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Evaluation of a Naive Model for Square Wave Voltammetry at a Disk Microelectrode.

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Abstract

A square wave voltammetric waveform (SWV) was applied to an inlaid microdisk electrode in a solution of $K_4[Fe(CN)_6]$. A simple model relying on the assumption of steady state current throughout the scan was used to model the current potential behaviour. However, experimental peak current magnitudes were between 30% and 50% greater than those predicted by the model. The model predicts an increase of peak current and peak width at half height with pulse height Esw and no effect of the parameters frequency, f and step height, ΔEs. Experimental peak current magnitudes and peak current magnitudes predicted by the model both increased with increasing Esw but were not affected by f or ΔEs.

Keywords: microelectrode, square wave voltammetry.

1. Introduction

Microelectrode have found many uses in electroanalysis as single disks or arrays. The use of square wave voltammetry (SWV) has traditionally been employed for anodic stripping methods, for example in the determination of epinephrine[1] and more commonly for the detection of heavy metals, Cd^{2+}, Pb^{2+} and Cu^{2+}[2-4]. However organics such as paraquat[5,6], chloroamphenicol[7] and vanillin[8] have been determined using SWV at microelectrodes. There has been work done in modelling SWV at microelectrodes by Whelan et al [9]. Furthermore the application of SWV has been modelled at spherical electrodes[10] and spherical microelectrodes[11]. In this short communication, we evaluate the application of and empirical model, used previously for differential pulse voltammetry at a microelectrode [12] and a rotating disk electrode [13], to SWV at a microelectrode disk.

2. The steady state model

This model relies on the rapid achievement of a microelectrode steady state current on application of SWV pulses. The square wave voltammetric waveform arises from the superimposition of two waveforms, an incremental staircase potential of amplitude ΔEs, which has a square wave amplitude waveform superimposed on it of magnitude Esw[14,15]. The current is sampled at the lower potential of the Esw, at tp, and then at the higher potential, at 2tp where tp is related to the frequency of the square wave waveform, as $f = 1/(2tp)$, and the difference between these two currents is output. The

pulse of length tp corresponds to half the period of the applied staircase potential. At the lower potential the current is given by

$$i_1 = \frac{4nFrDC}{1+\varepsilon_1} \qquad (1)$$

where r is the microelectrode radius, D the diffusion coefficient of the electroactive species in solution, C its concentration and ε_1 is a function of the applied potential E_i:

$$\varepsilon_1 = \exp\left(\frac{-nF(E_i - E^o)}{RT}\right) \qquad (2)$$

E_i is the initial potential and E^o is the formal potential of the electroactive couple. On application of the pulse Esw, the current sampled is

$$i_2 = \frac{4nFrDC}{1+\varepsilon_2} \qquad (3)$$

where

$$\varepsilon_2 = \exp\left(\frac{-nF(E_i + 2Esw - E^0)}{RT}\right) \qquad (4)$$

And in the next time increment the base potential E_i will increment by ΔEs. The output current is

$$\delta i = i_2 - i_1. \qquad (5)$$

Typically the current output is plotted against the mid point potential of each square wave cycle[9]. As an approximation, the Taylor series expansion of the exponential function is given by:

$$\left(\frac{1}{1+e^x}\right) \approx 1/2 - x/4 + x^3/48 + O(x^4) \qquad (6)$$

and this may be used to obtain an estimate for δi.

3. Experimental

Experiments were carried out at room temperature (20 ± 3^{o}C) using a microelectrode, with a nominal 10 μm or 25μm diameter Pt disk (source = IJ Cambria Scientific Ltd, 11 Gwscwm Road, Burry Port , Carms, SA16 OBS UK) in a three electrode one compartment cell. The reference electrode was a saturated calomel electrode and the auxiliary electrode was Pt wire. Potentials were controlled using a CHI 620A Electrochemical Analyser. Chemicals were reagent grade and solutions were prepared in deionised water.

4. Results and Discussion

From initial linear sweep voltammetric experiments with the two electrodes in 5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl, the current was determined to be 5.1 nA and 14.1 nA from which effective radii were calculated to be 4.1 microns and 11.2 microns respectively, using a diffusion coefficient of 6.5 x 10^{-6} cm^2s^{-1}[16].

Following this, square wave potential waveforms were applied to determine the nature of the current response.

The parameters varied for the SWV were the pulse height Esw, the step height ΔEs and the frequency. The parameter which has the greatest effect on the peak current is the pulse height Esw. Figure 1 shows the experimental current profile for a range of Esw values. It can be seen that the peak current and the peak width at half height increases with Esw. The peak current magnitude varies linearly with the Esw up to and Esw value

approximately 50mV ($Y = 104 X + 0.27$, $R^2 = 0.98$, Y is in nA and X is in V). At higher Esw values, the magnitude of the peak current levels off with increasing Esw.

When (6) is substituted into (5) the approximation is

$$\delta i \approx 2 n^2F^2rDCEsw/(RT) \qquad (7)$$

which predicts a linear behaviour between the peak current and Esw. From an analytical viewpoint, changing Esw will increase the sensitivity of the analytical method.

Figure 2 shows the modelled profile predicted by model for the experimental conditions of Figure 1. It can be seen that the current potential profile of Figure 2 mirrors that of Figure 1. Table 1 displays the characteristic parameters of the profiles. It can be seen that there is an increase in δi_p with Esw. The notable difference between the model and experimental results is the peak current magnitude. At low Esw values the difference between theory and experimental is relatively constant. This difference cannot be explained by double layer charging current or residual current since there is not enough residual current in the experimental plots to warrant this assertion. The greater experimental current may be due to a redox cycling effect where the $[Fe(CN)]^{3-}$ generated on the forward pulse is reduced on the subsequent reverse pulse and *vice versa*.

The difference is consistent at low Esw values for both electrodes. At higher Esw values the percent difference increases as the pulses are larger which means that the currents are deviating from steady state and the current is being sampled during a Cottrell regime.

Changing ΔEs from 4 to 15 mV at the 4.1 μm radius microelectrode yielded a peak current of 1.3 nA. The model also predicts no effect of ΔEs on peak current magnitude.

Similarly at low frequencies (f<15Hz), the frequency has no effect on the peak current magnitude; which is also predicted by the model.

5. Conclusion

This simple model predicts that there is an increase in sensitivity with increasing pulse amplitude, Esw. This is borne out with experimental results. In addition there is no increase in sensitivity with step height, ΔEs or frequency. In addition there is no shift in the peak current position with all three of these parameters. However there is a large discrepancy between the experimental and modelled current.

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Figure legends

Figure 1 Experimental output for SWV at a 4.1 micron radius Pt microelectrode. ΔEs = 4 mV, $K_4[Fe(CN)_6]$ = 5 mM in 0.1M KCl, f = 5 Hz and the values of Esw are 5, 15, 25, 35, 45, 60 and 80mV in order of increasing current magnitude..

Figure 2. Simulated output using the Model for SWV at a 4.1 micron radius microelectrode. Esw = 5, 15, 25, 35, 45, 60 and 80 mV. Other conditions are as in Figure 1.

Table 1. Experimental and model I simulation outputs. f = 5Hz, ΔEs = 0.004 V and C = 5 mM. The δi% difference is the calculated as 100(experimental – theory)/theory

		Model		Experimental		
Electrode Radius μm	Esw /mV	Ep/ V	δi_p/ nA	Ep/V	δi_p /nA	δi%
4.1	15	0.179	1.48	0.176	2.00	34
4.1	25	0.181	2.36	0.176	3.11	32
4.1	35	0.179	3.08	0.176	4.17	35
4.1	45	0.181	3.66	0.180	4.96	35
4.1	60	0.180	4.27	0.180	6.09	32
11.2	5	0.181	1.39	0.180	1.99	44
11.2	10	0.178	2.80	0.184	3.97	44
11.2	15	0.179	4.06	0.184	5.92	46
11.2	20	0.180	5.31	0.184	8.20	54
11.2	25	0.181	6.45	0.184	10.10	56
11.2	35	0.179	8.45	0.184	13.34	54
11.2	45	0.181	10.03	0.184	16.93	69
11.2	60	0.180	11.69	0.188	20.13	72