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## Characterization of adsorbates by transient measurements in Scanning Electrochemical Microscopy

Dao Trinh, Michel Keddam, Xosé Ramon Novoa, Vincent Vivier

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Dao Trinh, Michel Keddam, Xosé Ramon Novoa, Vincent Vivier. Characterization of adsorbates by transient measurements in Scanning Electrochemical Microscopy. *Electrochimica Acta*, 2014, 131, pp.28-35. 10.1016/j.electacta.2014.02.002 . hal-01020311

**HAL Id: hal-01020311**

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Submitted on 18 Jul 2014

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2 **Characterization of adsorbates by**  
3 **transient measurements in Scanning**  
4 **Electrochemical Microscopy**  
5

6 Dao TRINH<sup>a,b,†,1</sup>, Michel KEDDAM<sup>a,b</sup>, Xosé Ramón NÓVOA<sup>c,1</sup>,  
7 and Vincent VIVIER<sup>a,b,1,\*</sup>  
8

9 <sup>a</sup> CNRS, UPR15, Laboratoire Interfaces et Systèmes Electrochimiques, F-75005 Paris,  
10 France

11 <sup>b</sup> UPMC Université P. et M. Curie, UPR15, LISE, 4 place Jussieu, F-75005 Paris,  
12 France

13 <sup>c</sup> ENCOMAT group, E.E.I, Universidade de Vigo, Campus Universitario, 36310 Vigo,  
14 Spain.

15  
16  
17  
18 <sup>1</sup> ISE member

19 <sup>†</sup> Present address: Université de la Rochelle, Laboratoire des Sciences de l'Ingénieur  
20 pour l'Environnement, F-17000 La Rochelle, France

21 \* Corresponding author:  [vincent.vivier@upmc.fr](mailto:vincent.vivier@upmc.fr)

22  +33(0)1 4427 4158  
23  
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1       **Abstract**

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

11

12      ***Keywords:*** *Scanning Electrochemical Microscopy; AC-SECM; Adsorbate intermediate;*  
13      *Competitive adsorption; Electrochemical impedance spectroscopy.*

14  
15

## 1 **1 Introduction**

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

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

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

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

5 In this paper, we report on possibility of studying elementary steps by transient SECM.  
6 Two different examples are presented: the reduction of proton on a polycrystalline Pt  
7 electrode compared with the competitive adsorption of bromide ions and the dissolution  
8 of iron in acidic solution. In both cases, the mechanisms are assumed to involve adsorbate  
9 intermediates.

## 10 **2 Experimental**

### 11 *2.1 Experimental setup*

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

1 configuration (2 working electrodes, one reference electrode, and one counter electrode)  
2 was used as described previously [33, 34].

### 3 *2.2 Materials and Reagents*

4 Microelectrodes were made from 10 and 40  $\mu\text{m}$ -diameter platinum wires, sealed in a  
5 glass capillary by using a microforge. A polycrystalline platinum electrode of 5 mm in  
6 diameter isolated by an epoxy resin was used as substrate.

7 All solutions were prepared in distilled water from analytical-grade chemicals. A 0.5 M  
8  $\text{H}_2\text{SO}_4$  solution was used for the study of the proton reduction and the adsorption of  
9 hydrogen on polycrystalline platinum electrode. In order to study the competitive  
10 adsorption between hydrogen and bromine on platinum, a mixture of 0.1 M  $\text{HClO}_4$  and 5  
11 mM KBr was used. Prior to the experiments, Pt electrodes were cleaned by performing  
12 repetitive scans over one hour between the HER and the OER reaction in sulfuric acid  
13 solution.

14 The iron used in this study was a massive high-purity iron (99.99%) purchased from  
15 Johnson-Matthey. It was firstly annealed during 4 h at  $995^\circ\text{C}$  in vacuum and then  
16 quenched in water. The rod was laterally insulated with a cataphoretic paint and  
17 embedded in an epoxy resin. Prior to each experiment, the electrode was polished with  
18 SiC paper down to grade 2400, cleaned in water in an ultrasonic bath and then dried with  
19 warm air. The anodic dissolution of iron was investigated in 0.5 M  $\text{H}_2\text{SO}_4$  solution.

### 20 *2.3 SECM measurements*

21 The dimensionless size of the microelectrode tip  $RG$  ( $RG = r_g/a$ , where  $r_g$  is the total  
22 external diameter of the microelectrode and  $a$  the disc microelectrode radius) and the

1 dimensionless tip-to-substrate distance  $L$  ( $L = d/a$  where  $d$  is the actual tip-to-substrate  
2 distance) were determined by performing approach curves in negative feedback mode.  
3 The SECM experiments in transient mode and the electrochemical impedance  
4 spectroscopy were performed under potentiostatic regulation of the substrate with a  
5 50 mV peak-to-peak sine wave perturbation signal. This amplitude was chosen to  
6 improve the signal-to-noise ratio, while the linearity condition for the electrochemical  
7 system is maintained. The frequency was varied from 10 kHz down to 50 mHz with 7  
8 frequencies per decade.

### 9 **3 Basic of the transient SECM measurements**

10 The transient technique used in this study is based on the former works of Albery et al.  
11 [12-14] and Benzekri et al. [18, 19] devised for rotating ring-disk electrode. In  
12 generator/collector mode, an obvious analogy exists between the SECM and the RRDE:  
13 redox species generated at one electrode can be detected at the second electrode, the time-  
14 of-flight being governed by the distance between the probe and the substrate of the  
15 SECM experiment, and by the rotation rate and the interelectrode distance in the case of  
16 the RRDE. In addition, the collection efficiency can be defined as the ratio of the current  
17 of the collecting electrode to that of the generating one. Similar to a usual electrochemical  
18 impedance measurement, a small sine-wave perturbation can be superimposed to the dc  
19 component of the substrate (at steady-state), allowing the complex transfer function  
20  $N(\omega)$  corresponding to the complex collection efficiency to be defined as:

$$21 \quad N(\omega) = \frac{\Delta I_{ip}(\omega)}{\Delta I_{sub}(\omega)} \quad (1)$$

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

$$4 \quad N(\omega) = \frac{\Delta I_{tip}(\omega)}{\Delta\Phi_{tip}(\omega)} \cdot \frac{\Delta\Phi_{tip}(\omega)}{\Delta\Phi_{sub}(\omega)} \cdot \frac{\Delta\Phi_{sub}(\omega)}{\Delta I_{sub}(\omega)} \quad (2)$$

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

9 The second term is the complex transport coefficient,  $N_t(\omega) = \frac{\Delta\Phi_{tip}(\omega)}{\Delta\Phi_{sub}(\omega)}$ , corresponding  
 10 to the mass transport contribution of electroactive species between the substrate and the  
 11 tip collector electrode. This contribution always exists and can be determined  
 12 experimentally. Fig. 1 shows an example of the Nyquist representation of the complex  
 13 collection efficiency measured for a SECM experiment when using ferricyanide as redox  
 14 mediator. The potential of the Pt substrate was set at 0.465 V/SHE and the Pt-  
 15 microelectrode (tip) was biased at 0.745 V/SHE to oxidize the collected  $Fe^{2+}$  species.  
 16 When an ac-perturbation was applied to the substrate, the ferrocyanide ions diffuse in  
 17 solution and are detected at the tip. The shape of the curve (a semi-cardioid) is very  
 18 similar to the curves obtained with the RRDE system [18, 19] or with a channel flow  
 19 double electrode system [20]. The low frequency limit corresponds to the steady-state

1 collection efficiency, whereas the high frequency limit was about 100 Hz, which is larger  
 2 than with other generator / collector systems and depends on the probe-to-substrate  
 3 distance as expected [20]. At higher frequency, the small tail was ascribed to the ohmic  
 4 coupling between the two working electrodes as already pointed out for a generator /  
 5 collector system by Gabrielli et al. [40]. Thus, the collection response is similar to that of  
 6 a low-pass filter [18, 20] and Trinh et al. have also shown that this contribution can be  
 7 evaluated numerically by using finite element simulations [33].

8 ----- *Figure 1* -----

9 The last term in the right hand-side of Eq.(2) is the complex emission efficiency of the  
 10 substrate,  $N_{sub}(\omega) = \frac{\Delta\Phi_{sub}(\omega)}{\Delta I_{sub}(\omega)}$ , which is the quantity of interest in this study. It can be  
 11 calculated from the independent determination of both the complex collection efficiency  
 12 and  $N_{sub}(\omega)$ . Further, if the double-layer charging is neglected, the non-steady-state  
 13 current measured at the substrate is the sum of the flux of species released in solution,  
 14  $\Delta\Phi_{sub}$ , and of the Faradaic charge stored at the interface,  $\Delta Q_{sub}$ , corresponding to the  
 15 formation of adsorbate intermediates or thin solid films:

$$16 \quad \Delta I_{sub} = n_{sub} F \Delta\Phi_{sub} + \frac{d\Delta Q_{sub}}{dt} \quad (3)$$

17 where  $n_{sub}$  is the number of electrons involved in the electrochemical reaction at the  
 18 substrate, and  $F$  the Faraday constant. In the frequency domain, Eq.(3) can be rewritten in  
 19 dimensionless form as:

$$20 \quad n_{sub} F N_{sub} + j\omega \frac{\Delta Q_{sub}(\omega)}{\Delta I_{sub}(\omega)} = 1 \quad (4)$$

1 In a Nyquist representation Eq.(4) corresponds to a semi circle in which  $j\omega \frac{\Delta Q_{sub}(\omega)}{\Delta I_{sub}(\omega)}$  is  
2 the contribution of the charge exchanged for the formation of the adsorbates at the  
3 substrate. The high frequency limit of Eq.(4) corresponds to the kinetics of processes  
4 taking place at the substrate when controlled by the charge transfer resistance.  
5 Conversely, at the low frequency limit, the right hand-side term is null and the steady-  
6 state requires that the flux and the current are linked through the Faraday constant.

7 The experimental setup used in this work allows the simultaneous measurement of the  
8 complex collection efficiency and the electrochemical impedance of the substrate,  
9  $Z_{sub}(\omega)$ . Thus from Eq.(4), the differential capacitance of the substrate,  $C_d$ , can be then  
10 calculated as:

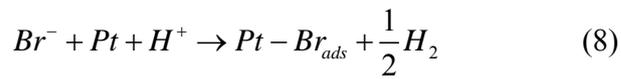
$$11 \quad C_d(\omega) = \frac{\Delta Q_{sub}(\omega)}{\Delta E_{sub}(\omega)} = \frac{1 - n_{sub} F \Delta N_{sub}(\omega)}{j\omega Z_{sub}(\omega)} \quad (5)$$

12 This provides a unique way of determining the relaxation ascribed to the charge stored at  
13 the interface during the electrochemical process.

14 In the following section, this new technique will be used for the study of competitive  
15 adsorption between hydrogen and bromide ions on a Pt substrate and for the dissolution  
16 mechanism of iron.



1 in a solution of HClO<sub>4</sub>. They showed that the presence of bromide significantly alters the  
2 adsorption of hydrogen that was attributed to the competitive adsorption of bromine  
3 through the following reaction:



5 The presence of bromide significantly alters the adsorption of hydrogen resulting in the  
6 gradual disappearance of the adsorption/desorption peak at about 0.260 V/SHE.  
7 Concomitantly, the peak at 0.135 V/SHE increases with the bromide ion concentration,  
8 which confirms the competitive adsorption of bromine and hydrogen.

9 In this case, the total exchanged charge involved through the competitive formation of the  
10 hydrogen and bromine absorbed layer is the sum of the charge required for the adsorption  
11 of each species,  $\Delta Q_{sub}^H$  and  $\Delta Q_{sub}^{Br}$ , respectively.

$$12 \quad \Delta Q_{sub} = \Delta Q_{sub}^H + \Delta Q_{sub}^{Br} \quad (9)$$

13 The potential corresponding to the adsorption reaction of bromine is very close to the  
14 adsorption potential of hydrogen and it is difficult to distinguish between these two  
15 phenomena by conventional electrochemical methods, especially on a single  
16 voltammogram. By performing the transient SECM measurements while detecting  
17 different species generated from the substrate, specific information about each adsorption  
18 process can be gathered and the competitive reaction between the adsorption of bromine  
19 and hydrogen can be selectively studied.

1 Figure 4 shows the differential capacitance  $\frac{\Delta Q_{sub}}{\Delta E_{sub}}$  calculated from the experimental  
 2 complex collection efficiency according to Eq. (5) in the case of bromine and hydrogen  
 3 adsorption. The transient SECM measurements were performed at  $E_{sub} = 1.19$  V/SHE for  
 4 bromine and  $E_{sub} = -0.005$  V/SHE for hydrogen. For electrode potential value lower than  
 5  $-0.005$  V/SHE, the HER occurs on the substrate to form dissolved hydrogen which is then  
 6 captured and oxidized by the tip (the tip is biased at 0.645 V/SHE). This reaction involves  
 7 adsorbed intermediate according to the Volmer – Tafel or Volmer – Heyrovsky  
 8 mechanism.

9 ----- Figure 4 -----

10 At 1.19 V/SHE,  $Br^-$  is oxidized to  $Br_2$  ( $Br_3^-$ ) which is then detected at the tip (tip potential  
 11 is maintained at 0.645 V/SHE to reduce the  $Br_2$  generated at the substrate). In both cases,  
 12 the HF limit tends towards 0 because in the frequency domain, the impedance is governed  
 13 purely by the charge transfer resistance. The low frequency limit corresponds to the  
 14 charge accumulation at the electrode surface, *i.e.*, 1 mFcm<sup>-2</sup> for hydrogen and 1.2 mF  
 15 mFcm<sup>-2</sup> for bromine (Table 1). The latter value corresponds to the accumulation of  
 16 charge on the substrate associated with the competitive adsorption between  $H_{ads}$  and  
 17  $Br_{ads}$ .

18 ----- Table 1 -----

19 Thus, varying the electrode potential allows the different contribution of adsorbed species  
 20 to be evaluated and the sum of charges involved in the formation of  $H_{ads}$  and  $Br_{ads}$  is  
 21 given by  $\Delta Q_{sub} = \Delta Q_{sub}^H + \Delta Q_{sub}^{Br} = 71 + 85 = 156 \mu C cm^{-2}$ . This value (156  $\mu C cm^{-2}$ ) is

1 smaller than the one obtained for a monolayer of adsorbed hydrogen in the absence of  
2 bromide ions ( $212 \mu\text{C cm}^{-2}$ ) which confirms the hypothesis of competitive adsorption of  
3 bromide ions on the site occupied by hydrogen on platinum substrate. It should also be  
4 mentioned that because both electrodes (tip and substrate) are made from the same  
5 material and were prepared following the same experimental procedure (grinding,  
6 washing, electrochemical cleaning), the roughness factor for each electrode was assumed  
7 to be the same. This allows expecting that the complex collection efficiency to be  
8 independent of this roughness factor.

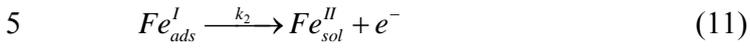
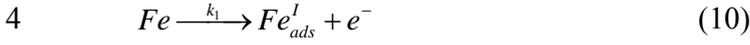
9 In addition, the time-constant for the relaxation of  $H_{ads}$  at the electrode surface without  
10 the bromide ion in solution is about 2 Hz [34]. This frequency points to a kinetics ten  
11 times faster than the value determined in presence of bromide ions (Figure 4). All the  
12 characteristic constants extracted from these experiments are reported in Table 1. This  
13 behavior indicates a change in the mechanism and kinetics of adsorption of hydrogen in  
14 presence of a competitive adsorption.

#### 15 *4.2 Mechanism of iron dissolution in acidic solution*

16 The dissolution mechanism of iron in an acidic solution has been the topic of controversy  
17 [44]. Two different mechanisms were considered based on the interpretation of current  
18 potential curves and electrochemical impedance diagrams [44-46], in which adsorbed  
19 monovalent iron species act as an intermediate in the transfer of the first and second  
20 electrons of Fe (mechanism proposed by J. O'M. Bockris, et al. [45]) whereas Heusler  
21 [46] suggested that it acts as a catalyst in the dissolution of divalent Fe cations in acidic  
22 solutions.

1 These two mechanisms can be summarized as follows:

2 Bockris' mechanism [45] is described by two successive and irreversible elementary  
3 steps involving  $Fe_{ads}^I$  as adsorbate intermediate:



6 Thus, mass and charge balances can be expressed as

$$7 \quad \beta \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta \quad (12)$$

$$8 \quad i_{sub} = F(k_1(1-\theta) + k_2\theta) \quad (13)$$

9 where  $\theta$  is the fractional surface coverage of  $Fe_{ads}^I$  and  $\beta$  is the maximum of surface  
10 concentration of adsorbate intermediate. The flux of electrogenerated species at the  
11 substrate is then given by

$$12 \quad \Phi_{sub} = k_2\theta \quad (14)$$

13 At steady-state, the fractional surface coverage is given by

$$14 \quad \bar{\theta} = \frac{k_1}{k_1 + k_2} \quad (15)$$

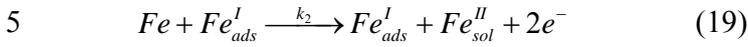
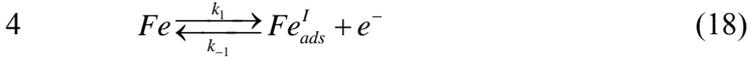
15 The impedance of the substrate is given by

$$16 \quad \frac{1}{Z_{sub}} = F \left[ (b_1 + b_2)k_2\bar{\theta} - (k_1 - k_2) \frac{(b_1 - b_2)k_2\bar{\theta}}{k_1 + k_2 + \beta j\omega} \right] \quad (16)$$

17 allowing the collection efficiency to be calculated as

$$N_{sub} = \left( b_2 k_2 \bar{\theta} + k_2 \frac{(b_1 - b_2) k_2 \bar{\theta}}{k_1 + k_2 + \beta j \omega} \right) \times Z_{sub} \quad (17)$$

The mechanism proposed by Heusler [46] also involves  $Fe_{ads}^I$  as adsorbate intermediate, but the later acts as a catalyst:



The mass and charge balances can then be expressed as

$$\beta \frac{d\theta}{dt} = k_1 (1 - \theta) - k_{-1} \theta \quad (20)$$

$$i_{sub} = F (k_1 (1 - \theta) - k_{-1} \theta + 2k_2 \theta) \quad (21)$$

The flux of electrogenerated species at the substrate is also given by

$$\Phi_{sub} = k_2 \theta \quad (22)$$

At steady-state, the fractional surface coverage is given by

$$\bar{\theta} = \frac{k_1}{k_1 + k_{-1}} \quad (23)$$

The impedance of the substrate is given by

$$\frac{1}{Z_{sub}} = F \left[ (b_1 - b_{-1}) k_{-1} \bar{\theta} + 2k_2 b_2 \bar{\theta} - (k_1 + k_{-1} - 2k_2) \frac{k_{-1} (b_1 - b_{-1}) \bar{\theta}}{k_1 + k_{-1} + \beta j \omega} \right] \quad (24)$$

allowing the collection efficiency to be calculated as

$$N_{sub} = \left( b_2 k_2 \bar{\theta} + k_2 \frac{k_{-1} (b_1 - b_{-1}) \bar{\theta}}{k_1 + k_{-1} + \beta j \omega} \right) \times Z_{sub} \quad (25)$$

----- Figure 5 -----

Fig. 5 shows the experimental impedance diagrams measured at the onset of the dissolution peak of pure iron as a function of the electrode potential. In each case two loops are evidenced, a high frequency capacitive one corresponding to the double layer capacity-charge transfer resistance and a low frequency inductive one generated by the frequency response of the surface coverage by the adsorbed reaction intermediate. These diagrams are characterized by a decrease of the impedance (larger value of the dissolution current) and a shift of the characteristic frequency towards shorter time-constant as the potential increases for both loops. Assuming that electrochemical steps follow Tafel kinetics and using the linearized expression of the currents given by Eq.(13) and Eq.(21), it is possible to calculate the impedance response as shown in Fig. 6a for the Bockris' mechanism and Fig. 6b Heusler's mechanism. Independently of the kinetic constants used for the simulation, in both cases the shape of the impedance diagrams are very similar to those obtained experimentally. Both the amplitude and time-constants vary in the same way. It is thus difficult to decide which mechanism is the most suited.

----- Figure 6 -----

----- Figure 7 -----

Fig. 7 shows the calculated collection efficiency of the substrate using the same set of parameters as those used for the impedance diagrams presented in Fig. 6. Interestingly, a

1 different behavior is observed. In the case of Bockris' mechanism, the collection  
2 efficiency locus overlap in amplitude and a small frequency shift can be observed (Fig.  
3 7a) whereas for Heusler's mechanism, the amplitude of the complex collection efficiency  
4 is potential dependent (Fig. 7b). As the potential increases, the high frequency limit  
5 increases corresponding to a change of the kinetic process at the substrate under the  
6 assumption of vanishing variations of the superficial concentration.

7 ----- *Figure 8* -----

8 Fig. 8 shows the experimental complex collection efficiency of the substrate measured  
9 simultaneously with the impedance diagrams presented in Fig. 5. The shape of the  
10 transfer function does not depend on the potential and a small frequency shift is observed.  
11 These results compare favorably with the theoretical curves presented in Fig. 7a  
12 indicating that the Bockris' mechanism allows a quantitative description of the iron  
13 dissolution valid at low current densities and low pH [1, 2]. Thus the transient SECM  
14 allows distinguishing between different possible mechanisms. It should be mentioned that  
15 for experiments performed at higher potentials (thus for larger steady-state dissolution  
16 current), no reliable results could have been obtained. This was ascribed to the fact that  
17 under high dissolution rates the distance between the Pt-probe and the iron substrate  
18 varies too quickly compared to the time-scale of the impedance acquisition rate.

## 19 **5 Conclusions**

20 In this work, we have highlighted different intakes that can be obtained using the SECM  
21 in transient mode in order to characterize an electrified interface.

1 In the case of competitive adsorption between halide ions and hydrogen, it was shown  
2 that it is possible to discriminate between the different species and to evaluate  
3 independently the charge exchanged for each adsorbate.

4 In the case of the formation of an adsorbate intermediates like Fe(I) species, the complex  
5 collection efficiency of the substrate can decide between different mechanisms and  
6 appears to be a complementary approach to the usual impedance measurements.

7 The perspectives of this work are the investigation of reaction mechanism on well  
8 oriented materials such as the absorption and the competitive adsorption on single  
9 crystals and the investigation of the passive film formation and passive film reactivity as  
10 a function of the grain orientation.

## 11 **Acknowledgements**

12 The authors gratefully acknowledge D. Rose (UPR15) for technical support.

13

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## Figure captions

**Figure 1:** Complex experimental collection efficiency for a 50 mM  $\text{Fe}(\text{CN})_6^{3-}$  + 0.5 M KCl solution with the tip-to-substrate distance as a parameter. The tip was a Pt microelectrode, 20  $\mu\text{m}$  in diameter, biased at 0.745 V/SHE and the Pt substrate at 0.465 V/SHE

**Figure 2:** Schematic representation of a monolayer of hydrogen adsorbed on platinum (a) and the competitive adsorption between hydrogen and bromine on platinum (b).

**Figure 3:** Cyclic voltammogram of the polycrystalline platinum electrode (0.5 cm in diameter) in a 5 mM KBr + 0.1 M  $\text{HClO}_4$  solution – initial potential 0.445 V/SHE – 5 cycles at 50  $\text{mVs}^{-1}$ .

**Figure 4:** Differential capacitances calculated from the complex experimental collection efficiency according to Eq. (5)  $E_{sub} = -0.005$  V/SHE, Pt-tip: 20  $\mu\text{m}$  in radius, Pt-substrate 0.5 cm diameter. Solution: 0.1 M  $\text{HClO}_4$  + 5 mM KBr.

**Figure 5:** Electrochemical impedance diagrams of pure iron in sulfuric acid solution (0.5 M) as a function of the electrode potential.

**Figure 6:** Simulated electrochemical impedance diagrams for pure iron in sulfuric acid solution as a function of the electrode potential using Refs. [1, 2] for the choice of kinetic constants. (a) Bockris' mechanism:  $k_1 = 0.4 \cdot 10^6 e^{b_1 \cdot E}$ ;  $b_1 = 38.4 \text{ V}^{-1}$ ;  $k_2 = 8 \cdot 10^{-4} e^{b_2 \cdot E}$ ;  $b_2 = 7 \text{ V}^{-1}$ ;  $\beta = 10^{-8} \text{ mol} \cdot \text{cm}^{-2}$ ;  $C_d = 100 \mu\text{F}$  (b) Heusler's mechanism:  $k_1 = 10 e^{b_1 \cdot E}$ ;

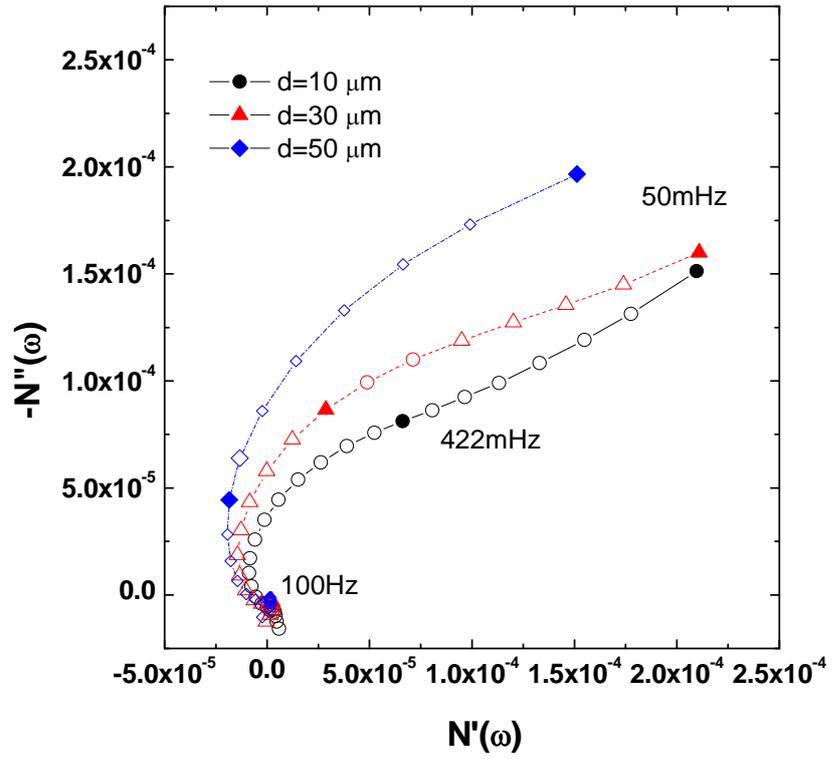
1  $b_1 = 19.2 \text{ V}^{-1}; \quad k_{-1} = 15 \cdot 10^{-18} e^{-b_{-1} \cdot E}; \quad b_{-1} = 19.2 \text{ V}^{-1}; k_2 = 8 \cdot 10^{-4} e^{b_2 \cdot E}; \quad b_2 = 7 \text{ V}^{-1};$   
2  $\beta = 10^{-8} \text{ mol} \cdot \text{cm}^{-2}; C_d = 100 \text{ } \mu\text{F}.$

3 **Figure 7:** Simulated collection efficiency of the substrate for pure iron in sulfuric acid  
4 solution as a function of the electrode potential (same kinetic constants as in Fig. 6). (a)  
5 Bockris' mechanism, (b) Heusler's mechanism.

6 **Figure 8:** Experimental collection efficiency of the substrate for pure iron in sulfuric acid  
7 solution (0.5 M) as a function of the electrode potential.

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9 **Table 1:** Capacitance, charge and time constant of the adsorption processes for the  
10 different experiments performed.

1 *Figure 1*



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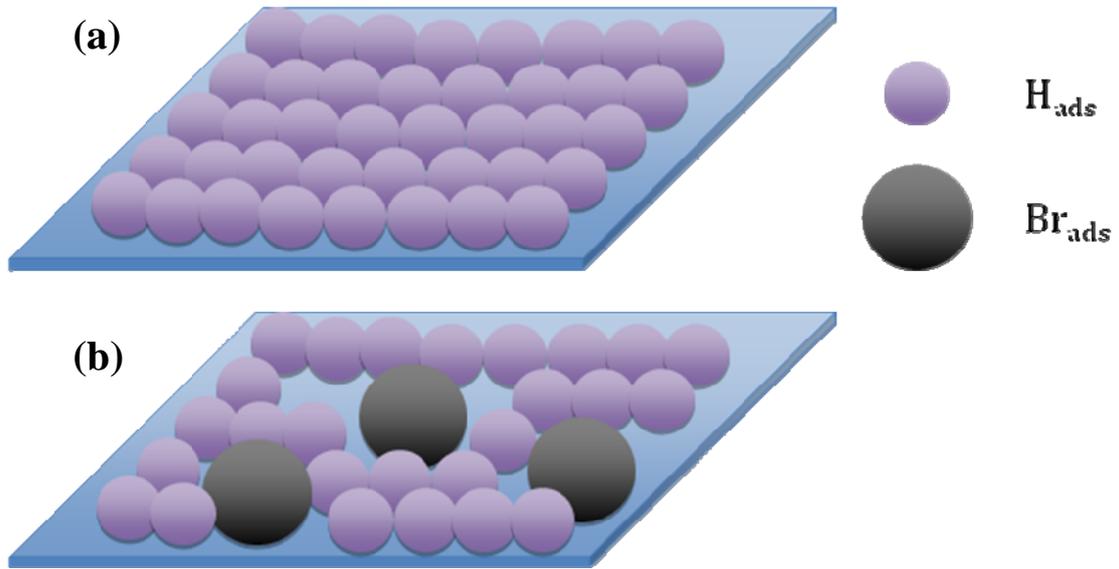
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*Figure 2*

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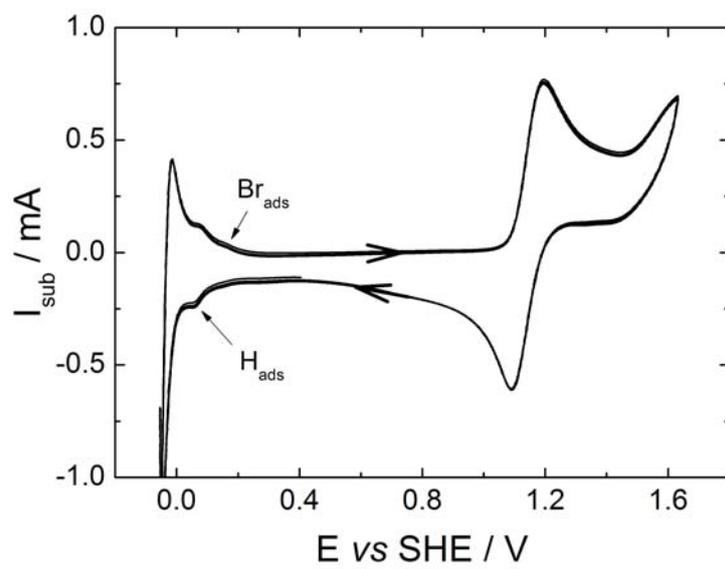
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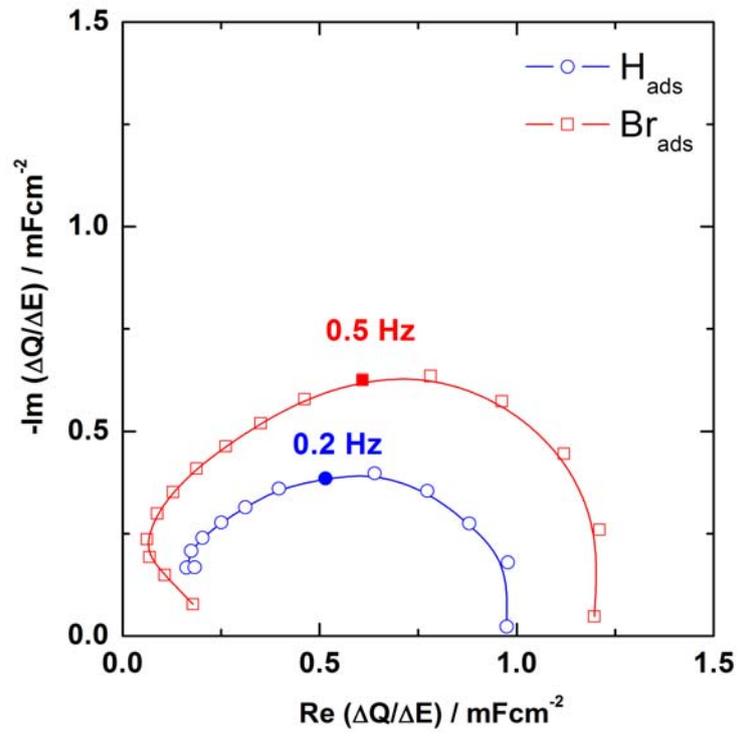
**Figure 3**



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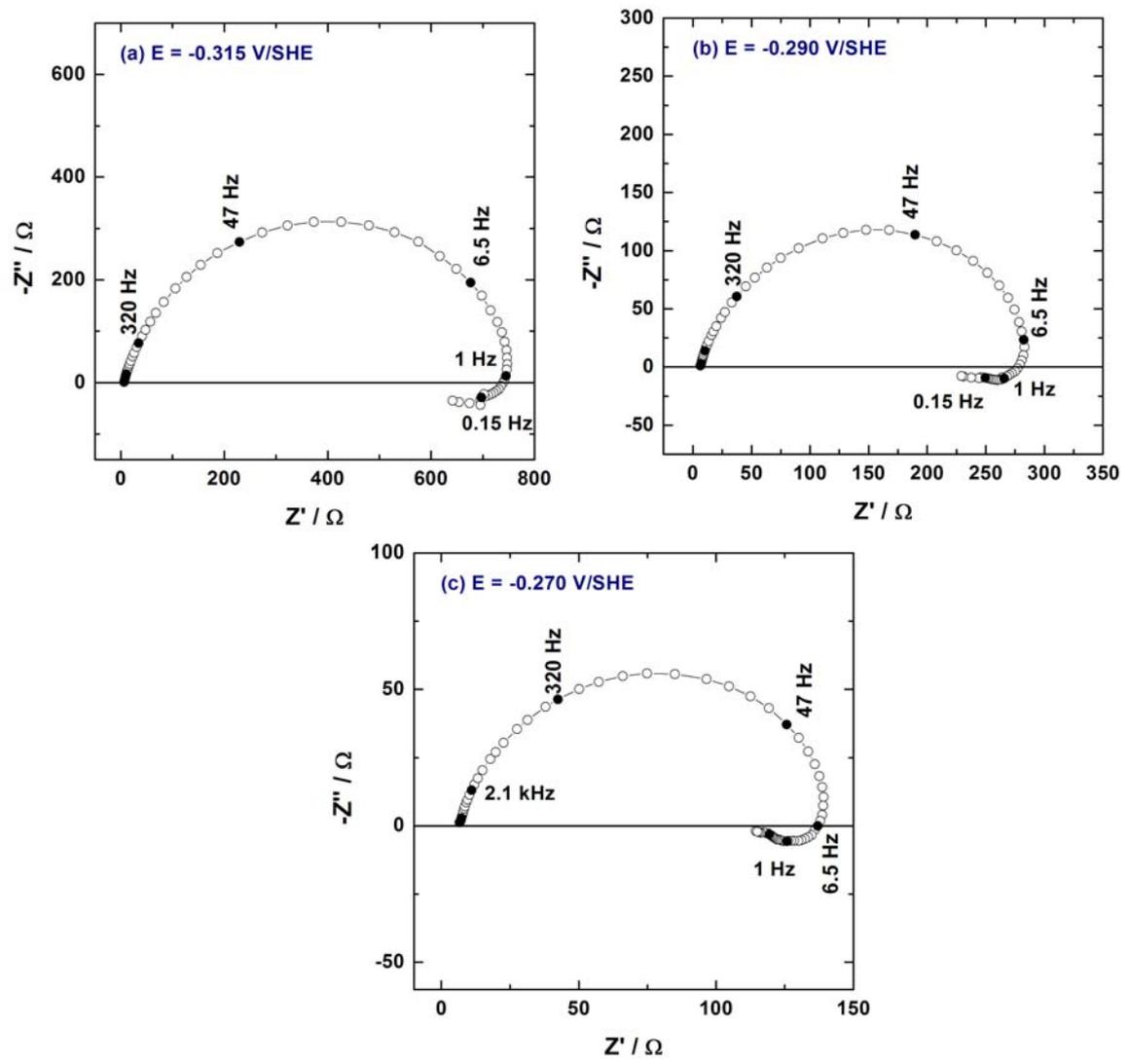
*Figure 4*



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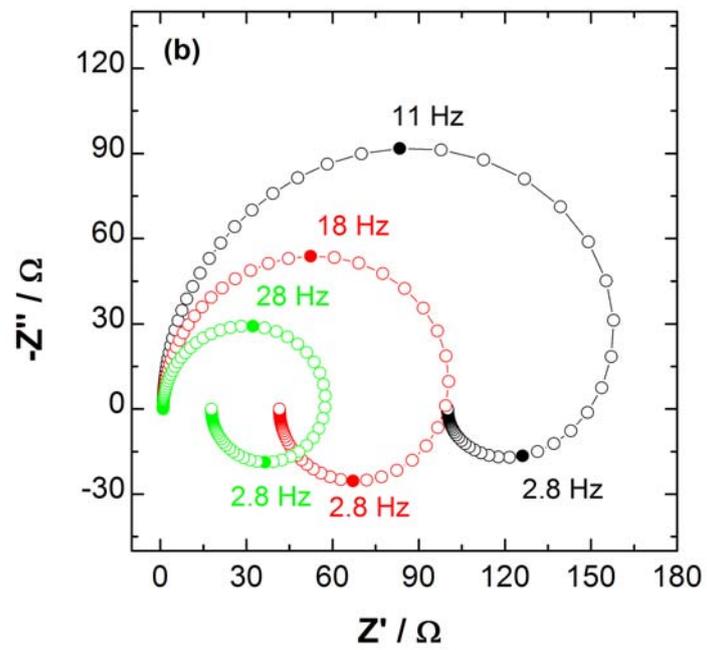
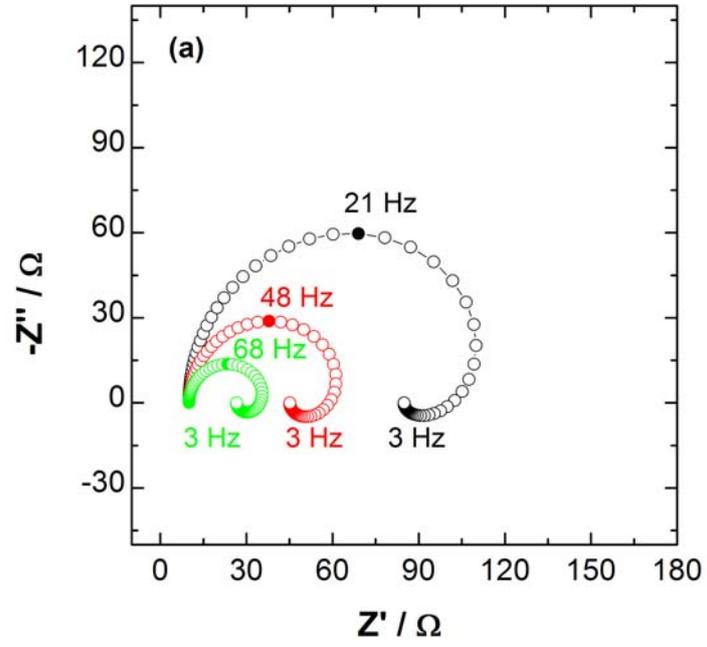
Figure 5



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1 *Figure 6*

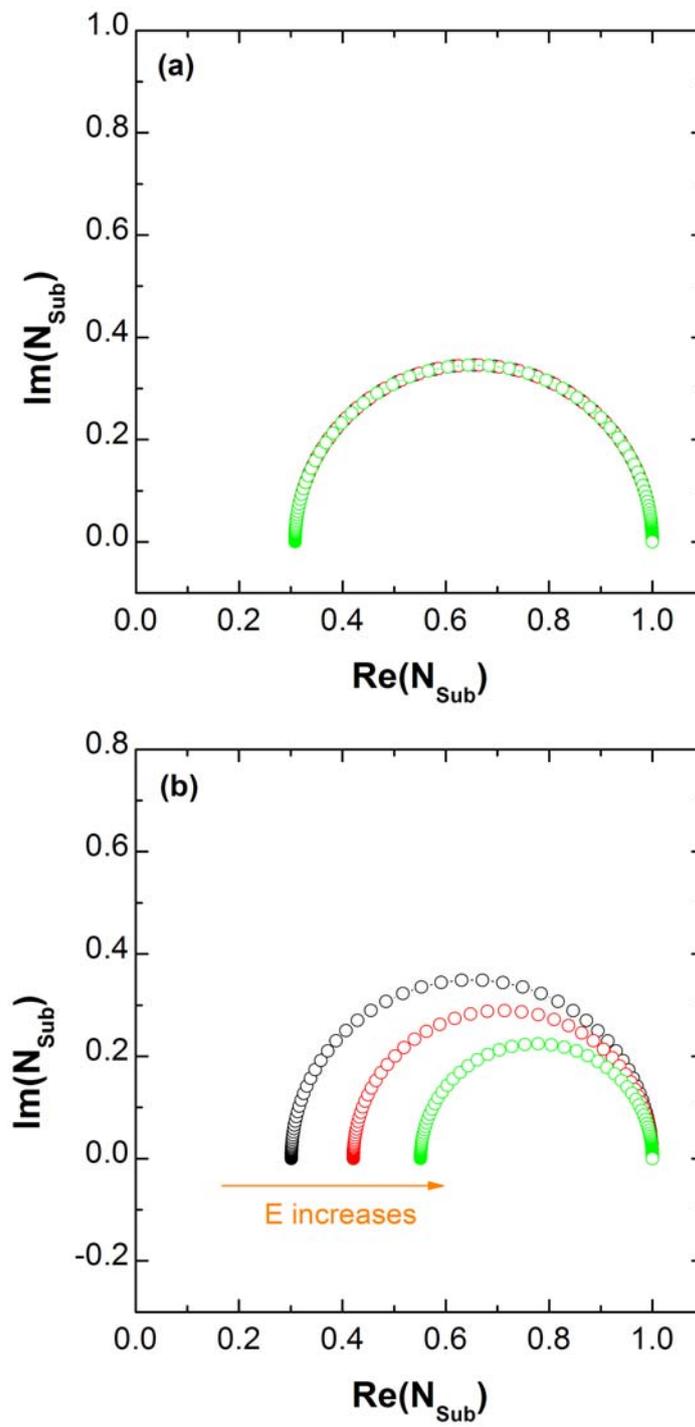
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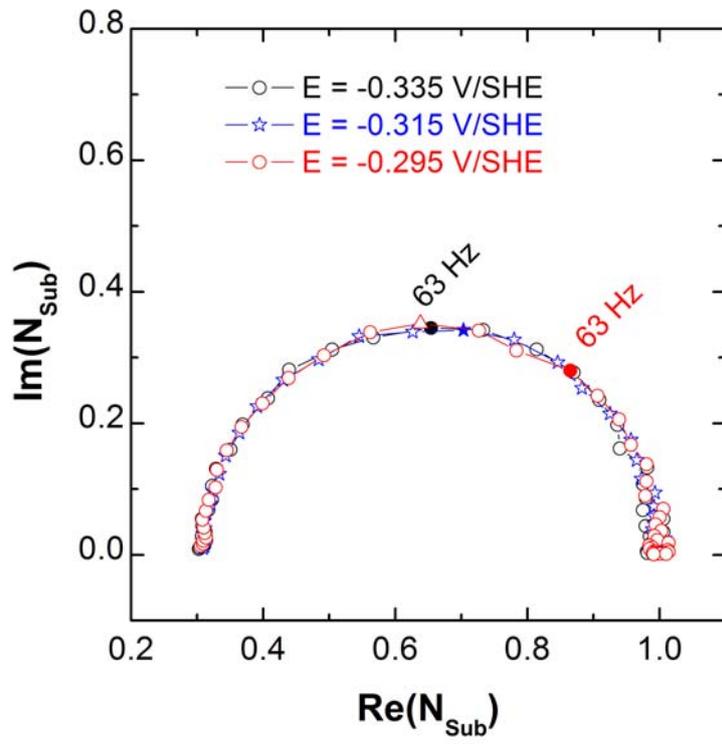
*Figure 7*



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1 *Figure 8*

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**Table 1**

	Capacitance / mF cm <sup>-2</sup>	Charge / μC cm <sup>-2</sup>	Characteristic Frequency / Hz
Only H <sub>ads</sub> (without the presence of Br)	<b>3</b>	<b>212</b>	<b>2</b>
H <sub>ads</sub> competitive with Br <sub>ads</sub>	<b>1</b>	<b>71</b>	<b>0.2</b>
Br <sub>ads</sub> competitive with H <sub>ads</sub>	<b>1.2</b>	<b>85</b>	<b>0.5</b>

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