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Extending the operation procedures of scanning electrochemical microscopy to unveil corrosion and protection mechanisms

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Keynote: The Scanning Electrochemical Microscopy (SECM) technique has gained considerable attention for surface characterization since its invention in the late 80s. By using a microelectrode as scanning probe moving in the vicinity of a surface-electrolyte interface, electrochemical signalling within the diffusion layer can be used to sense redox species involved in the heterogeneous reactions and/or interacting with the substrate under investigation. Consequently, not only reacting redox species are locally determined, but also certain properties such as surface conductivity or passivation phenomena are regularly imaged with the aim to discern the mechanisms of those processes occurring on reactive materials. Despite the great versatility of SECM, the related methods for corrosion research have been mostly restricted to potentiostatic procedures and the conventional operation modes remain blind to many chemical species of interest. Meanwhile, modelling of signals acquired at fixed locations have served to evaluate kinetic constants, but mostly for specific electron transfer reactions at the surface, which may not entirely relate to the surface condition. However, the adequate combination of diverse electrochemical measurement routines, which are rarely explored, as well as fundamental data analysis may allow the acquisition of additional valuable information, thus addressing reaction pathways and physicochemical parameters of the material. In this sense, this contribution will provide some examples further deepening in the capabilities of the SECM, in order to visualize and quantify those phenomena, also revealing the role of micro- and macrogalvanic interaction by complementary techniques as well as the chemical and electrochemical effects induced by corrosion inhibitors.