UNIVERSITE, Faculty: University of Lille, Faculty of Science and Technology

Scientific field, Specialty: solid chemistry, heterogeneous catalysis, spectroscopy

Title of thesis: In-depth investigation of perovskite oxides used as electrocatalysts.

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Laboratory(s) of Connection: Unit of Catalysis and Solid-state Chemistry (UCCS, UMR-CNRS 8181)

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Programme de Rattachement : Projet Horizon Europe KNOWSKITE-X | knowskite-x.eu

SUBJECT OF THESE

Context - In an electrolyzer, electrical energy is used to activate a redox reaction such as the transformation of water into hydrogen or the reduction of carbon dioxide and produce molecules of interest such as H_2 from water. This topic is thus part of the European overall strategy towards upgrading and sustaining the hydrogen sector. It also responds to the need to adapt the energy grid to the drastic increase in the share of renewable energy sources, whose production is often intermittent. This involves storing the energy produced when demand is low and returning it in the form of zero-carbon fuel (H_2).

At the core of this device, solid electrodes are used to activate reagent molecules in the gas or liquid phase and transport ions to the other side of the cell *via* an electrolyte. The electrode materials therefore have a catalytic active phase while having satisfactory electrical and ionic conduction properties. The scientific objective of this thesis is to better understand all the processes involved at the electrodes: diffusion of reagents at the fluid/ solid interface, adsorption, and activation of reactive species in the presence of an electric potential gradient, product desorption, and transport of O^{2-}oxide ions or H^+ protons, depending on the device studied.

At present, solid oxide electrolyzer (SOE) electrodes consist of mixed oxides of lanthanum, strontium, iron, cobalt, and/or magnesium for the so-called "air" electrode and nickel on stabilized zirconium for the so-called "hydrogen" electrode. In the context of this thesis, we will be particularly interested in perovskite structures that host at least 2 cations: A and B within an ABO_3 formula. It is possible to enrich this composition to obtain more complex formulations like (AA'A"…)(BB'B"…)O_3, which may also include dopant(s) *d* introduced in tiny quantities.

Description – This thesis is based on two working hypotheses:

The adjustment of the composition of perovskites (A'A"…)(B'B"…)dO_3 is the key to improving the final performance, but the number of possible formulations in a given system is far too high to engage in a systematic approach. The fine understanding of key phenomena in the right place (surface, subsurface, and/ or volume) and under relevant experimental conditions (temperature, electrical potential, concentration—or partial pressure—of reagents) is an essential step in the development of new materials.

An original approach based on the study under relevant conditions (shaping, temperature, atmosphere) of discrete models can provide specific answers with a significant saving of time. For example, we plan to study specifically the surface reactivity of active phases by an approach borrowed from the field of heterogeneous catalysis, for example, programmed reduction in temperature and determination of activation energies. Regarding the study of surface and subsurface exchanges

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(especially the exploration of the phenomenon of ex-solution under redox cycling), we will use a methodology validated by our team of investigation resolved on the surface of polycrystalline model films.

This thesis work will include the following steps:

- Refinement of formulations of electrode materials-presumably to be selected within the (La,Ce,Ba,Ca)(Zr,Fe,Cu,Ni,Y,Pr)O_3 system-and targeted electrolysis operation parameters (temperature, bias, feed…) against the most recent literature.
- Study of surface catalytic reactivity on powders: temperature-programmed reactions with H_2 and O_2, (electro)catalytic cracking of water, reduction of CO_2 in the presence of H_2 or CO…
- Investigation by in situ *spectroscopies* and surface techniques of the effect of redox cycling on surface/ subsurface model films.
- Evaluation under relevant conditions of the most promising electrode materials: electrolyzer cell, electro-catalytic reduction of CO_2.

The objective is the preparation and characterization in the relevant context of mixed oxide models of increasing complexity (discrete models) to acquire new and decisive knowledge in the field of solid oxide electrolyzers.

The objectives of these scientific objectives are based on the acquisition of new knowledge about the relationships between structure, property, and performance of an active material and the rationalization of this knowledge on a scientific basis.

Depending on the candidate's/candidate's profile, it may be considered to consolidate the study through a theoretical chemistry approach (DFT) or the discovery of new formulations using machine learning.

Candidate/applicant profile: The successful candidate holds a M2 in chemistry, physics, spectroscopy, chemistry-physics, or materials and has completed a successful research experience (M2 internship). The academic level and scientific aspirations of the candidate must be consistent with the subject, in particular its multidisciplinary nature. He or she must be able and interested in working collaboratively in an international context across Europe. Furthermore, a perfect command of English is essential for writing and speaking.

Desired recruitment date: 1st October 2025

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