## Premio Nacional SOCIEMAT Mejor Carrera Científica en Ciencia y Tecnología de Materiales

# OPERANDO CHEMICAL IMAGING OF CORROSION REACTIONS

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**Summary**: SOCIEMAT distinguishes outstanding scientific achievements in Materials Science and Technology through its National Award for the Best Scientific Career, that has been awarded to Prof. Ricardo M. Souto in 2024 to recognize excellence in corrosion research and technical contributions to the field of corrosion science and technology. His h-index is 55 according to Google Scholar and 46 according to Scopus.

**Keywords**: ***Corrosion***; spatially-resolved corrosion; localized corrosion; passivity; galvanic corrosion; underfilm corrosion; corrosion protection; biomaterials characterization***. Electrochemical methods***; Conventional electrochemical techniques; electrochemical noise measurements; Scanning electrochemical microscopy; ion-selective microelectrodes; localized impedance; Scanning vibrating electrode technique; localized electrochemical impedance spectroscopy; combined atomic force and scanning electrochemical microscopies.

## 1. SHORT BIOGRAPHICAL DATA.

Ricardo M. Souto is Full Professor at the University of La Laguna (ULL, Canary Islands, Spain) since 2008. He received the MSc degree in Chemistry from ULL, and a PhD degree at the University of Utrecht (The Netherlands). The doctoral training focused on the study of the multistep reaction mechanism of electrode processes and the catalytic effect of adsorbable species using first and second order AC electrochemical techniques.

His return to ULL happened with the foundation of the Electrochemistry and Corrosion research group (ELECOR). Research focus was shifted to the study of localized corrosion processes in passive metals by using conventional electrochemical techniques in combination with surface characterization techniques, whereas also studying corrosion protection by corrosion inhibiting organic substances or applying polymeric barrier coatings.

Aware of the limitations of conventional electrochemical methods to analyse the origins of localized corrosion processes in passivated metals, in 1994 a fruitful collaboration was initiated for more than a decade with prof. G.T. Burstein at the University of Cambridge (UK), where the use of microelectrodes for the study of nucleation events of individual pitting on steels and titanium-based materials began, using electrochemical noise analysis techniques. Although major advances in the knowledge of the mechanism of localised corrosion were achieved, the need for microelectrochemical techniques with spatial resolution became evident. Then, activities focused on the application of scanning electrochemical microscopes and other combined near-field probes for the investigation of corrosion and corrosion protection processes, expanding from systems of industrial interest to the biocompatibility of implant materials in the human body.

The electrochemical scanning microscope (SECM) was gradually introduced, proposing new operation modes for the study of interfacial reactions on reactive solid surfaces (namely, redox competition mode, combined potentiometric/amperometric operation, the measurement of impedances in the probe conforming AC-SECM or Scanning Electrochemical Impedance Microscopy (SEIM), as well as combined AFM-SECM operation).

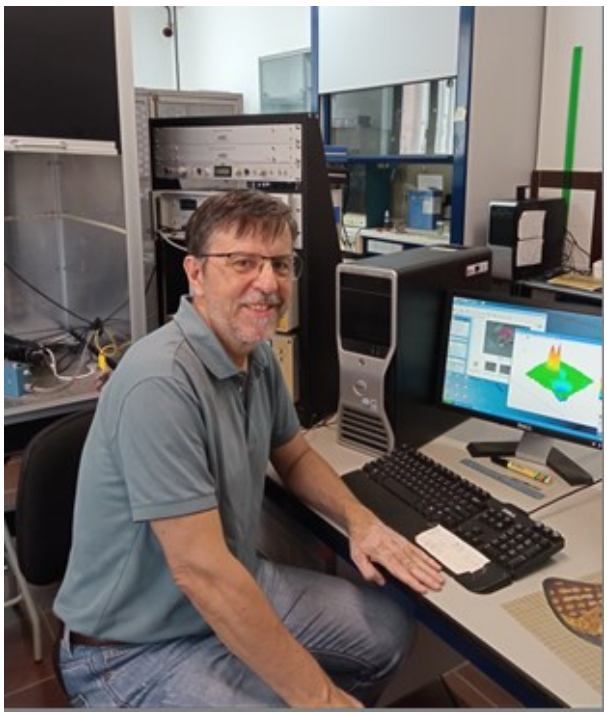

**Figure 1.** Prof. Ricardo M. Souto at his laboratory.

## 2. OPERANDO CHEMICAL IMAGING OF CORROSION REACTIONS

The function of most metallic components is ultimately limited by the loss of their properties due to corrosion. Corrosion refers to the investigation of environmentally induced degradation of a material that involves a chemical reaction. Research in Corrosion Science covers mechanisms of corrosion and passivation, methods to control corrosion, either by employing protection procedures such as corrosion inhibition and protective coating layers, or the development of novel processing techniques that would originate materials with improved surface properties.

Corrosion reactions are of an electrochemical nature, and despite their diversity they all initiate from sites with micro- and submicrometric dimensions, thus demanding operando techniques that resolve the heterogeneous processes occurring at metallic surfaces, either pristine or modified under surface modification or coating procedures. Advanced research is mainly directed to the better understanding of micrometer- and submicrometer-level chemical processes, the application of new instrumentation not previously available to enable the investigation of various phenomena, advances in materials modelling and simulation, and responding to new societal expectations concerning better quality of life (i.e., leading to more environmentally-friendly corrosion mitigation strategies, as well as producing tailored materials for specific environments and applications including a new generation of alloys and surface protection layers).

Innovative methods based on measurements of potential, current and electrochemical impedance by scanning electrochemical microscopy (SECM) allow revealing the early stages of localized corrosion reactions as well as characterizing the protective performance of coatings and inhibitor systems. These observations are fundamental for the accurate study of the electrochemical behaviour of materials under corrosion reactions.

SECM is a microelectrochemical method that most adequately addresses such demand, and it has been demonstrated to be very efficient to reveal corrosion reactions associated with pitting corrosion, metal dissolution, galvanic corrosion, dealloying, passivity and its breakdown, formation of corrosion inhibitor layers, transport processes through coatings, delamination and blistering. Metals, alloys, even surface modifications such as welds, have also been satisfactorily imaged. Very importantly, the versatility of SECM arises from the wide variety of techniques and operation modes that can be classified into amperometric, potentiometric and AC modes, as well as its inherent ability to be hyphenated to other surface analytical techniques such as atomic force microscopy (AFM).

## 3. THE ELECTROCHEMISTRY AND CORROSION RESEARCH GROUP OF THE UNIVERSITY OF LA LAGUNA.

The research group has gained its reputation in the scientific areas of Electrochemistry and Corrosion (ELECOR), mostly through the generation of new knowledge at the fundamental level, as well as developing new scientific methodologies for surface monitoring and characterization. In addition, research contracts on materials selection for specific applications and environments, detection of corrosion failure origin, materials rehabilitation and extended life-time expectancies, are frequently established with companies and governmental agencies in the Canary Islands (Spain). Thus, activities have been performed concerning cooling reactors in power stations, mechanical components in solar farms, durability essays of mirror lenses for astrophysical telescopes, corrosion processes in buildings, transport basis, roads, etc.

Yet the main area of expertise and highest reputation concerns the Application of scanning microelectrochemical methods in Corrosion Science, leading to assemble a rather unique laboratory where a number of SECM instruments designed to cover this wide range of SECM operation modes is distributed along other scanning microelectrochemical techniques, namely the Scanning Vibrating Electrode Technique (SVET), Scanning Ion Electrode Technique (SIET), Localized Electrochemical Impedance Spectroscopy (LEIS) and Scanning Kelvin Probe Force Microscopy (SKPFM). A selection of main achievements is listed here:

(1) Use of the microelectrode probe in the SECM in a device for the measurement of electrochemical noise, which allowed to record passivity currents with resolution below the pA range, making accessible the visualization of localized passivity breakdown for the first time (https://doi.org/10.1016/j.elecom.2004.04.018).

(2) Development of a new mode of operation for the SECM that uses alternating current and impedance analysis (SEIM). This has facilitated the detection of local variations in the surface conductivity of thin films on metals containing organic molecules with corrosion-inhibiting characteristics, a highly chemical sensitive method with superior lateral resolution than AFM and Kelvin probe (https://doi.org/10.1002/cplu.201500398).

(3) Use of the SECM microscope probe as ion source for the controlled initiation of pitting corrosion processes at selected positions of a passivated metal surface at the submicrometer dimension, providing powerfool tools for the investigation of the early stages of pitting corrosion phenomena (https://doi.org/10.1016/j.elecom.2014.11.017).

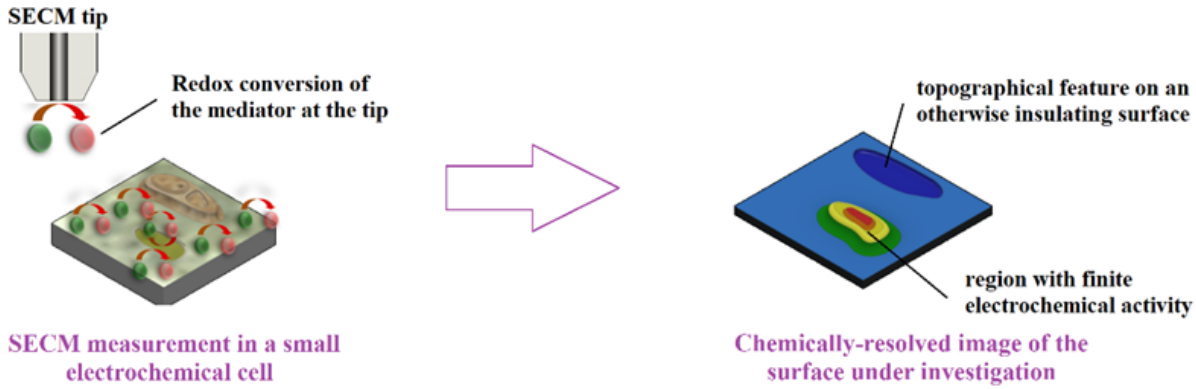


**Figure 2.** Scanning electrochemical microscopy (SECM) allow revealing the early stages of localized corrosion reactions as well as characterizing the protective performance of coatings and inhibitor systems.

(4) Introduction of the potentiometric operation of SECM in corrosion science with enhanced chemical sensitivity and selectivity, by the construction of pH sensitive probes and solid contact ion-selective microelectrodes for faster acquisition rates (https://doi.org/10.1149/2.001310jes).

(5) Development of multi-barrel probes with internal reference to avoid high electric field effects related to galvanic coupling reactions, interfering in the surface chemical analysis (https://doi.org/10.1149/2.0671805jes).

(6) Combined AFM-SECM operation for the unambiguous monitoring of chemical and morphology evolution during the early stages of metal dissolution at the submicrometer range (https://doi.org/10.1016/j.electacta.2017.07.042).

(7) Monitoring of transport processes through insulating polymer layers relevant to coating swelling and early blister formation at the metal/coating interface (https://doi.org/10.1016/j.corsci.2004.06.002).

(8) Development of a new method based on the use of the redox competition SECM mode established during oxygen consumption upon corrosion reaction, for the detection of chemical activity around defects, pores and cut-edges of metal-coating systems (https://doi.org/10.1016/j.electacta.2014.11.192).

(9) Introduction of potentiometric SECM for the characterization of composite coating systems for corrosion protection (https://doi.org/10.1016/j.corsci.2016.06.002).