

# ITI HiFunMat Master Internship Proposal

M 1

M 2

**Design of Electrochemical Interfaces to Facilitate the Electrochemical Reduction of N<sub>2</sub> in NH<sub>3</sub> as an Alternative to the Haber-Bosch Process**

## Internship supervisor

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Laboratory	ICPEES
Collaboration with a HiFunMat member ( <i>please indicate their name</i> )	<input type="checkbox"/> No <input checked="" type="checkbox"/> Yes : Elena Savinova

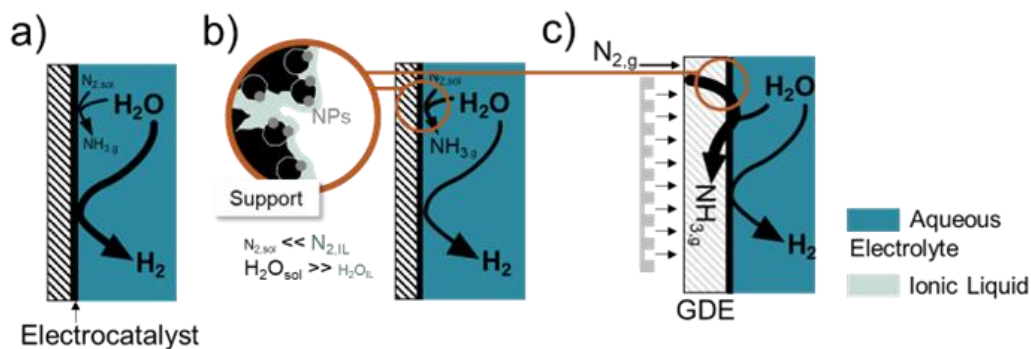
## Student profile looked for

Master program ( <i>more than one box can be ticked</i> )	<input checked="" type="checkbox"/> Material science and engineering <input checked="" type="checkbox"/> Chemistry <input checked="" type="checkbox"/> Physics
Other indications if necessary	The core topic of the internship shall be 'electrochemistry'

## Internship description

The key role played by ammonia in our modern society requires the development of alternatives for the Haber-Bosch process (*i.e.*, the N<sub>2</sub> hydrogenation at high temperature/high pressure in presence of an iron catalyst to produce NH<sub>3</sub>), to reduce its energy and CO<sub>2</sub> generation costs. Indeed, the H<sub>2</sub> used in the Haber-Bosch process mainly comes from fossil sources, and the aforementioned process is responsible for **ca. 2%** of the world yearly energetic consumption. An alternative lies in the electrochemical reduction of N<sub>2</sub> in NH<sub>3</sub> in near-ambient conditions. However, to make the latter possible, several objectives must be tackled. The nitrogen reduction reaction (NRR, N<sub>2</sub> + 6H<sup>+</sup> + 6e<sup>-</sup> → 2NH<sub>3</sub>) occurs in the same potential range as the hydrogen evolution reaction (HER, 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>). The latter, being far simpler and faster, dominates the catalytic activity. This domination is further increased owing to the fact that the N<sub>2</sub> solubility in aqueous media is extremely low, which also impact the NRR relative activity *vs.* the HER. Hence, the electrode interface at which the NRR happens must be tuned accordingly: (i) the local concentration of protons should be decreased to limit the HER, while still being sufficient to insure the NRR; (ii) the local concentration of N<sub>2</sub> should be drastically increased.

This internship aims to explore these approaches, by designing innovative interfaces on electrodeposited metallic ruthenium and metallic nickel, hence moving away from 'classical' interface as illustrated in **Fig. 1A**: (i) through the use of ionic liquids, *i.e.*, electrolytes only composed of liquid salts at room temperature, that shall be either used as encapsulating agents for the nanoparticles or as bulk electrolyte with various concentration of water or other protons carriers (see **Fig. 1B**); (ii) through the development of gas/liquid interfaces to ease the access of the N<sub>2</sub> under gaseous form at the reactive interface, thus greatly diminishing the limitations induced by its low solubility (see **Fig. 1C**).



**Figure 1.** Schematic representation of the different types of interfaces to be envisioned for the nitrogen reduction reaction (NRR): (a) the ‘conventional’ interface, with aqueous environment and  $N_2$  dissolved in  $H_2O$ , leading to a hydrogen evolution reaction (HER) dominated interface; (b) an aqueous interface with the active material encapsulated in ionic liquid (IL), thus tuning the solubility of the reactants at the interface; (c) a ‘gas diffusion electrode’ design, in which the  $N_2$  is provided under gaseous form directly at the interface. Adapted from [1].

Specifically, the intern will:

- Using the preliminary results obtained by our team, optimize the design of electrodeposited Ru and Ni nanoparticles adapted to the study of innovative interfaces.
- Characterize their reactivity for the NRR (and the nitrate reduction reaction) in (a) aqueous media, in (b) presence of a fluor-rich ionic liquid (EMPA- $C_4F_9SO_3$ ) as encapsulating agent or electrolyte and in (c) a so-called GDE cell (similar to the design in **Fig. 1C**) by electrochemistry and spectroscopy.

The internship might eventually extend to the design of disruptive electrocatalysts and to the use of anion exchange membranes, instead of aqueous electrolyte, in the GDE cell.

[1] T. Asset, “The runt of ammonia production by  $N_2$  reduction: Electrocatalysis in aqueous media”, *Curr. Opin. Electro.* 39 (2023) 101301, DOI: 10.1016/j.coelec.2023.101301