Characterization of adsorbates by transient measurements in Scanning Electrochemical Microscopy

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ABSTRACT

In this work, we demonstrate that the use of the scanning electrochemical microscopy in transient mode allows the investigation of adsorbate intermediates at a polarized interface. Two different systems were studied. In the case of a competitive adsorption involving halide and hydrogen, the contribution of each element was monitored independently. Interestingly, the simultaneous measurement of the electrochemical impedance allowed the complex differential capacitance for each adsorbed species to be calculated. In the case of the iron dissolution, the formation of a monovalent Fe species was evidenced allowing to discriminate between different dissolution mechanisms previously described in the literature.

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1. Introduction

Electrochemical impedance spectroscopy, EIS, has been widely used for investigating complex electrochemical mechanisms such as those involved in corrosion or metal dissolution [1–5]. When combined with one or more other potential-modulation based techniques, it allows multiple transfer functions to be determined offering the possibility of gathering simultaneously various type of data. For instance, the kinetics and the exchange of ions and molecules inside a thin polymer film has been investigated using ac-electrogravimetry method [6–8], whereas the use of a double-excitation technique allowed the investigation of the double layer relaxation [9–11].

It has also been shown that the rotating ring-disk electrode (RRDE) allows the investigation of electrochemical and coupled chemical reactions [12–14]. In their pioneering work, the group of Albery has used the alternating current measurements for defining a complex collection efficiency as the ratio of the ac-current collected at the ring to the ac-current generated at the disk [15–17]. This approach was successfully used for characterizing the formation of thin films at an electrode surface [18,19], and was extended to channel flow double electrode for the study of the iron dissolution [20].

Scanning electrochemical microscopy (SECM) also allows the investigation of the electrochemical interface using a microelectrode as a collecting electrode [21,22]. SECM has been successfully used to investigate intricate systems such as those encountered in corrosion [23–29], for performing the dosing of adsorbed intermediates (electro)generated on a substrate using the surface interrogation mode (SI-SECM) [30–32]. Recently, Trinh et al. [33,34] have shown that a transient SECM (similarly to what has been done for the RRDE) allowed a quantitative study of adsorption processes.

It is generally difficult to identify intermediate species involved in multistep reactions. For instance, halide and hydrogen adsorption have a competitive character [35–37] and various mechanisms involved in corrosion refer to the formation of adsorbates or thin films [1,2,19].

In this paper, we report on possibility of studying elementary steps by transient SECM. Two different examples are presented: the reduction of proton on a polycrystalline Pt electrode compared with the competitive adsorption of bromide ions and the dissolution of

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iron in acidic solution. In both cases, the mechanisms are assumed to involve adsorbate intermediates.

2. Experimental

2.1. Experimental setup

All experiments were performed with a homemade SECM device already described elsewhere [38,39]. Briefly, it consisted in a 3-axis positioning system (VP-25XA, Newport) driven by a motion encoder (ESP300, Newport) allowing a 3-axis displacement with a 100 nm resolution. The electrochemical measurements were performed with a homemade bi-potentiostat coupled to a low noise current-to-voltage transducer (Femto DLPCA200, BFI Optilas) with adjustable gain (10^3-10^{11} V/A). Current and potential measurements were performed with an AD/DA card (PCI-6281–National Instruments), and the whole experimental device is controlled by a homemade software allowing usual SECM experiment to be achieved, but also multiple transfer functions to be obtained from the different input channels of the data acquisition card. A four-electrode configuration (2 working electrodes, one reference electrode, and one counter electrode) was used as described previously [33,34].

2.2. Materials and Reagents

Microelectrodes were made from 10 and 40 μm-diameter platinum wires, sealed in a glass capillary by using a microforge. A polycrystalline platinum electrode of 5 mm in diameter isolated by an epoxy resin was used as substrate.

All solutions were prepared in distilled water from analytical-grade chemicals. A 0.5 M H_2SO_4 solution was used for the study of the proton reduction and the adsorption of hydrogen on polycrystalline platinum electrode. In order to study the competitive adsorption between hydrogen and bromine on platinum, a mixture of 0.1 M $HClO_4$ and 5 mM KBr was used. Prior to the experiments, Pt electrodes were cleaned by performing repetitive scans over one hour between the HER and the OER reaction in sulfuric acid solution.

The iron used in this study was a massive high-purity iron (99.99%) purchased from Johnson-Matthey. It was firstly annealed during 4 h at 995 °C in vacuum and then quenched in water. The rod was laterally insulated with a cataphoretic paint and embedded in an epoxy resin. Prior to each experiment, the electrode was polished with SiC paper down to grade 2400, cleaned in water in an ultrasonic bath and then dried with warm air. The anodic dissolution of iron was investigated in 0.5 M H_2SO_4 solution.

2.3. SECM measurements

The dimensionless size of the microelectrode tip RG ($RG = r_g/a$, where r_g is the total external diameter of the microelectrode and a the disc microelectrode radius) and the dimensionless tip-to-substrate distance L ($L = d/a$ where d is the actual tip-to-substrate distance) were determined by performing approach curves in negative feedback mode. The SECM experiments in transient mode and the electrochemical impedance spectroscopy were performed under potentiostatic regulation of the substrate with a 50 mV peak-to-peak sine wave perturbation signal. This amplitude was chosen to improve the signal-to-noise ratio, while the linearity condition for the electrochemical system is maintained. The frequency was varied from 10 kHz down to 50 mHz with 7 frequencies per decade.

3. Basic of the transient SECM measurements

The transient technique used in this study is based on the former works of Albery et al. [12–14] and Benzekri et al. [18,19] devised for rotating ring-disk electrode. In generator/collector mode, an obvious analogy exists between the SECM and the RRDE: redox species generated at one electrode can be detected at the second electrode, the time-of-flight being governed by the distance between the probe and the substrate of the SECM experiment, and by the rotation rate and the interelectrode distance in the case of the RRDE. In addition, the collection efficiency can be defined as the ratio of the current of the collecting electrode to that of the generating one. Similar to a usual electrochemical impedance measurement, a small sine-wave perturbation can be superimposed to the dc component of the substrate (at steady-state), allowing the complex transfer function $N(\omega)$ corresponding to the complex collection efficiency to be defined as:

$$N(\omega) = \frac{\Delta I_{tip}(\omega)}{\Delta I_{sub}(\omega)} \tag{1}$$

where $\Delta I_{tip}(\omega)$ and $\Delta I_{sub}(\omega)$ are the ac-components of the tip and substrate currents, respectively. The introduction of the electrochemical fluxes at the substrate, $\Delta \Phi_{sub}(\omega)$, and at the tip, $\Delta \Phi_{tip}(\omega)$, in Eq. (1) allows the rewriting of $N(\omega)$ as:

$$N(\omega) = \frac{\Delta I_{tip}(\omega)}{\Delta \Phi_{tip}(\omega)} \cdot \frac{\Delta \Phi_{tip}(\omega)}{\Delta \Phi_{sub}(\omega)} \cdot \frac{\Delta \Phi_{sub}(\omega)}{\Delta I_{sub}(\omega)} \tag{2}$$

In the right hand-side of Eq. (2), the first term is the inverse of the complex collection efficiency on the tip, $N_{tip}(\omega) = \frac{\Delta \Phi_{tip}(\omega)}{\Delta I_{tip}(\omega)}$. For this technique, a simple redox reaction has to be chosen on the tip (*i.e.* a kinetically fast electrochemical reaction non complicated by any coupled chemical reaction) in order to maintain its value frequency independent.

The second term is the complex transport coefficient, $N_t(\omega) = \frac{\Delta \Phi_{tip}(\omega)}{\Delta \Phi_{sub}(\omega)}$, corresponding to the mass transport contribution of electroactive species between the substrate and the tip collector electrode. This contribution always exists and can be determined experimentally. Fig. 1 shows an example of the Nyquist
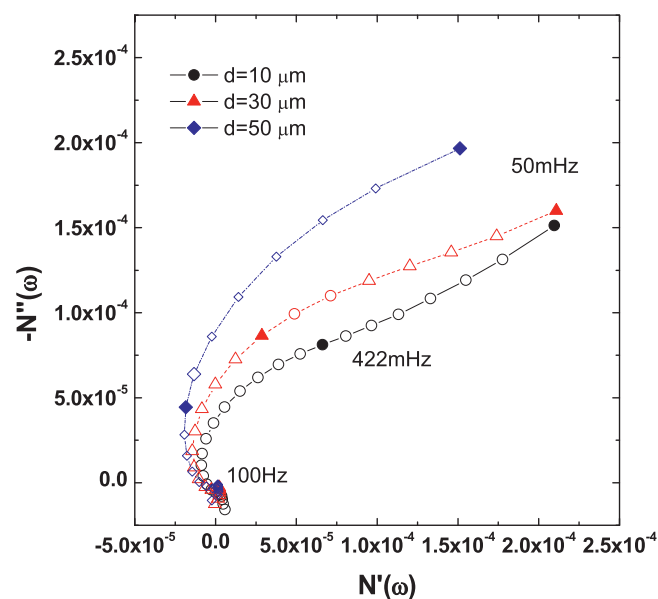
Fig. 1. Complex experimental collection efficiency for a 50 mM $Fe(CN)_6^{3-}$ + 0.5 M KCl solution with the tip-to-substrate distance as a parameter. The tip was a Pt microelectrode, 20 μm in diameter, biased at 0.745 V/SHE and the Pt substrate at 0.465 V/SHE.