



Transient Analysis of a Porous Electrode

Sheba Devan,^{a,*} Venkat R. Subramanian,^{b,**} and Ralph E. White^{a,***,z}

^aCenter for Electrochemical Engineering, Department of Chemical Engineering, Swearingen Engineering Center, University of South Carolina, Columbia, South Carolina 29208, USA

^bDepartment of Chemical Engineering, Tennessee Tech University, Cookeville, Tennessee 38505, USA

An analytical expression is presented for the voltage response including the transient voltage for a simple (*i.e.*, no concentration gradients) porous electrode model subject to a sinusoidal input current density. The transient voltage response as a function of the frequency, exchange current density, and double layer capacitance is studied independent of the periodic (steady state) voltage response. The change in the voltage response in the transient region is compared to that of the periodic voltage response with respect to the parameters. The physical properties of the porous electrode can be estimated using the voltage response in the transient region is presented. The methodology for doing this is described.

© 2005 The Electrochemical Society. [DOI: 10.1149/1.1884786] All rights reserved.

Manuscript submitted August 20, 2004; revised manuscript received November 22, 2004. Available electronically April 1, 2005.

The transient techniques employed to measure the physical properties of a porous electrode and in fact any electrochemical system are based on the concept of perturbing the system about its initial condition using potential, current, or charge and measuring the response of the system. Because the rates of each processes such as interfacial charge transfer, mass transport etc., are time dependent, the analysis of the time dependence gives information to obtain these properties. When any system is perturbed, the current or voltage response changes from one steady state (initial state) to another steady state. The transition from an initial state to steady state occurs within a region and the response in this region is called the transient response. Hence, the complete response of a system consists of two parts: the transient response and the steady state response.¹

The perturbation can be of many different kinds such as step, ramp, pulse, sinusoidal, etc.² To maintain a linear response the amplitude of the perturbations are often very small. Some of the transient techniques take into consideration only the steady state response of the system for example electrochemical impedance spectroscopy (EIS).³ Most of the other techniques include the measurement of both transient and the steady state responses for example potential step or sweep.^{2,4} We will only consider the techniques that take into consideration the transient response of the system. In this case, the analysis of the system response is often carried out using a combination of the transient and steady state response. However, the transient response is a strong function of the properties of the system. Moreover, the transient response occurs at very short times. Consequently, we expect that there is a wealth of information that can be obtained in very short time periods using just the response in the transient region. In the past, instrumental limitations posed a serious problem to measuring the response at very short time periods (a few milliseconds).² With the advancement of the electrochemical instrumentation this problem has been solved and the measurements at short time periods have been used by some researchers to estimate certain parameters in case of porous electrodes⁵⁻⁷ and thin films.^{8,9} However the potential of the transient response has not been fully utilized.

In this paper, we stress the importance of the transient response of a porous electrode using a simple porous electrode model. The model equations presented below describe the porous electrode under very low rates of discharge when the concentration gradients in the solution phase are not important and when the size of the particles in the electrode are very small so that there is no solid-phase diffusion limitation as well. An analytical solution is developed for the voltage response of a porous electrode subjected to sinusoidal perturbation in current. The response includes the transient voltage

response and the uniform and sustained periodic (sinusoidal steady state) voltage response. Note that the steady state response in periodic input perturbation such as a sinusoidal signal is also a periodic response with the same frequency but with a different amplitude and phase angle with respect to the input perturbations. The input sinusoidal perturbations could have been replaced by other kind of perturbations such as step input,⁶ ramp input,⁷ etc. However, the advantages of analyzing the system response using sinusoidal perturbations are (i) perturbations as sine waves are easy to generate compared to the other wave forms¹⁰ (ii) using sinusoidal signals specified as a function of time and frequency facilitates the use of frequency as another variable apart from time that can be varied at ease, and (iii) the sinusoidal signal can be expressed using standard mathematical functions that makes modeling the system and the subsequent theoretical analysis easier.

In this paper, we analyze the voltage response in the transient region as a function of frequency, exchange current density, and double layer capacitance and compare it with the change in the periodic voltage response (sinusoidal steady state response) of the porous electrode with respect to the same set of parameters. By evaluating the limiting expressions of the derived analytical solution for the voltage response we establish the possibility of estimating the physical parameters of the system using only the voltage response in the transient region. The proposed methodology can be used to estimate parameters accurately within very short time periods.

Model Development

Consider the geometry of the porous electrode illustrated in Fig. 1. The following assumptions are made:

- (1) Porous electrode theory in one dimension is applicable.¹¹
- (2) No concentration gradients exist inside the electrode.
- (3) Both double layer charging and a linear faradi c reaction occur.
- (4) The material properties ($a, \sigma, \kappa, \alpha_a, \alpha_c$) are assumed to be constants.
- (5) The double layer capacitance (C_{dl}) is a constant.
- (6) The open circuit potential is set equal to zero.

With no concentration gradients, the matrix phase current density, i_1 and solution phase current density, i_2 are given by Ohm's law¹¹

$$i_1 = -\sigma_{\text{eff}} \frac{\partial \phi_1}{\partial x} \quad [1]$$

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.

*** Electrochemical Society Fellow.

^z E-mail: white@enr.sc.edu

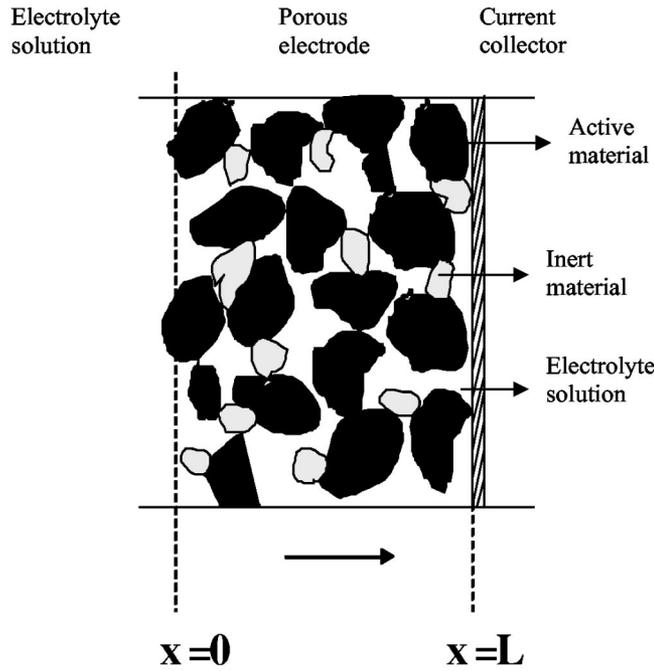


Figure 1. Geometry of the porous electrode.

$$i_2 = -\kappa_{\text{eff}} \frac{\partial \phi_2}{\partial x} \quad [2]$$

where σ_{eff} and κ_{eff} are the effective matrix phase and solution phase conductivities, which are related to the respective bulk conductivities through the Bruggeman's correlation

$$\sigma_{\text{eff}} = (1 - \varepsilon - \varepsilon_{\text{inert}})^{1.5} \sigma \quad [3]$$

$$\kappa_{\text{eff}} = \varepsilon^{1.5} \kappa \quad [4]$$

The total current density $I(t)$ is the sum of the matrix and solution phase current densities

$$i_1 + i_2 = I(t) \quad [5]$$

where $I(t)$ is the applied current density as a function of time. The current transferred from the matrix phase to the solution phase is expressed in terms of the interfacial current density, j_n ¹¹

$$-\frac{\partial i_1}{\partial x} = \frac{\partial i_2}{\partial x} = a j_n \quad [6]$$

where a is the surface area per unit volume of the porous electrode (estimated here as a collection of uniform sphere of radius R_s , see list of symbols¹²). The interfacial current density (j_n) is the sum of the double layer charging current density and the faradic current density

$$j_n = C_{\text{dl}} \frac{\partial(\phi_1 - \phi_2)}{\partial t} + j_{n,f} \quad [7]$$

where C_{dl} is the double layer capacitance and the faradic current density ($j_{n,f}$) is given by the linearized Butler-Volmer kinetic expression^{5,13}

$$j_{n,f} = \frac{i_0 F (\alpha_a + \alpha_c)}{RT} (\phi_1 - \phi_2) \quad [8]$$

where $\alpha_a + \alpha_c = n$ and the open circuit potential has been set equal to zero. Substituting Eq. 8 in Eq. 7 yields

$$j_n = C_{\text{dl}} \frac{\partial(\phi_1 - \phi_2)}{\partial t} + \frac{i_0 (\alpha_a + \alpha_c) F}{RT} (\phi_1 - \phi_2) \quad [9]$$

The overpotential is given by $\eta = \phi_1 - \phi_2$ when the open circuit potential is set equal to zero. For a constant value for the open-circuit potential ($U \neq 0$) the quantity $(\phi_1 - \phi_2)$ in Eq. 8 and consequently in Eq. 9 should be replaced with $(\phi_1 - \phi_2 - U)$. Now the overpotential is given by $\eta = \phi_1 - \phi_2 - U$. The equations derived from this point and on are in terms of the overpotential that is the same for both cases; when U is a constant value and for U set equal to zero. The initial and boundary conditions for the overpotential are given by

$$\phi_1 = 0 \text{ and } \phi_2 = 0 \Rightarrow \eta = 0 \text{ at } t = 0 \text{ for } 0 \leq x \leq L \quad [10]$$

$$i_1 = 0 \text{ and } i_2 = I(t) \Rightarrow \frac{\partial \eta}{\partial x} = \frac{I(t)}{\kappa_{\text{eff}}} \text{ at } x = 0 \text{ and for } t > 0 \quad [11]$$

$$i_1 = I(t) \text{ and } i_2 = 0 \Rightarrow \frac{\partial \eta}{\partial x} = \frac{-I(t)}{\sigma_{\text{eff}}} \text{ at } x = L \text{ and for } t > 0 \quad [12]$$

Equations 1, 2, 6, and 9 can be used to derive the following equation for the overpotential in dimensionless form¹⁷

$$\frac{\partial \eta^*}{\partial \tau} = \frac{\partial^2 \eta^*}{\partial X^2} - \nu^2 \eta^* \quad [13]$$

where ν^2 (dimensionless exchange current density) is

$$\nu^2 = \frac{a i_0 (\alpha_a + \alpha_c) F L^2}{RT} \left(\frac{1}{\sigma_{\text{eff}}} + \frac{1}{\kappa_{\text{eff}}} \right) \quad [14]$$

and

$$X = \frac{x}{L}; \tau = \frac{t}{a C_{\text{dl}} \left(\frac{1}{\kappa_{\text{eff}}} + \frac{1}{\sigma_{\text{eff}}} \right) L^2}; \eta^* = \frac{\eta F}{RT} \quad [15]$$

The corresponding dimensionless initial and boundary conditions are

$$\eta^* = 0 \text{ at } \tau = 0 \text{ and for } 0 \leq X \leq 1 \quad [16]$$

$$\frac{\partial \eta^*}{\partial X} = \delta \text{ at } X = 0 \text{ and for } \tau > 0 \quad [17]$$

$$\frac{\partial \eta^*}{\partial X} = -\delta \beta \text{ at } X = 1 \text{ and for } \tau > 0 \quad [18]$$

where β is the ratio of the effective solution phase to matrix phase conductivity ($\beta = \kappa_{\text{eff}} / \sigma_{\text{eff}}$) and δ is the dimensionless current density

$$\delta(\tau) = I(\tau) \left(\frac{FL}{\kappa_{\text{eff}} RT} \right) \quad [19]$$

The solution to Eq. 13 using the initial and boundary conditions given in Eq. 16-18 in the Laplace domain is

$$\bar{\eta}^*(s) = -\bar{\delta}(s) \left[\frac{\beta \cosh(X \sqrt{\nu^2 + s}) + \cosh((1-X) \sqrt{\nu^2 + s})}{\sqrt{\nu^2 + s} \sinh(\sqrt{\nu^2 + s})} \right] \quad [20]$$

where the over bar represents the variables in the Laplace domain and

$$\bar{\delta}(s) = \bar{I}(s) \left(\frac{FL}{\kappa_{\text{eff}} RT} \right) \quad [21]$$

The potential drop across the porous electrode can be defined as

$$V^* = (\phi_1|_{X=1} - \phi_2|_{X=0}) \quad [22]$$

or

$$V^* = (\phi_1^*|_{X=1} - \phi_1^*|_{X=0}) + \eta^*|_{X=0} \quad [23]$$

Having solved for the overpotential of the electrode in the Laplace domain it is convenient to derive the voltage drop across the porous electrode in terms of the dimensionless overpotential. Hence we determine the potential drop in the solid phase ($\phi_1^*|_{X=1} - \phi_1^*|_{X=0}$) in terms of the overpotential in the subsequent equations that can be later substituted in Eq. 23 to obtain voltage drop as a function of overpotential in the dimensionless form.

Combining Eq. 1, 6, and 9 gives the equation for solid phase potential as

$$\sigma_{\text{eff}} \frac{\partial^2 \phi_1}{\partial X^2} = aC_{\text{dl}} \frac{\partial \eta}{\partial t} + \frac{a i_0 (\alpha_a + \alpha_c) F}{RT} \eta \quad [24]$$

Substitution of the dimensionless variables as defined in Eq. 14 and 15 into Eq. 24 and letting

$$\phi_1^* = \frac{\phi_1 F}{RT} \quad [25]$$

yields an equation for the dimensionless solid phase potential

$$\frac{\partial^2 \phi_1^*}{\partial X^2} = \frac{\beta}{1 + \beta} \left[\frac{\partial \eta^*}{\partial \tau} + \nu^2 \eta^* \right] \quad [26]$$

Using Eq. 13, Eq. 26 can be rewritten as

$$\frac{\partial^2 \phi_1^*}{\partial X^2} = \frac{\beta}{1 + \beta} \frac{\partial^2 \eta^*}{\partial X^2} \quad [27]$$

The boundary conditions for ϕ_1^* and η^* in Eq. 27 are

$$\frac{\partial \phi_1^*}{\partial X} = 0 \text{ and } \frac{\partial \eta^*}{\partial X} = \delta \text{ at } X = 0 \quad [28]$$

$$\frac{\partial \phi_1^*}{\partial X} = -\delta\beta \text{ and } \frac{\partial \eta^*}{\partial X} = -\delta\beta \text{ at } X = 1 \quad [29]$$

Equation 27 can be integrated once with respect to X to yield

$$\frac{\partial \phi_1^*}{\partial X} = \frac{\beta}{1 + \beta} \frac{\partial \eta^*}{\partial X} + C \quad [30]$$

where C is an integration constant that can be determined using one of the boundary conditions (Eq. 28 or 29)

$$C = -\frac{\delta\beta}{1 + \beta} \quad [31]$$

Integrating Eq. 30 between the limits X = 0 to 1 gives the change in the dimensionless solid phase potential across the electrode

$$\phi_1^*|_{X=1} - \phi_1^*|_{X=0} = \frac{\beta}{1 + \beta} (\eta^*|_{X=1} - \eta^*|_{X=0}) - \frac{\delta\beta}{1 + \beta} \quad [32]$$

By substituting Eq. 32 into Eq. 23, we get the dimensionless voltage drop across the electrode as

$$V^* = \left[\frac{\eta^*|_{X=0} + \beta \eta^*|_{X=1} - \delta\beta}{1 + \beta} \right] \quad [33]$$

This dimensional voltage response of the porous electrode in the Laplace domain is obtained using the expression for dimensionless overpotential (Eq. 20 and Eq. 33) in the Laplace domain as

$$\bar{V}^*(s) = \bar{\delta}(s) \left[\frac{\beta^2 \cosh(\sqrt{\nu^2 + s}) + 2\beta + \cosh(\sqrt{\nu^2 + s})}{(\beta + 1)\sqrt{\nu^2 + s} \sinh(\sqrt{\nu^2 + s})} + \frac{\beta}{(\beta + 1)} \right] \quad [34]$$

Laplace inverse of Eq. 34 is determined using the standard theorems as explained below. The Laplace inverse of the second term of Eq. 34 can be determined directly

$$L^{-1} \left[\frac{\bar{\delta}(s)\beta}{(\beta + 1)} \right] = \frac{\delta(\tau)\beta}{(\beta + 1)} \quad [35]$$

A is the amplitude and ω^* is dimensionless frequency of the input perturbation defined as

$$\omega^* = aC_{\text{dl}} \left(\frac{1}{\kappa_{\text{eff}}} + \frac{1}{\sigma_{\text{eff}}} \right) L^2 \omega \quad [36]$$

Now the Laplace inverse of Eq. 34 is given by

$$L^{-1}[\bar{V}^*(s)] = L^{-1}[\bar{\delta}(s)G(s + \nu^2)] + \frac{\beta}{(\beta + 1)} \delta(\tau) \quad [37]$$

where

$$G(s + \nu^2) = \frac{\beta^2 \cosh(\sqrt{\nu^2 + s}) + 2\beta + \cosh(\sqrt{\nu^2 + s})}{(\beta + 1)\sqrt{\nu^2 + s} \sinh(\sqrt{\nu^2 + s})} \quad [38]$$

The Laplace inverse of the function $G(s + \nu^2)$ can be determined by applying the shifting theorem and the Heaviside expansion theorem¹⁴⁻¹⁶ as

$$g(\tau) = e^{-\nu^2 \tau} L^{-1}[G(s)] = -(\beta + 1)e^{-\nu^2 \tau} - \sum_{k=1}^{\infty} \frac{2e^{-(\nu^2 + k^2 \pi^2)\tau} ((-1)^k (\beta + 1) + 2\beta)}{(-1)^k (\beta + 1)} \quad [39]$$

Substituting for the inverse Laplace of the functions $G(s + \nu^2)$ and $\bar{\delta}(s)$ and applying convolution theorem¹⁴ we obtain the Laplace inverse of the first term in Eq. 37

$$L^{-1}[\bar{\delta}(s)G(s + \nu^2)] = \int_0^{\tau} \delta(\xi)g(\tau - \xi)d\xi \quad [40]$$

In general the dimensionless voltage response in the time domain for a porous electrode with a time dependent input current can be derived using the expression

$$V^*(\tau) = \int_0^{\tau} \delta(\xi)g(\tau - \xi)d\xi + \frac{\beta}{(\beta + 1)} \delta(\tau) \quad [41]$$

$$V^* = \frac{VF}{RT} \quad [42]$$

or in dimensional form Eq. 41 is given by

$$V(t) = \frac{L}{\kappa_{\text{eff}}} \left[\int_0^t I(\xi)g(t - \xi) d\xi + \frac{\beta}{(\beta + 1)} I(t) \right] \quad [43]$$

For the case of a sinusoidal input perturbation applied as a current density ($I(t) = A \cos(\omega t)$) to the system, the dimensionless current density becomes

$$\delta(\tau) = A \cos(\omega^* \tau) \left(\frac{FL}{\kappa_{\text{eff}} RT} \right) \quad [44]$$

The voltage response of the porous electrode to the applied sinusoidal perturbation in the time domain is determined by evaluating the integral in Eq. 40 and substituting the result into Eq. 37

$$V(t, \omega) = \frac{c_1 (\beta + 1) \nu^2 e^{-\nu^2 \frac{t}{\tau_0}}}{(\nu^4 + (\omega \tau_0)^2)} + c_1 \sum_{n=1}^{\infty} A_k \left(\frac{(\nu^2 + k^2 \pi^2) e^{-(\nu^2 + k^2 \pi^2) \frac{t}{\tau_0}}}{((\nu^2 + k^2 \pi^2)^2 + (\omega \tau_0)^2)} \right) + V_{\text{ss}} \quad [45]$$

where the uniform and sustained periodic voltage response which is commonly called the steady state voltage response is given by

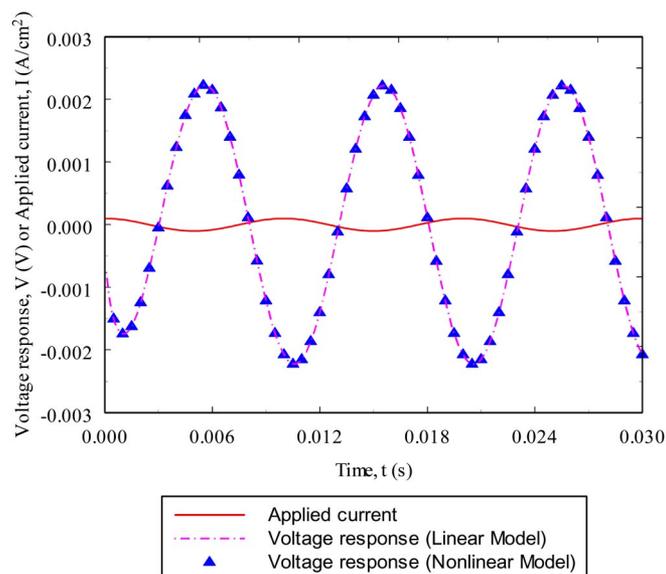


Figure 2. Input current density and voltage response plotted at a frequency of $f = 100$ Hz. All the other values are given in Table I.

$$V_{ss} = -\frac{c_1(\beta + 1)(v^2 \cos(\omega t) + \omega t_0 \sin(\omega t))}{(v^4 + (\omega t_0)^2)} - 2c_1 \sum_{k=1}^{\infty} A_k \left(\frac{\cos(\omega t)(v^2 + k^2 \pi^2) + \omega t_0 \sin(\omega t)}{((v^2 + k^2 \pi^2)^2 + (\omega t_0)^2)} \right) - \frac{c_1 \cos(\omega t) \beta}{\beta + 1} \quad [46]$$

with

$$A_k = \frac{((-1)^k(\beta^2 + 1) + 2\beta)}{(-1)^k(\beta + 1)} \quad [47]$$

$$c_1 = \frac{AL}{\kappa_{eff}} \quad [48]$$

and

$$t_0 = aC_{dl}L^2 \left(\frac{1}{\kappa_{eff}} + \frac{1}{\sigma_{eff}} \right) \quad [49]$$

The angular frequency ω that appears in all of the above equations is given in rad/s, which is related to the frequency 'f' given in Hz as $\omega = 2\pi f$.

Results and Discussion

The voltage response to an input sinusoidal current signal is also a sinusoidal wave with the same frequency as the input but with a different phase angle and amplitude. Figure 2 shows these differences between the input current density and the voltage response for a fixed frequency ($f = 100$ Hz). The voltage response is function of the frequency of the input perturbation, time and the dimensionless parameters that include v^2 , β and t_0 (see Eq. 45). The dimensionless parameters are in turn functions of the properties of the porous electrode: exchange current density, electric double layer at the interface and the effective conductivities in the solid and solution phase (see Eq. 14 and 15). The values of the parameters used to simulate the voltage response in Fig. 2 are given in Table I. In deriving the analytical expression for the voltage response we have assumed linear electrochemical kinetics. Hence, the model presented in this paper is limited to cases where the perturbation to the system is very small ($A = 0.1 \text{ mA/cm}^2$ or less) and when the exchange current den-

Table I. Parameter values.

Parameter	Value
i_0	0.00018 A/cm ²
κ_{eff}	2.055×10^{-4} S/cm
σ_{eff}	0.16185 S/cm
L	0.016 cm
ε	0.63
ε_{inert}	0.073 (Ref. 5)
R_s	8.5 μm
C_{dl}	10 $\mu\text{F/cm}^2$
n	1
$\alpha_a + \alpha_c$	1
A	0.0001 A/cm ²
a	$3(1 - \varepsilon - \varepsilon_{inert})/R_s = 1408.1 \text{ cm}^{-1}$
T	298.15 K
t_0	0.01307 s
v^2	9.1599
t_0/v^2	1.427 ms

sity is high ($i_0 = 1.8 \times 10^{-4}$ A/cm² or greater). We confirmed our results for the linear kinetics case presented here by replacing Eq. 8 with the Butler-Volmer equation and solving the resulting equation numerically. In plotting the voltage response using the analytical solution one has to be careful with the number of terms used in the series. The number of terms required in the series solution is a function of the frequency. The number of terms (k) required is proportional to the frequency hence when the expression is used to simulate the voltage response at high frequencies a larger number of terms is needed (for example, for $f = 100$ Hz $k = 1600$).

The short time voltage response and the periodic part of the total voltage are represented in Fig. 3. The periodic part is a uniform and sustained periodic state that can otherwise be called as the sinusoidal steady state. Henceforth, when we refer as the periodic response it should be understood as the sinusoidal steady state response. The short time voltage response is given by the first two terms of Eq. 45 ($V - V_{ss}$) that goes to zero at longer times. Note: Short time voltage response occurs only at times less than a few time constants (constant multiplied by t_0/v^2), while transient voltage response is the total voltage response in the transient region. Transient region refers

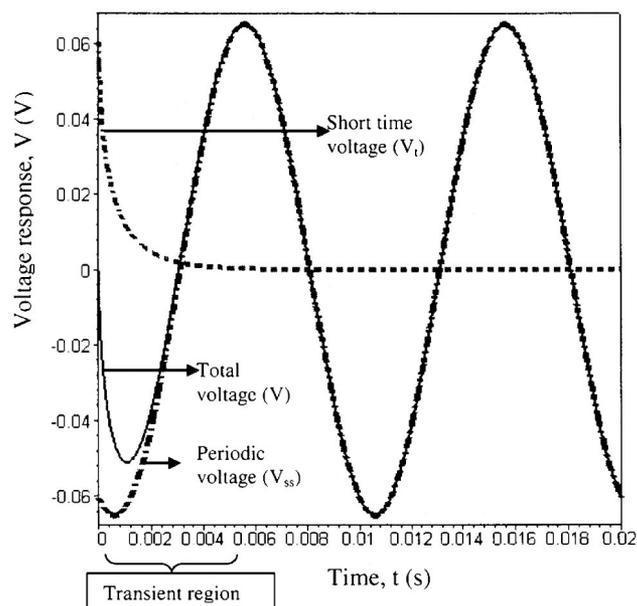


Figure 3. Transient voltage and the steady state voltage that make up the total voltage response of the porous electrode ($f = 100$ Hz).

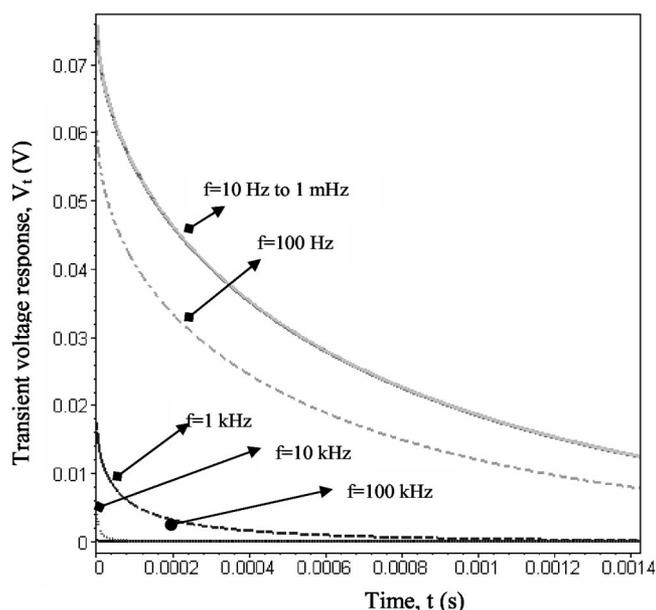


Figure 4. Short time voltage response as a function of time for various frequency values.

to time less than the time constant, t_0/ν^2 ($=1.427$ ms; see Table I) and steady-state region (longer times) refers to $t \gg t_0/\nu^2$.

Transient voltage response.—In this section, we focus on the behavior of the transient voltage response. The change in the transient voltage as a function of the frequency is shown in Fig. 4. A frequency range of 100 kHz to 10 mHz over which the same system would yield a squashed semicircle in the frequency domain is used to analyze the response in time domain.⁶ We observe that the short time voltage changes for higher frequency values but for frequencies less than or equal to 10 Hz the short time voltage becomes constant. The frequency of 10 Hz is termed the limiting frequency (f_l) because the short time voltage at frequencies lower than f_l can be determined by evaluating the limit of the total voltage response at $\omega = 0$. The short time voltage response is indicated as $V_{l|f_l}$ can be written as

$$V|_{f_l} = c_1 \underbrace{\left[\frac{(\beta + 1)e^{\frac{\nu^2 t}{t_0}}}{\nu^2} + \sum_{k=1}^{\infty} A_k e^{-(\nu^2 + k^2 \pi^2) \frac{t}{t_0}} \right]}_{V_{l|f_l}} - c_1 \underbrace{\left[\frac{(\beta + 1)}{\nu^2} + \sum_{k=1}^{\infty} A_k + \frac{\beta}{(\beta + 1)} \right]}_{V_{ss|f_l}} \quad [50]$$

Figure 5 gives the total voltage response for $t \leq t_0/\nu^2$ at different frequency values. Because the short time response dominates the total voltage response over the transient region, it shows a constant voltage response for $f \leq f_l$ as observed in Fig. 4 for just the short time voltage response. Also, the total voltage response in Fig. 5 is characterized by a constant slope in the initial part of the response and a constant value for voltage at $t = 0$ at all frequencies. The values of these constants can be determined by evaluating the following limiting cases of Eq. 45

$$V|_{t=0} = \frac{AL}{(\kappa_{\text{eff}} + \sigma_{\text{eff}})} \quad [51]$$

and

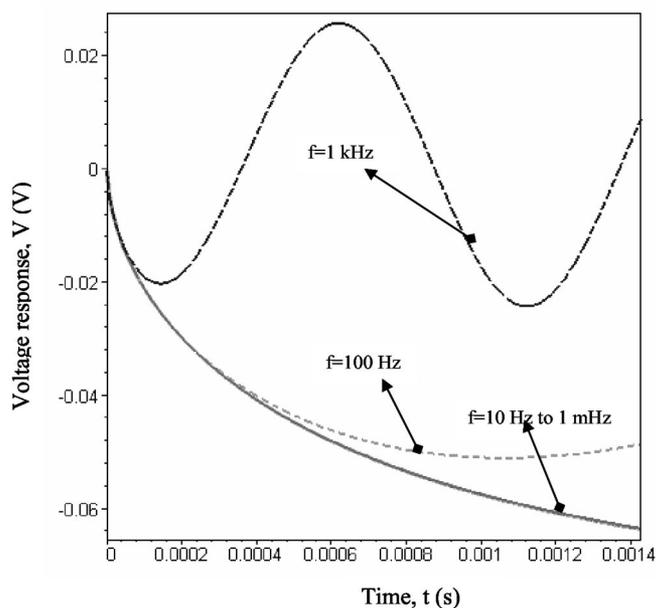


Figure 5. Transient voltage response region for various frequency values. Note that the initial slope at all frequencies is equal. ($t_0 = 0.01307$ s and $(\nu^2 = 9.1599)$).

$$\left(\frac{dV}{dt} \right)_{t=0} = -\frac{c_1}{t_0} \left[(\beta + 1) + \sum_{k=1}^{\infty} A_k \right] \quad [52]$$

Equation 51 can otherwise be obtained by substituting the initial condition for the overpotential at $X = 0$ and $X = 1$ ($\eta^*|_{X=0}$ and $\eta^*|_{X=1}$ both of which are zero) into Eq. 33. Also dV/dt at $t = 0$ can be obtained by differentiating both sides of Eq. 33 with respect to t , provided an expression for η as a function of time valid for short time periods is known (such an expression can be obtained by determining the Laplace inverse of Eq. 20). Both Eq. 51 and 52 are independent of frequency. Note that the voltage at time $t = 0$ is determined by the ohmic properties of the material (solution phase conductivity and solid phase conductivity). The initial slope of the voltage response (see Eq. 52) is independent of the electrode kinetics.

At low frequencies the input perturbation tends to become a step input ($\lim_{\omega \rightarrow 0} [A \cos(\omega t)] = A$). Hence the voltage response at low frequencies for sinusoidal perturbation should agree with the voltage response for a step input that consists of a transient and a steady state response (not periodic). This is evident from a plot of the voltage response at f_l for sinusoidal perturbation (Eq. 50) and the voltage response with a step input as shown in Fig. 6. An analytical solution for the voltage response of a porous electrode in the case of applied potential step was published earlier.^{5,6,17} Unfortunately, typos exist in all of them; in Ref. 5 the negative sign before the term within the exponential that is before $\sinh(\nu)$ in Eq. B-9 should be omitted, in Ref. 6 $C_m^1 = 2(-1)^m \nu / (m^2 \pi^2 + \nu^2) [A^1 \sinh(\nu) + B^1 \cosh(\nu) - B^1(-1)^m]$ in the voltage expression (Eq. 10) instead of the expression given in Eq. 11 and in Ref. 17 coefficient of the series term in the voltage expression (Eq. 39) should be $2\delta / (1 + \beta)$.

Unlike the constant steady state voltage response for a step input, the constant voltage response in the steady state region as $\omega \rightarrow 0$ indicates that the periodic voltage response is characterized by constant amplitude. This is because of the nature of the two input perturbations. In linear systems the steady state response of the system takes the same form as the input perturbation (when the input is a periodic perturbation the corresponding output will also be periodic). The constant amplitude of the periodic signal for low frequen-

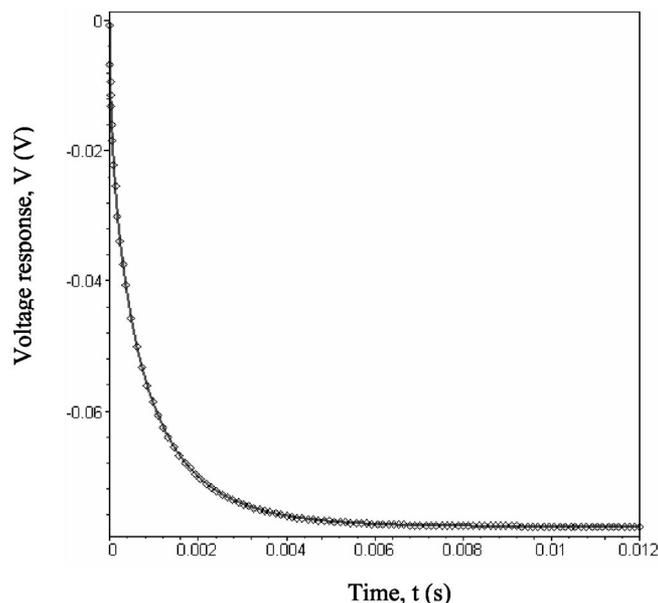


Figure 6. Comparing the voltage response at the limiting frequency for a sinusoidal input (Eq. 50) given by continuous line with that of the voltage response for a potential step as the input (see Ref. 5 and 6, or 16) represented by symbols.

cies is evident from Fig. 7 that gives a plot of the amplitude of the periodic ($V_{ss, amp}$) response as a function of the frequency in a semi log scale. In obtaining the $V_{ss, amp}$ at very high frequency one has to pay utmost attention to the sample spacing. Sample spacing is defined as the time period between two consecutive data samples. For higher frequency values very small sample spacing has to be used to obtain an accurate value of the amplitude. The amplitude of the periodic voltage response is inversely proportional to the frequency. At lower frequency values $f \leq 10$ Hz a constant value of $V_{ss, amp}$ is obtained as determined using the voltage response at the limiting frequency, f_1 . The amplitude for $f \leq f_1$ is given by $V_{ss|f_1}$ (Eq. 52). The value of the limiting frequency for the periodic voltage is same as that of the transient voltage. The amplitude of the periodic voltage response is also constant at high frequencies and is given by Eq. 51, the value of the voltage at time $t = 0$ in the transient region. At

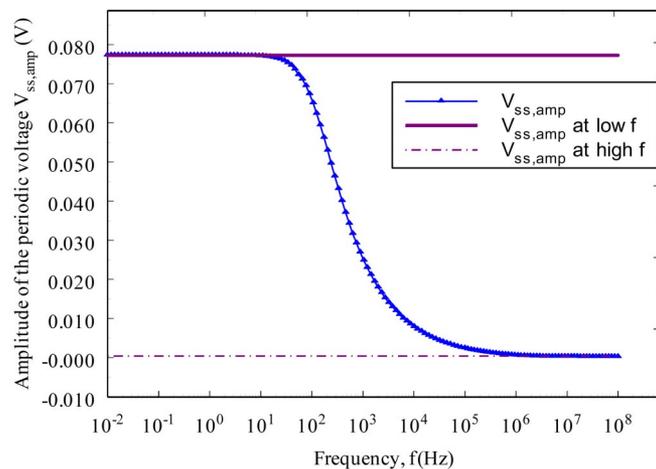


Figure 7. Amplitude of the steady state voltage (V_{ss} , Eq. 46) plotted as a function of the frequency. The straight lines at high and low frequency are plotted using Eq. 5 and 52, respectively.

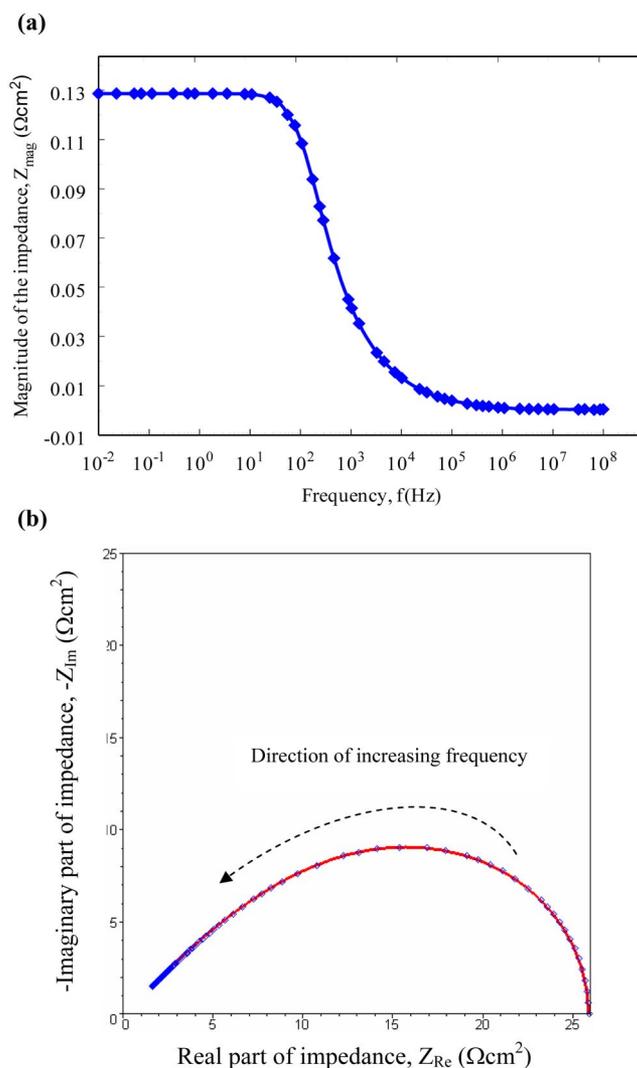


Figure 8. (a) The Bode plot of the impedance vs. frequency. (b) Nyquist plot of the impedance of a porous electrode. Continuous line represents the plot obtained using the impedance expression in the literature. Symbols denote the plot determined from the expression for steady state voltage response (Eq. 46).

this point it is worth mentioning that a plot of the ratio of the amplitude of the periodic signal to the amplitude of the input current, $V_{ss, amp}$ vs. log frequency yields the well-known Bode magnitude plot of impedance as shown in Fig. 8a along with the Bode plot obtained using the impedance expression.^{5,6} We would also mention that the impedance plots can be obtained from the expression of the voltage response and the input current presented in this paper by applying simple concepts: we know that the real part of the impedance is given by the part of the voltage response that is in phase and the imaginary part is given by the part of the response that is out of phase with respect to the input perturbation. Z_{Re} and Z_{Im} are equal to the coefficient of $\cos(\omega t)$ divided by A and $\sin(\omega t)$ divided by A of Eq. 46, respectively. The Nyquist plot obtained using the impedance expression^{5,6} is compared to that obtained using Eq. 46 as described above are given in Fig. 8b.

In porous electrodes designed for the electrochemical capacitors, the performance of the porous electrode is limited only by the electrical double layer charging. In this case, the voltage response is given by (limit of Eq. 45 as $\nu^2 \rightarrow 1$)

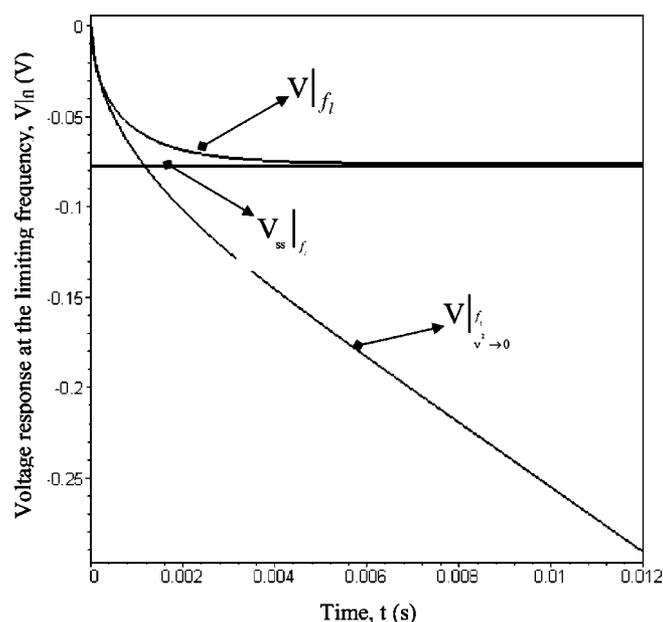


Figure 9. Voltage response at the limiting frequency for different cases as indicated in the figure. All the parameter values are indicated in Table I.

$$V|_{v^2 \rightarrow 0} = -\frac{c_1(\beta + 1)\sin(\omega t)}{\omega t_0} - c_1 \sum_{k=1}^{\infty} A_k \left(\frac{k^2 \pi^2 \cos(\omega t) + \omega t_0 \sin(\omega t) - k^2 \pi^2 e^{-k^2 \pi^2 \frac{t}{t_0}}}{((k^2 \pi^2)^2 + (\omega t_0)^2)} \right) - \frac{c_1 \cos(\omega t) \beta}{\beta + 1} \quad [53]$$

and at $f \ll f_1$ we have (limit of Eq. 53 as $\omega \rightarrow 0$)

$$V|_{v^2 \rightarrow 0, f_1} = c_1 \left[\sum_{k=1}^{\infty} A_k \frac{e^{-k^2 \pi^2 \frac{t}{t_0}}}{k^2 \pi^2} \right] - c_1 \left[\frac{(\beta + 1)}{t_0} + \sum_{k=1}^{\infty} \frac{A_k}{k^2 \pi^2} + \frac{\beta}{(\beta + 1)} \right] \quad [54]$$

Unless mentioned we will only deal with a porous electrode governed by both linear kinetics and double layer charging. Figure 9 shows a comparison of the voltage profiles of a porous electrode at the limiting frequency for the two cases; 1) with both linear kinetics and double layer charging (Eq. 50 and 2) with double layer charging only (Eq. 54). The voltage response in the transient region for the latter case can be approximated by a straight line while in the later case the transient response is a curve. In the porous electrode limited by double layer charging only the figure shows a linear increase in the voltage response with time well beyond the borderline between the transient region and the steady state region that is at $t = t_0/v^2$.

Because we determined that the transient voltage response becomes a constant at the limiting current density the effect of the exchange current density and double layer capacitance is studied using the voltage response at the limiting frequency (Eq. 50). A plot of the voltage response for various values of i_0 and C_{dl} are presented in Fig. 10 and 11, respectively. For now, we will discuss the effect of the voltage response only in transient region. The effect of the parameters on the periodic voltage response will be dealt in detail later. In the transient region the voltage response changes with the value of i_0 . However one should remember that the slope at $t = 0$ remains a constant since the value of C_{dl} is not varied (see Eq. 52). In Fig. 10 the initial slope of the voltage response curve and the voltage re-

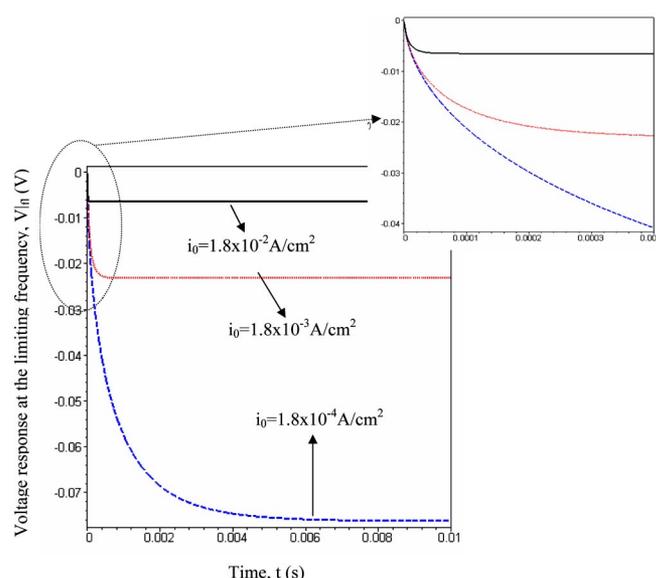


Figure 10. Voltage response at the limiting frequency, (Eq. 50) plotted for various values of the exchange current density, i_0 in A/cm^2 as indicated in the figure. All the other parameter values are given in Table I.

sponse in the latter part of the transient region changes as evident from Eq. 52. It is also important to remember that in both the figures the voltage at time $t = 0$ is constant given by Eq. 51 and is independent of i_0 and C_{dl} . In Fig. 10 and 11, the time taken for the transient response to attain sinusoidal steady state response varies with the parameters. The time taken for the transient response to attain sinusoidal steady state response is nothing but the time range in which the transient response occurs which is the time constant t_0/v^2 where t_0 and v^2 are functions of the parameters. The changes in the parameter values also introduce a shift of the limiting frequency (see Table

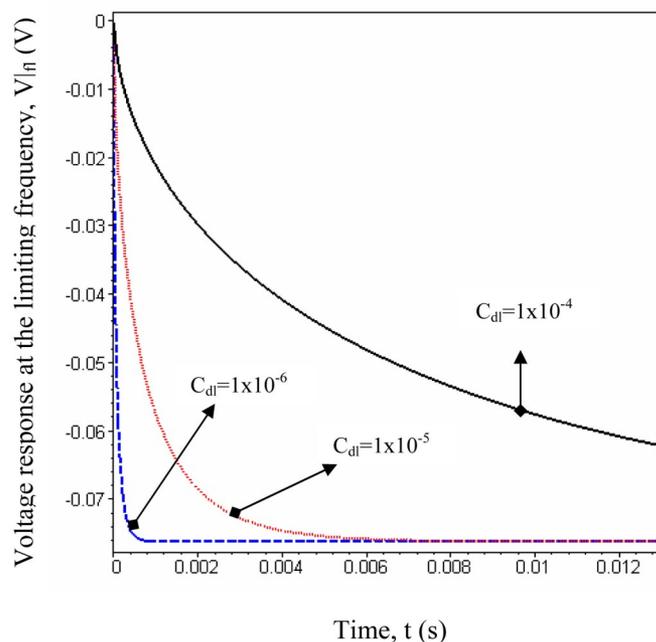


Figure 11. Voltage response at the limiting frequency (Eq. 50) plotted for various values of the double layer capacitance, C_{dl} in F/cm^2 as indicated in the figure. All the other parameter values are given in Table I.

Table II. Limiting frequency values as a function of the (a) exchange current density and (b) double layer capacitance.

(a) Exchange current density, i_0 (A/cm ²)	Limiting frequency, f_1 (Hz) ^a
1.8×10^{-2}	1 Hz
1.8×10^{-3}	10 Hz
1.8×10^{-4}	0.1 Hz
(b) Double layer capacitance, C_{dl} (μ F/cm ²)	Limiting frequency, f_1 (Hz) ^b
1 00	1 Hz
10	10 Hz
1	0.1 Hz

^a The limiting current density is determined with the parameter values given in Table I except for i_0 (whose values are specified above).

^b The limiting current density is determined with the parameter values given in Table I except for C_{dl} (whose values are specified above).

II). From the tabulated values we see that f_1 is directly proportional to i_0 / C_{dl} . Because we know that frequency is the inverse of time, we can conclude that $f_1 \propto 1/t_0/\nu^2$.

The effect of parameters on the periodic response at the limiting frequency can be explained based on Fig. 10 and 11. With the decrease in i_0 the amplitude of the periodic voltage response decreases while the change in C_{dl} does not influence the value of $V_{ss, amp}$. However change in both i_0 and C_{dl} values introduce a change in the time constant ($t_0 = \nu^2$) for the transient region. As the time constant increases the periodic (sinusoidal steady state) voltage response is pushed to longer and longer times and hence the limiting frequency becomes a smaller value. The change in f_1 with the exchange current density is clear from Fig. 12.

Parameter estimation.—So far we have analyzed the effect of frequency and the parameter values on the behavior of the transient voltage response. In this section, we will investigate the possibility of estimating parameters of the porous electrode using the transient voltage response only.

The value of the voltage at $t = 0$ yields the ratio of the solution phase conductivity to solid phase conductivity (Eq. 51). When one of the conductivity values is known (κ_{eff} or σ_{eff}) the other can be

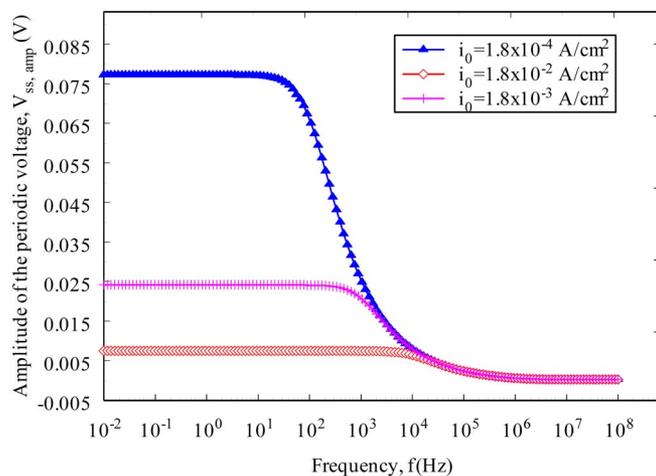


Figure 12. Amplitude of the steady state voltage response plotted as a function of frequency for three different values of the exchange current density as indicated in the figure.

determined from their ratio (β). Alternatively when the solid phase conductivity in a porous electrode is very high it can be neglected. Then Eq. 51 would yield a value for κ_{eff} .

The equation for the initial slope of the transient voltage (Eq. 52) can be used to determine the value of the double layer capacitance.

The exchange current density is obtained from the value of the voltage at a fixed frequency and at any point of time well within the transient region. It is convenient to use the moderate frequency range (100 Hz to 0.01 Hz) because the transient voltage response exists for a considerable time (in ms see Fig. 4) at these frequencies.

In cases where both conductivities are unknown, the following four equations can be solved simultaneously to estimate the parameter values: Eq. 51, Eq. 52, and the voltage response in the transient region at two different values of time at a fixed frequency or the voltage response in the transient region at two different values of the frequency at a fixed time. One has to be cautious in selecting the time and frequency values for parameter estimation. The moderate frequency value of about 100 to 0.01 Hz has to be used and also the value of time should be longer than the constant initial slope region but should also be within the transient region. These values can be determined by looking at the nature of the voltage response curves at very short times. A better method to estimate parameters would be to fit¹⁸ simultaneously the voltage response in the transient region for two or three different frequency values using nonlinear regression.

Conclusions

An analytical solution for the voltage response in the time domain for a porous electrode perturbed by a sinusoidal current density was derived. The voltage response of the porous electrode included the initial transients along with the periodic response. The effect of frequency, exchange current density and double layer charging on the transient voltage response was analyzed. The corresponding variation in the periodic voltage was presented and compared to that of the transient voltage response. Based on the results we conclude that the transient voltage response has a wealth of information that can be used independently to estimate all the parameters associated with a porous electrode model presented here.

Acknowledgments

The authors acknowledge with great appreciation financial support from the National Reconnaissance Office (NRO) under contract no. 000-03-C-0122.

The University of South Carolina assisted in meeting the publication costs of this article.

List of Symbols

- A amplitude of the applied current density, A/cm²
- A_k see Eq. 47
- a specific interfacial area, $3(1 - \epsilon - \epsilon_{inert})/R_s \text{ cm}^{-1}$
- C_{dl} double-layer capacitance, F/cm²
- c_1 see Eq. 48
- f frequency, Hz (1/s)
- f_1 limiting frequency, Hz
- F Faraday's constant, 96487 C/equiv
- I applied current density, $A \cos(\omega t)$, A/cm²
- i_0 exchange current density, A/cm²
- i_1 matrix phase current density, A/cm²
- i_2 solution phase current density, A/cm²
- j_n interfacial current density, A/cm²
- $J_{n,f}$ faradaic interfacial current density, A/cm²
- L thickness of the porous electrode, cm
- n number of electrons transferred in the reaction, (=1)
- R universal gas constant, 8.313 J/mol. K
- R_s radius of a particle, cm
- T temperature, K
- t time, s
- t_0 time constant for double layer charging, s (see Eq. 49)
- V^* dimensionless voltage across the porous electrode
- V voltage (total voltage) response across the porous electrode, V (see Eq. 45)
- V_{ss} steady state voltage response across the porous electrode, V (see Eq. 46)

$V_{ss, amp}$	amplitude of the steady state voltage response across the porous electrode, V (see Eq. 46)
V_t	short time voltage response across the porous electrode, V (first two expressions of Eq. 45)
X	dimensionless distance, x/L
x	distance, cm
Greek	
α_a, α_c	anodic and cathodic transfer coefficients respectively ($\alpha_a + \alpha_c = n$)
ε	porosity of the electrode, dimensionless
ε_{inert}	volume fraction of the inert material of the porous electrode, dimensionless
β	ratio of the effective solution phase and matrix phase conductivities, $\kappa_{eff}/\sigma_{eff}$
δ	dimensionless current density, $I(t)(FL/\kappa_{eff}RT)$ (see Eq. 19)
ϕ_1	solid phase potential, V
ϕ_1^*	dimensionless solid phase potential, ϕ_1F/RT
ϕ_2	solution phase potential, V
η	overpotential ($\phi_1 - \phi_2$), V
η^*	dimensionless overpotential, $\eta F/RT$ (see Eq. 15)
κ	solution phase conductivity, S/cm
κ_{eff}	effective solution phase conductivity, see Eq. 4, S/cm
ν^2	dimensionless exchange current density, $ai_0(\alpha_a + \alpha_c)FL^2/RT(1/\sigma_{eff} + 1/\kappa_{eff})$ (see Eq. 14)
σ	matrix phase conductivity, S/cm
σ_{eff}	effective matrix phase conductivity, see Eq. 3, S/cm
τ	dimensionless time, $t/aC_{dl}(1/\kappa_{eff} + 1/\sigma_{eff})L^2$ (see Eq. 15)
ω	frequency of the applied current, rad/s ($=2\pi f$)
ω^*	dimensionless frequency of the applied current, (see Eq. 36)
ξ	dummy variable of integration
Subscripts	
t	variable in the transient region
ss	variable in steady state region

References

1. J. McClellan, R. W. Schafer, and M. A. Yoder, *DSP First: A Multimedia Approach*, Prentice Hall, Upper Saddle River, NJ (1998).
2. D. D. Macdonald, *Transient Techniques in Electrochemistry*, Plenum Press, New York (1977).
3. D. D. Macdonald and M. C. H. Mckubre, in *Modern Aspects of Electrochemistry*, Vol. 14, B. E. Conway, J. O' M. Bockris, and R. E. White, Editors, Plenum Publishers, New York (1982).
4. A. J. Bard and L. R. Faulkner, in *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., John Wiley & Sons, New York (2001).
5. I. J. Ong and J. Newman, *J. Electrochem. Soc.*, **146**, 4360 (1999).
6. P. M. Gomadam, J. W. Weidner, T. A. Zawodzinski, and A. P. Saab, *J. Electrochem. Soc.*, **150**, E371 (2003).
7. A. Lundquist and G. Lindbergh, *Electrochim. Acta*, **44**, 2523 (1999).
8. C. Montella, *J. Electroanal. Chem.*, **518**, 61 (2002).
9. A. V. Churikov and A. V. Ivanishev, *Electrochim. Acta*, **48**, 3677 (2003).
10. B. A. Ogunnaike and W. H. Ray, *Process Dynamics, Modeling and Control*, p. 82, Oxford University Press, New York (1994).
11. J. S. Newman, *Electrochemical Systems*, 2nd ed., Prentice Hall, Englewood Cliffs, NJ (1991).
12. Q. Guo, V. R. Subramanian, J. W. Weidner, and R. E. White, *J. Electrochem. Soc.*, **149**, A307 (2002).
13. S. Devan, V. R. Subramanian, and R. E. White, *J. Electrochem. Soc.*, **151**, A905 (2004).
14. A. Constantinides and N. Mostoufi, *Numerical Methods for Chemical Engineers with Matlab Applications*, p. 449, Prentice Hall, Upper Saddle River, NJ (1999).
15. R. E. White and V. R. Subramanian, *Computational Methods in Chemical Engineering with Maple Applications*, Springer Verlag, In preparation.
16. V. R. Subramanian and R. E. White, *Chem. Eng. Ed.*, **34**, 328 (2000).
17. V. R. Subramanian, S. Devan, and R. E. White, *J. Power Sources*, **135**, 361 (2004).
18. Q. Guo, V. A. Sethuraman, and R. E. White, *J. Electrochem. Soc.*, **151**, A983 (2004).