



HAL
open science

Combinatorial synthesis & High Throughput Screening of LiPO(N) solid electrolyte as a study case for methodology validation

William Berthou, Maxime Legallais, Vincent Motto-Ros, Brigitte Pecquenard,
Frédéric Le Cras

► To cite this version:

William Berthou, Maxime Legallais, Vincent Motto-Ros, Brigitte Pecquenard, Frédéric Le Cras. Combinatorial synthesis & High Throughput Screening of LiPO(N) solid electrolyte as a study case for methodology validation. LIBD 2023 - 10ème Lithium Batteries Discussions - "Electrode Materials", Jun 2023, Arcachon, France. cea-04211212

HAL Id: cea-04211212

<https://cea.hal.science/cea-04211212>

Submitted on 19 Sep 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Combinatorial synthesis & High Throughput Screening of LiPO(N) solid electrolyte as a steady-case methodology validation

William Berthou^{a,b}, Maxime Legallais^a, Vincent Motto-Ros^c, Brigitte Pecquenard^b, Frédéric Le Cras^{a,b,d}

^a Univ. Grenoble Alpes, CEA, CTREG, DNAQ, 28 Avenue Gustave Eiffel, 33600 Pessac, France

^b CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB – UMR 5026, 87 Av. du Dr Schweitzer 33608 Pessac, France

^c Institut Lumière Matière, UMR 5306, Université Lyon 1 – CNRS, 69622 Villeurbanne, France

^d Univ. Grenoble Alpes, CEA, LITEN, 38054 Grenoble, France

Since its introduction in pharmacological research⁽¹⁾, High Throughput Screening (HTS) approaches are developed in many fields. The latter aim at coupling combinatorial methods in order to synthesize a wide range of material libraries, and automated, fast characterization techniques. In material science, the goal is to accelerate the discovery of new keys organic, inorganic or composite breakthrough materials. This coupling may also bring beyond 'classical' iterative method regarding the study of complex systems (ternary, quaternary...)⁽³⁾.

Amorphous lithium phosphate is used since 25 years as state-of-the-art solid electrolyte into all-solid-state thin film microbatteries. This vitreous amorphous material stands as an isotropic and homogeneous medium, free from phase boundaries, with beneficial mechanical properties. Its low electronic conductivity and its electrochemical quasi-stability over a wide potential range ($\sim[4-0]$ V vs. Li^+/Li^0) are remarkable properties. Under its LiPON form, its conductivity can be raised up 2.10^{-6} S.cm⁻¹, which is quite modest but that can be partially overcome by a very small thickness (~ 1 μm). Anyway, enhanced ionic conductivity of those materials is still crucial for their use as solid electrolyte or electrode passivation layer (artificial SEI-CEI) into All-Solid-State Lithium Batteries (Li-ASSB).

Conduction properties into LiPO-compounds are driven by its glass structure and its atomic composition, closely linked altogether. Increased disorder facilitates lithium ions migration into the material. This can be induced through two main mechanisms: the mixed former effect⁽⁵⁾ (Si, P, B...) and the mixed anion effect⁽⁶⁾ (O, N, S...). Hence, variety into LiPO-type compounds Li(P, Si, B, Ge...)(O, N, S...) is wide. **This study aims at setting a methodology based on combinatorial synthesis paths coupled with HTS characterizations.**

Combinatorial synthesis is achieved through co-sputtering, using three tilted targets.

In order to validate this methodology, LiPO(N) compounds synthesized at start from a single Li_3PO_4 tilted target are chosen as study-case. Thin film samples are obtained by sputtering the target in a pure Ar or N_2 atmosphere on a 4'' silicon substrate. Deposition through a shadow mask allows the synthesis of 76 distinct $\text{Li}_w\text{P}_x\text{O}_y\text{N}_z$ materials with various thicknesses and compositions in one experiment. Moreover, varying sputtering parameters, i.e. target-substrate distance, power, chamber pressure, discharge gas type..., allows to tune thin film growth.

A High Throughput Screening approach based on relevant automated characterization techniques is then applied to these thin film material libraries spread on 4'' substrates. In the frame of our material application, morphological (thickness), physical-chemical (composition & structure) and functional properties (ionic/electronic conductivities) are studied. More specifically, thin film composition analysis stands as a bottleneck due to multiple constraints: (i) difficulties for light elements analysis, especially lithium; (ii) needs of localized analysis (mapping) on few mm² over large substrate (4'' wafer); (iii) scarce material quantity available ($\sim \mu\text{g}$) and finally (iv) fast analysis. Finally, only Laser Induced Breakdown Spectroscopy technique (LIBS) seems to fulfil each requirement⁽⁸⁾. However, its implementation into our methodology still requires important developments.

To this purpose, this presentation shows methodology results on LiPO(N)-compounds synthesized with several magnetron sputtering parameters. The material library is then characterized following the HTS approach developed.

References

1. Á. Furka, *J. Solid State Chem.* **7**, 4 (2002).
2. J. R. Dahn *et al.*, *Chem. Mater.* **14**, 3519–3523 (2002).
3. E. J. Amis, X.-D. Xiang, J.-C. Zhao, *MRS Bull.* **27**, 295–300 (2002).
4. G. Zhao *et al.*, *J. Solid State Chem.* **292**, 121651 (2020).
5. Y. Su *et al.*, *Phys. Status Solidi B.* **254**, 1600088 (2017).
6. N. Mascaraque, J. L. G. Fierro, A. Durán, F. Muñoz, *Solid State Ion.* **233**, 73–79 (2013).
7. V. Lacivita *et al.*, *J. Am. Chem. Soc.* **140** (2018), doi:10.1021/jacs.8b05192.
8. R. Pamu *et al.*, *ACS Appl. Energy Mater.* **4**, 7259–7267 (2021).