Call 2018 for a PhD position in Materials Science at the University of Poitiers, France

Subject. 'Mechanical and structural properties correlated to electrocatalytic activity in energy conversion and storage devices: application to molybdenum disulfur MoS_2'

Contact (Deadline for application : April 30, 2018 / PhD Start : Before December 2018)

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Salary. 1768 € per month (raw salary) for 3 years, possibility of complementary teaching activities (see *www.campusfrance.org/en/make-our-planet-great-again-en* for financial support)

Keywords. Mechanical properties; Stress; Dislocations, 2D Materials, Atomic structures Hydrogen Production; Water Electrolysis

Experimental techniques.
Near field AFM/STM microscopy, LEED/Auger/STS spectroscopy, Electrochemical experiments, Temperature mechanical testing, Ultra high vacuum systems, Voltammetry

Candidate Profile. The PhD candidate should be skilled in Materials Science and Physics, while showing a strong interest in experimental work. Some knowledge in Scanning probe microscopy, electron spectrometry and associated characterization techniques of crystalline materials would be highly valuable, as well as in physical chemistry and electrochemistry.

Partnership. Two interdisciplinary laboratories are involved at University of Poitiers in the PhD project (1) Pprime Institute, UPR 3346 CNRS, University of Poitiers, France (www.pprime.fr) (2) IC2MP, UMR 7285 CNRS, University of Poitiers, France (ic2mp.labo.univ-poitiers.fr).
In addition, atomistic simulations using interaction potentials for mechanical behavior and/or DFT ab initio calculations for electronic band structures could be performed in a collaboration with Y. Dapp (CEA Saclay, France), to compare with our experimental data.
Finally, the PhD project will be a great opportunity to deepen our existing scientific collaboration with the Center for Computational Design of functional layered Materials (CCDM) based at Temple University (Philadelphia, Pennsylvania, USA).

Context and Motivation. The development of low-cost and earth-abundant electrode materials in energy conversion and storage applications such as hydrogen production, is defying conventional paradigms in the state-of-the-art in catalysis where noble and scarce metals (PGMs) had long been deemed the only efficient electrode materials for use in fuel cells and water electrolyzers. The large-scale hydrogen production can be undertaken from the reforming process providing 96% of the environmentally friendly energy carrier. As the reforming process based on fossil hydrocarbons includes CO and CO_2 emissions (which requires a purification step), another sustainable approach based on water electrolysis (4-5% of H_2 production) merits to be developed for an environmental benefit. This issue will be thoroughly "green" with a production of hydrogen from a solid polymer electrolyte electrolyzer that can be supplied with a renewable and intermittent power source (photovoltaic or wind).

According to its theoretical specific energy density (32.7 kWh kg^{-1} *vs.* 10.5 kWh kg^{-1} for gasoline), H_2 is considered as an ideal and environmentally friendly energy carrier. Thus, hydrogen economy addresses challenges faced by modern societies by allowing the production of electricity using fuel cells.

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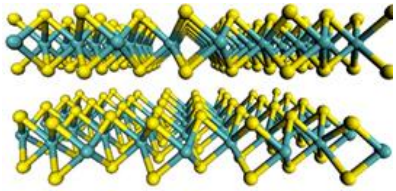
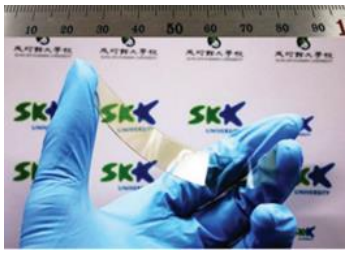
The use of H_2 as energy carrier will actually play a key role in the transition from an oil-based economy to a CO_2-free one. Furthermore, the large-scale use of electric vehicles is currently hampered by two factors: battery cost and short driving range. The use of H_2 can overcome these two bottlenecks and social impacts such as noise nuisance and urban pollution. To date, several automotive manufacturers are almost ready to commercialize H_2 fuel cell vehicles (HFCV). It was recently shown that 600 km can be driven with a 700 bars on-board H_2 reservoir filled in less than 3 min. Thus, HFCVs could be commercially marketed if high purity H_2 fuel can be produced and distributed on the roads of France.

Scientific Objectives.

Since 2010, the European Union has paid attention to the use of critical raw materials such as PGMs. Therefore, we recently developed a synthesis method to prepare very active nickel-cobalt spinels as anode for splitting efficiently water at potentials lower than 2 V [Abidat 2017]. The present challenge consists now in replacing the carbon supported Pt cathode materials by 2D Materials in the water-to-H_2 conversion. 2D materials present the interest of an ultimate thickness of only a few atomic layers. Indeed, they offer new ways for technological challenges in various domains [Ding 2016; Luo 2017], like microelectronics, photovoltaic or catalytic chemistry. It is also believed that these foils can be locally strained (or stressed) to modify their electronic properties, and consequently to enhance their electrocatalytic properties.



Crystallographic structure of MoS_2 foils (Mo in green, S in yellow).



MoS_2 foils after transfers on polymeric, flexible and transparent substrates.

The PhD project will be focused on molybdenum disulfur sheets (MoS_2) consisting of only three alternating S-Mo-S atomic layers, as promising earth-abundant and low-cost cathode material. The main issue is to understand how these 2D materials behave under external applied stresses and to identify how their local morphological changes may modify, or even control, their electrocatalytic activity. The catalytic performances of stressed-MoS_2 will be then investigated in a half-cell and in a single water electrolyzer in which a spinel-based catalyst will compose the anode to promote for instance diffusion limitation and hydrogen adsorption energy.

Methodology and Planning. We intend to advance this PhD project by taking advantage of the close multidisciplinary expertise in Physics (Pprime Institute) and Chemistry (IC2MP Institute) at the University of Poitiers, France. The PhD project is divided in four interconnected tasks listed below.

Task 1. Synthesis and characterization (IC2MP/Pprime)

First, MoS_2 sheets received in the framework of a scientific collaboration with the Center for Computational Design of functional layered Materials (CCDM) based at Temple University (Philadelphia, Pennsylvania, USA) will be investigated. MoS_2 2D materials will be also synthetized at IC2MP by AP-CVD, transferred if necessary on metallic substrates of interest and characterized by different techniques such as Raman spectroscopy, TEM, SEM, EBSD…

Task 2. Mechanical behavior at atomic scale (Pprime)

Metallic single crystal substrates (like Nb or Co…) coated by MoS_2 foils will be strained using the original Nanoplast equipment [Nahas 2013]. This experimental device allows following by

scanning tunneling microscopy under ultra-high vacuum (UHV AFM/STM) the *in situ* evolution of surface, down to the atomic scale, at increasing stress or strain [Coupeau 2016, Chauraud 2017]. Dislocations nucleated in the bulk will propagate towards the MoS_2/metal interface in order to locally modify the morphology of the covering foils in interaction. The role of key-parameters (such as substrate materials, adhesion properties, structure and thickness of the stacked foils, deformation temperature, crystallography of substrates…) will be studied.

Task 3. Electrochemical characterizations (IC2MP)

Free-stress and stressed-MoS_2 sheets will be investigated by voltammetry for extracting kinetic parameters such as Tafel slope and overpotential…A second step will consist in modifying MoS_2 sheets by incorporating other elements (M-MoS_3, M= Mn, Fe, Co, and Ni). In particular, due to their amorphous nature, the M–MoS_3 materials contain many defect sites, which may out-number the available edge sites in well-defined MoS_2 nanocrystals.

Task 4. Tests of H_2 production in a single water electrolyzer in alkaline medium (IC2MP)

The testing protocol will evaluate both performances under different temperatures, purity of the obtained gas and ageing of the MEA to assess the durability in alkaline medium. These results will be compared with the state-of-the-art of proton exchange membrane water electrolysis in terms of kWh/Nm^3 and €/Nm^3 at the same loading. This short cost analysis will be based only on the MEA components and preparation. Post mortem characterization will be performed by evaluating/examining the morphology of MEAs (cross section) using SEM technique, Linear Sweep Voltage curves. From these data, the catalyst layer ageing will be studied.

Periods of international mobility, congress/seminar attendances, doctoral formation (for example, scientific integrity, ethics,…), meeting on “after PhD defense” will be included in the PhD student Gantt diagram.

Position of the Project in Relation with the MOPGA Scientific Domains.

Hydrogen is an environmentally friendly decarbonaceous energy carrier, which has many advantages such as noise nuisance and urban pollution in vehicle (no CO and CO_2 emissions). H_2 results from water splitting in an electrolyzer; conversely, its combustion provides spontaneously energy, heat and recombined water as sole reaction product, safe for the Planet. With a solar energy profile, we have demonstrated in a Proton Exchange Membrane Water electrolyzer a durability of anode materials prepared in IC2MP (1200h) with 1 A cm^{-2} and a cell voltage at 1.7 V.

As energy transition, Jules Verne thought Hydrogen as one the promising solution for the close future:

…“- And what we will burn to the place of coal? Water, replied C. Smith….I believe that water will one day be used as fuel, that hydrogen and oxygen, which compose it, used separately or simultaneously, will provide a source of heat and inexhaustible light and of an intensity that coal cannot have” (“L’Île mystérieuse”, 1874, pp. 670).

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