

A MODEL FOR THE *ac*-IMPEDANCE OF AN ELECTRODE COATED BY A PRECIPITATED SALT FILM

F K CRUNDWELL

Department of Chemical Engineering, University of the Witwatersrand, P O Wits 2050, South Africa

(Received 22 May 1990, in revised form 26 September 1990)

Abstract—The *ac*-impedance of an electrode which is coated by a precipitated salt film is described. An important aspect of this model is that it describes the modulation of the film thickness which displays an impedance spectrum typical of that of an RC-series circuit (i.e. a vertical straight line on the Nyquist diagram) at frequencies below 1 Hz, in addition to the spectrum for diffusion through a layer of fixed thickness (i.e. a loop on the Nyquist diagram that is similar in shape to that of convective diffusion). A model for the dissolution of Cu in HCl solutions in the limiting-current region that describes the modulation of the thickness of the precipitated CuCl film is derived and is shown to be a good description of the experimental results.

Key words *ac*-impedance, salt film, limiting-current region, dissolution, precipitation

INTRODUCTION

The precipitation of a porous salt film on the surface of an electrode occurs in a number of electrochemical systems. Russel and Newman[1, 2] observed that the iron electrode surface is covered by a porous FeSO₄ film, and presented a model for the passivation of iron in which the passivation potential is a function of the pH at the electrode-salt film interface. Nobe and co-workers[3-6] observed that the copper electrode surface is covered by a CuCl film in the limiting-current region, and presented a model in which the rate of reaction is controlled by the diffusion of Cl⁻ ions through the porous layer to the electrode surface.

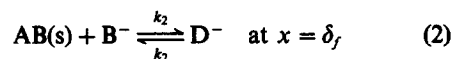
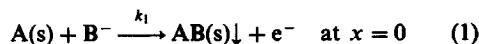
Steady-state measurements have been carried out in these and similar systems in which the electrode surface is covered by a porous salt film, but few studies have made use of transient techniques, such as frequency response analysis (*ac*-impedance analysis). One exception is that of Clerc and Landolt[7] who used this technique to study the anodic films on Ni in the limiting-current region in concentrated LiCl solutions. They proposed a model in which the electrode surface is covered with a compact oxide layer and a looser salt layer, and obtained good fits of their model to the data.

In this paper the analysis of the impedance spectrum is extended to include the case of an electrode reaction in which the electrode is coated with a precipitated salt. This analysis focuses on the effect of the diffusion of the reactants through the salt film on the low-frequency impedance spectrum.

MATHEMATICAL FORMULATION

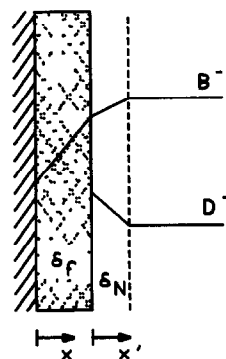
A typical electrode system in which a porous salt film has precipitated on the electrode surface is

illustrated in Fig 1. A reactant B⁻ diffuses through the convective diffusion barrier and the porous salt layer, and reacts at the electrode surface to produce more salt film. The salt film dissolves chemically at the salt-solution boundary, and the products diffuse to the bulk solution. This scheme is



The concentration gradient of B⁻ is distributed between the convective diffusion boundary layer, and the porous salt layer. In the porous salt layer concentration gradient of B⁻ is determined by molecular diffusion

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial x^2} \quad 0 < x < \delta_f \quad (3)$$



Electrode Film Solution

Fig 1 Schematic diagram illustrating the various diffusion processes occurring during the dissolution of an electrode onto which a porous salt film has precipitated

and in the solution boundary layer, the concentration gradient of B^- is determined by convective diffusion

$$\frac{\partial c'_1}{\partial t} = D'_1 \frac{\partial^2 c'_1}{\partial x'^2} - v_x \frac{\partial c'_1}{\partial x'} \quad 0 < x' < \delta_N \quad (4)$$

The origin of the x -coordinate is taken at the electrode-salt interface, while that of the x' -coordinate is taken at the salt-solution interface (i.e. $x' = x - \delta_f$)

The concentration gradient of the products, D^- , is determined by convective diffusion

$$\frac{\partial c'_2}{\partial t} = D'_2 \frac{\partial^2 c'_2}{\partial x'^2} - v_x \frac{\partial c'_2}{\partial x'} \quad 0 < x' < \delta_N \quad (5)$$

This model has neglected all effects, such as field-assisted migration, that are not described by convective or molecular diffusion. It has also assumed that there are no variations other than those in the x -direction, and the interfaces are planar and perpendicular to the axis of rotation.

Since the diffusion velocity for most ions in solution is about $1 \mu\text{m/s}$, and the rate of removal of metal ions from the surface results in the electrode interface receding by about 1nm/s , the electrode interface is essentially stationary relative to diffusion of ions in solution. This is the well-known pseudo-steady-state assumption, which will be applied in this model.

Associated with the transport equations (3)–(5) are the boundary conditions involving the flux and concentration of the diffusing species. These differential equations are therefore subject to the following boundary conditions

$$x = 0 \quad N_1(0) = i/F = k_1 c_1(0) \quad (6)$$

$$x = \delta_f \quad c_1(\delta_f) = c'_1(0) \quad (7)$$

$$x' = 0 \quad N_1(0) - k_2 c_1(\delta_f) + k_{-2} c_2(0) = N'_1(0) \quad (8)$$

$$x' = \delta_N \quad c'_1(\delta_N) = C_b \quad (9)$$

$$x' = 0 \quad N_2(0) = k_2 c_1(\delta_f) - k_{-2} c_2(0) \quad (10)$$

$$x' = \delta_N \quad c_2(\delta_N) = 0, \quad (11)$$

where N_1 , N'_1 and N_2 are the fluxes of c_1 , c'_1 , and c_2 , respectively, δ_f is the thickness of the salt layer, δ_N is the Nernst diffusion layer thickness, k_1 is the electrochemical rate constant for reaction (1).

In addition the mass balance over the film gives

$$\rho(1 - \epsilon) \frac{d\delta_f}{dt} = i/F - k_2 c_1(\delta_f) + k_{-2} c_2(0), \quad (12)$$

where ρ is the molar density of the salt, and ϵ is the porosity of the salt. This model assumes that ϵ is constant throughout the film thickness.

Steady-state solution

The steady-state solution of equations (4) and (5) is given by

$$c(\infty) = a_1 \int_0^\infty \exp\left\{1/D \int_0^z v_x(z) dz\right\} dt + c(0) \quad (13)$$

Designating the integral by δ_N , where $\delta_N = 1.61 (D/v)^{1/3} (v/\Omega)^{1/2}$ and applying the boundary condition (9) we get

$$C_b = a_1 \delta_N + a_2 \quad (14)$$

Applying the boundary condition, equation (11) we get that

$$0 = a_3 \delta_N + a_4 \quad (15)$$

and substituting this into the boundary condition equation (10) we get

$$N_2(0) = \frac{D_2}{\delta_N} \frac{k_2 c_1(\delta_f)}{D_2/\delta_N + k_{-2}} \quad (16)$$

This flux is potentially important since it can be measured at the ring in a ring-disk electrode experiment if the ring is set at a potential that will reduce or oxidize D^- ions only.

The steady-state solution of equation (3) is

$$c_1(x) = a_5 x + c_1(0) \quad (17)$$

Applying the boundary conditions, equations (6)–(8), and by noting that $N'_1(0) = N_1(0) = k_1 c_1(0)$ we get the following expression for the current at steady state

$$\frac{i}{F} = \frac{C_b}{1/k_1 + \delta_f/D_1 + \delta_N/D'_1 - K}, \quad (18)$$

where

$$K = \frac{\delta_N/D'_1 D_2/\delta_N k_2/k_1 (k_1 \delta_f/D_1 + 1)}{D_2/\delta_N + k_{-2}}$$

The mass balance over the film together with the substitution of the value of $c'_1(0) = c_1(\delta_f)$ from equation (17) and the boundary conditions equations (6) and (7) yields an equation for the film thickness in terms of the mass transfer coefficient D_2/δ_N for D^- ions

$$\frac{\delta_f}{D_1} = \frac{1}{k_2} - \frac{1}{k_1} + \frac{k_{-2} \delta_N}{k_2 D_2} \quad (19)$$

Substituting this into equation (17), we get

$$\frac{i}{F} = \frac{C_b}{k_{-2}/k_2 \delta_N/D_2 + 1/k_2} \quad (20)$$

Unsteady-state solution and ac-impedance analysis

For small perturbations of the voltage, the current can be expressed as a truncated Taylor series

$$i = \bar{i} + \frac{\partial i}{\partial V} \tilde{V} + \frac{\partial i}{\partial c} \tilde{c} \quad (21)$$

The faradaic impedance, \tilde{V}/\tilde{i} , is then given by

$$Z_f = R_t \left\{ 1 - \frac{\partial i}{\partial c} \frac{\tilde{c}}{\tilde{i}} \right\}, \quad (22)$$

where $R_t = \partial V/\partial i$ is the charge-transfer resistance. Equations (3)–(5) become

$$\frac{\partial \tilde{c}_1}{\partial t} = D_1 \frac{\partial^2 \tilde{c}_1}{\partial x^2} \quad 0 < x < \delta_f \quad (23)$$

$$\frac{\partial \tilde{c}'_1}{\partial t} = D'_1 \frac{\partial^2 \tilde{c}'_1}{\partial x'^2} - v_x \frac{\partial \tilde{c}'_1}{\partial x'} \quad 0 < x' < \delta_N \quad (24)$$

$$\frac{\partial \tilde{c}'_2}{\partial t} = D'_2 \frac{\partial^2 \tilde{c}'_2}{\partial x'^2} - v_x \quad 0 < x' < \delta_N \quad (25)$$

and the boundary conditions become

$$x = 0 \quad \tilde{N}_1(0) = \tilde{i}/F = k_1 \tilde{c}_1(0) \quad (26)$$

$$x = \delta_f \quad \tilde{c}_1(\delta_f) = \tilde{c}'_1(0) \quad (27)$$

$$x' = 0 \quad \tilde{N}_1(0) - k_2 \tilde{c}_1(\delta_f) + k_{-2} \tilde{c}_2(0) = \tilde{N}'_1(0) \quad (28)$$

$$x' = \delta N \quad \tilde{c}'_1(\delta_N) = 0 \tag{29}$$

$$x' = 0 \quad \tilde{N}_2(0) = k_2 \tilde{c}_1(\delta_f) - k_{-2} \tilde{c}_2(0) \tag{30}$$

$$x' = \delta_N \quad \tilde{c}_2(\delta_N) = 0 \tag{31}$$

The mass balance over the film becomes

$$\rho(1 - \epsilon) \frac{d\delta_f}{dt} = \tilde{i}/F - k_2 \tilde{c}_1(\delta_f) + k_{-2} \tilde{c}_2(0) \tag{32}$$

From equation (32) we would expect the thickness of the film to vary when a low-frequency perturbation is superimposed on the voltage. This variation in the film thickness will affect the flux through the salt layer. The flux through the salt layer can be expanded as a Taylor series about its steady-state value

$$N_2 = \bar{N}_2 + \frac{\partial N_2}{\partial c_2} \tilde{c}_2 + \frac{\partial N_2}{\partial \delta_f} \delta_f \tag{33}$$

From Fick's first law, we get that

$$\tilde{N}_2 = D_2 \frac{d\tilde{c}_2}{dx} - \frac{D_2}{\delta_f} \frac{d\tilde{c}_2}{dx} \delta_f \tag{34}$$

Equations (24) and (25) have been discussed in detail [8, 9] and the numerical solution is usually presented in terms of the convective Warburg impedance, $\theta'_N(0)$. The fluxes at the salt-solution interface are given by

$$\tilde{N}'_1(0) = D'_1 \left. \frac{d\tilde{c}'_1}{dx'} \right|_{x=0} = \tilde{c}'_1(0) \frac{D'_1}{\delta_N} \theta'_N(0) = \tilde{c}'_1(0) K_1 \tag{35}$$

$$\tilde{N}_2(0) = D_2 \left. \frac{d\tilde{c}_2}{dx} \right|_{x=0} = \tilde{c}_2(0) \frac{D_2}{\delta_N} \theta'_N(0) = \tilde{c}_2(0) K_2 \tag{36}$$

Taking the Laplace transform of equation (32) with respect to time and substituting equation (36) we get that

$$\delta_f = \frac{1}{\gamma s} (\tilde{i}/F - \tilde{c}_2(0) K_2), \tag{37}$$

where $\gamma = \rho(1 - \epsilon)$ and s is the temporal Laplace coordinate

Taking the Laplace transform of equation (23), applying the boundary conditions equations (26) and (27) and substituting equations (34) and (35), we get that

$$Z_f = R_f \left\{ 1 + \frac{k_1(1 + B/\gamma s)(\tanh(\alpha)/\sqrt{sD_1} - G_1)}{1 - \sqrt{sD_1} \tanh(\alpha) G_1} \right\}, \tag{38}$$

where

$$G_1 = \left\{ \frac{1 + B/\gamma s \frac{K_2 k_2 \sinh(\alpha)}{(k_{-2} + K_2)\sqrt{sD_1}}}{K_1 + \frac{K_2 k_2}{k_{-2} + K_2} (1 - (E/\gamma s - B/\gamma s \cosh(\alpha)))} \right\}$$

$$\alpha = \sqrt{(s/D_1)} \delta_f \quad B = \frac{D_1}{\delta_f} \left. \frac{d\tilde{c}_1}{dx} \right|_{x=0} \quad E = \frac{D_1}{\delta_f} \left. \frac{d\tilde{c}_1}{dx} \right|_{x=\delta_f}$$

Some limiting cases

Of interest are solutions corresponding to cases where one or more of the convective diffusion barriers is zero, or where B or E (the parameters which determine the size of the fluctuation in the film thickness) are zero

Case (i). $K_1 = K_2 = 0$ Should this hold then the boundary condition equation (27) becomes $\tilde{c}'_1(\delta_f) = 0$ and the solution to equations (33) and (34) is

$$Z_f = R_f \{ 1 + k_1(1 + B/\gamma s) \tanh(\alpha) / \sqrt{(sD_1)} \} \tag{39}$$

This indicates clearly the effect of the modulation of the film thickness of the porous layer

Case (ii) $K_2 = 0, B = E = 0$ This corresponds to the case when the film is inert and the reaction is governed by the diffusion of the reactant to the surface

$$Z_f = R_f \left\{ 1 + \frac{k_1(\tanh(\alpha)/\sqrt{(sD_1)} - 1/K_1)}{1 - \sqrt{sD_1} \tanh(\alpha)/K_1} \right\} \tag{40}$$

The convective Warburg impedance can be approximated by the solution to Fick's equation for a Nernst layer. Then

$$K_1 \approx -\frac{\sqrt{(sD'_1)}}{\tanh \beta} \quad \beta = \sqrt{(s/D'_1)} \delta_N$$

$$Z_f = R_f \left\{ 1 + \frac{k_1(\tanh(\alpha)/\sqrt{(sD_1)} + \tanh(\beta)/\sqrt{(sD'_1)})}{1 + \tanh(\alpha) \tanh(\beta) \sqrt{(sD_1)}/\sqrt{(sD'_1)}} \right\} \tag{41}$$

RESULTS

The electrode impedance is given by the faradaic impedance shunted by the double-layer capacitance. For a sinusoidal perturbation of voltage, the frequency response is obtained by substituting $j\omega$ for s . Calculated impedance results are presented here for the two cases examined. For all the calculated impedance spectra the same values for charge-transfer resistance, the solution resistance, and the double-layer capacitance are used. These are 5Ω , 10Ω and $3.5 \times 10^{-6} \mu\text{F}$, respectively.

Case (i) Figures 2-4 show equation (39) calculated for various values of the parameters D_1 , δ_f and B , respectively. The figures illustrate a shape similar to that typical of the convective Warburg impedance diagram at frequencies between 1 kHz and 10 Hz, but then below 10 Hz the effect of the modulation of the

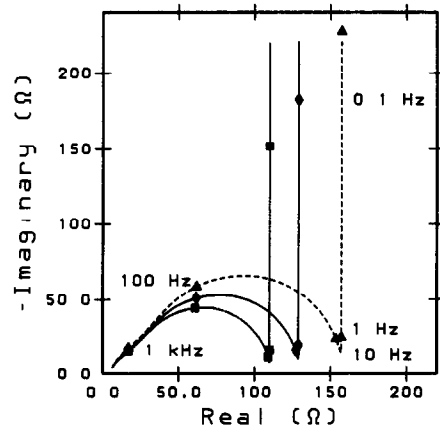


Fig 2 *ac*-Impedance spectra for equation (39) for three different values of the diffusion coefficient --- 2.8×10^{-5} , — 3.5×10^{-5} , — — $4.2 \times 10^{-5} \text{ cm}^2/\text{s}$ $\delta_f = 4 \times 10^{-4} \text{ cm}$, $k_1 = 10 \text{ m/s}$, $B/\gamma = 1$

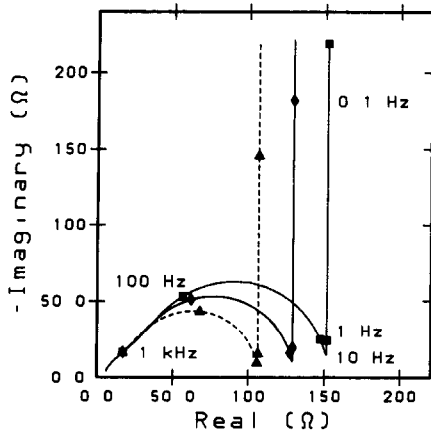


Fig 3 *ac*-Impedance spectra for equation (39) for three different values of the film thickness --- 3.2×10^{-4} , — 4.0×10^{-4} , — 4.8×10^{-4} cm $D_1 = 3.5 \times 10^{-5}$ cm²/s, $k_1 = 10$ m/s, $B/\gamma = 1$

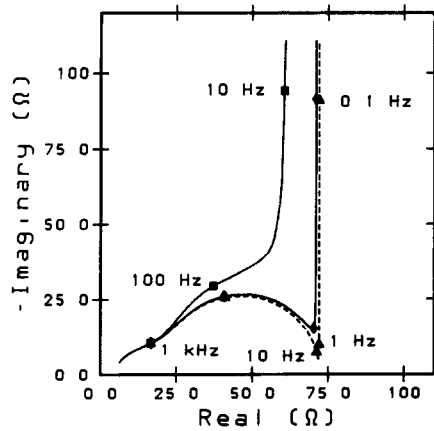


Fig 4 *ac*-Impedance spectra for equation (39) for three different values of the constant B/γ --- 1, — 10, — 100 $D_1 = 3.5 \times 10^{-5}$ cm²/s, $\delta_f = 4 \times 10^{-4}$ cm, $k_1 = 10$ m/s

film thickness, described by the term in $B/\gamma s$, becomes dominant. This term displays typical RC-series impedance, i.e. a vertical straight line on the Nyquist diagram.

Figure 2 shows the effect of a variation in the value of the diffusion coefficient. The dashed lines are 20% above and below the solid curve. This illustrates the sensitivity of the model to the value of the diffusion coefficient. Similar results are shown in Fig 3 for a variation in the value of the film thickness, indicating that the model is also very sensitive to the value of the film thickness. The effect of variation in the value of B is shown in Fig 4.

Case (ii) Figures 5–8 show equation (41) calculated for various values of the parameters D_1 , δ_f , D'_1 and δ'_N , respectively. These figures illustrate the distortion of the typical convective Warburg impedance diagrams (at frequencies above 1 kHz).

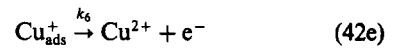
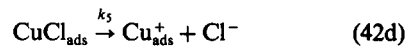
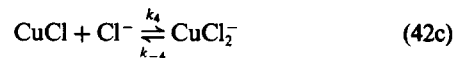
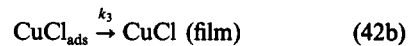
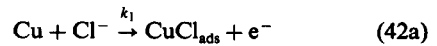
The dashed lines are 20% above and below the solid curve, illustrating the sensitivity of the model to the various parameters.

Analysis of the ac-impedance of copper dissolution in the limiting-current region

The anodic dissolution of copper in hydrochloric acid solutions in the limiting-current region is first order in the concentration of chloride ions. It has been established that a CuCl porous layer forms on

the electrode surface, and it has been postulated that the diffusion of chloride through this porous layer controls the rate of reaction[3–6].

The following mechanism has been proposed for the dissolution of copper in the limiting-current region



Reactions (42a, b, d, e) occur at the electrode surface, while reaction (42c) occurs at the film–solution boundary.

The change in the rate of the electrochemical reaction (42a) in the limiting current region is given by

$$\frac{\tilde{i}_1}{F} = k_1(1 - \bar{\theta})\bar{c}_1(0), \quad (43)$$

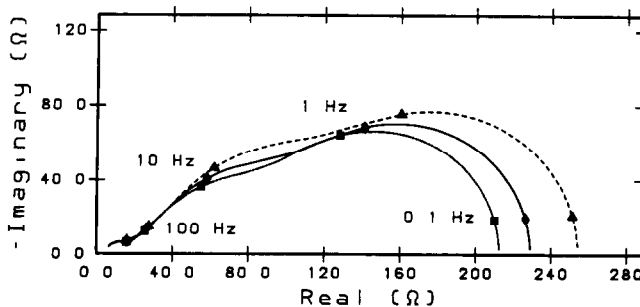


Fig 5 *ac*-Impedance spectra for equation (41) for three different values of the diffusion coefficient in the porous film --- 0.4×10^{-5} , — 0.5×10^{-5} , — 0.6×10^{-5} cm²/s $\delta_f = 4 \times 10^{-4}$ cm $D'_1 = 3.5 \times 10^{-5}$ cm²/s, $\delta'_N = 0.004$ cm, $k_1 = 1$ m/s

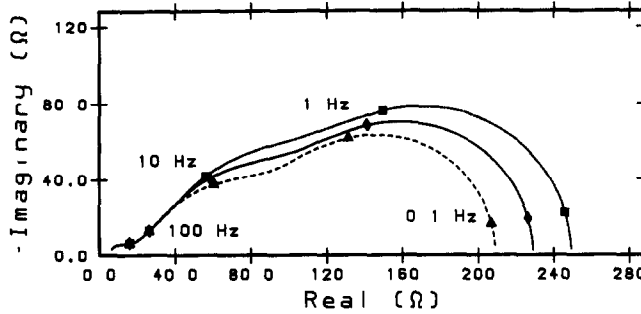


Fig 6 *ac*-Impedance spectra for equation (41) for three different values of the porous film thickness --- 4×10^{-4} , — 5×10^{-4} — 6×10^{-4} cm $D_1 = 5 \times 10^{-6}$ cm²/s, $D'_1 = 3.5 \times 10^{-5}$ cm²/s, $\delta_f = 0.004$ cm, $k_1 = 1$ m/s

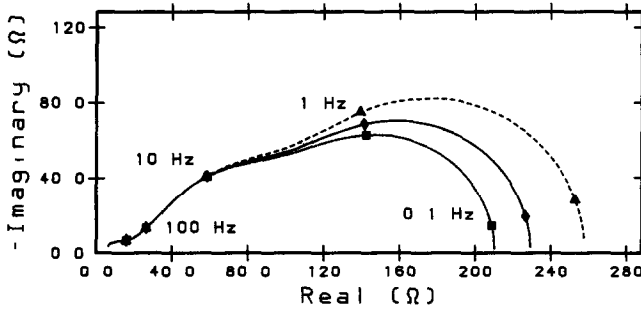


Fig 7 *ac*-Impedance spectra for equation (41) for three different values of the diffusion coefficient --- 2.8×10^{-5} , — 3.5×10^{-5} , — 4.2×10^{-5} cm²/s $D_1 = 5 \times 10^{-6}$ cm²/s, $\delta_f = 0.0005$ cm, $\delta_N = 0.004$ cm, $k_1 = 1$ m/s

where $\bar{\theta}$ is the surface concentration of the CuCl_{ads} intermediate, and $\bar{c}_1(0)$ is the change in the concentration of Cl^- at the Cu surface. The change in the rate of the electrochemical reaction (42e) is given by

$$\frac{\bar{i}_2}{F} = k_6 \bar{F}, \quad (44)$$

where \bar{F} is the change in the surface coverage of the Cu_{ads}^+ intermediate. The rate of the formation of CuCl_{ads} is governed by the mass balance

$$\frac{d\bar{\theta}}{dt} = \frac{\bar{i}_1}{F} - k_3 \bar{\theta} - k_5 \bar{\theta} \quad (45)$$

while the formation and dissolution of the porous film is given by

$$\rho_{\text{CuCl}}(1 - \epsilon) \frac{d\delta_f}{dt} = k_3 \bar{\theta} \quad (46)$$

ρ_{CuCl} is the molar density of CuCl and ϵ and δ_f are the porosity and thickness of the CuCl porous film. A mass balance of the Cu_{ads}^+ intermediate formed by reaction (42d) is given by

$$\frac{d\bar{F}}{dt} = k_5 \bar{\theta} - k_6 \bar{F} \quad (47)$$

Equation (23) describes the diffusion of the limiting species through the porous salt layer and is subject to the boundary conditions

$$x = 0 \quad \bar{N}_1(0) = \frac{\bar{i}_1}{F} - k_5 \bar{\theta} \quad (48)$$

$$x = \delta_f \quad \bar{c}_1(\delta_f) = 0 \quad (49)$$

From equation (46) we would expect the thickness of the film to vary when a low-frequency sinusoidal voltage is superimposed on its steady-state value, and this variation in the film thickness would affect the

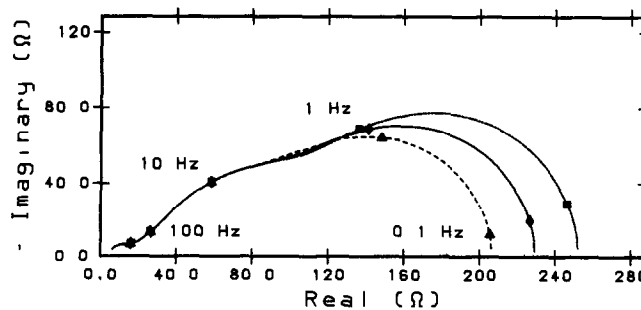


Fig 8 *ac*-Impedance spectra for equation (41) for three different values of the Nernst diffusion layer thickness --- 3.2×10^{-3} , — 4×10^{-3} — 4.8×10^{-3} cm $D_1 = 5 \times 10^{-6}$ cm²/s, $D'_1 = 3.5 \times 10^{-5}$ cm²/s, $\delta_f = 0.0005$ cm, $k_1 = 1$ m/s

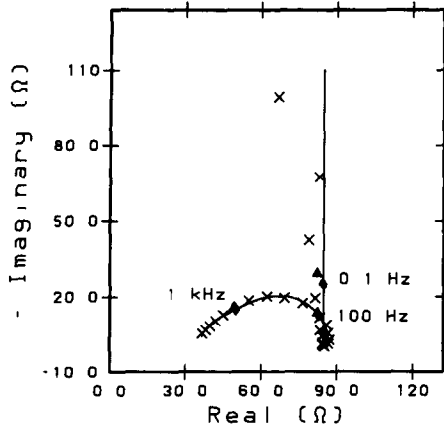


Fig 9 *ac*-Impedance spectra for the dissolution of copper in the limiting-current region in 0.1 M HCl $V_D = -27$ mV, $i = 0.284$ mA

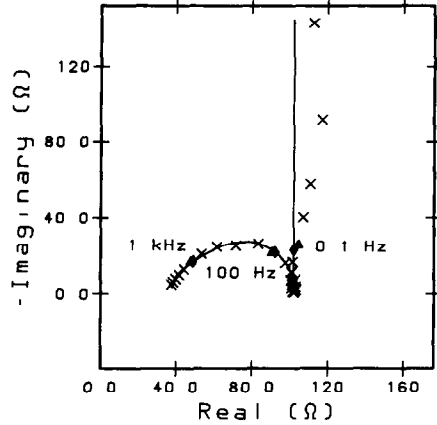


Fig 11 *ac*-Impedance spectra for the dissolution of copper in the limiting-current region in 0.1 M HCl $V_D = -20$ mV, $i = 0.30$ mA

flux through the porous layer. The flux of Cl^- can be expanded as a Taylor series about its steady-state value, and equation (34) applies.

Taking the Laplace transform of equations (43)–(49), and substituting the boundary conditions, together with equation (34), we get the following expression for the faradaic impedance for the dissolution of the Cu electrode in HCl solutions in the limiting current region

$$Z_f = R_s \left\{ 1 + \frac{k_1(1-\theta)(s + k_3 + Bk_3/\gamma s) \tanh \psi}{\sqrt{(sD_1)(s + k_3 + k_5)}} \right\}, \quad (50)$$

where $\gamma = \rho_{\text{CuCl}}(1 - \epsilon)$, $\psi = \sqrt{(s/D_1)\delta_f}$

The electrode impedance is given by the faradaic impedance shunted by the double-layer capacitance. For a sinusoidal perturbation of the voltage, the frequency response is obtained by substituting $j\omega$ for s in equation (50). The electrode impedance, plotted as a Nyquist diagram, consists of four loops, three of which are capacitive and a fourth that is inductive. These loops are the charge-transfer resistance double-layer capacitance loop, and the loops describing the intermediates $\text{CuCu}_{\text{ads}}^+$ and Cu_{ads}^+ , and the mass trans-

fer of Cl^- through the porous CuCl layer. The term involving $s/(s + k_3 + k_5)$ is the inductive loop and arises from the reaction (42d). The term involving $B/\gamma s$ represents the modulation of the film thickness. This term represents a RC-series impedance at low frequencies, i.e. a vertical line on a Nyquist diagram.

Figures 9–11 show equation (50) fitted to experimental data for the dissolution of Cu in HCl solutions. The lines represent the model and the points the experimental impedance spectra. The diamonds and the triangles represent the model and the experimental values at the same frequencies, indicating the close correspondence between this model and the data. Table 1 gives the values of the parameters fitted to equation (50) for the experimental results presented in Figs 9–11.

These results indicate that the modulation of the film thickness has a significant effect on the impedance spectra at low frequencies, and that this is described by the model outlined in this paper.

CONCLUSIONS

The problem of the frequency response of an electrode which is coated with a porous salt film has been solved, and simplifying cases that illustrate the main points of the analysis have been examined. The analysis is then shown to describe the results of the dissolution Cu in the limiting-current region, in which

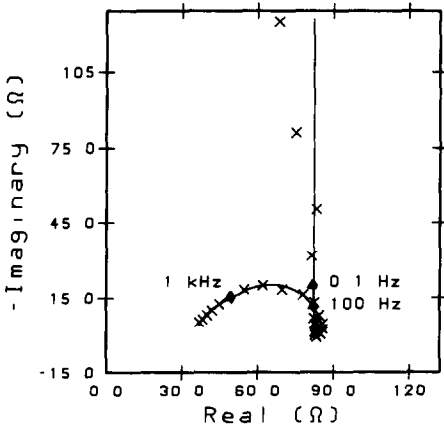


Fig 10 *ac*-Impedance spectra for the dissolution of copper in the limiting-current region in 0.1 M HCl $V_D = -27$ mV, $i = 0.298$ mA

Table 1 Parameters for the impedance spectra in the limiting-current region

Parameter	Units	V_D (mV vs sce)		
		-27	-27	-20
D_2	$\text{cm}^2/\text{s} \times 10^{-5}$	1.10	0.89	0.68
δ_f	$\text{cm} \times 10^{-4}$	1.14	0.95	1.02
$k_1(1-\theta)$	cm/s	0.17	0.16	0.12
k_3	1/s	27.6	27.6	32.5
E/γ	1/s	0.51	0.44	0.33
k_5	1/s	1.8	3.0	0.5
R_i	Ω	18.5	18.2	22.6
R_s	Ω	36.0	36.1	37.2
C_{dl}	μF	4.0	4.0	5.0

a precipitated film of CuCl covers the surface of the electrode

REFERENCES

- 1 P Russel and J Newman, *J Electrochem Soc* **133**, 59 (1986)
- 2 P Russel and J Newman, *J Electrochem Soc* **134**, 1051 (1987)
- 3 H P Lee and K Nobe, *J Electrochem Soc* **133**, 2035-2043 (1986)
- 4 M Braun and K Nobe, *J Electrochem Soc* **126**, 1666-1671 (1979)
- 5 H P Lee, K Nobe and A Pearlstein, *J Electrochem Soc* **132**, 1031-1037 (1985)
- 6 A Pearlstein, H P Lee and K Nobe, *J Electrochem Soc* **132**, 2159-2165 (1985)
- 7 C Clerc and D Landolt, *Electrochim Acta* **33**, 859 (1988)
- 8 E Levart and D Schuhmann, *J Electrochem Soc* **55**, 77 (1974)
- 9 R V Homsey and J Newman, *J Electrochem Soc* **121**, 521 (1974)