Position Description

1. General Information

Name of the position	**Hydride-based materials for electrochemical storage**
Foreseen enrolment date	1 October 2024
Position is funded by	• COFUND, Marie Skłodowska-Curie Actions (MSCA), Horizon Europe, European Union • Institut de Chimie et des Matériaux Paris-Est (ICMPE/UPEC-CNRS) • The University of Sydney (USYD)
Research Host	Institut de Chimie et des Matériaux Paris-Est (ICMPE/UPEC-CNRS)
PhD awarding institutions	Université Paris-Est Créteil & The University of Sydney
Locations	Primary: Thiais, France Secondary: Sydney, Australia
Supervisors	Dr. Fermin Cuevas (ICMPE/UPEC-CNRS), Assoc. Prof. Mickaël Mateos (ICMPE/UPEC) Prof. François-Aguey Zinsou (USYD)
Group of discipline	Chemistry, Materials science, Solid-state chemistry, Electrochemistry

2. Research topics (only one of these projects will be funded)

Project 1: *Hydrides as conversion anodes of Li and Na-ion batteries operating at room temperature*
Metal hydrides, MH, are promising anodes for Li-ion batteries. Through the conversion reaction MH_x + xLi <-> M + *x*LiH, metal hydrides provide high gravimetric (1000-2000 mAh/g) and volumetric (2000-4000 mAh/cm^3) capacities with a typical operating potential below 0.6 V vs Li^+/Li [1]. However, the reversibility of the conversion reaction is poor unless temperatures as high as 120°C are used. It has been suggested that kinetic limitations of the conversion reaction are due to the slow diffusion of either H and Li or the nucleation and growth of the hydride at the M/LiH interface [2]. This PhD project aims to achieve higher levels of reversibility in the electrochemical conversion metal hydrides with lithium at room temperature with fast kinetics. For overcoming current hurdles, several strategies will be investigated and this will include novel composite hydrides based on light alkali-earth (Mg, Ca) and 3d-metals (Ti, V). To reduce the length of diffusion paths, efforts will be dedicated to enhancing the hydride nanostructuration.

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Further engineering of the composite electrode, e.g. through the wet shaping on the composite electrode, will allow to increase the available area of M/LiH interface for reaction.

Electrochemical studies to understand the reaction mechanisms and evaluate the performances of novel hydride materials will be first done by using classical liquid organic electrolytes in half-cell. This will be later expanded to all solid-state battery investigation, by utilising solid Li^+ conductors developed in our laboratories [3,4]. Finally, this new knowledge acquired around the Li-ion technology will be translated to novel hydride materials in Na-ion cells.

[1] S. Sartori, F. Cuevas, M. Latroche, "Metal hydrides as negative electrodes for Li-ion batteries", App. Phys. A, 122 (2016) 135, http://dx.doi.org/10.1007/s00339-016-9674-x.

[2] N. Berti, E. Hadjixenophontos, F. Cuevas, J. Zhang, A. Lacoste, P. Dubot, G. Schmitz, M. Latroche, *"Thin films as model system for understanding the electrochemical reaction mechanisms in conversion reaction of MgH_2 with lithium"*, J. Power Sources, 402 (2018) 99-106, https://doi.org/10.1016/j.jpowsour.2018.09.033.

[3] A. H. Dao, P. López-Aranguren, R. Cerny, O. Guiader, J. Zhang, F. Cuevas, M. Latroche, C. Jordy, "Improvement of the ionic conductivity on new substituted borohydride argyrodites", Solid State Ionics, 339 (2019) 114987, http://dx.doi.org/10.1016/j.ssi.2019.05.022.

[4] X.X. Luo, A.Rawal, C. Cazorla, K.-F. Aguey-Zinsou "Facile Self-Forming Superionic Conductors Based on Complex Borohydride Surface Oxidation" Adv. Sustainable Syst.4 (2020) 1900113, https://doi.org/10.1002/adsu.201900113.

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Non-academic Supervisor : Mr Jean-Marie Guitera- H2potential

Research Fields: Solid-state chemistry, electrochemistry, hydrides, all-solid-state batteries, metal-ion batteries

Project 2: *Towards all-hydride based solid-state Li-ion batteries*

Hydrides have outstanding properties as both negative electrodes and solid electrolytes for Li-ion batteries. Metal hydrides can operate as anodes through the conversion reaction $MH_x + xLi <-> M + xLiH$ leading to high gravimetric (1000-2000 mAh/g) and volumetric (2000-4000 mAh/cm^3) capacities with a typical potential < 0.6 V [1]. As solid electrolytes, complex hydrides have superior mechanical deformability and promising Li-ion conductivity of the order of 0.1 mS/cm at room temperature [2]. The association of hydrides both as anode and solid electrolyte materials is also expected to ensure chemical compatibility of all the battery components and thus superior performances. However, the reversibility of the electrochemical conversion reaction of metal hydrides with lithium is poor and the level of Li-ion conductivity in complex hydrides at room temperature is still too low.

This PhD project will be devoted to study the association of novel metal hydrides as anode materials and complex hydrides as solid electrolytes for advancing all hydride-based Li-ion batteries working at room temperature [3]. For overcoming current hurdles, novel hydride nanocomposites will be prepared with phase composition allowing for fast Li-mobility at room temperature. The goal will be to encompass fast Li-mobility in the active material of the electrode with high Li-conductivity in the solid electrolyte to gain a synergetic effect between the two components. The conductivity of the solid electrolyte will be improved in line with current nanocomposite strategies [4].

Electrochemical studies to evaluate the performances of solid half-cells will be first done at high temperatures to minimize kinetic limitations and then this work will be progressed toward room temperature operation. If results are successful, the concept will be extended to Na-ion cells.

[1] S. Sartori, F. Cuevas, M. Latroche, "Metal hydrides as negative electrodes for Li-ion batteries", App. Phys. A, 122 (2016) 135, http://dx.doi.org/10.1007/s00339-016-9674-x.

[2] J. Monnier, J. Zhang, F. Cuevas, M. Latroche, *"Hydrides compounds for electrochemical applications"*, Curr. Opin. Electrochem., 32 (2022) 100921-100929, https://doi.org/10.1016/j.coelec.2021.100921

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[3] M. Latroche, D. Blanchard, F. Cuevas, A. E. Kharbachi, B. C. Hauback, T. R. Jensen, P. E. d. Jongh, S. Kim, N. S. Nazer, P. Ngene, S. I. Orimo, D. B. Ravnsbæk, V. A. Yartys, *"Full-cell hydride-based solid-state Li batteries for energy storage"*, Int. J. Hydrogen Energy, 44 (2019) 7875-7887, doi: https://doi.org/10.1016/j.ijhydene.2018.12.200

[4] L.-M. de Kort, V. Gulino, P.-E. de Jongh, P. Ngene "Ionic conductivity in complex metal hydride-based nanocomposite materials: The impact of nanostructuring and nanocomposite formation", J. Alloys Compd. 901 (2022) 163474. https://doi.org/10.1016/j.jallcom.2021.163474

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Project 3: *High-conducting hydride-based materials as solid-electrolytes of Li-ion and Na-ion batteries*

Complex Hydrides have unique properties as solid electrolytes of Li and Na-ion batteries [1]. Their soft mechanical properties allow for the formation of intimate interfaces with electrode materials. Moreover, they are light materials and have a large electrochemical stability window. However, their ionic conductivity is still low for optimal room temperature operation, the chemical compatibility towards electrode materials is rarely demonstrated, and electrolyte synthesis is often intricate and costly.

This PhD project aims at synthetizing novel hydride-based materials with ionic conductivity reaching 1 mS/cm at room temperature and good chemical compatibility with high-performance electrode materials. The targeted electrolytes will be synthetized as nanocomposites with a high density of interfaces and defects allowing for fast Li-ion and Na-ion conduction [2]. Novel synthetic routes are envisaged to reduce cost, especially for Na-ion electrolytes.

Full electrochemical cells will be implemented by association of hydride electrolytes with positive and negative electrode materials [3]. For the positive side, low potential electrodes will be first studied (e.g. TiS_2 for Li-ion) and more challenging ones with high potential (e.g. $LiFePO_4$ for Li-ion and $NaCrO_2$ for Na ion) will be tested in a second step. On the negative side Li and Na metal will be targeted as ultimate high-capacity electrodes with the alternative of using of metal hydrides instead if these demonstrate better chemical compatibility than pure metals.

[1] J. Monnier, J. Zhang, F. Cuevas, M. Latroche, *"Hydrides compounds for electrochemical applications"*, Curr. Opin. Electrochem., 32 (2022) 100921-100929, https://doi.org/10.1016/j.coelec.2021.100921

[2]L.-M. de Kort, V. Gulino, P.-E. de Jongh, P. Ngene "Ionic conductivity in complex metal hydride-based nanocomposite materials: The impact of nanostructuring and nanocomposite formation", J. Alloys Compd. 901 (2022) 163474. https://doi.org/10.1016/j.jallcom.2021.163474

[3] M. Latroche, D. Blanchard, F. Cuevas, A. E. Kharbachi, B. C. Hauback, T. R. Jensen, P. E. d. Jongh, S. Kim, N. S. Nazer, P. Ngene, S. I. Orimo, D. B. Ravnsbæk, V. A. Yartys, *"Full-cell hydride-based solid-state Li batteries for energy storage"*, Int. J. Hydrogen Energy, 44 (2019) 7875-7887, doi: https://doi.org/10.1016/j.ijhydene.2018.12.200.

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3. Employment Benefits and Conditions

The Institut de Chimie et des Matériaux Paris-Est (ICMPE) - Université de Paris-Est Créteil (UPEC) / Centre National de la Recherche Scientifique (CNRS) offers a 36-months full-time work contract (with the option to extend up to a maximum of 42 months). A probation period of 2 month will apply. The legal working time is 38 h and 40 min per week.

The remuneration, in line with the European Commission rules for Marie Skłodowska-Curie grant holders, will consist of a gross annual salary of 28,800 EUR. Of this amount, the estimated net salary to be perceived by the Researcher is 1,850 EUR per month. However, the definite amount to be received by the Researcher is subject to national tax legislation.

Benefits include

- Becoming a Marie Skłodowska-Curie fellow and be invited to join the Marie Curie Alumni Association.
- Access to all the necessary facilities and laboratories at ICMPE – UPEC/CNRS and The University of Sydney.
- Tuition fees exemption at both PhD awarding institutions.
- Yearly travel allowance to cover flights and accommodation for participating in AUFRANDE events.
- 10,000 EUR allowance to cover flights and living expenses for 12 months in Australia.
- Industry placement over a month where the candidate will gain exposure to the industrial world in particular along the translation of R&D to the market.
- 45 days paid per year holiday leave.
- Affiliation to the French social security system and its legislation on accidents at work.

4. PhD enrolment

Successful candidates for this position will be enrolled by the following institutions and must comply with their specific entry requirements, in addition to AUFRANDE's conditions.

Applicants must hold a Master's degree or equivalent qualification performed at a high academic standard, and which includes a substantial component of original research.

Applicants must prove English language proficiency (see: https://www.sydney.edu.au/study/how-to-apply/international-students/english-language-requirements.html).

More information on UPEC's requirements

Approval of the CNRS and/or UPEC defence security officer may be required before the starting of employment. In case of denial, the employment will not be carried out.

Visit the website: https://www.paris-est-sup.fr/ecoles-doctorales/ecole-doctorale-sciences-ingenierie-et-environnement-sie/accueil/

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More information on the University of Sydney's requirements

Meeting the minimum requirements for eligibility does not guarantee admission. Admission remains at the discretion of the Associate Dean (Higher Degree by Research) for each faculty.

For more information on admission requirements, please visit the University of Sydney's website: https://www.sydney.edu.au/study/applying/how-to-apply/postgraduate-research.html

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