

'Dip'-formation in phase-sensitive ac-voltammetry as a result of the uncompensated resistance

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Short communication

“DIP”-FORMATION IN PHASE-SENSITIVE AC-VOLTAMMETRY AS A RESULT OF THE UNCOMPENSATED RESISTANCE

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During research [1] on surface modified electrodes (SME), we encountered a remarkable phenomenon in the phase-sensitive ($\lambda = 90^\circ$) ac-voltammograms of a cobalt-tetra(*p*-aminophenyl)porphyrin (CoT(pNH₂)PP) modified glassy carbon (Cg) electrode. Upon increasing the frequency, a dip arises in the redox peak, exactly at its peak potential (Fig. 1a). Further increase of the frequency turns the peak upside down and then forces an increase in this direction. Finally, this peak decreases again ($f > 150$ Hz) and only the double-layer charging current is observed. This unexpected behaviour could not be explained at first, but simulation of the ac-voltammogram made it clear that this effect is due to the uncompensated (electrolyte) resistance (R_u). For this simulation, the equivalent circuit shown in Fig. 2 was used. The current (i) for the phase-sensitive ac-voltammogram, at a detection angle (λ) of 90° , is expressed by

$$i(\lambda = 90^\circ) = \epsilon Y'' \cos \omega t = \epsilon \frac{Z''}{(Z')^2 + (Z'')^2} \cos \omega t \quad (1)$$

where ϵ is the modulation amplitude, ω the angular frequency, and Y'' the imaginary part of the admittance, which is composed of the real (Z') and the imaginary (Z'') part of the impedance. For the equivalent circuit used, Z' and Z'' are given by

$$Z' = R_u + \frac{R_f C_f^2}{(C_f + C_d)^2 + (\omega R_f C_f C_d)^2} \quad (2)$$

$$Z'' = \frac{C_d + C_f + (\omega R_f C_f)^2 C_d}{\omega [(C_f + C_d)^2 + (\omega R_f C_f C_d)^2]} \quad (3)$$

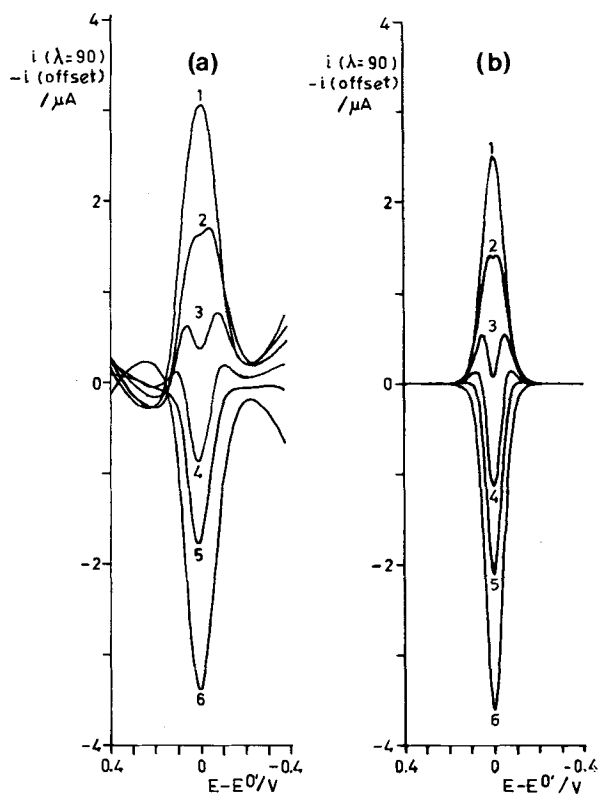
where C_d is the double-layer capacity and R_u the uncompensated solution resistance, which can be calculated from [2]:

$$R_u = (2\kappa d)^{-1} \quad (4)$$

for a disc electrode (diameter d) in the case of a primary current distribution (κ

being the specific conductivity). The faradaic resistance (R_f) and capacity (C_f), however, depend on the electrode potential as expressed by [3] (quasi-reversible charge transfer):

$$R_f = \frac{RT}{n^2 F^2 A \Gamma_T k_s} (\xi^\alpha + \xi^{\alpha-1}) \quad (5)$$



	f/Hz	Offset	
		Measured	Simulated
1	30	10.6	9.0
2	40	10.2	11.0
3	50	11.4	12.3
4	60	12.3	13.1
5	70	12.8	13.6
6	150	12.4	11.3

Fig. 1. Phase-selective ac-voltammograms of a Co(II)T(pNH₂)PP modified Cg-electrode. (a) Measured for different frequencies in 0.1 M TEAP/DMSO ($\kappa = 2.44 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$), $\lambda = 90^\circ$, $\epsilon = 0.01 \text{ V (rms)}$, $v = 0.02 \text{ V s}^{-1}$. (b) Simulated with $\lambda = 90^\circ$, $\epsilon = 0.01 \text{ V}$, $R_u = 90 \Omega \text{cm}^2$, $C_d = 22.2 \mu\text{F cm}^{-2}$, $\Gamma_T = 1.5 \times 10^{-11} \text{ mol cm}^{-2}$, $A = 0.246 \text{ cm}^2$, and $k_s = 590 \text{ s}^{-1}$ ($C_f = 14.1 \mu\text{F cm}^{-2}$ and $R_f = 60 \Omega \text{cm}^2$ at $E = E^{0'}$).

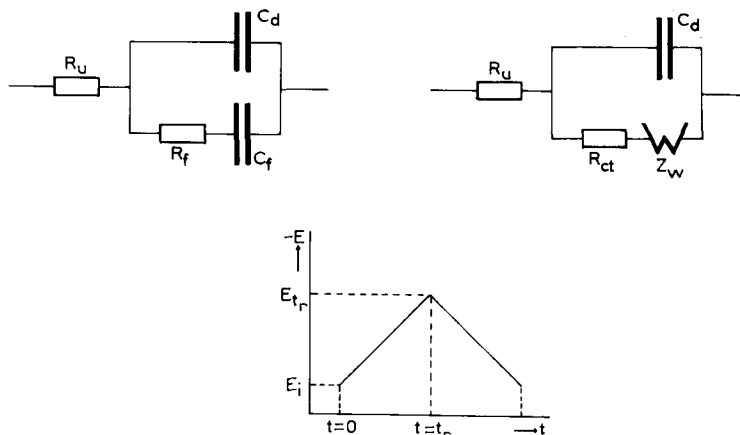


Fig. 2. Equivalent circuit for surface modified electrode; both O and R attached to the surface. R_u , Uncompensated resistance; C_d , double-layer capacity; R_f , faradaic resistance; C_f , faradaic capacity; R_{ct} , charge transfer resistance; Z_w , Warburg impedance.

and

$$C_f = \frac{n^2 F^2 A \Gamma_T}{RT} \frac{\xi}{(1 + \xi)^2} \quad (6)$$

where

$$\xi = \exp(nF/RT)(E - E^{o'})$$

The symbols α , n , F , R , T , and E have their usual meaning and k_s (s^{-1}) stands for the rate constant of the surface reaction. The double-layer capacity (C_d) and the total surface concentration (Γ_T) are determined from the ac-voltammogram at 30 Hz. Substitution of eqns. (2)–(6) into eqn. (1) yields a general expression for the ac-voltammogram, at a detection angle (λ) of 90° , in which the uncompensated resistance is accounted for. This expression was used for simulation of the measured voltammograms. As can be seen from Fig. 1b, the simulations agree very well with the observed changes in the ac-voltammograms upon increasing the frequency (see Fig. 1a). This remarkable behaviour primarily results from the uncompensated (mainly electrolyte) resistance (R_u), but is intensified by the faradaic resistance, i.e. reaction rate. No dip-formation occurs when $R_u = 0$. For increasing values of R_f ($R_u \neq 0$), dip-formation occurs at lower frequencies. The best fit of the simulation was obtained for a surface reaction rate constant (k_s) of 590 s^{-1} . From cyclic voltammetry, a rate constant $k_s = 24 \text{ s}^{-1}$ was determined [1]. This value is probably too low since it was calculated from the peak potential difference (ΔE_p) which approached $\approx 15 \text{ mV}$ and not the expected zero value at low potential scan rates (v). If the graph $\cot \phi = f(\omega)$ is used for the determination of k_s , then not only R_u but also C_d must be taken into account because the faradaic phase angle (ϕ_f) and not the measured phase angle (ϕ) must be used.

It should also be noted that peak broadening occurs, which is frequency-dependent. This peak broadening, calculated from the simulation, does not completely explain the one experimentally observed, so non-ideal behaviour, as described by Brown and Anson [4] and Murray and co-workers [5], must still be taken into account. The appearance of a dip in the peak of the ac-voltammogram results, for a certain frequency region, in apparently two peaks, which can be very confusing for interpretation.

A similar phenomenon can be observed if redox species in solution are detected by ac-voltammetry at a detection angle of 90° instead of 45° . Phase-sensitive ac-voltammetry should therefore be performed at different frequencies and in combination with cyclic voltammetry to avoid erroneous interpretations.

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