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Scanning Electrochemical Microscopy: Methodology for Construction of Ultramicroelectrodes with an Automatic Micropipette Extruder

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Abstract

Nowadays, in the Corrosion Research Centre (CICORR) of the Autonomous University of Campeche, an electrochemical characterization route is being developed using the Electrochemical Scanning Microscopy technique (SECM). It is been used on different systems oriented to the study of localized corrosion. This requires the construction of the ultramicroelectrodes (UME); which are essential instruments for the technique application; through which is possible to study high resolution electrochemical processes in the interface of a substrate in solution; by visualizing the electrochemistry of topographies and surface reactivities and films. The ultramicroelectrodes construction is performed quickly and systematically using an automatic micropipette extruder Sutter Instrument P-1000; by previously defining the glass characteristics, filament type and ultramicroelectrode type to be obtained. Based on this, the equipment can be programmed minimizing errors for the required purposes. Subsequently, the properly manufactured instruments are subjected to the respective calibration process.

Keywords: Ultramicroelectrodes, SECM, Localized Corrosion.

Microscopía Electroquímica de Barrido: Metodología para la Construcción de Ultramicroelectrodos con un Extrusor Automático de Micropipetas

Resumen

Actualmente, en el Centro de Investigación de la Corrosión (CICORR), de la Universidad Autónoma de Campeche, se está desarrollando una ruta de caracterización electroquímica utilizando la técnica de Microscopía Electroquímica de Barrido (SECM), en diferentes sistemas orientados al estudio de la corrosión localizada. Esto requiere la construcción de ultramicroelectrodos (UME); instrumentos fundamentales para la aplicación de la técnica a través de la cual es posible estudiar procesos electroquímicos de alta resolución en la interfaz de un sustrato en solución, visualizando la electroquímica de topografías y reactividades de superficies y películas. La construcción de los ultramicroelectrodos se lleva a cabo de forma rápida y sistemática utilizando un extrusor de micropipetas automático Sutter Instrument P-1000, definiendo previamente las características del vidrio, tipo de filamento y tipo de ultramicroelectrodo que se desea obtener. En base a esto, el equipo se puede programar minimizando los errores para los fines requeridos. Posteriormente, los instrumentos debidamente fabricados se someten al proceso de calibración respectivo.

Palabras clave: Ultramicroelectrodos, SECM, Corrosión Localizada.

Introduction

The scanning electrochemical miscroscopy (SECM) technique allows the study in high resolution of the electrochemical processes that occur at the electrified interphase substrate-electrolyte, visualizing the electrochemistry of topographies and reactivities of surfaces and films. For this purpose, the ultramicroelectrodes (UME), topographic sweep scan probes previously constructed, are used. The procedure is based on small movements of the tip thereof under potentiostatic or potentiodynamic operation [1]. The ultramicroelectrodes (UME) can have ion-selective tips according to the required purposes and can detect the reactions that occur in close proximity to the studied surface, obtaining images of chemical reactivity thereof and quantitative measurements of the reaction rates [2-3].

The complete electrochemical equipment consists of a digital signal generator/plotter computer with the integrated CHI 12.26 software, three-dimensional movement piezoelectric/nano-positioner, with maximum spacing distance of 50 mm; a bipotentiostat/galvanostat with data acquisition circuits of high resolution, range of ± 10 mV and ±250 mA up to the order of the picometers; and a three-electrode measuring cell [3].

The goal is the construction of ultramicroelectrodes through an automated process, using an automatic micropipette extruder; whih is generally employed for the micropipettes construction with medical or biological uses; reprogramming the equipment for the required purposes.

Experimental Section

Automatic Micropipette Extruder Sutter Instrument P-1000

As a fundamental step for the technique development, the ultramicroelectrodes (UME) must be designed and manufactured [2-3]. The construction involves the manufacturing of a glass scanning probe in a fast and systematized way, using an automatic Sutter Instrument P-1000 micropipette extruder [4]. The equipment performance is focused on the ultramicroelectrodes construction (UME) used in electrochemical measurements by the scanning electrochemical microscopy technique (SECM). The glass characteristics, the filament and the capillaries type, are previously determined and specified. Based on this, the equipment is programmed minimizing errors for the required purposes through a color touch screen that provides an intuitive interface and has a library of previously loaded programs and the option of programming new instructions for the construction of micropipettes, quickly and automatically.

Ultramicroelectrodes and Scanning Electrochemical Microscopy, CH Instruments CHI920C

The performance of the CHI 12.26 software associated with the operation of the scanning electrochemical microscope is tested through a dummy cell or dummy electrochemical cell, with a resistance of 100 KΩ, selecting a potential range of 0.5 V to -0.5 V with a series of commands and help parameters in the configuration menu. Subsequently, a piezoelectric/nano-positioner is calibrated with an installed ultramicroelectrode (UME) previously manufactured, immersed in a solution of 1 mM ferrocemethanol plus 0.1 M KNO_3. This compound is soluble in water, has a reversible redox reaction with reproducible data and does not contaminate the microelectrodes tip. A small flat platinum disc is used as a working electrode and is inserted into the electrochemical microcell of the scanning electrochemical microscope. A saline bridge, a counter electrode and the Ag/AgCl reference electrode are connected. The solution is poured into the teflon cell. The ultramicroelectrode tip (UME) is positioned close to the substrate surface with help of the XYZ movement command from the software options menu, avoiding the impact and breaking of the ultamicroelectrode tip on the metal surface (Figure 1). When the tip is fairly close to the surface, cyclic voltammetry curves are obtained to characterize the recorded potential values at both, the ultramicroelectrode tip and the test substrate. These data are used as base for subsequent generation of the Approach Curves (PAC) [5].

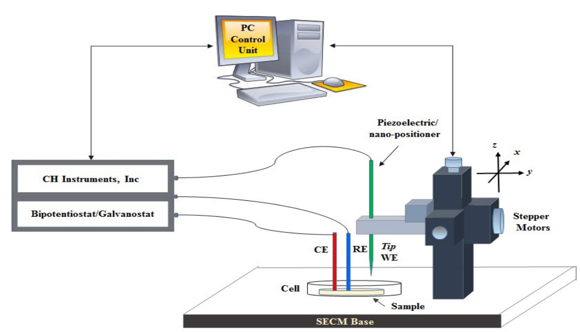

Figure 1. Scanning electrochemical microscopy CH Instruments CHI920C. Scheme of the experimental device for scanning electrochemical microscopy.

Results and Discussion

Extruder Sutter´s Calibration

The extruder calibration consists in determining the ramp temperature. The breaking of the borosilicate glass capillary introduced into the heating jaw of the equipment will be reached. This temperature guarantees a clean and fast capillary breakage after a few seconds. The ultramicroelectrodes with more resistant cones were obtained at 525°C ramp temperature.

Ultramicroelectrodes (UME) Construction

The characteristics of the used borosilicate glass pieces are 4± 0.125 cm in length, with internal diameter of 1± mm and external diameter of 2±0.05 cm, King Precision Glass, Inc. brand. Inside it a platinum fiber of 10 mm is introduced. A 4 mm^2 square heating jaw is installed into the equipment as a resistance for heat transfer. A piece of glass is positioned and aligned in the center of the jaw, supported horizontally by special screws. Subsequently, it is inserted through it. The chamber humidity is controlled and determined if the capillary is correctly aligned from left to right. For the software equipment, the necessary characteristics to be obtained are set and identified: glass type of the capillaries, filament type and micropipette type. Next, an adequate program will be identified and available for use, minimizing errors and simplifying the equipment programming for the required purposes. Later, an adequate program will be identified and available for use, minimizing errors and simplifying the equipment programming for the required purposes. If the pre-loaded specifications are not adequate, the parameters for automatic programming could be determined based on trial and error tests, until the necessary pipettes are obtained. An interactive screen is programmed with the previously determined parameters. These parameters must be the heat of the jaw or ramp temperature (°C), pushing force (pull), rate or velocity (units/ms), pressure (psi), waiting time or delay for the separation (ms), capillaries characteristics and used glass type. When the equipment has been calibrated and all the necessary parameters has been programmed, the micropipettes can be produced. Immediately, after several cycles of heat and force application, the glass can be separated in two identical pipettes, which will potentially be ultramicroelectrodes (UME) used for characterization with scanning electrochemical microscopy (SECM). The electrical connection is made using a copper fiber and silver conductive epoxy resin, Atom Adhesive brand, model AA DUCT 2979. Subsequently, properly manufactured ultramicroelectrodes are subjected to a review and calibration process. Figure 2 shows the scanning electron microscopy micrographs of micropipettes characteristics for ultramicoelectrodes, manufactured automatically with the Sutter Instrument Model P-1000. The images were taken with a Scanning Electron Microscope Hitachi FlexSEM 1000, at accelerating voltage 5 kV and magnification of 25x.

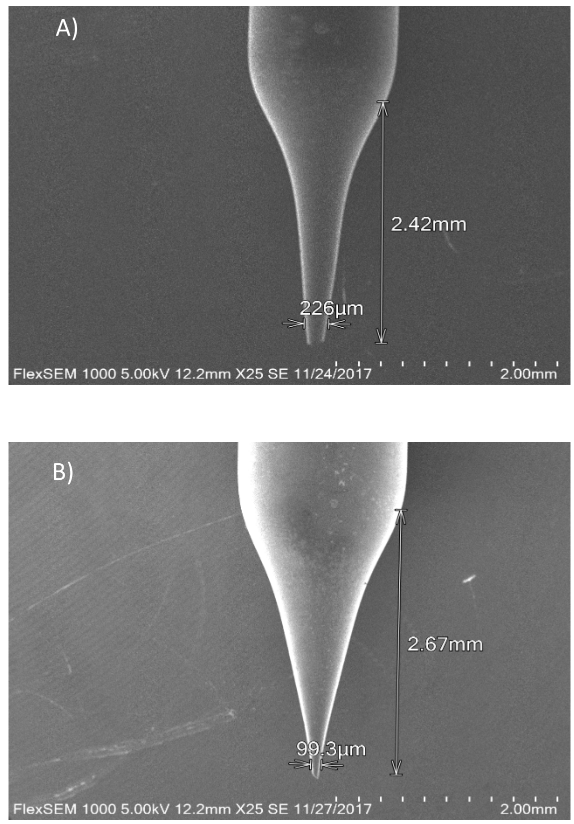

Figure 2. Scanning Electron Microscope micrograph of a micropipette with: A) Short cones, thin and elongated tips, thin borosilicate glass, low resistance. B) Short cones and wide tips, thin borosilicate glass, high resistance.

The characteristic configuration of most desired tips are those that have a cone shape with high mechanical resistance which allows the micro-electrode interacting propperly with the substrate during the electric current application by the bi-potentiostat. As well, Figure 3 shows photos of the final manufactured product of ultramicroelectrodes samples.

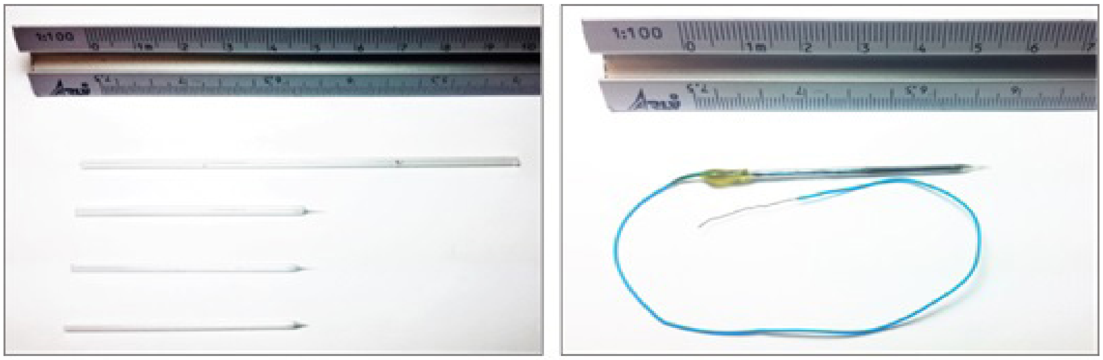

Figure 3. Ultramicroelectrodes (UME) manufactured automatically with the equipment Sutter Instrument Model P-1000.

When the piezoelectric/nano-positioner is calibrated with one of the manufactured ultramicroelectrodes (UME) previously installed, the maximum distance between the ultramicroelectrode tip and the interface of the studied substrate, conductor or insulator is determined [5, 6-7]. The tip is approached at the correct distance and the Surface Scanning Curves (PSC) are carried out, determining the boundary between the insulator and the conductor, obtaining border images.

Ultramicroelectrodes (UME) Calibration

Figure 4 shows one of the calibration curves obtained from a platinum ultramicroelectrode (UME) in a solution of 1 mM ferrocemethanol plus 0.1 M KNO_3. The values of the current response (A) from both; the tip of the ultramicroelecrode (UME) and the conductor substrate; are obtained. The data are used, subsequently to obtain the Approximation Curves (PAC) for that especific ultramicro-electrode. A straight line with soft slope must be obtained in the case of a propperly manufactured ultramicro-electrode.

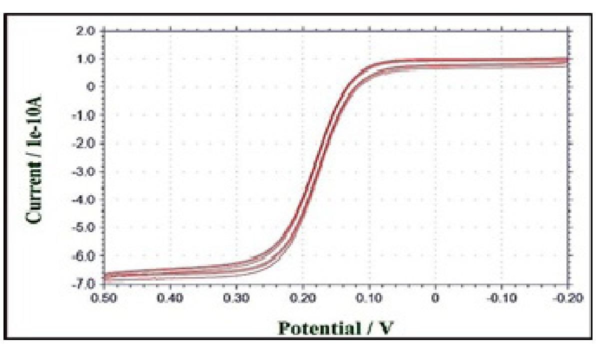

Figure 4. Ultramicroelectrode (UME) calibration curve for platinum, ferrocemethanol 1 mM + 0,1 M KNO_3 solution.

Figure 5 shows the maximum approximation curves of the ultramicroelectrode (UME) obtained from a conductive substrate and a non-conductive substrate [3-4, 7]. The obtained data is used to finally perform characterizations with scanning electrochemical microscopy (SECM).

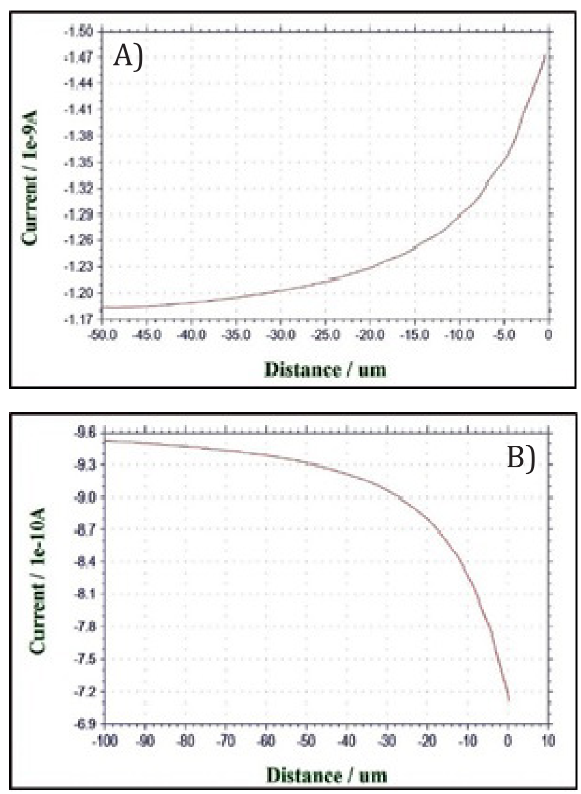

Figure 5. Approximation curve for platinum on A) conductive substrate, B) non-conductive substrate.

Conclusions

The construction of ultramicoelectrodes (UME) through a well-established and controlled elegant methodology allows the application of the technique to study the red-ox reactions and faradaic phenomena on metals surfaces with controlled resolution which can be improved up to a nanometric range.

The micropipettes with more resistant cones were obtained at 525°C ramp temperature, with a speed between 16-18 units/ms, without pushing force, 500 psi pressure and waiting time for the separation 1 ms.

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