LABORATOIRE DE CHIMIE ENS DE LYON

ÉCOLE NORMALE SUPÉRIEURE DE LYON

Sujet de Thèse (2022-2025)

« Modélisation Théorique Multi-échelles des Structures de Nanocages Bimétalliques et de leur Réactivité pour des Applications dans les Piles à Combustibles»

« Multiscale Modeling of Bimetallic Nanoframe Structures and their Reactivity for Applications in Fuel Cells »

Context : In the automotive sector, there is currently a real challenge in proposing new clean energy conversion systems that are economically viable and within the framework of sustainable development. At the dawn of a new era potentially dominated by all-electric vehicles, questions remain about the abundance of battery component materials, their stability, long-term durability and recycling. For nearly 20 years, an interesting alternative has been considered in this sector: proton exchange membrane fuel cells (PEMFCs). Their principle is to convert the chemical energy of hydrogen fuel into electrical energy by means of a metallic catalyst (usually platinum in the form of nanoparticles supported on carbon at the cathode of the cell). However, several difficulties prevent the large-scale commercialization of this device in a new generation of fuel-cell vehicles: in particular the performance of the catalyst at the cathode towards the oxygen reduction reaction (ORR), its high cost (rare metal), the durability of the catalytic system and of the fuel cell after several thousand operating cycles. A North-American group of researchers (Stamenkovic et al.) proposed a few years ago hollow nanoframes of PtNi alloys, of a relatively modest size (diameter of 15 nm), as a cost-effective solution to modify the nature of the catalyst. In fact, the substitution in these nanocages of a significant part of the platinum by nickel (less expensive) reduces the cost of the catalyst while increasing its performance and preserving its durability. Other similar bimetallic systems have been proposed in the literature without truly equaling the performance of PtNi nanoframes and above all without reducing the platinum content as much (larger nanoframes). However, the remarkable catalytic properties of these new materials remain misunderstood at the atomic scale, to date.

Objectives : in this project, the PhD student will use a multi-scale theoretical approach to study the three-dimensional structures, the chemical composition and the reactivity of PtNi nanomaterials and especially nanoframes. At small size (3.5 nm), the catalyst models will be optimized by means of density functional theory (DFT) calculations. These reference results will make it possible to parameterize an effective potential in order to be able to explore the phase space of hollow and excavated PtNi nanocages at a more realistic size by means of Monte Carlo simulations. The combination of theoretical approaches aims to better understand the structure of these nanomaterials, their spatial arrangement, their composition and their reactivity towards ORR. This theoretical approach can be validated by comparison with the experimental measurements already available. These works will finally make it possible to progress in the understanding of these catalytic systems, an essential step for designing other materials that are even more efficient and economical in the field of PEMFCs.

Localisation : Laboratoire de Chimie de l'ENS de Lyon.

Partnership : these research works will be carried out in collaboration with Dr Christine Mottet (CINaM Marseille), Dr Federico Calle-Vallejo (Université de Barcelone), and in partnership with Pr Vojislav Stamenkovic (ANL, Argonne USA), who invented these catalysts.

Contact : David Loffreda Directeur de Recherche CNRS Président CT8/GENCI	Université de Lyon Ecole Normale Supérieure de Lyon CNRS, Laboratoire de Chimie, UMR 5182 F-69342 Lyon, France	Phone: (+33) 4 72 72 88 43 Email:david.loffreda@ens-lyon.fr http://www.ens-lyon.fr