

Master thesis proposal

Combinatorial mapping of the electrochemical reactivity of composition-gradient thin films with operando Raman and contact angle monitoring

Keywords: Combinatorial mapping, advanced magnetron co-sputtering, oxide thin films, operando Raman and electrochemical monitoring, operando drop-cell measurements.

SCIENTIFIC DESCRIPTION:

Multicomponent thin films are today a major research avenue to accelerate the discovery and optimization of functional materials. The so-called “combinatorial” approach makes it possible to deposit, in a single step, thin layers exhibiting composition gradients, thereby enabling the systematic exploration of broad chemical composition spaces. These films, prepared by magnetron sputtering, can be considered as true material libraries in which each region of the sample possesses a slightly different composition. Their study allows one to establish direct correlations between structure, composition, and functional properties, and to rapidly identify the most promising formulations for applications in electrocatalysis, interfacial stability, or electrochromic devices.

In this context, two laboratories (ICMCB – Bordeaux and LRS – Paris) have joined forces to combine their complementary expertise. The first one is specialized in the broad sense in materials chemistry synthesis using advanced magnetron sputtering including various modes RF, DC or co-sputtering configuration allowing a careful control of the films structure, composition and morphology in particular for applications in the field of electrochromism combining optical and electrochemical characterizations. The second has recognized know-how in operando electrochemical analysis, with original tools developed to study surfaces under confined electrolyte droplets, to couple electrochemical measurements with optical and spectroscopic probes, and to characterize interfacial dynamics in real time.

The aim of the proposed internship is to exploit this synergy by setting up a genuine combinatorial mapping of the electrochemical reactivities of thin films. The starting materials include amorphous WO₃ layers of about 200 nm deposited on transparent conductive substrates (ITO). These films are of particular interest because they show strong Raman responses and pronounced abilities for reversible ion insertion and deinsertion (H⁺, Li⁺). They are therefore ideal models for operando spectroscopic monitoring, since they allow direct observation, through Raman spectroscopy, of the evolution of the W–O vibrational modes as a function of applied potential and ionic environment. The internship will start with WO₃, a state-of-the-art electrochromic oxide that serves as a model material, before extending the methodology to other compositions.

The internship will first focus on establishing a basic electrochemical mapping of the films, using a confined droplet cell mounted on a goniometer. This approach makes it possible to scan the surface of the films with a lateral resolution of a few hundred micrometers and to acquire, point by point, electrochemical data such as cyclic voltammograms or electrochemical impedance spectra. These measurements will give access to two-dimensional maps of electrochemical activity, capacitance, and charge-transfer resistance as a function of local composition. These first datasets will serve to identify representative regions for more detailed investigations.

In a second step, operando experiments will be carried out by coupling electrochemistry with Raman spectroscopy. The objective is to monitor in real time, on selected areas, the evolution of characteristic vibrational bands during electrochemical cycling, in order to correlate local reactivity with the



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chemical structure and oxidation state of the material. This approach will be particularly relevant for WO₃ films, whose Raman signatures are sensitive to ion insertion. These data will provide unique insights into interfacial modifications, which are likely to strongly influence electrochemical activity and stability.

The explored electrochemical environments will cover both aqueous electrolytes, such as 0.1 M H₃PO₄ or phosphate buffers, and non-aqueous electrolytes as ionic liquids based on TFSI anions. These different electrolytes will allow the exploration of varied potential windows and the assessment of the robustness and reactivity of the films in contrasting environments.

This internship therefore offers the candidate the opportunity to become immersed in an interdisciplinary research project associating materials science and electrochemistry, and to contribute to the development of an advanced combinatorial methodology for the discovery of new functional materials. The high-throughput synthesis and characterization of functional materials provide the foundation for the reliable use of machine learning and artificial intelligence in advanced materials discovery. Joint supervision by two laboratories, each supported by a DIADEM project, will guarantee a stimulating and structuring research environment at the interface between synthesis, structural characterization, and operando analysis of electrochemical interfaces.

Techniques/methods in use: Library of WO_x films will be deposited by magnetron sputtering using both RF and DC modes from ceramic WO₃ or W targets in single and co-sputtering configurations on conductive substrate. Physico-chemical characterizations will include XRD, SEM, profilometry measurements, as well as operando spectroelectrochemical methods (Raman, cyclic voltammetry) and electrochemical measurement performed in a droplet cell (small volume, contact angle...)

Budget description and use : The grant will be used to pay for the master's internship. The research costs will be covered by the two laboratories

Applicant skills: Student in 2nd year of Master or 3rd year of engineering school with a good background in physical chemistry and electrochemistry and/or material science.

Autonomous, meticulous, rigorous

A good level of English is required

Industrial partnership: No

Internship supervisor(s):

- Aline ROUGIER, aline.rougier@icmcb.cnrs.fr
- Vincent VIVIER, vincent.vivier@sorbonne-universite.fr

Internship location: Laboratoire de Réactivité de Surface – Sorbonne Université – Paris

Possibility for a Doctoral thesis: Yes

