New method for measuring the differential capacity in electrochemistry

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Electrical behavior of the ideally polarizable metal–solution interface is similar to a RC series circuit. The dc polarization, E, of the interface is potentiostatically controlled and differential capacity, C, measurements are carried out with a linear variation of E versus time. A precise measurement method of C is described in the case where the time constant of the circuit is rather high ($\approx 10^{-2}$ s). The principle of this method is to impose on the interface an ac current perturbation, I_ω, and to measure the ac potential response, E_ω. A system composed of a low bandwidth potentiostat (<1 Hz) and a galvanostat controls the dc potential, E, and produces the ac current, I_ω. In- and out-of-phase components of the ac potential response, E_ω, are analyzed by means of a lock-in amplifier. An ohmic drop compensation technique with suppression of the residual common mode is used to improve the determination of the $E_\omega(90°)$. Using a dummy cell, comparison between the new method and the classic potentiostatic technique is carried out. Results show that it is possible to measure C with a relative error less than 1% in a frequency range up to 2 kHz whereas with the classic potentiostatic technique the frequency range is limited to around 100 Hz. © *1998 American Institute of Physics.* [S0034-6748(98)02807-X]

I. INTRODUCTION

Studies of the interfacial region between the electrode and the solution are of fundamental interest because the elementary steps of electrochemical processes take place in this region.

Given the simple case of an ideally polarized metal–solution interface, in the defined potential range, there is no charge transfer due to faradic reactions between the metal and the solution. The accumulation of electrical charges on the metal and ionic charges in the solution lead to the formation of the electrochemical double layer. The electrical behavior of the metal–solution interface is analogous to a capacitor. Using the Gouy–Chapman theory, the potential of zero charge (pzc)[1] of the interface is determined from the differential capacity-potential curves $C(E)$. This approach has been used to study the influence of the metal crystalline anisotropy on the pzc at single-crystal surfaces of gold[2] and silver.[3] The knowledge of the surface charge density on the electrode versus the potential is essential in studies of polarized metal–solution interfaces.[4–6] By integrating the capacity-potential curves, the charge-potential curves, $\sigma(E)$, are obtained. The integration constant is determined from the pzc. The precision on the determination of σ is linked to the precision of the pzc determination and to the precision of the differential capacity measurement.

On the $C(E)$ curves, the pzc corresponds to the minimum of C. Its amplitude increases with the electrolyte dilution. With a dilute electrolyte, the minimum is very well marked and the precision of the pzc determination is good. On gold and silver electrodes, the pzc determination of different orientation is achieved with a precision of ± 10 mV. The pzc determination does not introduce a major error in the σ determination.

On the other hand, differential capacity measurement is generally relatively imprecise which introduces errors in the σ determination. The measured capacity values vary with the frequency of the interfacial perturbation ac tension, E_ω, used and depend on the experimental conditions. In a previous article,[7] the source of the frequency dispersion of C has been discussed. It has been shown that the classic potentiostatic method used for C measurement could be at the origin of the main errors. With this method, in normal experimental conditions, frequencies higher than 100 Hz cannot be used. These low frequencies are not sufficient to eliminate parasitic phenomena such as slow residual faradic reactions which could lead to some measurement dispersions.

The aim of the present work is to present a new method for differential capacity measurement which allows the use of higher frequencies.

II. METHODS FOR THE MEASUREMENT OF DIFFERENTIAL CAPACITY

The starting point of the measurement of the differential capacity is the determination of the impedance Z of the metal–solution interface.[8] Using classic electrical model of an ideally polarized metal–solution interface, where a resistance, R_e, and a capacity, C, are in series, the impedance, Z, of the interfacial region between the working electrode, (WE), and the reference electrode, (RE), for the dc potential, E, is given by the equation:

$$Z = R_e + \frac{1}{jC\omega}, \tag{1}$$

where R_e is the electrolyte resistance, C the differential capacity of the double layer, and ω the angular frequency of the ac perturbation.

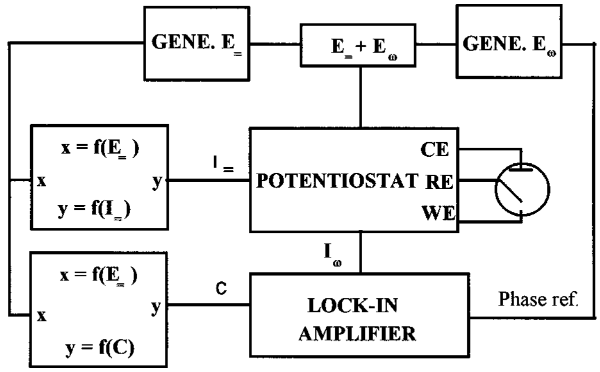

FIG. 1. Diagram of a potentiostatic feedback device for measuring the differential capacity using ac potential perturbation technique.

A. Brief overview of classic potentiostatic measurement

With solid electrodes, a reproducible surface state can be achieved only by using polarization cycles with a linear variation of the dc potential, E. $C(E)$ measurements are carried out during the polarization sweep.

The principle of the potentiostatic method (Fig. 1) is to superpose to the dc potential, E, provided by a triangular voltage generator a perturbation ac tension, E_ω, provided by a sinusoidal voltage generator. The differential capacity is obtained from the measurement by a lock-in amplifier of the response ac current, I_ω, flowing in the potentiostatic circuit.

In a recent article[6] we showed that the error of the measurement increases both with the time constant of the potentiostatic circuit and the frequency. In normal measurement conditions, the time constant is around 10^{-2} s, the potentiostat bandwidth is 1 MHz. So the highest available frequency is about of 100 Hz. In conclusion, we suggest in this article that the C measurement at frequency >100 Hz could be possible if the effect of the potentiostatic control of dc potential, E, over the measurement is eliminated. For that the potentiostatic control of dc potential, E, and the interfacial ac perturbation must be dissociated.

B. Improved method

The principle is that differential capacity measurements are carried out using an ac perturbation of the interface without any intervention of the control system on the dc potential, E. Thus the characteristics of the potentiostat must satisfy two antagonistic conditions. The potentiostatic control system must have:

(1) a sufficient fast time response to control the dc potential, E, when it varies linearly with time with a sweep rate of about 10 mV s^{-1};
(2) a sufficiently low time response to have no reactions when the frequency of the ac perturbation is higher than 10 Hz.

These conditions will define the bandwidth of the potentiostat.

In a classic experiment, the dc potential sweep rate is typically 10 mV s^{-1}, the potential range is around 2 V so the fundamental frequency of the potentiostatic control is approximately 5×10^{-3} Hz. The $E(t)$ function of the dc potential is a symmetric ''saw tooth'' varying between $E_{\max}$ and $E_{\min}$. The Fourier transform is

$$E_{\mathrm{FT}}(t)=|E_{\max}-E_{\min}|\left(\frac{1}{2}+\sum_{1}^{n}\left(\frac{2}{n\pi}\right)^2\cos n\omega t\right)+E_{\min}, \tag{2}$$

where n is an odd positive integer. According to this relation at $t=0$, which corresponds to the slope change, and for $n=99$ the difference between $E_{\mathrm{FT}}(t)$ and $E(t)$ is less than 2%. In these conditions a potentiostat with a low cut off frequency (≈ 0.1 Hz) can correctly control the dc potential, E, imposed to the interface.

If an ac current, I_ω, with a frequency of 10 Hz, value 100 times higher than the bandwidth of the potentiostat, goes through the interface, the ac tension, E_ω, induced by this perturbation will not be corrected by the potentiostatic control. For each E value imposed by the potentiostat the measurement of in- and out-of-phase components of the perturbation current, I_ω, and induced tension, E_ω, gives the true value of the differential capacity.

Thus it is possible to have a dc potential control without any perturbation of the differential capacity measurement.

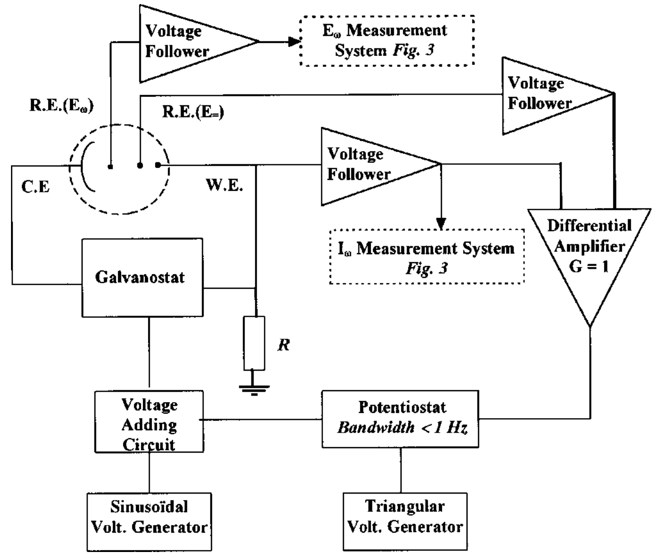

FIG. 2. Diagram of a galvanostatic feedback device for measuring the differential capacity using ac current perturbation technique.

III. EXPERIMENTAL SYSTEM

One problem in the design of the experimental system is to impose simultaneously the dc polarization, E, and the ac perturbation current, I_ω.

Figure 2 shows the principle of the method. The dc potential, E, of the working electrode is imposed by a reduced bandwidth potentiostat ($B_\omega\approx 1$ Hz) driving the galvanostat. The ac perturbation current, I_ω, generated by the ac voltage generator through the resistance, R, is imposed to the cell circuit by the mean of the galvanostat.

A detailed diagram of the system measurement is shown in Fig. 3. The ac tension response, E_ω, to the ac perturbation current, I_ω, is measured between the working electrode WE

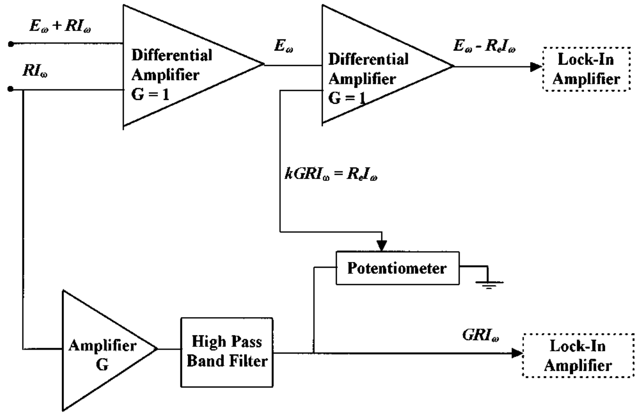

FIG. 3. Complementary diagram of Fig. 2: device for measuring the differential capacity with ohmic drop compensation.

and a special ac reference electrode, RE(E_ω), independent of the dc reference electrode, RE(E). The current, I_ω, and the tension, E_ω, are analyzed using two lock-in amplifiers. The phase of each lock-in is adjusted on the $I_\omega(0°)$ component. In these conditions $|I_\omega|$ is equal to the in-phase component $I_\omega(0°)$ and the components of E_ω are proportional to the components of the impedance, Z, which corresponds to the electrical circuit R_eC located between WE and RE(E_ω). From relation (1), by identification with the E_ω components, the resistance, R_e, and the differential capacity, C, can be determined:

$$Z(0°)=\frac{E_\omega(0°)}{I_\omega}=R_e, \tag{3}$$

$$Z(90°)=\frac{E_\omega(90°)}{I_\omega}=-\frac{1}{C\omega}. \tag{4}$$

Generally, the differential capacity of the interface is less than 100 μF and the electrolyte resistance is around 200 Ω. For a frequency range between 100 and 1000 Hz, the capacitance $|1/C\omega|$ is much smaller than R_e. The in-phase component $E_\omega(0°)$ which characterize the ohmic drop is then greater than the out-of-phase component $E_\omega(90°)$ which characterize the differential capacity. Obviously to have a precise measurement of $E_\omega(90°)$ without any saturation of the lock-in amplifier the ohmic drop must be compensated.

The compensation technique used is based on the one proposed by Gabrielli *et al.*[9] It consists of adding at E_ω (Fig. 3) a tension in phase opposition with a module equal to the ohmic drop $E_\omega(0°)$. This tension is obtained from the tension created by I_ω flowing through R by mean of a potentiometer $(0<k<1)$, an impedance adapter, and a differential amplifier. When $kGRI_\omega=R_eI_\omega=E_\omega(0°)$, the ohmic drop compensation is complete.

In the potential range where the electrode is ideally polarized, $E_\omega(0°)$ is constant and proportional to the resistance R_e. After the ohmic drop compensation, the lock-in input tension should be theoretically equal to

$$E_\omega-kGRI_\omega=jE_\omega(90°). \tag{5}$$

Relation (5) assumes that, in the studied frequency range, the differential amplifier used for compensation (Fig. 3) is ideal, i.e., its common mode rejection is infinite.

For a real differential amplifier, the possible frequency range depends on the variations of its common mode rejection. The knowledge of this parameter leads to the determination of the frequency range where measurement could be carried out with precision better than 1%.

For an ideal differential amplifier, the input tensions $E_1=E_\omega(0°)+jE_\omega(90°)$ and $E_2=E_\omega(0°)$ give an ideal output tension $E_i=jE_\omega(90°)$.

For a nonideal differential amplifier, identical input tensions $E_1=E_2=E_\omega(0°)$ give the common mode output tension E_{mc}. A classic variation law of E_{mc} is

$$E_{mc}=E_\omega(0°)\,\frac{(1+j\omega T_{mc})}{G_{mc}}, \tag{6}$$

where T_{mc} is the time constant and G_{mc} is the common mode rejection gain.

For a real amplifier, input tensions $E_1=E_\omega(0°)+jE_\omega(90°)$ and $E_2=E_\omega(0°)$ give the measured output tension:

$$E_m=E_i+E_{mc}=jE_\omega(90°)+E_\omega(0°)\,\frac{(1+j\omega T_{mc})}{G_{mc}}. \tag{7}$$

By definition the error function, Φ, of the differential capacity measurement is equal to the ratio between the measured capacity, C_m, and the true capacity, C:

$$\Phi=\frac{C_m}{C}=\frac{E_i}{E_m}. \tag{8}$$

Relations (7) and (8) lead to

$$\Phi=\frac{1}{1+\dfrac{E_\omega(0°)}{jE_\omega(90°)}\,\dfrac{1+j\omega T_{mc}}{G_{mc}}}. \tag{9}$$

By substituting $E_\omega(0°)$ and $E_\omega(90°)$ from Eqs. (3) and (4) into Eq. (9), we obtain

$$\Phi=\frac{1}{1-\dfrac{\omega^2TT_{mc}}{G_{mc}}+\dfrac{j\omega T}{G_{mc}}}, \tag{10}$$

where $T=R_eC$ is the interface time constant.

Expression (10) can be written

$$\Phi=\frac{1}{1-\left(\dfrac{\omega}{\omega_m}\right)^2+j2z\,\dfrac{\omega}{\omega_m}}, \tag{11}$$

where $B_{mc}=G_{mc}/T_{mc}$ is the common mode rejection bandwidth, $z=(TB_{mc})^{1/2}/2G_{mc}$ is the damping factor, and $\omega_m=(B_{mc}/T)^{1/2}$ is the limiting angular frequency.

For the amplifier used, values of parameters are: $1/T_{mc}\approx 1800$ Hz and $G_{mc}\approx 10^4=80$ dB. In these conditions, considering an interface time constant $T\approx 10^{-2}$ s, the limiting frequency value is $f_m\approx 4500$ Hz and the damping factor value is $z\approx 10^{-2}$. Expression (11) can be written in a simplified form:

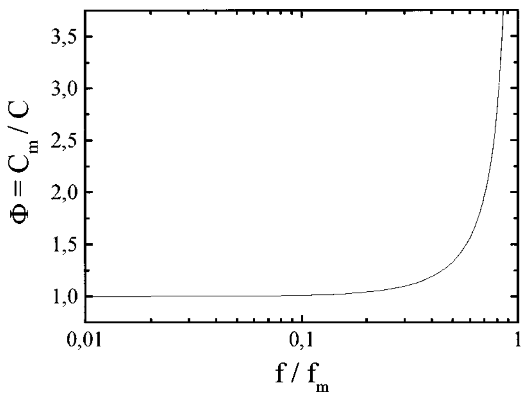

FIG. 4. Curve of the error function $\Phi = C_m/C$ vs the reduced frequency f/f_m for the differential capacity measurements with ohmic drop compensation [Eq. (12)].

$$\Phi = \frac{1}{1-\left(\frac{\omega}{\omega_m}\right)^2} = \frac{1}{1-\left(\frac{f}{f_m}\right)^2}. \tag{12}$$

The error function is below 1% if the frequency is below $0.1 f_m$ that means up to 450 Hz. Figure 4 shows the variation of the error function Φ versus reduced frequency f/f_m.

This frequency does not correspond to the highest usable frequency. From Eq. (7), the output tensions $E_S(90°)$ and $E_S(0°)$ of the lock-in are

$$E_s(90°) = E_\omega(90°) + E_\omega(0°)\ \frac{\omega T_{\text{mc}}}{G_{\text{mc}}}, \tag{13}$$

$$E_s(0°) = \frac{E_\omega(0°)}{G_{\text{mc}}} \approx 0. \tag{14}$$

Relation (13) shows that to get $E_\omega(90°)$ the stray term $E_\omega(0°)$. $\omega T_{\text{mc}}/G_{\text{mc}}$ which depends on the common mode rejection must be subtracted from the output tension $E_s(90°)$. At each frequency the determination of the stray term requires the measurement of the ohmic drop, R_e, by mean of the compensation potentiometer (Fig. 3). After that the electrochemical cell is replaced by a resistance equal to R_e. The measured tension $E_s(90°)$ corresponds to the stray term $E_\omega(0°)\omega T_{\text{mc}}/G_{\text{mc}}$. This term is subtracted from $E_s(90°)$ by shifting the ''zero'' of $E_s(90°)$ using the offset of the lock-in amplifier.

IV. EXPERIMENTAL RESULTS

Potentiostat and galvanostat (Fig. 2) are built with an operational amplifier ''OP-15''. Their characteristics are:

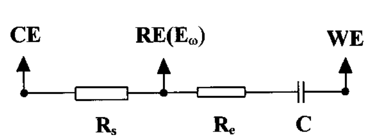

FIG. 5. Equivalent circuit of a dummy cell for the case where the metal–solution interface is ideally polarized.

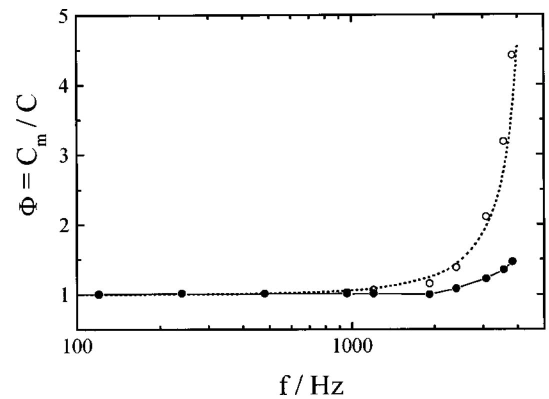

FIG. 6. Curves of the error function $\Phi = C_m/C$ vs frequency: ··· theoretical curve from Eq. (12). ○ experimental values with ohmic drop correction, —●— experimental values with ohmic drop correction and offset compensation.

(1) Potentiostat:
current capability: ± 10 mA; compliance voltage: ± 10 V; loop unity gain bandwidth: <1 Hz; current range: 1 V/mA.

(2) Galvanostat:
current capability: ± 10 mA; bandwidth: >100 kHz.

For testing this new method, a dummy cell is used. This one is schematically represented by the series electrical circuit in Fig. 5. R_s is the resistance of the electrolyte between the counter electrode, CE and the reference electrode RE(E_ω). The resistance values used $R_s = 500\ \Omega$ and $R_e = 200\ \Omega$ correspond to classic values for a real electrochemical cell.

The curves in Fig. 6 show the error function, Φ, versus the frequency, f, in the case of a calibrated capacity $C = 30\ \mu$F. The dotted line represents the theoretical curve obtained from Eq. (12) and the open circles correspond to measured values with ohmic drop correction without offset compensation. There is an excellent agreement between theoretical and experimental values. The error function is below 1% up to 450 Hz. The solid circles correspond to measured values with the ohmic drop compensation and the suppression of the effect of the common mode rejection, the curve shows that the error function is below 1% up to 2000

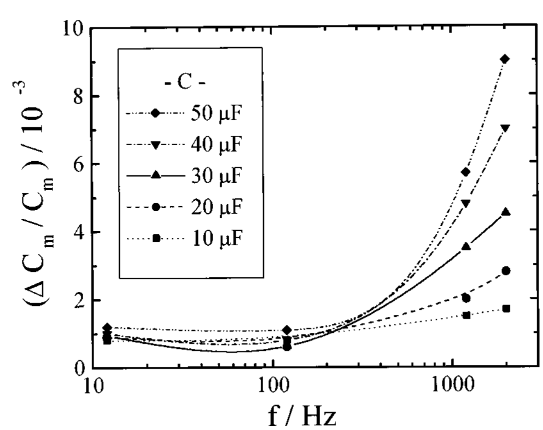

FIG. 7. Curves of the relative error $\Delta C_m/C$ for measured capacity C_m vs frequency for different calibrated capacity C.

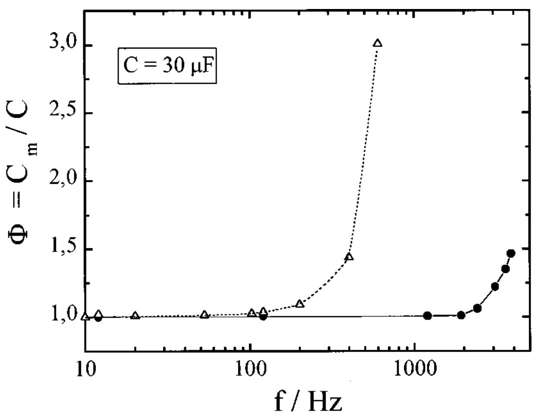

FIG. 8. Curves of the error function $\Phi = C_m / C$ vs frequency: ---△--- potentiostatic feedback control using ac potential perturbation technique; —■— galvanostatic feedback control using ac current perturbation technique.

Hz. The suppression of the effect of the common mode rejection strongly increases the available frequency range.

The curves in Fig. 7 represent the relative error $\Delta C_m / C_m$ for measured capacity, C_m, versus frequency for five calibrated capacities C:10, 20, 30, 40, and 50 μF. These curves show that the relative error does not exceed 0.1% for any C at frequencies up to 100 Hz. Between 100 and 2000 Hz, the relative error progressively increases with the frequency and the capacity. Nevertheless, the relative error is always less than 1%.

The comparison between this galvanostatic technique and the classic potentiostatic technique[6] is shown in Fig. 8. The curves represent the error function $\Phi = C_m / C$ versus frequency for each method with $R_e = 200\,\Omega$ and $C = 30\ \mu$F. These curves show clearly that this new method allows measurements with an error below 1% up to 2000 Hz whereas the potentiostatic method is limited to 100 Hz.

V. DISCUSSION

For an electrochemical interface which can be simulated by a series RC circuit with a time constant of about 10^{-2} s, the differential capacity can be measured when the dc polarization, E, and the interfacial perturbation ac current, I_ω, is imposed by a galvanostat associated with a low bandwidth potentiostat ($B_\omega < 1$ Hz).

Contrary to the potentiostatic method, in this new method the measurement precision does not depend on the characteristics of the control feedback circuit. The original feature of the method is to allow both a direct measurement of the perturbation ac current, I_ω, and of the response ac potential, E_ω, of the interface, between the working electrode, WE, and a reference electrode, RE(E_ω). With this new method, capacity measurement precision depends only on the measurement circuit performances as can be seen in Fig. 6. The frequency limit depends only on the common mode rejection of the differential amplifier used in the ohmic drop compensation.

The superiority of this galvanostatic method versus the classic potentiostatic method is clearly seen in Fig. 8. With the ohmic drop compensation and the suppression of the effect of the common mode rejection the error function is less than 1% up to 2000 Hz while with the classic potentiostatic method using ohmic drop correction the limiting frequency is 100 Hz.

[1] J. O'M. Bockris, B. E. Conway, and E. Yeager, *Comprehensive Treatise of Electrochemistry* (Plenum, New York, 1980), Vol. 1, p. 221.
[2] J. Lecoeur, J. Andro, and R. Parsons, Surf. Sci. **114**, 320 (1982).
[3] G. Valette, J. Electroanal. Chem. **178**, 179 (1984).
[4] J. P. Badiali, M. L. Rosinberg, and J. Goodisman, J. Electroanal. Chem. **130**, 31 (1981).
[5] S. Amokrane and J. P. Badiali, J. Electroanal. Chem. **266**, 21 (1989).
[6] F. Chao, M. Costa, J. Lecoeur, and J. P. Bellier, Electrochim. Acta **34**, 320 (1989).
[7] C. Koehler, J. Lecoeur, and J. P. Bellier, J. Electroanal. Chem. **395**, 29 (1995).
[8] R. E. White, J. O'M. Bockris, B. E. Conway, and E. Yeager, *Comprehensive Treatise of Electrochemistry* (Plenum, New York, 1984), Vol. 8, p. 3.
[9] C. Gabrielli, M. Ksouri, and R. Wiart, Electrochim. Acta **22**, 255 (1977).