



Short communication

The cavity-microelectrode as a tip for scanning electrochemical microscopy

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ABSTRACT

In this work, we present and discuss the use of cavity-microelectrodes (C-MEs) used as tip for the scanning electrochemical microscopy (SECM). Cavity-microelectrodes can be filled with a desired finely dispersed material thus compensating for the limited commercial availability of microwires. After discussing the possibility of filling and emptying a cavity-microelectrode with a desired tip shape, the consistency of negative and positive feedback approach curves obtained after filling a Au C-ME was verified. In addition, the tip/C-ME was tested under gas (oxygen) evolution condition, in order to demonstrate that the filling is stable in a wide range of gas fluxes thus extending the possible applications to tip generation/substrate collection mode. Finally, we introduce the use of the proposed system to quantify the rates of parallel reactions occurring at the material inserted in the tip under the tip generation/substrate collection mode.

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1. Introduction

Scanning electrochemical microscopy is undoubtedly one of the most rapidly developing electrochemical techniques for its versatility and in turn for its wide range of applications [1,2].

In the most typical SECM configuration, a disk microelectrode, the tip, is positioned in the solution with the metallic surface parallel to the sample of interest (the substrate) and can be moved in three dimensions thanks to the use of stepper or piezoelectric motors.

Tip and substrate, whose relative distance under operation conditions is typically less than one tip radius, have electrochemical potentials independently controlled by a bipotentiostat in a 4-electrode cell, that includes also a counter and a reference electrode [3]. The tip can be used as a probe, as a sensor, or as local generator of a reactant. SECM has an extremely wide variety of modes, depending on the experiment aim: determination of rate constants, screening of catalysts libraries, surface interrogation of reaction intermediates, study of semiconductor electronic configuration and so on.

In many cases what limits the possibilities of the techniques is the nature of the tip and its dimensions but a way to rapidly build a tip made of the material of interest is still missing. The nature of micrometer-sized wires useful to build tips is limited to a few metals (Au, Pt, Ag...) and carbon fibers (the latter harder to handle, leading to irreproducible tips). This limits the possibilities of SECM and can lead to uncertain results or

force the researchers to time consuming procedures to prepare custom tips. To give a few examples, in the screening of oxygen reduction reaction catalysts most researches adopted Au tips to locally produce oxygen at a constant rate while the tip screens the catalysts libraries [4]. However, Au dissolves under oxygen evolution reaction (OER) conditions and the catalyst library likely covers with a layer of Au. Notwithstanding Au is not a good catalyst for ORR, the presence of an undesired metal on the surface can in principle modify the materials features.

In another case, a Mn tip was desired but the researches needed to manually produce a Mn wire [5], that is not commercially available.

For all the above mentioned reasons, we here discuss the possibility of using cavity-microelectrodes as tip for the SECM. C-MEs consist in a micrometer-sized empty cylinder with glass walls and metallic bottom and can be easily and quickly filled with any powder of will. Cycles of C-ME filling/emptying with the same powder lead to highly reproducible results [6].

For these reason, C-MEs have been used in the last years to study materials in a wide range of applications: catalysts, batteries, enzymes, supercapacitors and so on [7].

Recently, the possibilities of C-MEs have been widened by showing that they can easily lead to quantitative analysis [8], for quantitative rapid screening [6] and for fine electrochemical characterization [9] thanks to the knowledge of the amount of material inserted in the cavity. C-MEs are typically prepared by recessing a metallic microdisk. The most commonly used materials are Pt, that is etched by hot aqua regia and Au, that can be etched by electrochemical dissolution in Cl⁻ or CN⁻ baths. The quality of C-ME geometry is improved using Au and

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the electrochemical dissolution that guarantees the dissolution kinetics. In turn, Au C-MEs lead to a more precise and accurate quantitative analysis [10] and allowed electrochemical noise measurements on oxygen evolution reaction electrocatalysts [11]. Very recently, double barrel C-MEs have been used to contain a catalyst sample and a reference one to precisely compare water oxidation onset potentials [12]. About the use of cavity-microelectrodes in SECM, Bard's group has already shown the preparation and use of etched microelectrodes as support to create carbon paste SECM tips [13]. Therefore, this work aims to explore in more details the possible use of C-MEs as SECM tips to be used in different modes: feedback, tip generation/substrate collection and substrate generation/tip collection. The possibility of conveniently studying parallel reactions occurring at a desired powder electrode material is also here introduced.

2. Materials and methods

C-ME tip preparation: A 25 μm radius gold wire (Goodfellow, 99.99% purity) was sealed into a flint glass capillary O.D./I.D 1.5/0.75 mm (#27-37-1, Frederik Haer & Co, Bowdoinham, ME) under vacuum. One end was then polished with 800 mesh sandpaper until the metal disk was exposed, then smoothed with 1000, 2400 and 4000 mesh abrasive paper and alumina suspensions in water down to 0.25 μm . Finally, the tip was sharpened, reaching the desired RG (ratio of glass to metal radius). A Ag conductive paste (Leit-silver, Aldrich) cured overnight at 80 $^{\circ}\text{C}$ was used to ensure the electric contact between the gold wire and a copper wire.

To recess the Au tip, we here update the procedure initially introduced in [10]: a galvanostatic square wave current profile (double step, DS) between +1.5 and -7 mA cm^{-2} in aqueous 0.5 M NaCl + 0.5 M HCl + 0.5 M H₂SO₄. The anodic step lasts twice than the cathodic one and the cycle frequency is 0.00028 s⁻¹. After the etching, the cavity bottom is made regular by cycling its potential (500 cycles at 500 mV s⁻¹) in the same solution between 0 and 1.1 V vs. Ag/AgCl (in 3 M KCl).

After the etching, the depth of the recess, l (μm), is determined as described in the literature [8,10,14]. In the case of the C-ME tip described and used in the present work, $l = 25.3 \mu\text{m}$ or $l = 60.0 \mu\text{m}$ (Fig. 2c and 4).

The cavity is now ready to be filled with the desired material by using the former as a pestle and then clean the glass surface from the powder excess with a piece of paper.

3. Results and discussion

Fig. 1 reports a picture of a filled C-ME Tip with RG between 5 and 6 filled with Vulcan XC72R (Cabot).

Note that the cavity filling does not extend beyond the cavity edge and this is likely at the bases of the filling reproducibility [6]. Observing

the tip at the microscope after each filling guarantees that the powder does not protrude from the cavity.

As a SECM tip, the electrode should fulfill the expected behavior of positive/negative feedback approach curves.

Therefore we filled a C-ME tip with Vulcan[®] XC72R (Cabot), immersed the electrode in a 0.1 M KClO₄ aqueous solution containing 1 mM ferrocenemethanol and approached it towards a substrate formed of a Pt disk embedded into plastics ($E_{\text{tip}} = 0.4 \text{ V vs. Ag/AgCl}$). In Fig. 2A and B, experimental approach curves are superimposed to the relevant fitting curves, the latter calculated using the conventional empirical equations [2].

The good correspondence of experimental results and predicted tip currents shown in Fig. 2A, B suggests that C-ME tips can be used in SECM for positioning and feedback experiments. This remains true until tip and substrate reactions are controlled by mass transport and the electroactive species reacts exclusively at the outer surface of the tip (i.e. more in proximity of the solution bulk). This effect was previously observed by us [10] and simulated by Barnes et al. [15], the latter having modeled the chronoamperometric behavior of a porous electrode on which a mass transport control reaction occurs. In this work, the authors observe an initial period in which thin layer diffusion within the layer sums to planar/semi-infinite one. After that, the reagent within the porous media is consumed, and the porous bed behaves like a planar electrode (follows Cottrell equation) where only the outer surface is electroactive. This model can be safely applied to the C-ME, provided that a mass transport controlled reaction is conducted at a conductive powder.

In fact, even changing the C-ME filling with another sufficiently high conductivity material like Co₃O₄ ($\sigma = 10^{-3}$ – $10^{-4} \Omega^{-1} \text{ cm}^{-1}$ [16]), the response is as expected: as shown in Fig. 2D, a feedback image recorded at the Pt/plastics boundary in ferrocenemethanol but with the tip filled with commercial Co₃O₄ (Sigma Aldrich) shows a high contrast between the conductive area (Pt, green) and the insulating one (plastics, red). Fig. 2D represents a proof of concept of the effectiveness of the C-ME as tip in one of the most conventional SECM experiments: a feedback image.

The choice of Co₃O₄ comes also from the need of having a good oxygen evolving catalyst as will be discussed in the following.

On the other hand, in the case of charge transfer controlled reaction at the tip, the C-ME likely behaves as a three-dimensional electrode, with the reacting species allowed to partially penetrate inside the cavity. This implies that the empiric equations used to fit approach curves for diffusion controlled systems are no longer useful and a new empirical equation is needed. This is the case of a tip (with $l = 60 \mu\text{m}$) filled with Co₃O₄ approached towards a Pt substrate in 0.1 M NaOH using dissolved oxygen as the redox mediator ($E_{\text{tip}} = -1.0 \text{ V vs. Ag/AgCl}$, that is less negative than water reduction onset). Oxygen reduction

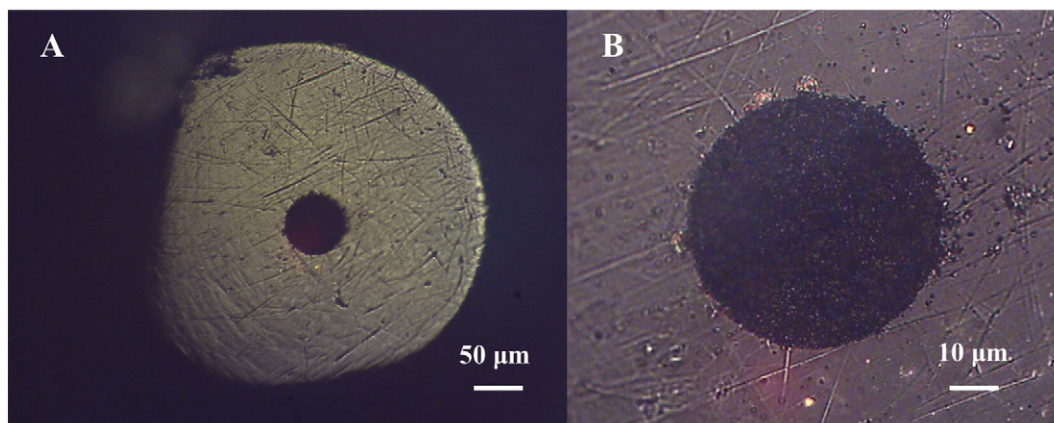


Fig. 1. Optical images of a 25 μm radius Au cavity-microelectrode filled with Pt/C at two different magnitudes.

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