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## Highlights

- Scanning electrochemical microscope to probe short lifetime reactive intermediate species.
- Detection of reactive intermediates involved in electrocatalytic processes.
- Adsorbed and dissolved reactive intermediates detected by various SECM methodologies
- Multiscale approach: from micro to nanometer scales.
- Numerical simulation to quantify the intermediates production and reactivity.

# Probing the reactive intermediate species generated during electrocatalysis by scanning electrochemical microscopy

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## Abstract:

Reactive intermediate species (RIS) are of major importance in many chemical and biological reactions. Due to the high reactivity their presence are usually confined at the place of their formation. Whereas electrochemical tools can electrogenerate them through various mechanistic paths, the local electrochemical probes, such as a micro/nanoelectrode tip of the scanning electrochemical microscopy (SECM), are by essence well adapted to catch their formation and reactivity at the location of their production. This review presents the recent local electrochemical probe strategies employed to probe RIS down to the nanometer scale, either immobilized on the surface of an electrode or within a reaction layer, in solution. It is illustrated by examples borrowed from the field of electrocatalysis, with emphasis on the contributions of numerical simulation to derive quantitative information.

**Keywords:** Scanning electrochemical microscopy, reactive intermediate species, nanoelectrochemistry, numerical simulation.

## Introduction

Reactive intermediate species (RIS) are key species involved in many chemical [1,2] and biological processes [3], and whereas their production must be encouraged in some applications, in others they must be avoided. In any case, a complete understanding of their formation as well as their quantification is needed. ESR (Electron Spin Resonance Spectroscopy) and chromatography are powerful methods to detect radical species trapped by conventional radical scavengers, including those electrochemically generated [1,4,5]. However, they are mostly limited to indirect detection and remain inoperative for local or time-resolved analysis. Alternatively, Raman spectroscopy, at different nanostructured surfaces for enhanced electromagnetic field, offers operando detection of RIS, but remains limited to surface-adsorbed reactive species with sub-second time resolution [6,7]. Due to their short lifetime,  $\tau$  in the sub-ms to sub- $\mu$ s, electroanalytical tools allowing to probe them at the earliest stage of their formation are needed. This can be performed by ultra-fast electrochemistry [8], although often difficult to implement and limited to electroactive intermediates.

Alternatively, RIS could be detected by electrochemical probes with size comparable to the characteristic distance they could travel  $\delta \approx (D\tau)^{1/2}$ , with  $D$  the diffusion coefficient of the RIS. Such small electrochemical probes, mostly used in the scanning electrochemical microscope (SECM) configuration, i.e. the probe facing a reacting interface, can then collect and/or identify RIS in a confined space nearby the location of their production [9].

Herein we review the different SECM methodologies employed to specifically probe molecular RIS either adsorbed at a surface or generated in the reaction layer of an electrode, in the context of molecular electrocatalysis.

## SECM modes used for the detection of reactive intermediate species

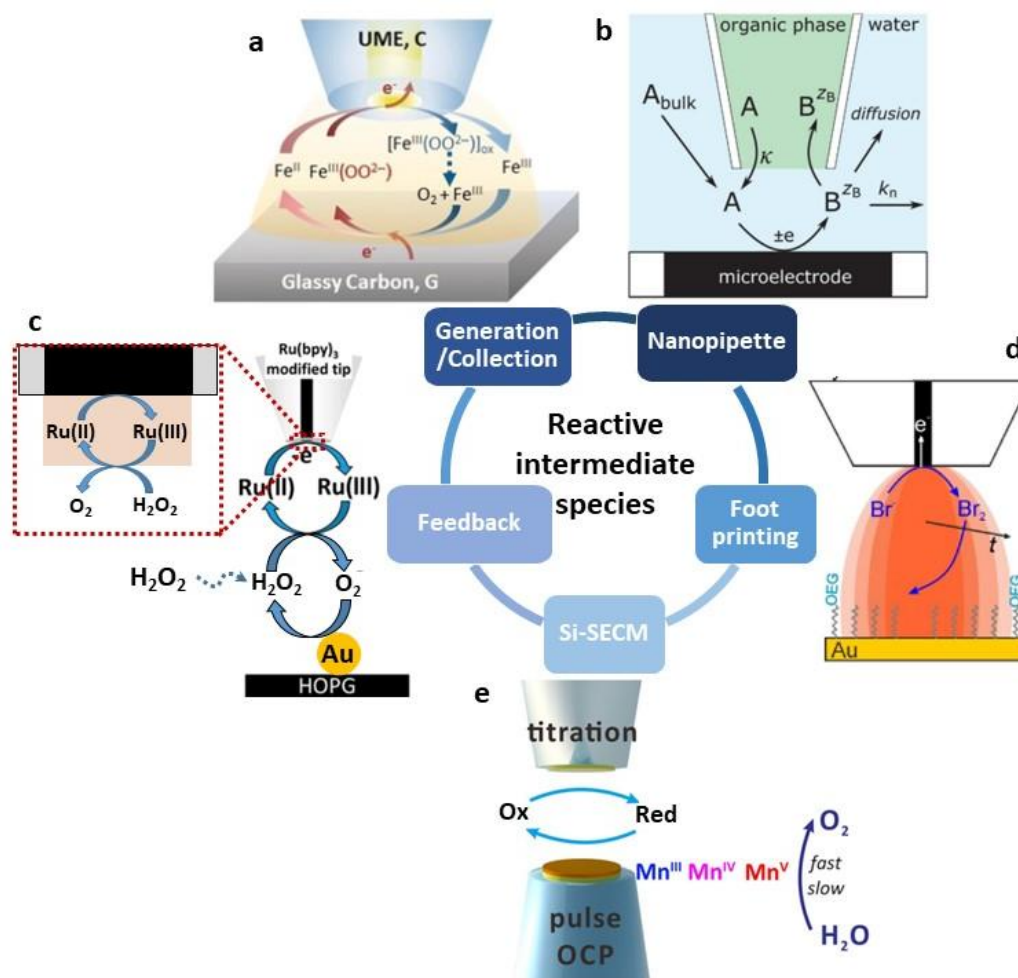
This section first presents the different modes of the SECM employed to identify and quantify various RIS generated in solution. Electroactive RIS are more often probed directly, where they are created using the generation collection mode (G/C) of the SECM. In this mode, inherited from the ring-disk electrode configuration, a generator electrode, G, triggers a reaction of interest while the collector one, C, facing G, collect the RIS produced at G. Figure 1a illustrates the substrate generation/tip collection (SG/TC) of  $\text{Fe}^{\text{III}}(\text{OO}^{2-})$  intermediates of ms lifetime produced during  $\text{O}_2$  reductive activation at iron porphyrins [10]. The reverse configuration (tip generation, substrate collection mode, TG/SC) was also employed with gap distances from  $10\mu\text{m}$  to  $500\text{nm}$ , using a classical or an hemispherical UME [11], or even down to  $73\text{ nm}$  employing nanoelectrodes (nanoSECM) [12]. In such a configuration,  $\tau \sim 1\mu\text{s}$  to  $\sim 10\text{ ns}$  lifetime RIS were directly probed [11,12]. However, the gap between the generator and the collector cannot be below  $\sim 3\text{nm}$  due to the direct electron tunneling occurring below this limit [13,14].

To push the detection of even shorter lifetime RIS, an elegant approach proposed to replace nanoelectrodes by a nanopipette filled with an organic phase, immiscible with the external aqueous solution, and to use it as a SECM tip (Figure 1b) [15–17]. The nanopipette delivers an electroactive species, A, to a polarized substrate that in turns electrogenerate the reactive intermediate, B,

subsequently transferred and collected in the nanopipette phase. Theoretical developments evidenced that extremely unstable RIS, with  $\tau \sim 1$  ns scale lifetime, require cyclic voltammetry collection at  $> 10^5$  V/s scan rates [15,18]. This nanopipette strategy can be useful for the detection and identification of many charged intermediates, electroactive or not, in both aqueous and nonaqueous solutions.

Indirect SECM detection modes have been also proposed, for example to probe non-electroactive RIS. The SECM feedback mode is one such powerful technique to quantitatively analyze electrochemical processes involving RIS. In this mode, RIS are detected indirectly through the use of a redox catalytic loop between a redox mediator activated by the SECM tip and the RIS present in the solution, as illustrated in Figure 1c for the feedback detection of  $\text{H}_2\text{O}_2$  from its oxidation by  $\text{Ru}^{\text{III}}$ . Even though  $\text{H}_2\text{O}_2$  is not strictly speaking a RIS, the strategy proposed could apply equivalently to RIS detection. The RIS ( $\text{H}_2\text{O}_2$ ) generated from a reaction of interest (either in the bulk or from a catalytically active NP) is revealed from its homogeneous reaction with a tip-electrogenerated redox mediator ( $\text{Ru}^{\text{III}}$  from a  $\text{Ru}^{\text{II}}$  solution in Figure 1c). This catalytic loop, often analyzed as an EC' mechanism, is probed by the catalytic tip current recorded for the redox mediator conversion [19–23]. It is sensitive to mass transfer of the RIS to the tip, which is controlled by the volume between the tip and an interface (either surface [21] or liquid/liquid [20]). The RIS are often detected experimentally by performing approach curves (variation of the tip-interface distance) and their concentration and lifetime can be quantified with the help of numerical simulation of the complex homogeneous reactions involved in the process [20,21]. The SECM tip can also work at fixed distance from the interface, in this case reactive intermediates with  $\tau$  in the ms range can be detected from current transients [19,23] or CVs [22]. To assess more unstable RIS and reach reaction occurring at the nanometer scale, a recent strategy proposed to confine the redox moieties in a thin layer coating the SECM tip, as illustrated in the inset of Figure 1c [24,25]. It further allows imaging indirectly the specific (electro)regeneration of the RIS at individual nanoparticles, as illustrated in Figure 1c [25].

Noteworthy, the G/C mode can also exploit such indirect detection of RIS produced from a substrate using a redox mediator either dissolved in the bulk, [26] or immobilized on the SECM tip (analogously to Figure 1c) [25]. This strategy was used to image the production of RIS both at the micrometer [26] and at the nanometer scale [25].



**Figure 1.** Illustration of the different SECM modes employed to investigate reactive intermediate species. a) generation/collection adapted from Ref. [10], b) nanopipette adapted from Ref. [15], c) feedback adapted from Ref. [24], d) foot printing adapted from Ref. [31] and e) surface interrogation adapted from Ref. [45].

Footprinting analysis (Figure 1d) is another indirect powerful methods to analyze local (electro)chemical reactions. A reactive footprint is performed by exposing a substrate modified by an organic coating [27,28] or self-assembled monolayers [29–32] to reactive intermediates, etchants, electrogenerated by a SECM tip. The reactivity between the reactive etchant and the organic layer leads most of the time to its irreversible local transformation (often destruction) producing a pattern with contrasted chemical functionalities. The footprint can be imaged post-mortem (SECM, AFM, condensation...) or operando (during its formation) using optical monitoring [33]. This methodology allows evidencing the bulk formation of reactive species [28] and to quantitatively characterize their reactivity with the layer [30–32] by analyzing the footprint expansion and/or width with the local electrogeneration time. It also allows studying competing reactions of the etchant or the layers with species present in solution such as radical scavengers [32]. Besides, this footprinting strategy can be exploited to develop methodologies and tools for the electrochemical micro/nanomachining of surfaces [34–36]. Noteworthy, the degradation of a layer deposited on the SECM tip by substrate-generated RIS is possible [33].

Finally, the SECM in the surface interrogation, SI, mode, illustrated in Figure 1e was widely employed to identify the formation of surface-bound RIS during photo(electro)chemical [37–40] or

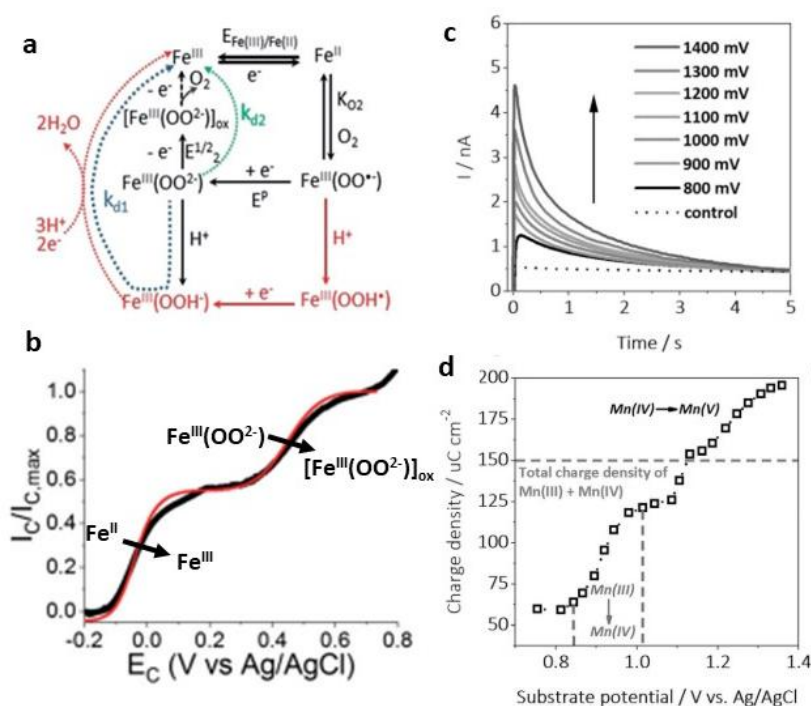
electrocatalytic processes [41–45]. Briefly, the SI-SECM operates in a transient feedback mode between two electrodes of comparable sizes. For instance, Figure 1e explores the ability of high-valent Mn oxides to catalyse the oxidation of water produced by a short oxidation potential pulse at a Mn-oxide substrate. While the substrate potential is returned to open circuit potential, the SECM tip, kept typically  $\sim 1 \mu\text{m}$  from the substrate, generates a titrant species (a redox mediator present in solution) which diffuses towards and reacts chemically (here is overall oxidized) with the surface species produced during the first step [44]. The SECM tip then provides a transient feedback current until the adsorbate has been entirely consumed. With the help of finite element simulation, such transient response yields the surface concentration of the reactive adsorbate. By carefully choosing the titrant redox potential, one can evidence the formation of different populations of surface RIS [41,45]. The SI-SECM can operate in cyclic voltammetry [41] to detect moderately RIS while chronoamperometry [37,39–46] grants access to highly RIS with ca.  $1 \mu\text{s}$  lifetime [42,43,45].

### Applications to electrocatalytic reactions

The different SECM modes described above were used to evidence the formation of many different RIS produced during various electrochemical processes. This is the case of reactive oxygen species (ROS) issued from the oxygen reduction reaction (ORR). For instance highly unstable superoxide ( $\text{O}_2^{\bullet-}$ ) ion in neutral pH aqueous media was evidenced [16]. It corresponds to 9% of the oxygen species reduced at Pt electrode, whereas its half-life was evaluated to be  $\sim 2 \mu\text{s}$ . Besides, the formation of very reactive hydroxyl radicals ( $\text{HO}^\bullet$ ) during the ORR on Prussian blue film [33], or on Pt microelectrode could be indirectly evidenced [28]. The production of  $\text{HO}^\bullet$ , also confirmed on Pt materials by EPR [4,47], may explain the nanoscale dissolution of Pt often observed during the ORR [48,49]. This very reactive intermediate was also identified indirectly during the ORR mediated, in a Fenton-like reaction, by a  $[\text{Cu}(\text{2CP-Bz-SMe})]^{2+}$  complex adsorbed on a gold surface [26]. ORR can also be triggered by organometallic complexes. It rather involves ROS in the form of adducts (as ligands of the metallic center). In the case of the reductive activation of  $\text{O}_2$  by Fe porphyrins in organic media (Figure 2A) [10], the SECM could only directly probe and quantify the  $\text{Fe}^{\text{III}}(\text{OO}^{2-})$  intermediates electrogenerated during the oxygen activation mechanism. Further numerical simulation of the LSV obtained at the SECM tip (red curve, Figure 2a), allowed extracting pertinent thermodynamic and kinetic parameters describing the overall catalytic cycle. With different ring-substituted porphyrin, such strategy offers structure–activity rationalization of the catalytic  $\text{O}_2$  activation in agreement with earlier DFT calculations [50]. By extension this strategy should be useful to study the different electrochemical activation pathways of small molecules ( $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ ).

Reactive radical intermediates are also involved in many complex redox catalytic reactions such as Belousov-Zhabotinsky oscillating reactions[21] or electro-chemiluminescence (ECL) [12,20,51], both of which were investigated by SECM. For the (BZ) oscillating reaction, a theoretical model involving a 11-reactions scheme allowed quantifying indirectly the concentration of reactive  $\text{BrO}_2^\bullet$  intermediates generated (down to  $7 \mu\text{mol L}^{-1}$  in a  $2 \mu\text{m}$  SECM gap) [21]. SECM could also demonstrate the ms lifetime of trialkylamine radical cations involved during anodic coreactant ECL [52]. These RIS are able to initiate new and strongly localized light emitting routes. They generate  $\mu\text{m}$  to  $\text{nm}$  localized ECL emission which can be imaged optically by footprinting the ECL RIS reactivity [53–55]. Besides amine coreactant oxidation, the oxalate oxidation process was quantitatively deciphered [12]. It required extremely small tip-substrate SECM gaps,  $d \approx 50\text{--}500 \text{ nm}$ , for the formation of the  $\text{C}_2\text{O}_4^{\bullet-}$  intermediate

with  $\tau=1.3 \mu\text{s}$  to be probed within gaps  $d < 73\text{nm}$ . Its later decomposition into  $\text{CO}_2^{\bullet-}$  was then revealed at longer distances,  $73\text{nm} < d < 500\text{nm}$  [12]. The detection of the latter RIS is promising for the investigation of  $\text{CO}_2$  reduction ( $\text{CO}_2\text{RR}$ ). The SECM could indeed trap  $\text{CO}_2^{\bullet-}$  formed during the  $\text{CO}_2\text{RR}$  within a sub-micro gap distance [11] allowing to determine its formal potential ( $E^0$ ), its heterogeneous formation rate constant ( $k^0$ ) and its dimerization rate ( $6.0 \times 10^8 \text{M}^{-1}\cdot\text{s}^{-1}$ ).



**Figure 2.** a) Mechanistic scheme of  $\text{O}_2$  activation by iron porphyrin deciphered by SECM, and b) the LSV recorded at the SECM tip showing the collection of the reaction intermediates adapted from Ref. [10]. c) Reductive titration of MnV and MnIV to MnIII intermediates generated during transient pulse of OER (Figure 1e) and d) corresponding integrated charge density showing the different species detected and their apparent predominance potential zone adapted from Ref. [45].

The SECM was also used to identify adsorbed RIS involved in the electrocatalytic oxygen evolution reaction (OER) using the SI-SECM mode [41–45]. Extensive studies of the reactive metal oxide RIS involved in OER electrocatalysis were proposed, such as cobalt [41,42], nickel/iron [43] or manganese [45] based catalysts. The different intermediates participating in the OER triggered by microelectrodes substrates coated with these catalysts were identified from the current transient associated to the conversion of redox titrant generated at the SECM tip (Figure 1e). It is illustrated in Figure 2c for the titration of Mn-oxide intermediates produced at different substrate potential. From the charge density extracted for each transient, the authors could draw nanoscale Pourbaix diagram showing the potential predominance and surface concentration in  $\text{Mn}^{\text{IV}}$  and  $\text{Mn}^{\text{V}}$  intermediates within electrochemically polarized amorphous  $\text{MnO}_x$  (Figure 2d).[45] Moreover, the quantitative analysis of the reaction rate between the catalysts intermediates and the water offered the possibility to determine the best environment needed to optimize the reactivity of the catalysts. The strategy is sound for benchmarking different OER electrocatalysts based on RIS identification. For example, the best OER kinetics with  $\text{Fe}^{\text{IV}}$  catalytic sites in  $\text{NiOOH}$  was obtained with a  $\text{Ni}_{0.82}\text{Fe}_{0.18}\text{OOH}$  structure. [43] Similarly,  $\text{Mn}^{\text{V}}$  sites were found to be more active in  $\text{CaMnO}_3$  Pervoskite than in amorphous  $\text{MnO}_x$  for which two different reactive  $\text{Mn}^{\text{V}}$  sites were proposed [45]. The strategy was extended to the identification of molecular RIS, such as surface-adsorbed ROS electrogenerated



during the OER at sp<sup>2</sup> carbon-containing BDD electrodes. the formation of at least two ROS was evidenced, one forming two orders of magnitude faster than the other but displaying a slower desorption rate [44]. If at that point the two populations of intermediates remain unknown, the role of pH and electrolyte on their surface concentration and reactivity was demonstrated. It opens interesting routes toward the study of other molecular RIS issued from other electrocatalytic reactions (ORR, HER, CO<sub>2</sub>RR..)

## Conclusions and outlooks

In this review, we demonstrated that confined environment in SECM configuration is a perfect condition to probe reactive intermediates involved in various (electro)chemical processes. The different methodologies of the SECM (Feedback, Generation/Collection, nanopipette, footprinting, and SI-SECM) already offered the possibility to probe numbers of reactive intermediates either generated on surfaces or in solution. The recent works have more particularly extended the limit of detection, enabling low concentrations and very low lifetimes (down to sub- $\mu$ s) ones. They also adapted to the description and understanding of more complex mechanisms involved in the electrocatalytic activation of small molecules through the ORR, OER and CO<sub>2</sub>RR or in ECL reactions. In the former case, detecting reaction intermediates is promising for the exploration of new mechanistic schemes, particularly in the field of molecular electrochemical activation of small molecules (O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, CO<sub>2</sub>) [56]. In the latter case, it has enabled the definition of ECL imaging modes, by visualizing optically the footprint of the reaction of the RIS, with continuous improvement of the limit of detection [53,57,58]. Beyond SECM micro/nanotip, other electrochemical nanoprobes such as nanopipettes are actively developed, allowing the confinement of a chemical reaction in femtomolar volume. For instance, through the confinement of a meniscus droplet, scanning electrochemical cell microscopy was able to probe reactive intermediates by producing nanoscale footprints on surfaces [59]. It is a promising tool for analyzing surface intermediates in electrocatalysis or corrosion sciences [60,61]. Nanopipettes can also be used as nanosamplers [62,63] or used as nanopores [64,65]. The possibility to produce a bipolar electrode at the mouth of the pore [65], opens promising routes for the combined production and detection of very reactive species. Besides, efforts should be made to generalize RIS probing strategies or their benchmarking. To this end, micro/nanofabrication offers a solution for the mass production of nanoelectrochemical devices. Indeed, nanofabricated electrochemical ring-disk nanocavities are touching single enzyme electrochemical activity with further possibility of optical monitoring [64] whereas nanofluidic electrochemical devices have already shown their ability to explore the role of adsorption in single (bio)molecule electrochemistry [66,67].

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