PhD GRANT

ÉCOLE DOCTORALE SCIENCES EXACTES ET LEURS APPLICATIONS - ED 211 / NATURAL SCIENCES DOCTORAL SCHOOL

Avenue de l'université BP 1155 64 013 PAU Cedex – France

PhD SUBJECT

TITLE: Reactivity of solid-solid interfaces. Towards an improvement of charge storage mechanisms in supercapacitors

ABSTRACT: *As part of the project "Engineering of electrode materials for the development of Li-ion batteries and supercapacitors with high energy density supported by the New Aquitaine authority", a PhD position is available to work on the charge storage mechanisms in Mn-Co nanocomposites for supercapacitors. The work will consist into:*

- The study of lamellar oxide nanocomposites of Mn and Co for the development of more efficient hybrid supercapacitors. These composite materials are designed by stacking nano-objects of different compositions so as to combine complementary properties to go towards the optimization of performance in terms of power and energy,

- the understanding of the properties at solid/solid interfaces between nano-layers, which govern the physico-chemical properties of the composite and its performance during cycling. A large part of the research will focus on the study of these solid/solid and solid/electrolyte interfaces of these systems by purely computational approaches or combining experience and theory.

Keywords: Chemical physics, solid states, supercapacitors, energy storage, computational chemistry, spectroscopy

WORKING CONDITIONS

Laboratoire : Institut des Sciences Analytiques et Physico-Chimique pour l'Environnement et les Matériaux (IPREM) **Site web :** https://iprem.univ-pau.fr

PhD Director: I. Baraille

PhD co-Director:

In Collaboration with ICMCB - Saft

Place: Pau - Aquitaine – France

Start: Octobre 2018	**Duration:** 3 years

Employer: Université de Pau et des Pays de l'Adour (UPPA)

monthly salary before taxes: 1685 €

HOST LABORATORY PROFILE

The Institute of Analytical Sciences and Physico-Chemistry for Environment and Materials (IPREM) is a Joint Research Unit CNRS / UPPA (UMR 5254). IPREM members are interested in the development of fundamental knowledge in physico-chemistry, analytical chemistry and microbiology, in relation to applications concerning the structure of the living, the management of the environment and the functional properties of different classes of materials. Their skills are based on analytical strategies, experimental and theoretical chemical-physics approaches, fine studies of structures and reactivity, development, characterization and implementation at different scales.

The skills of IPREM members in physical and theoretical chemistry and more particularly in the surfaces and interfaces characterization are implied in the study of complex chemical systems and more precisely, electronic structure properties and chemical reactivity. These skills rely on a large and

accurate technical platform based on mass spectrometries and photoélectron spectroscopies and a strong experience in surface analytical techniques and in the implementation of source code and computational strategies. Various computational ressources are available (local, and national computational centers) as well as X-ray photoelectron and Auger spectroscopy (XPS, AES), atomic force microscopy (AFM) and gas chemisorption.

MISSION - ACTIVITES PRINCIPALES / MISSION – PRINCIPAL ACTIVITIES

I. Scientific Context

This research project is part of the context of the electrochemical storage of energy by supercapacitors. The potential in terms of performance of supercapacitors, used for many years in small format devices (10 F / 2.5 V) for applications of the electronic power type, have led manufacturers to consider extending their applications to military, space, aeronautics or transport, to larger formats (several kW). However, supercapacitors still suffer from a too limited energy density (8Wh / kg approximately). In the context of hybrid vehicles, it is therefore necessary to increase energy densities, so that these systems can play their full role as a source of power, in addition to energy sources that are batteries. The performance of hybrid supercapacitor systems is closely related to the surface and interface phenomena of the materials that compose them, and more specifically it is the storage of charges and the insertion / de-insertion of surface ions which are at the origin of performance. A better understanding of the storage mechanisms of loads would better guide the optimization of materials for an increase in the density of power and energy. In this context, the development of materials with controlled morphologies associated with a thorough knowledge of the chemical mechanisms involved in surfaces and interfaces appears essential to meet the major challenges of hybrid supercapacitors.

II. Objectives

The project will focus on the identification and understanding of the differences in the reactivity of materials in relation to their morphology and the electronic structure of their surface for the improvement of electrochemical performances. The main objectives of the project are:

- the synthesis of nanocomposites based on $A_xH_yMO_2$ lamellar oxides / oxyhydroxides (M = Ni, Co, Mn) for hybrid supercapacitors, having morphologies, sizes, compositions and controlled structures,
- the study of the influence of surface modification of the active material on reactivity, by combining surface characterization methods and theoretical approaches at the atomic scale.
- control of surface phenomena and interfaces: the control of reactivity at the solid-solid and solid-liquid interfaces requires optimizing and understanding the mechanisms of charge storage on the surface of Mn oxyhydroxide particles and Co, and the respective role of these particles vis-à-vis the synergy of properties observed.

III. *Work plan*

The PhD student will work on nanocomposites of Mn and Co lamellar oxyhydroxides for positive electrodes of hybrid supercapacitors already synthesized and characterized (structurally and electrochemically) at the ICMCB.

- Computational study of the structural and electronic properties of nanocomposites using quantum chemistry methods
- Experimental characterization of surface properties of the materials (XPS, AES, microscopy)
- Investigation by means of a coupled experimental/computational approach of the surface reactivity through gas probe adsorption. combining

IV. Literature References

Andreu N., Flahaut D., Dedryvère R., Minvielle M., Martinez H., Gonbeau D., XPS investigation of surface reactivity of electrode materials: effect of the transition metal, Applied Materials and Interfaces 2015, 7, 6629-6636.

Quesne-Turin A., Flahaut D., Croguennec L., Vallverdu G., Allouche J., Charles-Blin Y., Chotard J.-N., Ménétrier M., Baraille I., The surface reactivity of Li2MnO3: First principles and experimental study Applied Materials and Interfaces. DOI 10.1021/acsami.7b14826

Martin, L.; Vallverdu, G.; Martinez, H.; Cras, F. L.; Baraille, I. First Principles Calculations of Solid–solid Interfaces: An Application to Conversion Materials for Lithium-Ion Batteries. J. Mater. Chem. **2012**, 22, 22063–22071

REQUIRED SKILLS

The candidates must have knowledge in:

- Physical chemistry and theoretical chemistry. Experience in supercapacitors will be appreciated.
- in characterization methods of materials in bulk (XRD, OCP, SEM and/or TEM) and/or surface (XPS, AES)

The candidates must demonstrate:

- a good organization;
- ability to present results issued from its research;
- ability to work in a team and to be capable of caring himself;

CRITÈRES D'ÉVALUATION DE LA CANDIDATURE / CRITERIA USED TO SELECT CANDIDATE

Selection process steps:

- Establishment of the selection comittee.
- evaluation of the applicants cv's
- Interview with the selected candidates and ranking.

Criteria used in selection of the candidate:

- The candidate's motivation, scientific maturity and curiosity.
- Candidate's knowledge in physical chemistry.
- Candidate's marks and rankings in M1 and M2.
- English proficiency

CONSTITUTION DU DOSSIER DE CANDIDATURE, DATE LIMITE DE DEPOT / REQUIRED DOSSIER, DATE

send an e-mail with your candidature containing:

- CV
- cover letter detailing candidate's motivations
- candidate's MSc marks and ranking
- any letters of recommendation with email
- contact details for 2 referees (at least)

CONTACTS

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