# From Traditional to Advanced Electrochemical Techniques for understanding Corrosion Mechanisms A Comprehensive Survey

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The conference will first give a short presentation of the tight relationship between electrochemistry and corrosion phenomena from the beginning of the 19th century. A series of outstanding theoretical and experimental advances in the first decades of the last century have opened a new era in corrosion investigations which took place only after World War II. Most studies were initially based on current-voltage relationship then extended to electrochemical impedance over an increasingly wide frequency range. The background of the impedance technique from both its instrumental and theoretical aspects will be restated by revisiting the usual description of an open-circuit corrosion potential case. From this most classical problem it is pointed out that the straightforward extrapolation of electrochemistry of inert electrodes to corroding materials is quite problematic. A specific field which can be defined as *corrosion electrochemistry* has to be progressively developed in the last decades. It includes essentially the multi-step reactions and their adsorbed intermediates species in the anodic dissolution of metals, the nucleation and growth of 2D and 3D surface films, the specific mass and charge transport conditions in localized corrosion sites, the change of surface morphology due to atoms removal…

The techniques developed in our group, and in several other ones, since the 60's can be regarded as an attempt to answer some of the specific problems raised by corrosion electrochemistry. It is to emphasize that progresses in the field were essentially possible owing to the tremendous advances in solid state electronics and computer science. The techniques will be presented focussing on a schematic representation of the main features of corroding interfaces, including generalized and localized attacks. Traditional impedance, techniques based on emitter-collector configuration able to provide a charge balance at interfaces, microbalance adding dynamic weight response of the interface. Association of these data allowed to derive far less "speculative" models of corrosion mechanisms.

Local corrosion can be specifically addressed by using various type of local probes. The most known of them are current sensitive probes likes SVET (Scanning Vibrating Electrode Technique) and bi-electrodes. SECM is able to provide both local surface morphology and reactivity data. All this techniques will be illustrated by their technological implementations, including sine wave polarization, their applications to various situations and their limitations commented.

More surprisingly, electrochemical approaches have been applied to more exotic or technological corrosion cases. Two different families of situation can be identified.

In the case of corrosion partly due to mechanical damages caused by solid impacts, straining the material, tribological effects…electrochemical techniques can still provide valuable information in the framework of the depassivation-repassivation mechanisms.

For understanding and optimizing the protection provided by coatings, electrochemistry is only partly involved but proved useful since it permitted to split the response of a coated metal in two distinct contributions, namely the defects of the coatings and the reactivity of the thence exposed fraction of the underlying metal. However most part of the global and long term protection depends on physicochemical properties of the coating material, either organic or inorganic.

Corrosion of reinforcing bars embedded in concrete can be dealt with in some extent by concepts to similar coated metal. A very recent advance is based on contact-less measurements applying the concept of contact-less electrochemistry or floating-electrode.

New possibilities of investigating the electrochemistry of corrosion products avoiding interferences with the underlying substrate will be also described.

Finally, the conclusions will try to draw the attention on several aspects deserving particular efforts of the scientific community.