Differential Pulse Voltammetry at Microelectrodes

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Microelectrodes have been cited to have many advantages over conventional electrodes [1-3]. However, a primary disadvantage is that the use of a microelectrode in a potential sweep mode results in a sigmoidal output which is difficult to interpret at low analyte concentrations. The aim of this work is to characterize the differential current response of a microelectrode. This may be done by numerical differentiation of a digitally acquired signal following a linear sweep which is trivial [4], or through the use of an applied differential pulse waveform.

The following assumptions were made in postulating the theory for differential pulse voltammetry at a planar disk microelectrode [5] and are the basis for Model 1.

a) The Cottrell equation may be used for characterization of the current response at short time periods following the pulse.

b) The current due to the potential ramp follows the traditional microelectrode behavior with a potential dependent component.

c) The above two currents, a) and b), are additive for the potential ramp before the pulse is applied, taking into account a steady-state current following the pulse.

d) The limiting steady-state current to be calculated after the pulse is applied.

The following assumptions were made in postulating the theory for differential pulse voltammetry at a planar disk microelectrode [5] and are the basis for Model 2.

i) The current due to the underlying ramp at time \( t \), \( i_d \), is less the current before the pulse, \( i_1 \).

ii) The potential defined by the potential ramp at time \( t \), \( \theta \), is the time at which the current is sampled after the pulse is applied and \( (\theta + \tau) \) is the time at which the current is sampled after the pulse is applied. \( \Delta E \) is the pulse amplitude and all other symbols have their usual meaning. The instrumental differential output is represented as follows by the sum of the current due to the underlying ramp at time \( \theta \), \( i_d \), and the current due to the pulse \( i_i \), less the current before the pulse, \( i_1 \).

\[
i(t) = i_1 + i_i - i_d
\]  

In practice during the timescale of the experiment the diffusion layer thickness was found to be of the same order of magnitude as the diameter of the microelectrode. This facilitated the presence of "edge effects" which leads to a steady-state current being reached within the pulse width (\( \delta t \)). By modifying the theory the differential current may be calculated as follows using Model 2.

\[
\delta t = i_4 - i_2
\]

where

\[
i_4 = \frac{4nF \sqrt{D}}{1 + \epsilon_3}
\]

and

\[
i_3 = \frac{4nF \sqrt{D} (E_2 + \Delta E - E_0)}{RT}
\]

where \( i_d \) is the steady-state current following the pulse and \( i_2 \) is the current due to the ramp potential before the pulse is applied. This modified theory allows for steady-state current to occur before and after the pulse.

From the limiting current \( i_L \) of the voltammetric response obtained by scanning the potential of a platinum microelectrode in a solution of \( 5 \times 10^{-3} M \) ferrocyanide in a solution of \( 0.1 M \) KCl, the electrode radius was found from Equation 7. Taking \( i_L \) to be \( 5.60 \times 10^{-9} \) A, and the diffusion coefficient \( (D) \) for \([Fe(CN)_6]^{3-}\) to be \( 6.5 \times 10^{-6} \) cm² s⁻¹ [6] the electrode radius \( r \) was calculated as \( 4.46 \times 10^{-6} \) m.

Figure 1 shows the response obtained by the application of a differential pulse waveform to a platinum microelectrode in a solution of \( 5 \) mM \([Fe(CN)_6]^{3-}\). It can be seen that the peak current heights increase with increasing pulse amplitude but at the expense of return to baseline. Closer investigation revealed that the increase in peak current height was linear with pulse amplitude over a
limited range. The effect of varying the differential pulse waveform
period (taken here to be the time between pulse applications) was
also investigated. It was found that long differential pulse
waveform periods (>10 s) resulted in stepped responses with ill-defined peaks
while shorter differential pulse waveform periods resulted in
smoother traces with well-defined peaks. The magnitude of the
differential pulse waveform period was found to have negligible
effect on peak current heights.

Figure 2 compares the experimental results obtained from the
numerical derivative of a sigmoidal experimental plot, Figure 2a,
and the response from the application of a differential pulse
waveform to the same electrode, Figure 2b. Also included are
simulated plots using Equation 8, Figure 2c, and Equation 9, Figure
2d. It is immediately obvious that Model 1 (Eq. 8), does not
correlate well with either of the experimental traces whereas Model 2
(Eq. 9) correlates well with both experimental traces.

Table 1 lists the peak current heights corresponding to each of
the experimental and simulations over a range of pulse
amplitudes. In the case of the differential pulse waveform the
correlation between experimental peak current heights and those
predicted by Model 2 occurs only over a narrow pulse amplitude
range. However it can be seen that the peak current heights obtained
by numerically differentiating the sigmoidal experimental plot
correlate well with those predicted by Model 2 over the complete
range of pulse amplitudes studied. It is therefore possible to enjoy
the advantage of a peaked response which is well-defined (Model 2)
over a wide range of pulse amplitudes without having to invest in
new and sophisticated equipment, the only system requirements
being a linear ramp waveform generator, a data acquisition unit and
a computer with relevant software, all of which are commonplace
in any electrochemistry laboratory.

The results for peak current from Model 2 and peak current
values from the numerical derivative of a linear sweep correlate
well. The reason for slight differences may be because of the fast
sweep rate used (10 mV/s). However the experimental differential
pulse response deviates from Model 2, indicating that there may be
some contribution to the response from the pulse and that a steady
state has not occurred in the timescale of the pulse width. This may
be due to slow electron transfer kinetics on such a short time scale
or a combination of slow electron transfer kinetics and diffusion
control.

As stated earlier Model 2 is based on the fact that a steady-state
current is reached within the pulse width due to the presence of edge
effects which in tum are due to the thickness of the diffusion layer
being of the same order of magnitude as the electrode diameter. The
diffusion layer thickness (d) is approximated by the equation
d = (xDr2)1/2 = 1.06 x 10-5 m where x = pulse width = 55 ms. Therefore
the thickness of the diffusion layer (d) is controlled by the pulse
width (x), and the diffusion coefficient (D), both of which are
constant for a given set of experimental conditions. It is clear that
the extent to which Model 2 can be applied to a given experimental
arrangement depends directly on the relative magnitudes of the
electrode diameter and the diffusion layer thickness.

A distinct advantage of applying a differential pulse to a
microelectrode can be seen at lower concentrations. This is evident
in Figure 3 where the response is shown both for direct current and
the differential current following the application of a differential
pulse. The direct current response is very difficult to interpret and
therefore almost useless in providing analytical information.
However for the differential pulse response there is useful
information to be gained as a peak is clearly seen at the potential
at which the electrochemical reaction in question is known to occur.
This has the effect of lowering the limits of detection relative to
the direct current experiments. Also a peaked response is more desirable
as a baseline can be drawn enabling peak current to be easily

<table>
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<tr>
<th>Pulse amplitude [mV]</th>
<th>Experimental peak height [nA]</th>
<th>Peak heights from Model 1 [nA]</th>
<th>Peak heights from Model 2 [nA]</th>
<th>Numerical derivative peak height [nA]</th>
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<td>0.65</td>
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<td>1.14</td>
<td>1.09</td>
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</table>

Fig. 1. Differential pulse output for a microelectrode in a solution of 5 mM
Fe(CN)63- in 0.1 M KCl. Instrumental time constant: 1 s, sweep rate:
10 mV/s. Differential pulse waveform period: 1.0 s, pulse width: 55 x 10^-5 s.
Pulse amplitudes are shown in the figure.

Fig. 2. a) Numerical point by point derivative of a linear sweep response for
5 mM Fe(CN)63- in 0.1 M KCl at a microelectrode (r = 4.46 x 10^-14 m)
where the sweep rate was 10 mV/s. Points which gave a pulse height of
60 mV were chosen. b) Experimental differential pulse output (AE =
60 mV), sweep rate: 10 mV/s, time constant: 1 s. c) Model 1, (Eq. 8)
calculated using the parameters as above. d) Model 2, (Eq. 9) calculated
using the parameters as above.
In conclusion, there is good correlation between Model 2 and the numerical derivative of a linear sweep potential waveform applied to a microelectrode. A differential pulse study does not correlate as well perhaps due to slow kinetics. Model 1 will apply for larger electrodes. Work on examining the effect of slow kinetics on the response is ongoing.

**Experimental**

The potentiostat used throughout this work was an Elr Model ECP 100 and a J.L. Lloyd X-Y chart recorder Model PL3 was used to chart the response. A three electrode system consisting of a carbon rod auxiliary, a saturated calomel reference electrode and an EG&G Pure platinum planar disk microelectrode was employed. All chemicals used were of reagent grade and all solutions were made up using deionized water. Solutions were degassed by bubbling with nitrogen for at least 15 min prior to recording any data. A Pasco Scientific CI-6510 analogue to digital converter was used to collect and store the data digitally and the simulations were carried out using a program written in Microsoft Excel.

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**References**