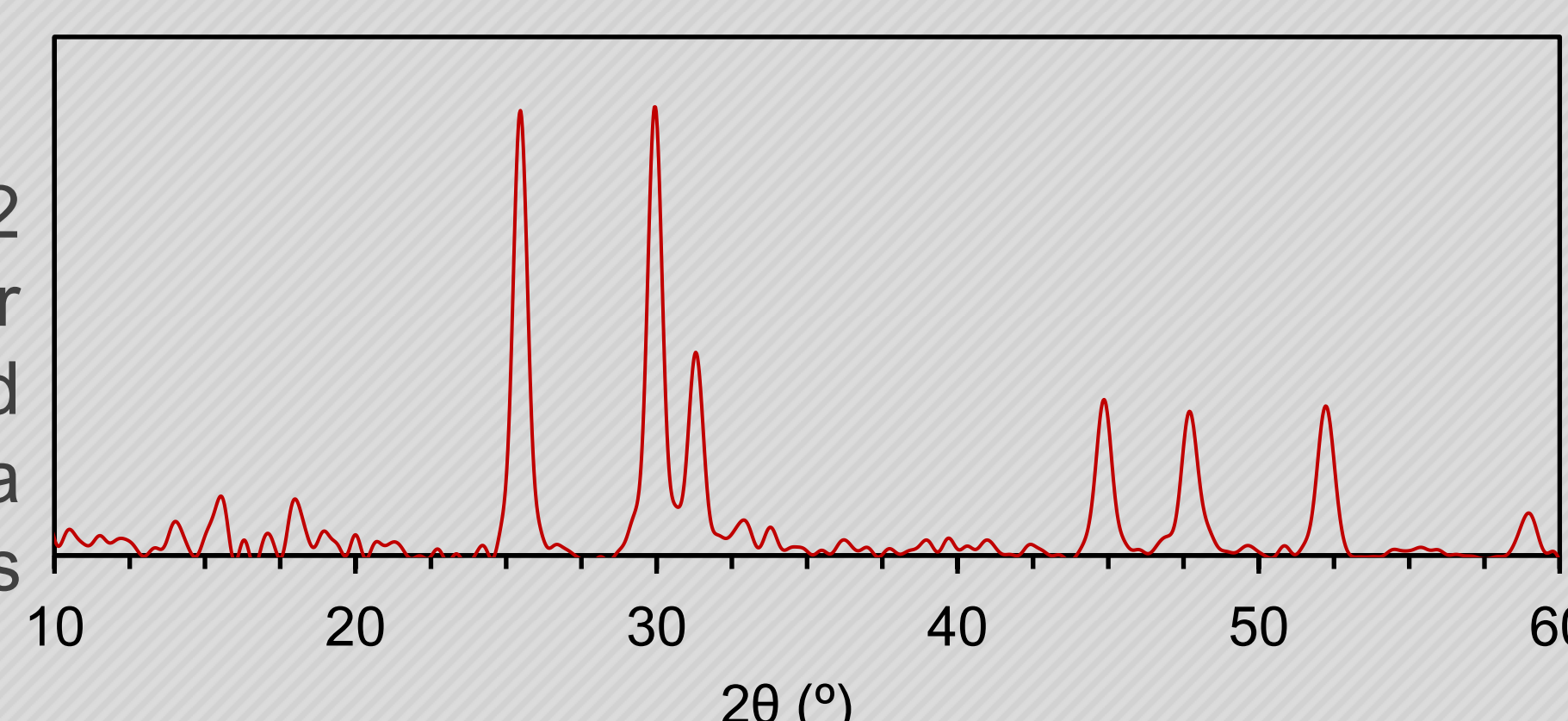
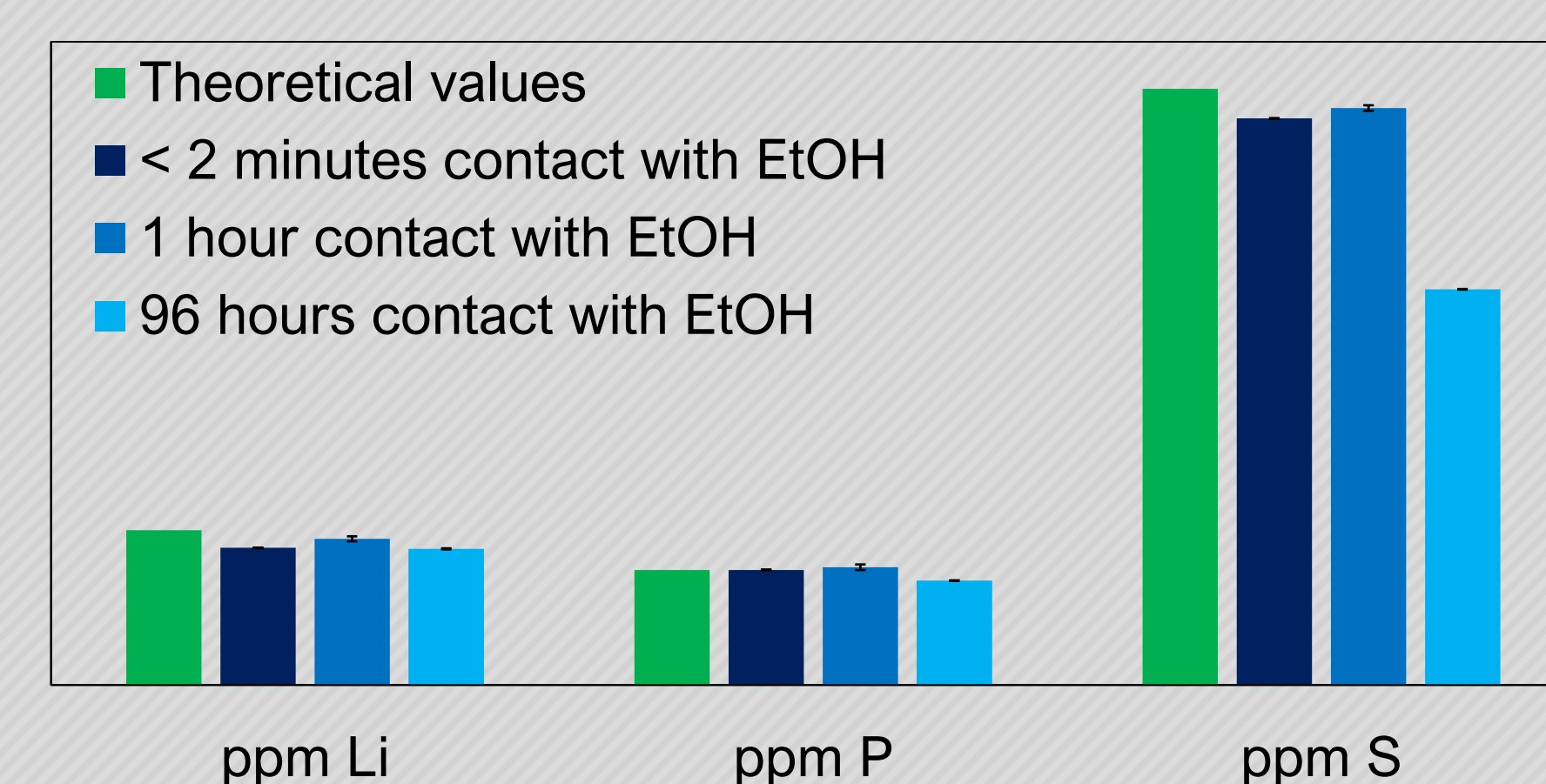
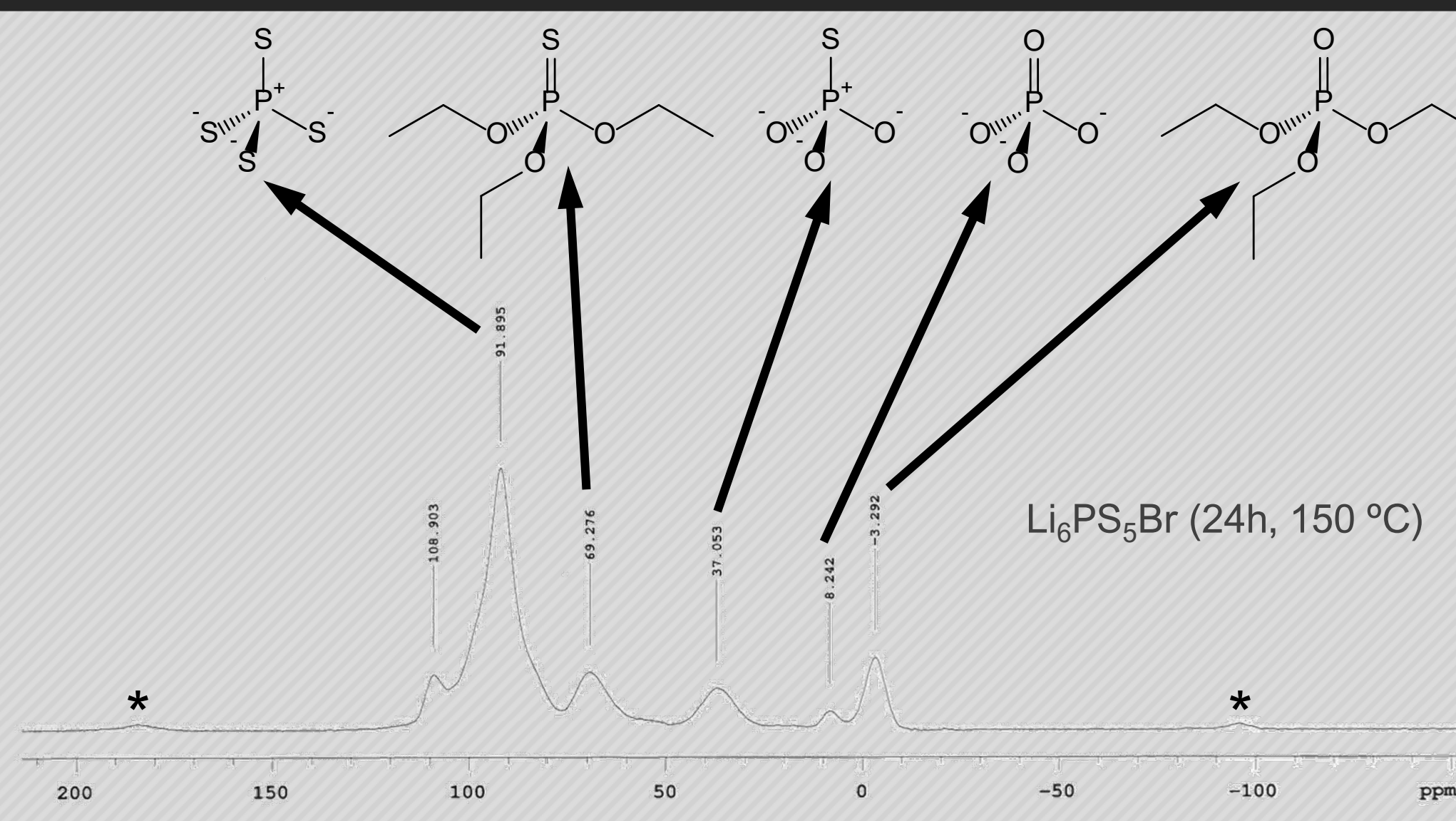
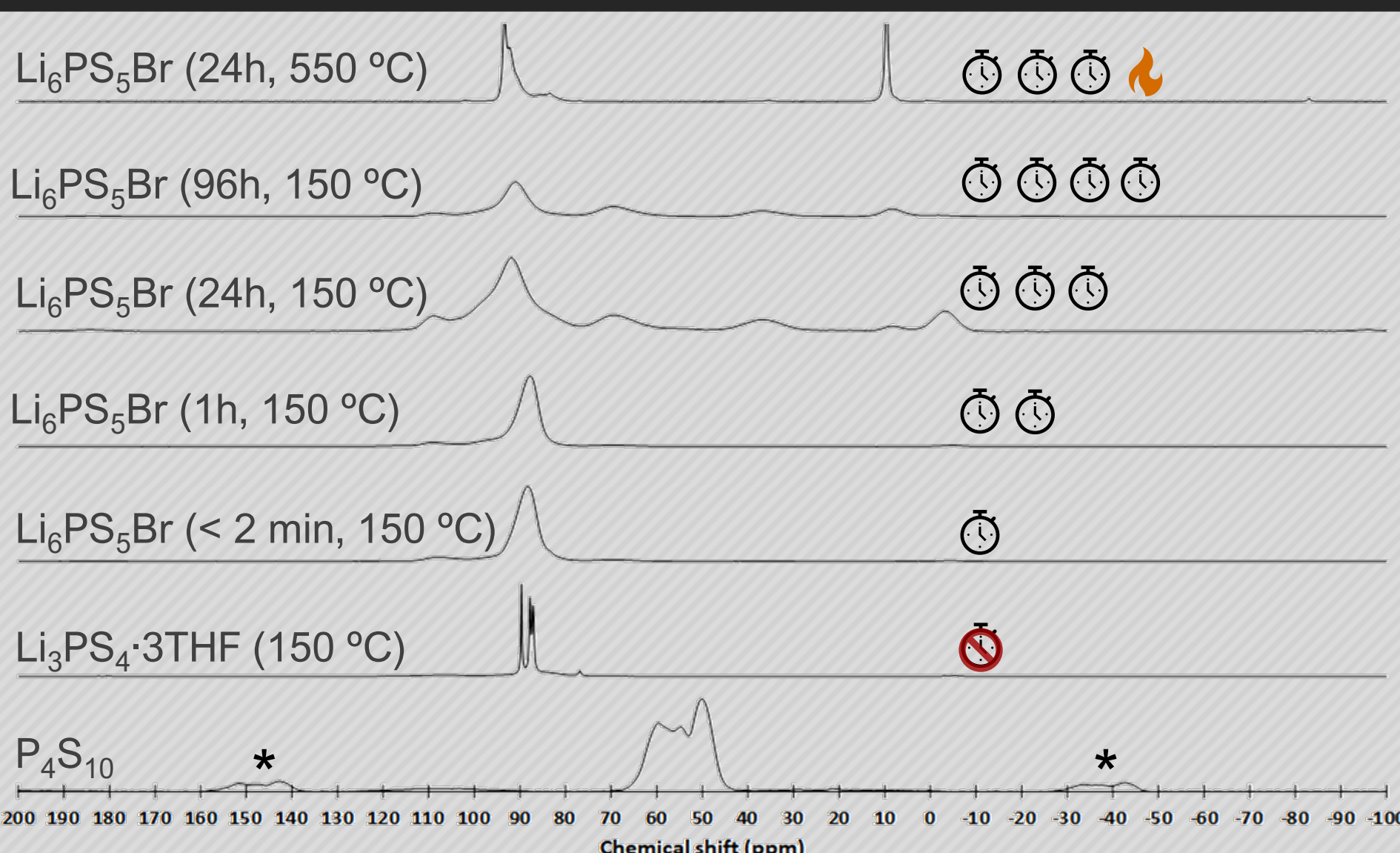
The need for sustainable transport leads to growth of the electric vehicle market. Solid-state batteries are seen as the next step in all roadmaps for Li-ion battery development. Sulfide-type solid-state electrolytes offer high ionic conductivity, and improved stability and safety compared to conventional liquid battery electrolytes.¹⁻⁴ Their use is hindered by a lack of data on optimal synthesis parameters and processing conditions. As many desirable sulfide solid-state electrolytes require thiophosphate units, the reaction route proposed by Yubuchi *et al.*⁵ (using ethanol to process Li_3PS_4 into the argyrodite-type electrolyte $\text{Li}_6\text{PS}_5\text{Br}$) is considered a fitting model for the synthesis of many sulfide solid-state electrolytes. The possible degradation in this ethanolic step was explored.

EXPERIMENTAL METHODS



Equimolar amounts of Li_3PS_4 , Li_2S , and LiBr were mixed in ethanol for varying amounts of time and subsequently dried *in vacuo* at 150 °C for 3 hours. The expected degradation reactions include simple nucleophilic substitution (as shown on the left), although rearrangements can also occur⁶ (as shown on the right) which shift the ethyl tail from an ethoxy-group to an available sulfur. Through rearrangement, it is possible to degrade into phosphates rather than thiophosphates, and the presence of Li_2S or of trace amounts of water may also enable the formation of phosphate anions (PO_4^{3-}).

RESULTS & DISCUSSION



³¹P-MAS-NMR spectroscopy of samples with increasing contact time with ethanol shows that after less than 2 minutes, only a loss of the highly ordered environment occurs without observable degradation. In fact, 1 hour of contact with ethanol gives the same result. At the 24 and 96 hour marks, several peaks are observed corresponding to ethanolic degradation products. Thermal treatment of such degraded samples results in a disproportionation into PS_4^{3-} and PO_4^{3-} units. ICP-OES confirms the trend of sulfur loss when contact time is considerably longer than 1 hour. Powder XRD confirms the presence of an argyrodite crystal structure.⁵

BIBLIOGRAPHY

- Ghidoui, M., Ruhl, J., Culver, S.P., and W.G. Zeier (2019). "Solution-based synthesis of lithium thiophosphate superionic conductors for solid-state batteries: a chemistry perspective." *Journal of Materials Chemistry A* 7(30): 17735-17753.
- Zheng, F., *et al.* (2018). "Review on solid electrolytes for all-solid-state lithium-ion batteries." *Journal of Power Sources* 389: 198-213.
- Manthiram, A., *et al.* (2017). "Lithium battery chemistries enabled by solid-state electrolytes." *Nature Reviews Materials* 2(4): 16103.
- Manthiram, A. (2017). "An Outlook on Lithium Ion Battery Technology." *ACS Central Science* 3(10): 1063-1069.
- Yubuchi, S., *et al.* (2019). "An argyrodite sulfide-based superionic conductor synthesized by a liquid-phase technique with tetrahydrofuran and ethanol." *Journal of Materials Chemistry A* 7(2): 558-566.
- Hatz, A.-K., *et al.* (2021). "Chemical Stability and Ionic Conductivity of LGPS-Type Solid Electrolyte Tetra-Li-SiPS₅ after Solvent Treatment." *ACS Applied Energy Materials* 4(9): 9932-9943.

³¹P-MAS-NMR assignments: Triethyl phosphate assignment as per Wiley SpectraBase entry, triethoxythiophosphate assignment as per "Practical Interpretation of P-31 NMR Spectra and Computer Assisted Structure Verification" by Quinn and Williams (2004, Toronto), all other peak assignments as per Hayashi, A., *et al.* (1999). "Structural Change Accompanying Crystallization in the Lithium Ion Conductive $\text{Li}_2\text{S-SiS}_2\text{-Li}_3\text{PO}_4$ Oxysulfide Glasses." *Journal of the Ceramic Society of Japan* 107(1246): 510-516.

ACKNOWLEDGEMENTS & CORRESPONDENCE

Raheed Bolia thanks Flanders Innovation & Entrepreneurship (VLAIO) for their financial support, Umicore for their financial support and research guidance, prof. dr. Peter Adriaensens and Gunter Reekmans for ³¹P-MAS-NMR and liquid ³¹P-NMR measurements and interpretation advice, and finally prof. dr. Wouter Marchal and An-Sofie Kelchtermans for ICP-OES measurements.

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