Chronoamperometry at Channel Electrodes. Experimental Applications of Double Electrodes

Richard G. Compton,* Barry A. Coles, and Justin J. Gooding

Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, United Kingdom

Adrian C. Fisher

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom

Timothy I. Cox

Defence Research Agency, St. Andrews Road, Malvern, Worcestershire WR14 3PS, United Kingdom Received: September 14, 1993; In Final Form: December 15, 1993[®]

Applications of transient experiments using double-channel electrodes are reported. The current response of a downstream detector electrode to a potential step at an upstream generator electrode is found to be in good agreement with theory. Such experiments are used to (i) demonstrate that the diffusion coefficient of the electrogenerated radical anion of *p*-chloranil in acetonitrile solution is 0.94×10^{-5} cm² s⁻¹, which contrasts markedly with that of the parent material $(1.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$, and (ii) characterize the nature of electrolytic processes occurring at the surface of porous silicon electrodes. The latter are shown to be electroactive throughout the depth of the porous surface layer.

Introduction

This series of papers is concerned with demonstrating the merits of channel electrodes for the fundamental study of electrode and interfacial processes. We have noted^{1,2} that their advantages include the wide range over which the rate of mass transport can be varied, operation under chemostatic conditions, and the mechanistically discriminatory power deriving from the nonuniformity of the diffusion layer thickness.³ The latter was illustrated with respect to the use of chronoamperometric measurements at single-channel electrodes for the resolution of the ECE/DISP problem.¹ We have predicted theoretically² that by employing two electrodes—a generator and a detector electrode—additional mechanistic information is experimentally accessible with high sensitivity. This paper describes experimental measurements made using double-channel electrodes, including one of novel geometry in which the two electrodes are located on opposite walls of the flow cell. The experiments vindicate the theory previously developed^{1,2} and show how double electrodes may be used to (a) examine the nature of electrolytic processes occurring at porous silicon electrodes and (b) interrogate electrode reaction mechanisms without the need for the usually made assumption that all participating species have a common diffusion coefficient. The configuration in which the electrodes are on opposing walls of the flow cell is found to be particularly sensitive.

Experimental Section

All channel electrode experiments were conducted using flow cells made to standard construction and dimensions⁴⁻⁶ capable of delivering flow rates in the range $10^{-4}-10^{-1}$ cm³ s⁻¹. Platinum foils (purity 99.95%, thickness 0.025 mm) of approximate size 4×4 mm,² supplied by Goodfellow Advanced Materials, were used as detector electrodes. Porous silicon films were fabricated by anodization of 50 m Ω cm p-type (100) silicon substrates in a 1:1 mixture of 40% HF and ethanol at a current density of 100 mA cm⁻² for varying times (Table 1). The thickness and average porosity of the porous silicon films were determined gravimetrically. By using a high current density for a short time, the chemical etching effect of the electrolyte was minimized and the depth dependence of the porosity is, therefore, also minimized. To within experimental error, the porosities of all three films are **TABLE 1**

sample	porosity/%	pore depth/µm	anodization time
PTC-5	67 ± 2	4 ± 0.1	50 s
PTC-7	69 ± 2	11 ± 0.2	2.5 min
PTC-9	71 ± 2	34 ± 0.7	8 min

the same. Unanodized substrates were also used as controls. The silicon samples were incorporated into the flow cell as working electrodes. The latter were masked so that they had dimensions similar to those of the detector electrodes. Precise dimensions were determined using a traveling microscope. A reference electrode was positioned in the flow system upstream, and a platinum gauze counter electrode located downstream, of the channel electrode. The former was either a silver wire pseudoreference electrode when nonaqueous media were under study or otherwise a saturated calomel electrode (SCE). The silver wire reference electrode was found to be steady throughout the period of our experiments: consistent values for the oxidation potential of N, N, N', N', tetramethyl-1,4-phenylenediamine (TMPD) were observed. Hence, potentials are reported relative to the saturated calomel electrode, +0.20 V being subtracted from the measured values to obtain the potentials quoted.

Conventional electrochemical measurements were made using an Oxford Electrodes potentiostat modified to boost the counter electrode voltage (up to 200 V). Double-electrode experiments were conducted with a purpose-built bipotentiostat which permitted the independent control of both detector and working electrode potentials relative to the reference electrode. Current transients were recorded on a digital storage oscilloscope. Other methodological details were as described previously.^{3,4} Complementary rotating disc measurements were conducted using Oxford Electrodes equipment. All experiments were carried out at 25 °C.

Experiments were performed using solutions of electroactive substrates (ca. $10^{-4}-10^{-3}$ M) in solutions made up in either dried⁷ acetonitrile (Fisons, dried, distilled) solution or doubly distilled deionized water as solvents. In the former case 0.1 M (recrystallized) tetrabutylammonium perchlorate (TBAP, Fluka, purum) was used as supporting electrolyte; in the latter, 0.2 M KCl (BDH, AnalaR Grade) was employed for the same purpose. *N*,*N*,*N*,*N*'. Tetramethylphenylenediamine, *p*-chloranil, and potassium ferricyanide were used as received from Aldrich (>99%). Solutions

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Figure 1. Schematic diagrams of a double-channel electrode illustrate the two possible cell geometries: (a) case A and (b) case B.

were purged of oxygen by outgassing with prepurified argon prior to electrolysis.

Results and Discussion

Two double-channel electrode geometries were considered in which the detector electrode was located either on the same side of the channel as the generator electrode or, alternatively, on the opposite wall. We refer to these as case A or case B geometry, respectively.²

We consider first steady-state experiments in which the upstream electrode is used to generate a species B from a suitable electroactive precursor, A:

$$A + e^{-} \rightleftharpoons B$$

while the detector electrode is potentiostated at a value corresponding to the transport-controlled reconversion of B (back into A). Systems based on two different solvents were selected for investigation. These were as follows: (i) the one-electron oxidation of tris(p-bromophenyl)amine (TPA) in acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and (ii) the one-electron reduction of potassium ferricyanide [K₃Fe(CN)₆] in water containing 0.2 M KCl as supporting electrolyte. The diffusion coefficients of the parent species, A (=TPA or Fe(CN)₆³⁻) are well-characterized: 1.47 $\times 10^{-5}$ cm² s⁻¹ {TPA}¹¹ and 7.6 $\times 10^{-6}$ cm² s⁻¹ {Fe(CN)₆⁴⁻}.¹² In all instances, the current flowing at the detector electrode was monitored as the potential of the generator electrode was swept through the oxidation wave of either TPA or TMPD. The detector current was measured as a function of the generator current, and in all cases a linear direct dependence was found, permitting the deduction of the steady-state collection efficiency^{2,8} defined as

$$CE = \frac{\text{detector electrode current}}{\text{generator electrode current}}$$
(1)

We have shown previously² how this quantity may be predicted from a knowledge of the double-electrode geometry and the solution flow rate and noted that, for case A, under experimental conditions where the Lévêque approximation is operative, the analytical theory^{9,10} gives a good basis for the prediction of CE which under those conditions is solely a function of the lengths x_1 , x_2 , and x_3 defined in Figure 1.

Experimental results for both chemical systems were found in the case A geometry to give excellent agreement with both analytical and computational theory, as has been found previ-



Figure 2. Collection efficiency for a double-channel electrode of the dimensions specified in the text for a case B cell geometry measured as a function of solution flow rate for different concentrations of TPA: 0.50 mM (\times), 1.0 mM (\odot), and 1.5 mM (+). The solid line shows the theoretically predicted behavior calculated from the cell geometry and the known diffusion coefficient of TPA.



Figure 3. Collection efficiency for a double-channel electrode for a case B cell geometry measured as a function of solution flow rate for the $Fe(CN)_6^{3-}$ (10 mM) system. The cell dimensions were 2h = 0.031 cm, $x_1 = 0.432$ cm, $x_2 = 1.161$ cm, and $x_3 = 1.533$ cm. The solid line shows the theoretically predicted behavior calculated from the cell geometry and the known diffusion coefficient of $Fe(CN)_6^{3-}$.

ously.^{10,13} We therefore turn to the case B electrode configuration. Figure 2 shows how the collection efficiency for the TPA system depends on solution flow rate for a channel cell of geometry cell depth = 0.346 cm, $x_1 = 0.48$ cm, $x_2 = 0.641$, and $x_3 = 1.165$ cm. Also shown is the theoretical behavior computed² for this geometry assuming that the radical cation of TPA has the diffusion coefficient quoted above. The different symbols in Figure 2 relate to three different concentrations of TPA; the measured independence of CE on [TPA] is entirely in accordance with theoretical prediction. Figure 3 shows a corresponding experiment conducted with the $Fe(CN)_{6^{3-}}$ system; again, excellent agreement between theory and experiment is found. In both cases it can be seen that CE varies from zero at high flow rates where the electrogenerated material, B, is swept out of the flow cell before it can diffuse across to the detector electrode, and CE approaches unity at very low flow rates where both electrodes effectively operate under a thin-layer regime and effect near-exhaustive electrolysis of all material flowing through the cell.

We consider next the transient response of the detector electrode, potentiostated as above, resulting from a potential step on the upstream electrode between potentials corresponding to zero current flow and to the transport limited discharge of A. The system examined first was the one-electron oxidation of N,N,N',N'tetramethylphenylenediamine (TMPD) in water containing 0.2 M KCl as supporting electrolyte. We report data for both case A and case B cell designs. Figures 4 and 5 show typical transient data measured for the two cases and for two different flow rates



Figure 4. Transient currents measured on the detector electrode resulting from a potential step at the generator for case A geometry. The solution contained 4×10^{-3} M TMPD and 0.2 M KCl. The data were recorded using solution flow rates of (a) 0.225 cm³ s⁻¹ and (b) $2.1_5 \times 10^{-3}$ cm³ s⁻¹. The cell geometry was 2h = 0.106 cm, $x_1 = 0.166$ cm, $x_2 = 0.307$ cm, and $x_3 = 0.505$ cm. The smooth lines drawn display the corresponding computed theoretical transients; boxes represent experimental points.

corresponding to typical fast and slow extremes. Also displayed are the theoretical transients computed as described elsewhere² assuming that both TMPD and its radical cation, TMPD^{•+}, have a diffusion coefficient of 6.3×10^{-6} cm² s⁻¹ equal to that reported in the literature.¹⁴ The excellent agreement between theory and experiment vindicates the theoretical model and computation strategy adopted² and also shows that the "equal diffusion coefficient" assumption is valid for the two systems studied.

We turn next to a system previously inferred⁷ not to satisfy the equal diffusion coefficient assumption and examine the oneelectron reduction of p-chloranil, CA, in acetonitrile solution using the case A cell geometry. Figures 6a and 7 show the measured transient responses of the generator and detector electrodes for a step between potentials corresponding to zero current and the transport-limited reduction of CA. Figure 6b shows the generator transient resulting from a double-potential step experiment in which the first step was as before, but the second step returned the electrode to a potential at which no steady-state current flowed. In all cases the detector electrode was potentiostated at -0.10 V (vs SCE), corresponding to the transport-limited conversion of B (the p-chloranil radical anion, CA^{\leftarrow}) back into A (CA). In the case of the generator transient the current normalized to its steadystate value was shown² to be a unique function of a dimensionless time parameter,

$$t' = t \left(\frac{4Dv_0^2}{h^2 x_1^2}\right)^{1/3} \tag{2}$$

and independent of [A]. Use of t'as the time coordinate in Figure 6a,b permits data from more than one experiment to be displayed simultaneously. Figure 6a includes a theoretical transient



Figure 5. Transient current measured on the detector electrode resulting from a potential step at the generator for case B geometry. The solution contained 4×10^{-3} M TMPD and 0.2 M KCl. The data were recorded using solution flow rates of (a) 2.0×10^{-3} cm³ s⁻¹ and (b) 4.5×10^{-4} cm³ s⁻¹. The cell geometry was 2h = 0.0257 cm, $x_1 = 0.392$ cm, $x_2 = 1.873$ cm, and $x_3 = 2.250$ cm. The smooth lines drawn display the corresponding computed theoretical transients; boxes represent experimental points.

computed^{1,2} using a value of $D_A = 1.75 \times 10^{-5}$ cm² s⁻¹ obtained from steady-state measurements of the transport-limited current at the generator electrode as a function of the rate of mass transport and which is in excellent agreement with literature reports.^{7,15} The very good agreement seen between theory and experiment using an independently deduced value of D_A justifies the model and theory proposed.^{1,2}

Figure 6b shows the generator electrode response resulting from the double step together with that predicted using the theory given previously¹ assuming values of $D_A = 1.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $D_B = 0.94 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. However, Figure 8 shows that the value of $D_{\rm B}$ selected to model the transients has only a tiny influence on the shape of the back generator transient (and has no influence whatsoever on the forward transient). It follows that chronoamperometry using single (channel) electrodes is inherently insensitive to variations in the ratio D_A/D_B . In contrast, Figure 7 shows the detector signal resulting from the same potential step. The theoretical transients depicted correspond to $D_A/D_B = 1$ and 0.54 ($D_A = 1.75 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), respectively. The large difference between the two theoretical curves indicates the power of double-electrode experiments in responding to differences in diffusion coefficients as predicted theoretically.² It can be seen that the values $D_{\rm A} = 1.75 \times 10^{-5} \, {\rm cm}^2 \, {\rm s}^{-1}$ and $D_{\rm B} =$ $0.94 \times 10^{-5} \mbox{ cm}^2 \mbox{ s}^{-1}$ give excellent agreement with experiment. The value for $D_{\rm B}$ is very close to that determined independently using a spectroelectrochemical technique,⁷ and we estimate $D_{\rm B}$ / $D_{\rm A} = 0.54 \pm 0.10$. The sensitivity of double-electrode experiments in elucidating electrode reaction mechanisms should be apparent.

We turn next to the use of double-electrode experiments for the characterization of interfacial processes. Illustrative calculations with respect to this problem were presented in ref 2. In



Figure 6. (a) Generator electrode transient measured for a cell of type A resulting from a single-potential step, as described in the text, for the reduction of CA in acetonitrile solution. The cell dimensions were 2h =0.038 cm and $x_1 = 0.413$ cm. The smooth line drawn displays the corresponding computed theoretical transient for $D_A = 1.75 \times 10^{-5} \text{ cm}^2$ s⁻¹; the symbols represent experimental points for three separate concentrations and flow rates: 0.67×10^{-3} M and 8.6×10^{-2} cm³ s⁻¹ (×), 1.02×10^{-3} M and 7.3×10^{-3} cm³ s⁻¹ (+), 0.21×10^{-3} M and 2.1×10^{-2} $cm^3 s^{-1}(O)$. (b) Generator electrode transient measured for a cell of type A resulting from a double-potential step, as described in the text, for the reduction of CA in acetonitrile solution. The cell dimensions were 2h =0.037 cm and $x_1 = 0.398$ cm. The smooth line drawn displays the corresponding computed theoretical transient for $D_{\rm A} = 1.75 \times 10^{-5} \, {\rm cm}^2$ s^{-1} and $D_B = 0.94 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; the symbols represent experimental points for two separate concentrations and flow rates: 0.21×10^{-3} M and 1.47×10^{-3} cm³ s⁻¹ (×), 1.5×10^{-4} M and 1.31×10^{-2} cm³ s⁻¹ (+). In both plots the current (I) has been normalized to the steady-state transportlimited current, I_{lim} , flowing at the generator electrode. The x axis represents normalized time (see text).



Figure 7. Detector electrode transient measured for a cell of type A resulting from a potential step, as described in the text, for the reduction of CA in acetonitrile solution. The cell dimensions were 2h = 0.037 cm, $x_1 = 0.40$ cm, $x_2 = 0.70$ cm, and $x_3 = 1.35$ cm. The symbols relate to different concentrations of CA: 2.1×10^{-4} M (×), 1.3×10^{-2} M (O). The solid lines are those generated theoretically for $D_A = 1.75 \times 10^{-5}$ cm²s⁻¹ and either $D_B = 1.75 \times 10^{-5}$ or 0.94×10^{-5} cm²s⁻¹. The current has been normalized to the steady-state current flowing at the detector electrode. The x axis represents *real* time.

particular, we examine the nature of electrolytic reactions taking place at a porous silicon electrode. Following the demonstration¹⁶ that porous silicon films can be fabricated which emit efficient visible photoluminescence at room temperature, there have been



Figure 8. Computed "back" transient relating to the reconversion of the *p*-chloranil radical anion to CA at the generator electrode, as in Figure 6b, for different values of $D_{\rm B}$: 1×10^{-5} , 0.8×10^{-5} , and 0.5×10^{-5} cm² s⁻¹. The current is normalized to the steady-state current attained after the forward step. The x axis represents *normalized* time (see text).

considerable efforts to produce efficient electroluminescent devices. To date, solid-state electroluminescent devices have proved rather inefficient. However, efficient electroluminescence has been achieved^{17,18} by using liquid contact systems in which the persulfate ion is used to achieve efficient injection of holes. In connection with the latter it is of importance to know whether electrolysis can occur throughout the full depth of the porous layer or else is confined to the pit of the pores, near the bulk silicon interface. To this end we have examined the three samples, with differing thicknesses of the porous layer, specified in Table 1 with the aim of demonstrating that significant electrolysis occurs on the surface of the material, thus implying that the porous layer is active throughout its depth.

We consider first the current/voltage curves measured on the various silicon samples, again relating to the one-electron reduction of CA in acetonitrile. Reduction at a nonporous silicon electrode showed a highly irreversible voltammetic feature with a halfwave potential of ca. -2.00 V (vs SCE). No decomposition of the solvent or supporting electrolyte system was observed at potentials anodic of -2.80 V. The magnitude of the voltammetric wave was significantly less (<40%) than that expected for mass transport control, possibly suggesting limitation by transport processes within the silicon. Turning to the porous silicon samples PTC-5, PTC-7, and PTC-9, it was found that the potential at which CA was reduced was markedly reduced as compared to the nonporous sample in all three cases. Clearly resolved voltammetric waves were seen in two cases with half-wave potentials of -1.20 V (PTC-5) and -1.05 V (PTC-7). The limiting current passed was consistent with mass transport control. In the case of PTC-9 the threshold potential for the discharge of the solvent system was markedly reduced compared to that for nonporous silicon and was found to occur at a voltage very close to that required for the reduction of CA. A half-wave potential of ca. -1.00 V was estimated for the reduction.

It is clear that as the depth of the silicon layer increases, the reduction potential for the discharge of CA is systematically decreased, as is the potential required for the reduction of the CH₃CN/0.1 M TBAP medium: increased pore depth lowers the overpotential required for both processes.

The sample PTC-9 had, by far, the deepest pores of all those studied. As such, it represented the optimal substrate for identifying the role of the pores in electrolysis processes occurring at porous silicon. However, it will be apparent that the direct voltammetric interrogation of such effects would be difficult using a single electrode alone due to the closeness of the reduction



Figure 9. Detector electrode response arising from a potential step on a nonporous silicon generator electrode as specified in the text. The current axis shows the transient normalized to the total current change induced by the transient. The x axis represents *real* time.



Figure 10. Detector electrode response arising from a potential step on a porous silicon generator electrode (sample PTC-5) as specified in the text. The current axis shows the transient normalized to the total current change induced by the transient. The x axis represents *real* time.

potentials of CA and the solvent system. Accordingly, a doublechannel electrode approach was adopted in which a platinum detector electrode was located downstream of the porous silicon electrode and used to monitor the concentration of CA surviving passage over the former as revealed by the current due to the one-electron reduction of CA.

We consider experiments in which the detector electrode is potentiostated at a value (-0.50 V, vs SCE) which corresponds to the transport-limited reduction of CA. In each experiment the potential of the silicon electrode is stepped between two values. The first of these corresponds to the transport-limited reduction of CA while the second, final potential is one at which *no* current due to the reduction of CA flows. In the case of nonporous silicon the two potentials were -2.60 and -1.90 V whereas for the three porous samples they were -1.60 and -0.70 V. In each case the current transient induced on the detector electrode was measured and showed a slow increase in current attributable to the enhanced levels of CA which can reach the detector electrode when the upstream silicon electrode is "switched off".

Initially, transients were measured for a nonporous silicon substrate using a range of flow rates. The transients were modeled using established theory,² and excellent agreement with experiment was found if a diffusion coefficient of 1.75×10^{-5} cm² s⁻¹ was assumed for CA (see above). A typical transient is shown in Figure 9 for which a flow rate of 1.6×10^{-3} cm³ s⁻¹ was used; a new steady-state current is reached on the platinum electrode approximately 12 s after the potential of the upstream electrode is stepped.

Figures 10, 11, and 12 show the detector electrode transients obtained for the samples PTC-5, PTC-7, and PTC-9 under exactly analogous conditions of flow rate as used to record Figure 9. It is immediately noticeable that the time scale of the transient increases as the pore depth of the substrate gets larger and in all cases is *significantly* longer than that recorded for the nonporous silicon.

The shape of the transients changes markedly between Figures 9, 10, 11, and 12. Consider first Figure 10, which relates to a porous electrode with pores of depth 3.6 μ m and which can be seen to contain two distinct portions: first, a sharp rise *exactly* corresponding to the time scale seen in Figure 9 where complications due to porosity effects are absent and, second, a much



Figure 11. Detector electrode response arising from a potential step on a porous silicon generator electrode (sample PTC-7) as specified in the text. The current axis shows the transient normalized to the total current change induced by the transient. The x axis represents *real* time.



Figure 12. Detector electrode response arising from a potential step on a porous silicon generator electrode (sample PTC-9) as specified in the text. The current axis shows the transient normalized to the total current change induced by the transient. The x axis represents *real* time.

slower increase over a period of tens of seconds in which the electrode slowly attains its steady-state current. Figure 11 relates to an electrode with pores of depth 10.9 μ m and is broadly similar in form to Figure 10, except that the slow portion of the curve extends over a longer period of time. Last examination of Figure 12, which corresponds to an electrode of pore depth 34.3 μ m, reveals a slow portion which is very substantially more pronounced than for the other two cases and which therefore dominates the overall form of the transient although an initial rapid component is still present. The time duration of the slow portion is even longer than in Figure 11.

We suggest that the initial portion of each transient reflects solution transport effects influenced by the switching off of the electrode reaction on and in the silicon electrode. The slow portion we attribute to transport of CA within the surface porous layer of the working electrode. In particular, when the silicon electrode is passing a current due to the reduction of CA, prior to the potential step, the pores will be substantially filled with CA.--When the current flow is terminated by the potential step, CA-will diffuse out of the porous layer into the flowing electrolyte in the channel. At the same time neutral CA will continue to diffuse into the pores until the concentration of CA within them has a value equal to that in bulk solution upstream of the platinum detector electrode. Thus, as interrogated by the detector electrode, the porous layer apparently continues to consume CA even when its potential is insufficient to reduce CA. The correlation of the time scale and magnitude of the slow contribution to the transient with the pore depth of the three electrodes examined suggests the veracity of this interpretation.

To illustrate the above inferences, we semiempirically modeled^{1,2} the transient response of the detector electrode in the following way. The current flowing at the working electrode is assumed to be transport limited and the steady-state concentration profile of CA in the channel above this electrode calculated using standard techniques^{1,2} in which the relevant transport equations are solved using a finite difference method which utilizes a grid of size $J \times K$ points in the zone of the working electrode.^{1,2} The flux of CA at each point k (0 < k < K) along the working electrode surface is evaluated: Experimental Applications of Double Electrodes



Figure 13. A set of theoretical detector transients computed using the model described in the text for the combinations of the parameters (1-f) and β shown in the diagram.

$$(\text{flux})_{k,t<0} = \left(D_{\text{CA}} \frac{\partial [\text{CA}]}{\partial y} \right)_{k,t<0}$$

where D_{CA} is the diffusion coefficient of CA. After the potential step (at t = 0) we assume the flux to be given by

$$(\text{flux})_{k,t>0} = \left(D_{\text{CA}} \frac{\partial [\text{CA}]}{\partial y} \right)_{k,t<0} f \exp(-\beta t)$$

where β controls the time scale of the slow transient and (1 - f)is the fraction of the current prior to the potential step arising from discharge at the surface of the electrode so that f is zero for a nonporous electrode.

Figure 13 shows a set of transients computed for the cell geometry used for the experiments reported above using the determined value of D_{CA} for different sets of the parameters (1 -f) and β . It can be seen that the simulated transients qualitatively mimic the form of the experimental transients. In particular, the sharply rising initial portion of the transient reflects the magnitude of (1 - f) and results from cessation of surface electrolysis. The empirical parameter β reflects the speed of diffusive transport within the porous layer and so dictates the time taken to establish a steady-state current on the detector electrode.

The model shows that when CA undergoes electrolytic reduction at porous silicon a significant amount of charge transfer must occur at the surface of the electrode; otherwise, the sharp part of the transient would be absent. In particular, if electrolysis were confined to the end of the pores where the porous layer terminates as bulk solid, only the slow transient would be observed. It follows that the porous layer is electroactive throughout its thickness.

The ability of transient experiments using double-channel electrodes to characterize the interfacial processes is evident.

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