

Investigations of the negative plate of lead/acid cells

3. Model calculations of the impedance of self-similar porous electrodes

Michel Saakes

TNO Environmental and Energy Research, P.O. Box 6011, 2600 JA Delft (Netherlands)

Willem H. Mulder

Department of Chemistry, University of the West Indies, Mona Campus, Kingston 7 (Jamaica)

(Received September 9, 1993; in revised form November 20, 1993; accepted November 21, 1993)

Abstract

In this paper a model for the calculation of the admittance (reciprocal impedance) of a porous metal electrode is derived, under anodic constant-current conditions, during precipitation of an insoluble salt at the metal/electrolyte interface. An example of the discharge, at low current density, of the negative plate in a lead/sulphuric acid battery during which lead sulphate is formed. The discussion is based on the assumption that porosity has a self-similar fractal character. The impedance of fractal electrodes will be discussed in terms of geometrical and physical parameters.

Introduction

The use of porous electrodes has proved to be essential for many applications. Examples are manifold: gas-diffusion electrodes (e.g., fuel cells); electrodes for battery applications (e.g., positive and negative plate of lead/acid cells), and electrodes for the removal of trace amounts of heavy metal impurities in waste-water treatment, etc. (e.g., carbon felt, granulate, fibers). In all these applications, the true interfacial electrode area is much larger than the apparent (geometrical) electrical area, which makes the space-time yield for the electrode reaction, of interest, much higher. The processes at porous electrodes have been described using many different mathematical approximations [1-7]. In this paper we will focus our attention on the well-known lead/lead sulphate system, i.e., a porous lead electrode that is discharged at constant current, at low current density, in sulphuric acid with the resulting formation of lead sulphate. The impedance of the lead/lead sulphate system in sulphuric acid is composed of four parameters, described in parts 1 and 2 of this series [8, 9]; the charge-transfer resistance, R_F , for the formation of lead ions, the Warburg impedance due to the diffusion of lead sulphate, the differential double-layer capacitance, C_d , and the crystallization resistance, R_k , due to the slow precipitation of lead sulphate.

Literature evaluation

Different models have been postulated for describing the porous interface (e.g., transmission line model [1], flooded agglomerate model [3], self-similar fractal roughness

model [10–17]. At porous electrodes, the parameters to be evaluated are both physical and geometrical. The possibility to extract the geometrical parameters from electrochemical measurements will be discussed first. The description of the system lead/lead sulphate in sulphuric acid, in case of a porous electrode, will be discussed in the context of the so-called self-similar roughness concept, as introduced by le Mehauté and Crépy [10], which has subsequently been adopted and elaborated by several authors [2, 6, 11–14, 17]. Very recently, Mulder [17] published a paper in which the influence of self-similar fractal roughness on the electrode admittance was quantitatively discussed for several cases involving both diffusion and adsorption. One case, which is of special interest, is the admittance spectrum for a d.c. reversible reaction at a fractal electrode. For this case the framework presented in ref. 17 for deriving the equation for the electrode admittance in case of fractal surface roughness can be used.

It has been shown [2, 17] that the electrode admittance, Y_{ei} , at a fractal electrode per unit of apparent surface area generally can be written as:

$$Y_{ei}(i\omega) = \sigma' \sigma^{1-\xi} y^\xi(i\omega) \quad (1)$$

where σ' is a geometry factor, σ the solution conductivity, ξ a number with a value between 1/2 and 1 and constant over a wide range of frequencies, and $y(i\omega)$ is the specific electrode admittance. The fractal or Hausdorff dimension, D_H , of the electrode is related to ξ via [11]:

$$\xi = 1/(D_H - 1) \quad (2)$$

In particular, this means that $\xi = 1$ for $D_H = 2$ (perfectly smooth surface).

The rate equation, which relates the faradaic-current density to the surface concentration of the electroactive species and the potential of the electrode, is used to derive the faradaic part of $y(i\omega)$ via $\Delta j_F = y_F(\phi_0 - \phi)$ where $\phi_0 - \phi$ is the local complex amplitude of the a.c. potential drop across the double layer. In order to get the total current density we have to add to this a contribution due to charging and discharging of the double layer, equal to $\Delta j_C = i\omega C_d(\phi_0 - \phi)$. The expression for $\Delta j = \Delta j_F + \Delta j_C$ can then be rewritten as:

$$\Delta j/\phi_0 = y(1 - \phi') \quad (3)$$

with $y = i\omega C_d + y_F$ and $\phi' = \phi/\phi_0$, the local deviation of the electrostatic potential just outside the double layer from the d.c. value, normalized with respect to the amplitude of the a.c. signal.

The local particle flux amplitude Δj_d towards or away from a fractal surface can be written in terms of the local interfacial concentration fluctuation, Δc_s , as [14, 17]:

$$\Delta j_d = -Q^{-1} D^{1-1/2\xi} (i\omega)^{1/2\xi} \Delta c_s \quad (4)$$

where Q is an average local geometry factor and D the diffusion coefficient.

The deviation from the stationary surface concentration, c_s , can then be found by combining eqn. (4) with the rate equation.

In the final expression for $Y_{ei}(i\omega)$ for an electrode which displays self-similar roughness three geometry factors appear: ξ , Q and σ' . In ref. 17 it was shown that in principle these three geometrical parameters as well as the total interfacial area, A_H , can be derived from a.c. impedance measurements.

Theory

The processes accompanying the anodic dissolution of lead in sulphuric acid are schematically represented in Fig. 1.

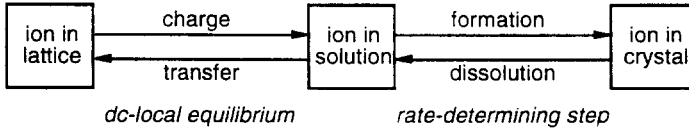


Fig. 1. Schematic representation of the process involved in the formation of lead sulphate if recrystallization is assumed to be the rate-determining step.

In deriving the rate equation for the system lead/lead sulphate in sulphuric acid, the mathematical description of the process of metal deposition can be used, if surface diffusion of adatoms is assumed to be rate determining [18].

The rate equation can be derived as follows. If we assume that dissolution at a surface coverage θ only proceeds at the uncovered surface, the dissolution-current density, j_{diss} , at the bare surface is given by:

$$j_{\text{diss}} = j_0 \exp(1 - \beta)\eta \quad (5)$$

where $\eta = (nF/RT)(\phi_0 - \phi)$, $\phi_0 - \phi$ is the local deviation from the equilibrium potential drop across the interface, $1 - \beta$ is the transfer coefficient for anodic dissolution ($0 \leq \beta \leq 1$) and j_0 is the exchange current density. Equation (5) is valid only for $\theta \ll 1$.

The deposition current, j_{dep} , depends on the average surface concentration, c_s , of lead sulphate. If c_0 represents the equilibrium concentration of lead sulphate, then j_{dep} is given by:

$$j_{\text{dep}} = j_0(c_s/c_0) \exp(-\beta\eta) \quad (6)$$

The net current density, j_F , (at $1 - \theta$) is given by:

$$j_F = j_{\text{diss}} - j_{\text{dep}} = j_0[\exp(1 - \beta)\eta - (c_s/c_0) \exp(-\beta\eta)] = j_0 \exp(-\beta\eta)[\exp(\eta) - c_s/c_0] \quad (7)$$

At small departure from equilibrium eqn. (7) can be linearized:

$$\Delta j_F = j_0(\Delta\eta - \Delta c_s/c_0) \quad (8)$$

where $\Delta c_s = c_s - c_0$ and $\Delta\eta = (nF/RT)(\phi_0 - \phi)$ is proportional to the local (complex) amplitude of the a.c. signal. This equation was derived before by Rybalka and co-workers [19-21].

Equation (7) is now used to obtain the first-order perturbation Δj_F :

$$\Delta j_F = j_0\{(1 - \beta)\Delta\eta \exp[(1 - \beta)\eta] + \beta\Delta\eta \exp(-\beta\eta) - (\Delta c_s/c_0) \exp(-\beta\eta)\} \quad (9)$$

Before Δj_F can be made explicit, Δc_s must be solved using Fick's laws. The flux equation for the process depicted in Fig. 1 is given by [18, 19]:

$$\Delta j_F/nF = k\Delta c_s - D(\partial\Delta c/\partial\nu)_s = k\Delta c_s - \Delta j_d \quad (10)$$

where k is the rate constant for the formation and dissolution of lead sulphate and $\partial/\partial\nu$ is the derivative at the interface taken along a unit vector ν normal to the surface, pointing towards the solution, and $n = 2$. Furthermore, it is assumed that the precipitate formation is a first-order process in the concentration of lead sulphate.

Inserting eqn. (3) into eqn. (10) leads to:

$$\Delta c_s = [k + Q^{-1}D^{1-1/2\xi}(i\omega)^{1/2\xi}]^{-1} \Delta j_F/nF \quad (11)$$

Now Δc_s can be introduced in the expression for Δj_F (eqn. (9)) which gives rise to the following equation:

$$\Delta j_F = R_F^{-1} \frac{\beta + (c_s/c_0)(1 - \beta)}{(c_s/c_0)^\beta + (j_0/nFc_0)/(k + Q^{-1}D^{1-1/2\xi}(i\omega)^{1/2\xi})} (\phi_0 - \phi) \quad (12)$$

where $R_F = (RT/nF)/j_0$.

Equation 12 can be simplified using $c_s/c_0 \approx 1$ (small d.c.-overpotential). This results in $(c_s/c_0)^\beta \approx 1$ and $\beta + (1 - \beta)c_s/c_0 \approx 1$ (only true for local equilibrium, so for d.c.-reversible reduction). The expression for Δj_F then reduces to:

$$\Delta j_F = R_F^{-1} [1 + (j_0/nFc_0)/(k + Q^{-1}D^{1-1/2\xi}(i\omega)^{1/2\xi})]^{-1} (\phi_0 - \phi) \quad (13)$$

The net local current density amplitude Δj is equal to $\Delta j_c + \Delta j_F$. The specific interfacial admittance, using eqns. (1) and (3), then reads:

$$y(i\omega) = [Y_{el}(i\omega)/(\sigma' \sigma^{-1\xi})]^{1/\xi} = i\omega C_d + R_F^{-1} [1 + (j_0/nFc_0)/(k + Q^{-1}D^{1-1/2\xi}(i\omega)^{1/2\xi})]^{-1} \\ \equiv i\omega C_d + a/[1 + b/(1 + c(i\omega)^{1/2\xi})] \quad (14)$$

where C_d is the differential double-layer capacitance, $a = R_F^{-1}$, $b = j_0/(nFc_0k)$ and $c = D^{1-1/2\xi}/Qk$. Identifying R_k with $RT/n^2F^2c_0k$, parameter b equals R_k/R_F . The geometrical parameters are σ' , Q and ξ . The physical parameters are C_d , R_F , k and D . Of the geometrical parameters ξ is obtained most easily by constant phase element (CPE) measurements for it is related to the constant phase angle, α , by $\alpha = \xi\pi/2$ [10]. It has been shown [17] that both σ' and Q as well as the total 'true' interfacial area can be obtained using only a.c. measurements. The value of σ' is obtained from measurements with a d.c.-reversible couple like $\text{Fe(III)[CN]}_6^{3-}/\text{Fe(II)[CN]}_6^{4-}$ as described in ref. 17. Once the geometrical parameters are known, the physical parameters can be found from linear fitting procedures [8].

Procedure for obtaining the physical parameters

The analysis of eqn. (14) will be outlined below. We can distinguish two limiting cases:

(i) $\omega \rightarrow 0$

In this case $y(i\omega)$ becomes:

$$y(i\omega)_{\omega \rightarrow 0} = a/(1 + b) \quad (15)$$

From this complex plane diagram for y'' versus y' , $a/(1 + b)$ is found as the intercept with the real axis.

(ii) $\omega \rightarrow \infty$

In this limit $y(i\omega)$ approaches the asymptote:

$$y(i\omega)_{\omega \rightarrow \infty} = i\omega C_d + a \quad (16)$$

From the complex plane diagram a is found as the intercept of this asymptote with the real axis. From both limits of ω the values of a, b and C_d are found. On the other hand, in order to find c it is necessary to perform a one-parameter fit. A linear relation is obtained using the expression:

$$b[a/(y(i\omega) - i\omega C_d) - 1]^{-1} = 1 + c(i\omega)^{1/2\xi} \quad (17)$$

Once Q is known, k is calculated c . Also, the exchange current density, j_0 , is obtained from the value of b .

The dependence of the electrode impedance, Z_{el} , on the fractal dimension of the electrode:

$$Z_{el} = Z' - iZ'' \alpha (i\omega C_d + a/[1 + b/(1 + c(i\omega)^{1/2\xi})])^{-\xi} \quad (18)$$

can be studied using fixed values of C_d , a , b and c and varying ξ between 1/2 and 1. In the case of a smooth electrode ($\sigma' = Q = \xi = 1$) a , b , c and C_d are obtained directly without the need to evaluate geometry parameters first.

D.c. reversible case

A simplification can be made assuming $a^{-1} = R_F = 0 (j_0 \rightarrow \infty)$. This results in:

$$Z_{el} \propto \{i\omega C_d + R_k^{-1}[(1 + c(i\omega)^{1/2\xi})]\}^{-\xi} \quad (19)$$

The parameter R_k contains the value of k which is essential for understanding the expander action.

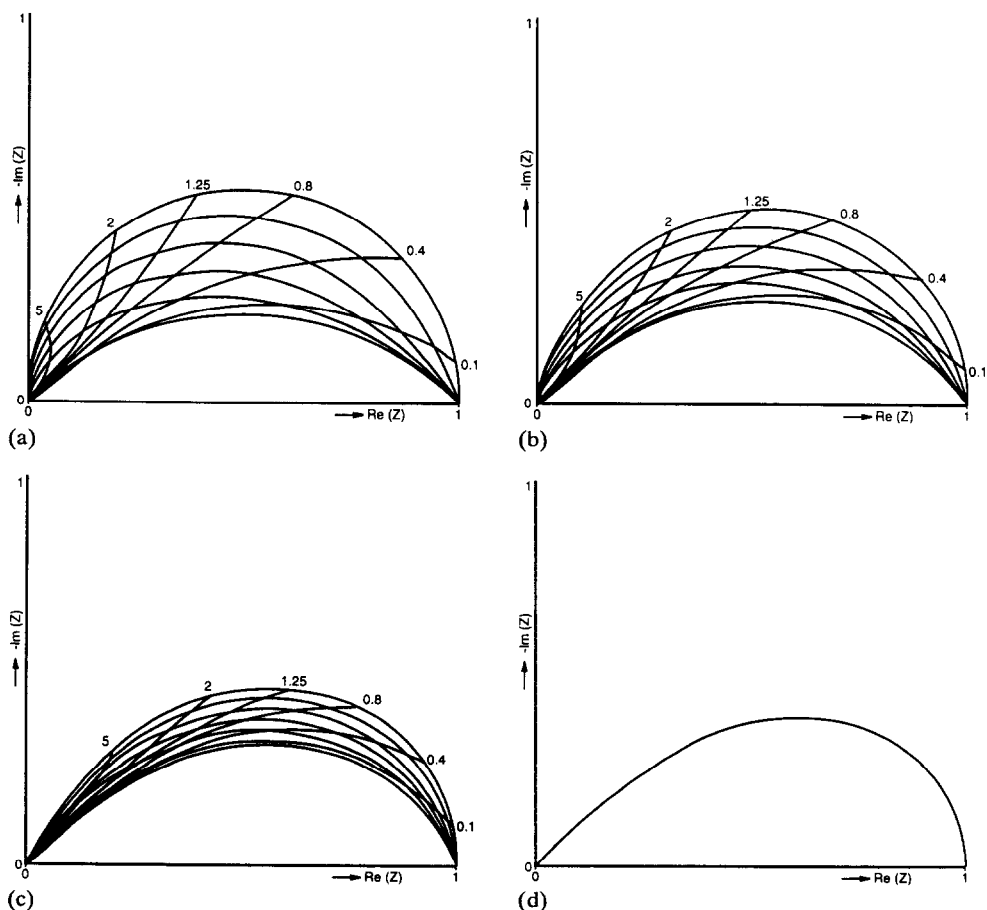


Fig. 2. Complex plane representation of eqn. (21) for $p=0, 0.2, 0.5, 1, 2$, and 10^5 (from top to bottom, respectively). Curves are drawn for (a) $\xi=1$ (perfectly smooth electrode), (b) $\xi=0.83$, (c) $\xi=0.67$, and (d) $\xi=0.5$ (completely porous electrode). Also curves of constants ω' are depicted with values as indicated.

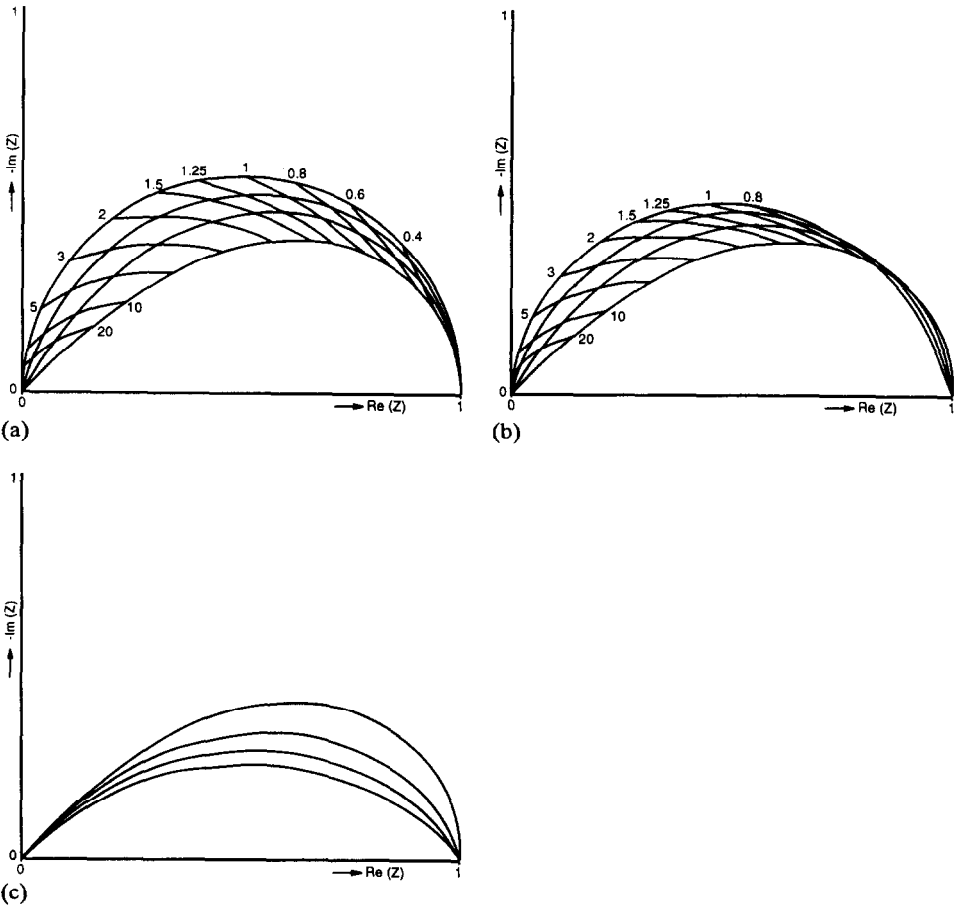


Fig. 3. Complex plane representation of eqn. (21) for $\xi=1, 0.83, 0.67$ and 0.5 . Curves are drawn for (a) $p=0$, (b) $p=0.2$ and (c) $p \rightarrow \infty$. In diagram (a) and (b) also lines of constant ω' values are indicated, corresponding to (from left to right) $\omega'=20, 10, 5, 3, 2, 1.5, 1, 0.8, 0.6$ and 0.4 .

The value of R_k can be found from the value of Z_{ei} in the low-frequency limit in which case:

$$(\sigma' \sigma^{1-\xi} Z_{ei}(i\omega)_{\omega \rightarrow 0})^{1/\xi} = R_k \tag{20}$$

In the case of d.c.-reversibility Z_{ei} can be rescaled to the form:

$$Z_{ei} \propto [1 + i\omega' + p(i\omega')^{1/2\xi}]^{-\xi} \tag{21}$$

where $\omega' = (RTC_d/n^2 F^2 c_0 k)\omega = R_k C_d \omega$ and $p = Q^{-1}(n^2 F^2 c_0 / RTC_d)^{1/2\xi} (D/k)^{1-1/2\xi}$. The limiting cases for eqn. (21) are: 1 for $\omega' \rightarrow 0$ and 0 for $\omega' \rightarrow \infty$.

In Figure 2(a)-(d) we have plotted Z_{ei} for $\xi=1.0, 0.83, 0.67$ and 0.5 . The a.c. frequency was varied between 10^{-15} to 10^{15} Hz. The values for p taken were $p=0, 0.2, 0.5, 1, 2$, and 10^5 . In each diagram (Fig. 2(a)-(c)) also lines of constant ω' values are indicated, corresponding to (from left to right) $\omega'=5, 2, 1.25, 0.8, 0.4$ and 0.1 .

In the case of $\xi=0.5$ eqn. (21) simplified to the form $Z_{ei} \propto (1 + i\omega'')^{-1/2}$ where $\omega'' = (p+1)\omega'$, one curve is found independent of the value of p . For $\xi=1$ (smooth

surface) and $p=0$ we find a semi-circle while for $p \rightarrow \infty$ a quarter-circle is found. The main difference in the impedance behaviour found is the change of the shape of the semi-circle for $\xi=1$, $p=0$ to a distorted semi-circle (lemniscate) for $1/2 < \xi < 1$, and the merging of all curves when $\xi \rightarrow 1/2$.

In Fig. 3 we have plotted the complex plane representation for $\xi=1$, 0.83, 0.67 and 0.5 for constant values of p ($p=0$, $p=0.2$ and $p \rightarrow \infty$). In this plot, for $p=0$ and $p=0.2$, lines of constant ω' values are drawn which represent the variation of the impedance for different ξ values and constant p .

Conclusions

A.c. impedance measurements can provide us with both the physical and geometrical parameters related to the discharge process of a porous lead electrode in sulphuric acid.

In the condition of a d.c.-reversible reaction the analysis is simplified. This condition holds for the discharge reaction of lead to lead sulphate in sulphuric acid.

In order to make the analysis of the impedance feasible, additional a.c. measurements are necessary to obtain σ' , Q and ξ . These measurements must be made at the same fractal electrode surface.

Acknowledgements

The authors wish to express their gratitude to Messrs. H.E. Wijers, B. van de Ploeg and C. Posthumus of the Royal Netherlands Navy for their stimulating contributions to the project. We further acknowledge the Royal Netherlands Navy, TNO Defence Research and TNO Environmental and Energy Research for their financial support. The work was carried out under contract no. A81/KM/074.

List of symbols

a	$1/R_F$
b	R_k/R_F
c	$D^{1-1/2\xi}/Qk$
c_s	surface concentration
Δc_s	first-order deviation from surface concentration
c_0	equilibrium concentration
C_d	differential double-layer capacitance
D	diffusion coefficient
D_H	Hausdorff dimension
F	Faraday constant
i	imaginary unit $\sqrt{-1}$
j_0	exchange-current density
Δj	total current density
Δj_C	double-layer part of current density
Δj_d	local particle flux amplitude
Δj_F	faradaic part of current density
k	crystallization rate constant
n	number of electrons transferred
Q	average local geometry factor

R	gas content
R_F	charge-transfer resistance
R_k	crystallization resistance
T	absolute temperature
y	specific electrode admittance
Y_{el}	electrode admittance
Z_{el}	electrode impedance
Z'	real part of impedance
Z''	imaginary part of impedance

Greek letters

α	constant phase angle
β	transfer coefficient
θ	fractional surface coverage
η	$(nF/RT)(\phi_0 - \phi)$
ξ	$1/(D_H - 1)$ CPE exponent
ϕ	potential amplitude just outside the double layer
ϕ_0	amplitude of applied a.c. signal
σ	solution conductivity
σ'	geometry factor
ν	unit vector
ω	angular frequency

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