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Irina Profatilova, Ivan Leteyi Mfiban, Victor Vanpeene, Vasily Tarnopolskiy, Lise Daniel, Magali Reytier, Sandrine Lyonnard, Oskar Thompson, Claire Villevieille, Marco Di Michel

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Deep Insight into Reactivity of Li_3PS_4 Electrolyte for Solid Li-Ion Batteries Towards Humidity Using Large Instruments

I. Profatlova, I. Leteyi Mfiban, V. Vanpeene, V. Tarnopolskiy (University Grenoble Alpes, CEA, LITEN, DEHT), O. Thompson, C. Villevieille (University Grenoble Alpes, University Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI), M. DiMichiel (ESRF - The European Synchrotron), L. Daniel (University Grenoble Alpes, CEA, LITEN, DEHT, Grenoble), S. Lyonnard (Univ. Grenoble Alpes, CEA, CNRS, Grenoble INP, IRIG, SyMMES), and M. Reytier (University Grenoble Alpes, CEA, LITEN, DEHT)

Abstract Text:

Wide commercialization of Li-ion batteries (LIBs) for electric transport stimulates a demand for safer batteries with higher energy density. Thiophosphate solid electrolytes (TSEs) for LIBs are one of the most promising candidates to replace a classical liquid electrolyte with volatile components owing to their high ionic conductivity values and appropriate mechanical properties for processing [1]. However, one of the main drawbacks of TSEs is their high sensitivity towards humidity even in trace amounts. The reactivity with water and moisture impacts the electrochemical properties of the electrolytes and leads to toxic H_2S emissions. This aspect plays a crucial role for the choice of LIB manufacturing environment (dry room characteristics) and requires fine understanding of underlying mechanisms to optimize a performance / cost ratio for solid-state batteries (SSBs).

In the present study, a unique combination of characterisation methods was applied to investigate the reaction between densified Li_3PS_4 pellet and different levels of humidity (dew point (DP) $-40\text{ }^\circ\text{C}$ and $\text{DP}=12\text{ }^\circ\text{C}$ for 15 min and 2 h) from chemical and morphological/microstructural points of view. H_2S gas evolution was accurately quantified upon a TSE exposure to humid atmosphere using a home-made flow-through setup with differentiation between surface and bulk pellet reactivity [2]. Further, top-view propagation of Li_3PS_4 pellet degradation was investigated using SEM and EDX techniques showing fractures generated through gas released leading to some increase in the pellet porosity at $\text{DP}= -40\text{ }^\circ\text{C}$; apparition of cracks and oxygen content raise in case of $\text{DP} = 12\text{ }^\circ\text{C}$ exposure. The bulk of the exposed pellets was probed using non-destructive X-ray nanotomography (ESRF, ID16b). Different scenarios were observed at low and high levels of humidity during 15 min and 2 h of the pellet exposure (see Fig.). Degradation front containing large pores and cracks propagated up to $50\text{ }\mu\text{m}$ to the depth of the pellet ($\sim 400\text{ }\mu\text{m}$ total thickness) after 2 h of exposure to $\text{DP}= 12\text{ }^\circ\text{C}$. X-ray diffraction-computed tomography (XRD-CT, ESRF, ID15a) was employed to observe structural changes in 3D for Li_3PS_4 SE upon its reaction with humidity at different depths. Minor changes were found in crystalline structure of Li_3PS_4 after $\text{DP}= -40\text{ }^\circ\text{C}$ exposure while a reaction at $\text{DP}=12\text{ }^\circ\text{C}$ provoked formation of new phases propagating up to $90\text{ }\mu\text{m}$ depth of the pellet. Some of newly formed compounds were identified, i.e. $\text{P}_2\text{S}_2\text{O}_3$, Li_2HPO_3 , P_2O_5 and $\text{Li}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$. Structural strains for Li_3PS_4 crystalline phase after its exposure to $\text{DP}=12\text{ }^\circ\text{C}$ were revealed thanks to advanced XRD-CT analysis. Finally, the impact of the pellet exposure to humidity at different conditions on its ionic conductivity was investigated.

As a result of this study, a solid link was found between the morphological, microstructural, chemical degradation of the TSE and its ionic conductivity upon reaction with water. It was evidenced that the crack formation and propagation to the bulk of TSE pellet is a result of a complex cyclic mechanism, which includes chemical attack of H_2O molecules on Li_3PS_4 pellet surface, creation of mechanical strain for the TSE lattice, formation of solid degradation products and gaseous H_2S , crack propagation due to the strain release and the gas evolution, further penetration of water to the bulk of the pellet, etc. To the best of our knowledge, this is a first comprehensive study of reaction between SSE and humidity taking into account all the aspects above. This work contributes to understanding of key triggers for TSE deterioration in contact with different concentrations of water and to definition of proper environment for solid-state batteries production and handling.

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[2] X. Randrema, I. Leteyi Mfiban, M. Soler, I. Profatilova et al, Towards a Practical Use of Sulfide Solid Electrolytes in Solid-State Batteries: Impact of Dry Room Exposure on H₂S Release and Material Properties, *Batteries & Supercaps* 2024, 7, e20230038.

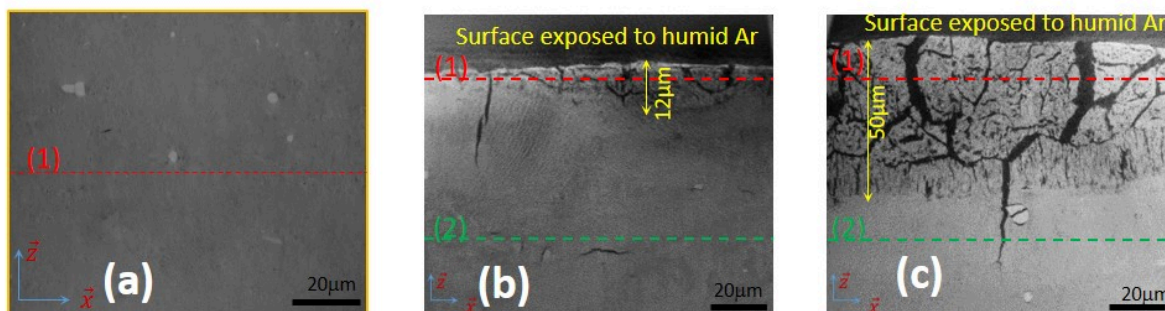


Fig. Longitudinal sections of pristine and humidity-exposed Li₃PS₄ pellets obtained by X-ray nanotomography. Pristine (a) 15 min at DP=12 °C- exposed (b) and 2h at DP=12 °C- exposed (c).

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Submitter's E-mail Address:

irina.profatilova@cea.fr

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First Corresponding Author

Dr Irina Profatilova

Affiliation(s): University Grenoble Alpes, CEA, LITEN, DEHT

Address:

17 rue des Martyrs
Grenoble, Isere, 38054
France

Phone Number:

E-mail Address: irina.profatilova@cea.fr

Second Author

Mr Ivan Leteyi Mfiban

Affiliation(s): University Grenoble Alpes, CEA, LITEN, DEHT

Phone Number: +33438785157

E-mail Address: ivan.leteyimfiban@cea.fr

Third Author

Dr Victor Vanpeene

Affiliation(s): University Grenoble Alpes, CEA, LITEN, DEHT

Phone Number:

E-mail Address: victor.vanpeene@cea.fr

Fourth Author

Dr Vasily Tarnopolskiy

Affiliation(s): University Grenoble Alpes, CEA, LITEN, DEHT

Phone Number:

E-mail Address: vasily.tarnopolskiy@cea.fr

Fifth Author

Oskar Thompson

Affiliation(s): University Grenoble Alpes, University Savoie Mont Blanc, CNRS; Grenoble INP, LEPMI

Phone Number:

E-mail Address: oskar.thompson@grenoble-inp.fr

Sixth Author

Prof Claire Villevieille

Affiliation(s): University Grenoble Alpes, University Savoie Mont Blanc, CNRS; Grenoble INP, LEPMI**Phone Number:****E-mail Address:** claire.villevieille@grenoble-inp.frSeventh Author

Dr Marco DiMichiel

Affiliation(s): ESRF - The European Synchrotron**Phone Number:****E-mail Address:** dimichie@esrf.frEighth Author

Mrs Lise Daniel

Affiliation(s): University Grenoble Alpes, CEA, LITEN, DEHT, Grenoble**Phone Number:****E-mail Address:** lise.daniel@cea.frNinth Author

Dr. Sandrine Lyonard

Affiliation(s): Univ. Grenoble Alpes, CEA, CNRS, Grenoble INP, IRIG, SyMMES**Phone Number:****E-mail Address:** sandrine.lyonnard@cea.frTenth Author

Dr Magali Reytier

Affiliation(s): University Grenoble Alpes, CEA, LITEN, DEHT**Phone Number:****E-mail Address:** magali.reytier@cea.fr

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