AUFRANDE

Position Description

1. General Information

Name of the position	**Diffusivity of lithium ions in high-energy positive electrode materials for lithium-ion batteries**
Foreseen enrolment date	Between 1 July and 1 October 2024
Position is funded by	• COFUND, Marie Skłodowska-Curie Actions (MSCA), Horizon Europe, European Union • Centre National de la Recherche Scientifique (CNRS) • The University of Sydney (USYD)
Research Host	Centre National de la Recherche Scientifique - Institut de Chimie de la Matière Condensée de Bordeaux (UMR5026)
PhD awarding institutions:	Université de Bordeaux & The University of Sydney
Locations	Primary: Pessac, France Secondary: Sydney, Australia
Supervisors	Dr Marie Guignard (CNRS ICMCB) Professor Maxim Avdeev (USYD & ANSTO)
Group of discipline	Solid-state chemistry, Materials science

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

Project 1: *New oxides with a $CaFe_2O_4$-type structure used as positive electrode for sodium-ion batteries*
This project is primarily a fundamental research project whose main goal is the exploration of new materials and new potentialities of electrochemical deintercalation and intercalation of sodium for a family of oxides that has thus far received little attention and that could be used as positive electrode materials in sodium ion batteries. More specifically, its objectives are: **- Exploring new $Na(M,M')_2O_4$ systems with $CaFe_2O_4$-type structure** by targeting ambient pressure synthesis conditions. Titanium- and ruthenium-based compounds will be selected as titanium and ruthenium can both help to stabilize this structure-type at ambient pressure. In order to explore more systems and/or to compare the structural and

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electrochemical properties of the new synthesized materials to those of existing ones (for example, $NaMn_2O_4$), HP-HT syntheses might also be necessary. All the syntheses could be performed at the ICMCB.

- Evaluating the electrochemical performance of all synthesized systems as positive electrode materials in a sodium battery. This task will provide a comprehensive state of the art appraisal of the most promising $CaFe_2O_4$-type $Na(M,M')_2O_4$ oxides candidates. In situ or operando X-ray powder diffraction experiments will also be performed during the charge/discharge of sodium batteries in order to study the structural mechanisms occurring in these materials during sodium electrochemical deintercalation and intercalation, as they have been the subject of a single publication. In particular, the structural mechanisms occurring during the discharge have never been studied. The electrochemical tests could all be performed at the ICMCB. In situ or operando experiments could be implemented either in the same laboratory or at large scale facilities.

- Understanding $Na(M,M')_2O_4$ structural details in order to elucidate mechanisms for sodium transport combining experimental and theoretical tools such as the Maximum Entropy Method (MEM) and Molecular Dynamics (MD). MEM analyses will rely on the analyses of high resolution powder diffraction patterns recorded at various temperatures at synchrotron or neutron sources. Optimization of electrochemical properties for any of the $Na(M,M')_2O_4$ systems will require a complete comprehension of percolation paths within their three-dimensional channel-type structures.

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Project 2: *Composition optimisation of the spinel-type $LiNi_{0.5}Mn_{1.5}O_4$ compound used as positive electrode for lithium-ion batteries*

This project is primarily a fundamental research project whose main goal is the composition optimization of a well-known compound used as positive electrode in lithium-ion batteries to improve it electronic and ionic conductivity. More specifically, its objectives are:

- **Limiting the amount of nickel in the spinel-like compound $LiNi_{0.5}Mn_{1.5}O_4$** by gradually replacing a total number of Ni^{2+} and Mn^{4+} ions by an equivalent number of Fe^{3+} ions until the composition $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ which exhibits an excellent thermal stability and which is able to deliver a high energy density. The syntheses will be carried out by sol-gel route in order to promote a homogeneous distribution of the three transition metal cations at the atomic scale.

- **Analysing in detail the average structure of the as-synthesised compounds** by synchrotron X-ray diffraction and by neutron diffraction. Neutron diffraction will indeed be of great scientific benefit, not only for locating lithium ions in the crystalline structure, but also for scattering factors. The synthesis conditions may affect the composition, the oxygen stoichiometry and the cationic order in the different octahedral and/or tetrahedral sites. This order is sometimes difficult to quantify by diffraction techniques which essentially provide information on the average structure. Therefore, the local structure of will also by studied by the analysis of the pair distribution functions (PDF).

- Understanding $Li(Ni,Mn,Fe)_2O_4$ structural details in order to elucidate mechanisms for lithium transport combining experimental and theoretical tools such as the Maximum Entropy Method (MEM) and Molecular Dynamics (MD). MEM analyses will rely on the analyses of high resolution powder diffraction patterns recorded at various temperatures at neutron sources. Optimization of electrochemical properties for any of the $Li(Ni,Mn,Fe)O_4$ systems will require a complete comprehension of percolation paths within their three-dimensional channel-type structures.

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Project 3: *Morphology optimisation of spinel-type $Li(Ni,Mn,Fe)O_4$ compounds used as positive electrode for lithium-ion batteries*
This project is primarily a fundamental research project whose main goal is the morphology optimization of spinel-like $Li(Ni,Mn,Fe)_2O_4$ compounds used as positive electrode in lithium-ion batteries to improve it electronic and ionic conductivity. More specifically, its objectives are: - **Exploring a wide range a particle morphology for the spinel-like compound** $LiNi_{1/3}Mn_{4/3}Fe_{1/3}O_4$ by synthetising it in different conditions (solid-state route, sol-gel route, molten-salt route..). The morphology of electrode material particles can dramatically affect lithium ion transport properties in them. A meticulous study will be carried out in order to understand the relationship between morphology and transport properties. - **Analysing in detail the average structure of the as-synthesised compounds** by synchrotron X-ray diffraction and by neutron diffraction. Neutron diffraction will indeed be of great scientific benefit, not only for locating lithium ions in the crystalline structure, but also for scattering factors. The synthesis conditions may affect the composition, the oxygen stoichiometry and the cationic order in the different octahedral and/or tetrahedral sites. This order is sometimes difficult to quantify by diffraction techniques which essentially provide information on the average structure. Therefore, the local structure of will also by studied by the analysis of the pair distribution functions (PDF). **- Understanding $Li(Ni,Mn,Fe)_2O_4$ structural details in order to elucidate mechanisms for lithium transport combining experimental and theoretical tools such as the Maximum Entropy Method (MEM) and Molecular Dynamics (MD).** MEM analyses will rely on the analyses of high-resolution powder diffraction patterns recorded at various temperatures at neutron sources. Optimization of electrochemical properties for any of the $Li(Ni,Mn,Fe)O_4$ systems will require a complete comprehension of percolation paths within their three-dimensional channel-type structures.
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3. Employment Benefits and Conditions

CNRS offers a 36-months full-time work contract (with the option to extend up to a maximum of 42 months). The total working hours per week is 38.5h.

The remuneration, in line with the European Commission rules for Marie Skłodowska-Curie grant holders, will consist of a gross annual salary EUR 27,000. Of this amount, the estimated net salary to be perceived by the Researcher is EUR 1,850 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 Institut de Chimie de la Matière Condensée de Bordeaux (UMR5026) 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 up to 12 months in Australia

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- 45 days paid holiday leave
- French Social security coverage
- Sick leave
- Parental leave

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 in chemistry, physics or a related field recognised in France performed at a high academic standard, and which includes a substantial component of original research; or an equivalent qualification that demonstrates research experience, excellence and capability.

Applicants must prove their English language proficiency equivalent to an overall IELTS score of 6.5 with no band below 6.0 (see: https://www.sydney.edu.au/study/how-to-apply/international-students/english-language-requirements.html).

More information on the Université de Bordeaux' requirements

Visit the website: https://college-doctoral.u-bordeaux.fr/en/Graduate-Research-School/The-Doctoral-Schools/Chemical-sciences

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.

Visit the website: https://www.sydney.edu.au/study/how-to-apply/postgraduate-research.html

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