Studying Electrocatalytic Activity Using Scanning Electrochemical Microscopy

by Carlos M. Sánchez-Sánchez

The use of single crystal electrodes in electrocatalysis have allowed researchers to understand some of the elementary steps in different reactions and to establish some relationships between the activity of an electrocatalyst and its surface structure. But the precise identification of the particular type of crystallographic site on a nanoparticle sized electrocatalyst where the reaction takes place at a higher rate (steps, kinks, or basal planes) still represents a challenge.

Scanning electrochemical microscopy is an excellent tool for studying electrocatalytic reactions at the nanometer scale, although it has not been much utilized for this purpose. So far, most of the electrocatalysis studies reported using SECM are mainly focused on the relationship between bulk chemical composition and electrochemical activity. This article presents some examples of electrocatalytic reactions studied by SECM using the tip generation-substrate collection (TG-SC), substrate generation-tip collection (SG-TC), redox competition (RC), and micropipette delivery-substrate collection (MD-SC) modes of SECM.

Electrocatalytic reactions[1] are generally considered heterogeneous inner-sphere reactions, where the reactants, intermediates, and/or products are specifically adsorbed on the electrode surface, allowing a decrease in the reaction energetic barrier. A variety of crystallographic sites may be present at the surface of each single crystal electrode as shown in Fig. 1. In the early 1980s, the use of single crystal electrodes in electrocatalysis was well established, thanks to the flame annealing cleaning method developed by Clavilier, *et al.,*[2] which facilitated obtaining a reproducible electrochemical response at single crystal electrodes while ensuring proper control of the type of site available on the surface. The use of single crystal electrodes, which, for instance in the case of platinum electrodes, need only three numbers to define the corresponding crystallographic Miller indexes (namely (111), (100), and (110)) for the three platinum basal planes, have allowed researchers to understand some of the elementary steps in different electrocatalytic reactions and to establish relationships between the electrocatalyst activity and electrocatalyst surface structure.[3] While a majority of these studies have been primarily devoted to the comparison of the three low-index Pt basal surfaces, efforts have also been made to study mixed surfaces — *i.e.,* surfaces with (111) terraces separated by monatomic (110) steps or surfaces with (110) terraces and (111) steps — to identify the most active site

at the electrode surface. All these studies have exhibited some limitations due to the difficulty associated with scaling up the single crystal electrode fabrication process.

Given the rapid development in the syntheses of nanomaterials, understanding particle size and surface structure effects on the electrocatalytic activity of unsupported and supported nanoparticles has become the next frontier in electrocatalysis. Nanoparticle electrocatalysts are very versatile and can be readily scaled for industrial applications. The electrocatalytic properties of nanoparticles are primarily determined by a set of physical parameters that include particle size, chemical composition (at the surface and in the bulk), and particle shape/surface structure. In particular, the effect of the crystallographic domains (facets) at the surface of the nanoparticles is currently a hot topic. The effect of the particle shape and, consequently, surface atomic arrangement and coordination, assumes particular importance given the significant progress in the synthesis of shape-controlled metal nanoparticles that has been achieved over the past decade.

Is it possible to investigate the catalytic activity provided by one single atomic step or kink on the surface of a catalytic nanoparticle? Identifying the particular zone on a single nanoparticle where the specific adsorption occurs during the redox reaction and where the activity is maximum for each particular electrocatalytic reaction would definitely help develop the surface structure versus reactivity relationship in electrocatalysis. This knowledge, if acquired at the nanometric scale, would be of considerable interest for further elaboration and design of future electrocatalytic nanomaterials. The unique

features of SECM[4] make it an attractive tool for studying electrocatalytic reactions at the nanometric scale.

The development of the SECM[5] in the late 1980s introduced a powerful electroanalytical probe technique based on the feedback current recorded when a redox mediator diffuses within the gap between an ultramicroelectrode (UME) acting as a tip, and a substrate of interest. This technique provides the great advantage of being able to map the chemical reactivity of the substrate material. In the past decades, several modes of actuation in the SECM have been developed beyond the initial feedback mode. Some of them are perhaps more relevant to surface characterization than to electrocatalysis. For instance, the surface interrogation (SI)[6] mode of the SECM is based on the generation of an electroactive titrant species at the tip electrode and the feedback current produced due to the chemical titration of the species adsorbed on the substrate. This technique represents one of the most relevant methodologies currently available for detecting and quantifying adsorbed species at micro-sized electrodes. More recently, Trinh, *et al.,*[7] have also developed the SECM in AC mode for the quantification of adsorbed reaction intermediates. While those two modes of the SECM are not commonly used for studying electrocatalytic activity, others modes have provided significant results. Table 1 summarizes some of them and includes the particular electrocatalytic reaction studied along with specific references.

More than one mode of the SECM has been utilized to extract the maximum amount of information and, in some cases,
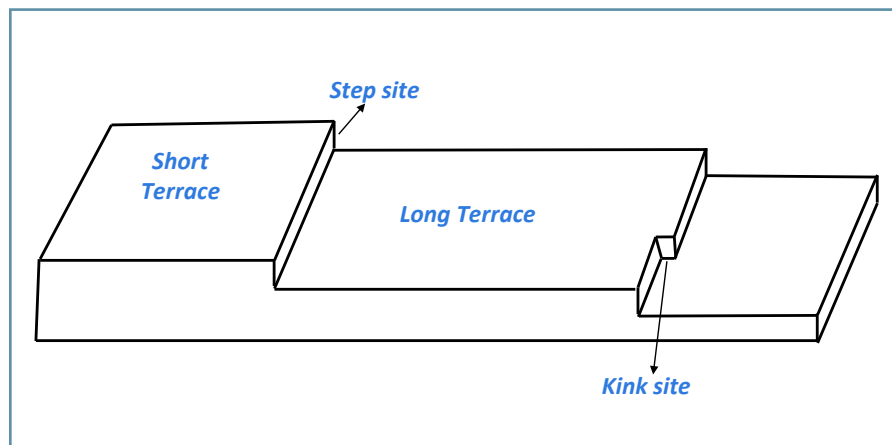
Fig. 1. *Scheme of the different type of sites on a single crystal electrode surface.*

to overcome the particular limitations. For instance, the generation-collection modes of SECM are not useful if reactant species of interest cannot be electrochemically generated in solution. Thus, in principle, the different modes of the SECM shown in Table 1 can be divided in two main groups: i) Modes based on electrochemically generated reactants, which include tip generation-substrate collection (TG-SC), substrate generation-tip collection (SG-TC), and redox competition (RC) modes, and ii) Modes based on non-electrochemically generated reactants, namely the micropipette delivery-substrate collection (MD-SC) mode.

In the TG-SC mode, a constant current or potential is applied to an UME tip to electrogenerate a constant flux of the species of interest. Then, the UME generator tip is brought close and held at a constant distance above an electrode array formed by different electrocatalyst nanoparticles and is scanned in the *X-Y* plane. The electrode array is held at a suitable potential to facilitate the electrocatalytic reaction of interest. An example of this type of SECM imaging is shown in Fig. 2. Panel A shows an optical image of a typical substrate electrode comprising two groups of nanoparticles deposited on a conductive current collector (in this case glassy carbon). Panel B displays the substrate current recorded as a function of tip position for the corresponding TG/SC image. The SECM image in Fig. 2 was obtained by generating H_2 under diffusion controlled conditions at the UME tip while scanning the tip in the *X-Y* plane at a constant distant from a substrate surface held at a potential suitable for performing the hydrogen oxidation reaction (HOR).

In contrast, the SG-TC mode has been mainly employed for obtaining mechanistic information such as the number of electrons transferred during the reaction on a given electrocatalyst, or for detecting short lifetime reaction intermediates. But applicability of this mode for electrocatalyt screening is limited because it does not strictly facilitate a time independent measurement; the diffusion layers of neighboring electrocatalysts may overlap as a function of time and the information collected by the tip sensor may be distorted. In spite of this limitation, this mode has been successfully employed for comparing the electrochemical activity of large bi-dimensional doped and undoped electrocatalyst coatings.[8] The SG-TC-shielded tip approach represents the unique case where this SECM mode has been successfully applied for the screening of different combinatorial electrocatalysts. In this approach, the UME tip outer walls are metal coated and connected under potentiostatic control to allow them to serve as a "drain" for the product generated by the electrocatalyst particles neighboring the nanoparticle under interrogation.

Table I. Some relevant electrocatalytic reactions already studied by SECM.
*(SG-TC) substrate generation-tip collection, (MD-SC) micropipette delivery-substrate collection, (TG-SC) tip generation-substrate collection, (RC) redox competition.

| Electrocatalytic Reactions	Reaction Abbreviations	SECM Modes*	References
$2H_2O \longrightarrow O_2 + 4H^+ + 4e$	OER	(SG-TC) (SG-TC-Shielded)	Näslund, *et al.*[8] Minguzzi, *et al.*[9]
$HCOOH \longrightarrow CO_2 + 2H^+ + 2e$	FAOR	(MD-SC) (TG-SC)	Lin, *et al.*[10] Jung, *et al.*[11]
$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e$	MOR	(MD-SC)	Lin, *et al.*[10]
$O_2 + 4H^+ + 4e \longrightarrow 2H_2O$	ORR	(TG-SC)	Fernandez, *et al.*[12] Sánchez-Sánchez, *et al.*[13]
$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$		(RC) (SG-TC)	Eckhard, *et al.*[14] Shen, *et al.*[15] Sánchez-Sánchez, *et al.*[16]
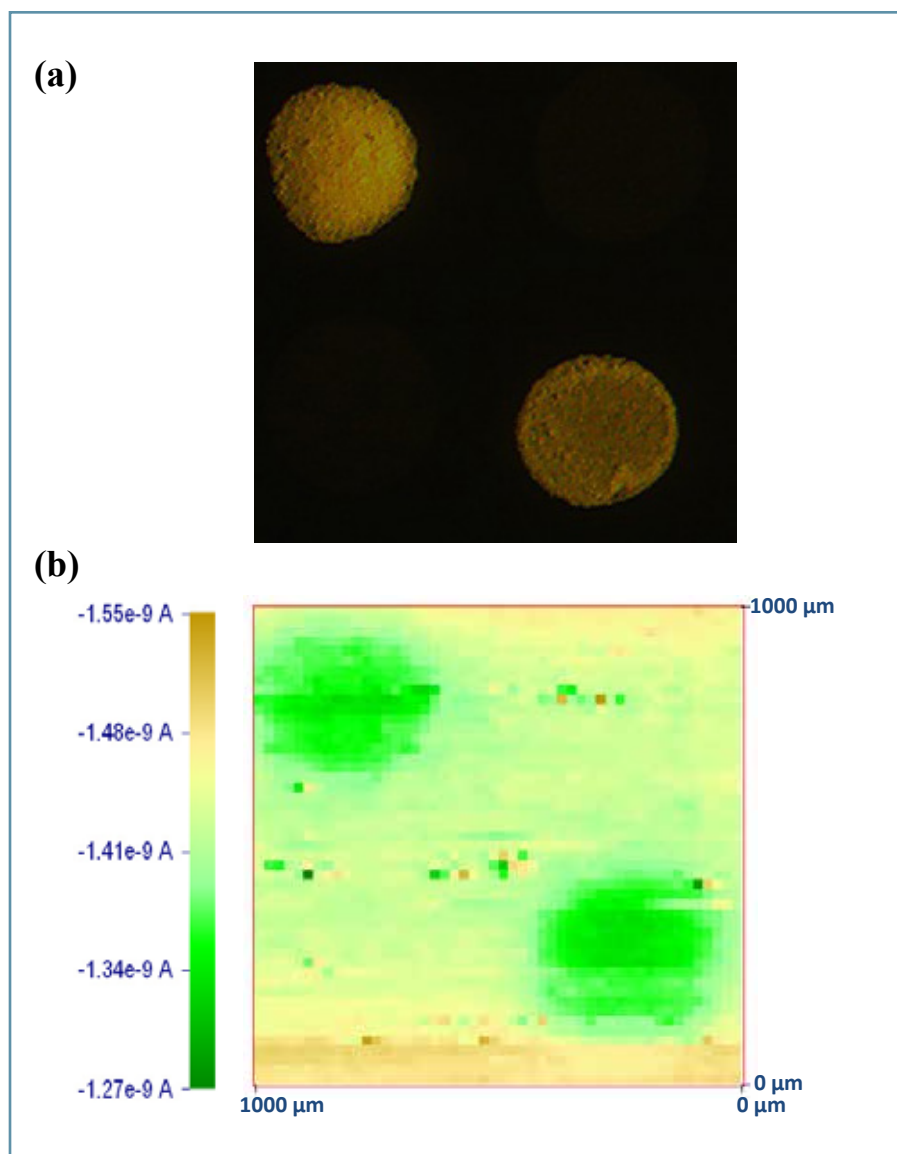
FIG. 2. *Equivalents optical and SECM images are shown in the upper and lower panels (a) and (b), respectively. The SECM TG/SC image displays the oxidation current collected at the substrate, meanwhile the tip scans its surface generating a constant flux of H_2.*

A couple of other SECM modes are worthy of mention. In the RC mode, both the tip and substrate are held at a potential that facilitates the electrochemical reaction of interest, allowing them to compete for the same electroactive species in solution. A predefined potential pulse profile at the SECM tip, which includes a regeneration step, is employed during the tip scanning process to avoid complete depletion of the species of interest. Finally, the MD-SC mode represents a paradigm wherein the reactants are not electrochemically generated. Herein, the different reactant of interest is delivered to the vicinity of an electrocatalyst array (held at appropriate potential) by scanning a micropipette over the X-Y plane at a constant tip-substrate distance. The resultant substrate current is recorded to yield a reactivity map.

Finally, SECM has been used to study the effect of surface structure on the activity of nanomaterials used in electrocatalytic reactions and has been shown to be a great technique to successfully translate single crystal electrode results to electrocatalysts based on shape-controlled platinum[13] and gold[17] nanoparticles. Activity trends in nanoparticle catalysts that are similar to established single crystal results have been demonstrated in several electrolytes using SECM. It has been unequivocally shown that the most active site/facet on the nanoparticle surface is identical to those identified in single crystal electrode studies. This finding opens up the door for designing new synthetic strategies to maximize a desired type of site/facet on the nanoparticle surface. It must be noted that all these studies devoted to extracting information about electrocatalytic reactions taking place on shape-controlled nanoparticles have employed a group of nanoparticles spread onto an conductive current collector and do not correspond to the interrogation of a single type of site or a single nanoparticle. Hence, the catalytic information extracted from these measurements corresponds to the average behavior of a group of nanoparticles and not the unique behavior of a single nanoparticle.

To summarize, this article reviews progress on the use of SECM to study electrocatalytic reactions, paying special attention to studying the surface structure effect on nanoparticles and translating of single crystal electrode results into electrocatalysts based on shape-controlled nanoparticles. SECM currently does have some limitations in terms of resolution of the interrogated nanometric domains. Hence, in the future, it will be necessary to develop new combined electrochemical probe techniques and nanoprobes to overcome said limitations and perhaps approach probing electrocatalysis at the surface of a single nanoparticle.

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About the Author

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