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Modulated hydrodynamic voltammetry using a small volume wall-tube cell

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A small-volume wall-tube electrode cell is shown to follow the dynamic voltammetric equations proposed for this type of electrode. It is used to demonstrate sinusoidal and square wave (or pulse) modulated hydrodynamic voltammetry.

Key Words: impinging jet electrode, hydrodynamic voltammetry, flow modulation

THE WALL-TUBE ELECTRODE IS A HYDRODYNAMIC ELECTRODE SYSTEM, one of a general class of impinging jet systems, in which a moving solution impinges against a planar electrode surface flush on a wall, from a tube whose internal diameter is bigger than that of the planar electrode's. Chin and Tsang (1) presented the hydrodynamic equations relating the current through the electrode to the dimensions of the electrode system and flow rate of the solution. Their limiting current equation was later reformulated to the more conventional electrical terms by Albery and Bruckenstein (2) who pointed out the close relation of the reformulated equation to the Levich equation used in characterizing the limiting current through a rotating disc electrode (RDE) (3). This limiting current equation, which we call the Ching-Tsang-Albery-Bruckenstein or CTAB equation, is given below with its perimeters illustrated in Figure 1.

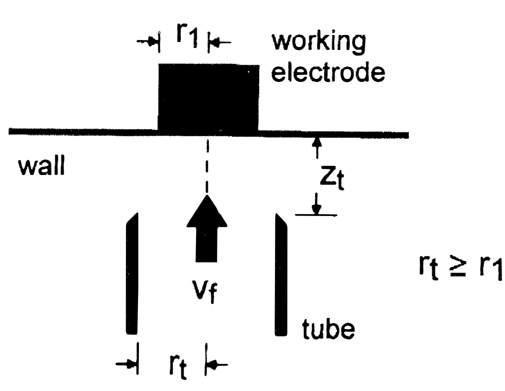

Figure 1. Wall-tube electrode system. Solution is pumped through a tube against a disc electrode flush on a wall.

$$i_{lim} = 0.624\, n\, F\, \pi\, r_1^{\,2}\, D^{2/3}\, \nu^{-1/6}\, (V_f / r_t^{\,3})^{1/2}\, C_0\, (r_t / z_t)^{0.054}$$

D	=	diffusion coefficient, cm^2/s
V_f	=	flow, cm^3/s
C_0	=	bulk solution concentration, mol/cm^3
r_1	=	disc electrode radius, cm
ν	=	kinematic viscosity, cm^2/s
r_t	=	tube radius, cm
z_t	=	tube to electrode distance, cm

We have designed an electrochemical cell using a wall-tube configuration which requires a small volume of solution. We show that its behavior follows closely that predicted by the CTAB equation, and demonstrate its use in modulated flow voltammetry.

Experimental

Cell Design. Figure 2 shows the schematic of a cell used in this paper. It is constructed from acrylic stock and can easily be taken apart for replacement or cleaning of the planar disc working electrode (Pt, Au or glassy carbon), the Ag/AgCl reference, and the Pt auxiliary electrode. With the use of calibrated shims, it is possible to set the distance between the tube and the planar disc precisely and therefore the ratio r_t/z_t in the CTAB equation. Values of the important dimensions and parameters are; $r_t = 0.116$ cm, $r_1 = 0.051$ cm, $z_t = 0.7$ to $3.0 \times r_t$ and $V_f = 2$ to 9 cm^3/min, for the set of experiments reported here. total volume of the cell is about 0.5 cm^3.

Reagents and materials. All reagents used are reagent grade and the water is distilled and deionized. The platinum used for the disc electrode and the auxiliary electrode is from Johnson Matthey.

Electrochemical Apparatus. A lab-built computerized data acquisition system is used. It has two independent sets of 12-bit analog to digital converters and digital to

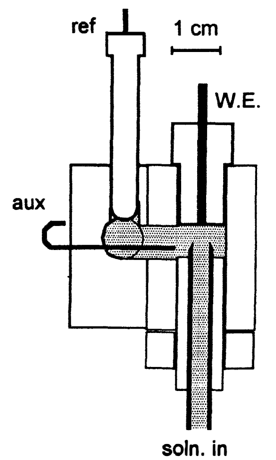

Figure 2. Small-volume electrochemical cell featuring the wall-tube electrode configuration.

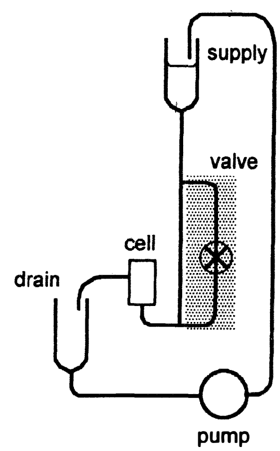

Figure 3. Hydraulic circuit for hydrodynamic voltammetry and modulated hydrodynamic voltammetry.

analog converters, and a potentiostat of standard configuration using LF411 operational amplifiers. Programs written in compiled Basic allow data acquisition at up to 5,000 readings per second of two parameters as well as time data accurate to one microsecond using a built-in crystal oscillator timer. Data is stored in diskette files for archiving and post-processing and can be displayed on the computer screen or output on a Yokogawa Electric Works model 3022 X-Y recorder for easily read hard copies.

Hydrodynamic voltammetry and modulated hydrodynamic voltammetry. The hydraulic circuit is shown in Figure 3. A Gilson Minipuls 2 variable speed peristaltic pump is used to scavenge the solution from the drain reservoir and return it to the supply reservoir. Rate of flow of the solution is a function of the hydraulic head and the resistance of the circuit from the supply to the drain. Rate of flow can be controlled either by keeping the resistance constant while varying the hydraulic head, or keeping the hydraulic head constant and varying the resistance. In doing the hydrodynamic voltammetry to characterize the small volume wall-tube cell at a constant flow rate, a large supply reservoir is used to keep the flow rate steady. In the modulated flow experiments, a small reservoir is attached to the pen-holder of a chart recorder which is placed on its side so that the supply reservoir is raised and lowered by the servo-mechanism. A function generator connected to the chart recorder's input is used to drive the reservoir sinusoidally up and down or in any waveform that the function generator is capable of putting out. To make sure that the signal recorded by the data acquisition system is a true representation of the reservoir's elevation, this voltage is taken from the feedback voltage from the servo's potentiometer.

In changing the flow rapidly from one value to another in square wave modulation of the flow (in pulsed flow voltammetry), an alternate path is added to the hydraulic circuit and is shown in the shaded part of Figure 3. Keeping the hydraulic head fixed, the flow rate is changed by a small amount by opening and closing a solenoid valve in series with this auxiliary circuit path. The maximum speed of the chart recorder used here is 4 Hz, which translates to approximately 80 msec for a 10 cm rise or fall, while a pinch valve can easily operate in about 15 msec. A modulated wave of reasonable square form of up to about 20 Hz can be produced by this method.

All the experiments reported in this paper involve the electrochemical reduction of varying concentrations of potassium ferricyanide solution in 0.1 M KCl at a Pt disc electrode. This reaction is well known and the parameters are well established in standard electrochemical literature. All experiments were run at 25 ± 1°C.

Results and Discussion

Hydrodynamic Voltammetry

Figure 4 shows a typical hydrodynamic voltammogram where the potential is scanned during the run from +0.4 V to -0.3 V (vs the 4 M Ag/AgCl reference) at 5 mV/s using a Pt disc working electrode. In this particular run, $r_t = 0.116$ cm, $r_1 = 0.051$ cm, $V_f = 0.153$ cm^3/s and $z_t = 0.150$ cm. Using 0.0101 cm^2/s for the kinematic viscosity and 7.6 x 10^{-6} cm^2/s for the diffusion coefficient of potassium ferricyanide in this medium (4) the calculated limiting current using the CTAB equation is 15.9 μA, while the actual experimental result is 16 μA, a result that is less than 1% different from the calculated value.

Figure 5 shows the linear dependence of the limiting current on the square root of the volume flow rate. The plot gives a linear correlation coefficient of 0.999.

Figure 6 shows that there is a distinct variation of limiting current with the position of the tube in relation to the planar electrode. Chin and Tsang included a dimensionless parameter, $(r_t/z_t)^{0.054}$, in their equation to take care of this. The figure shows that for the greatest accuracy, it is necessary to take this parameter into account. It can only be disregarded where the ratio is very close to or equal to unity.

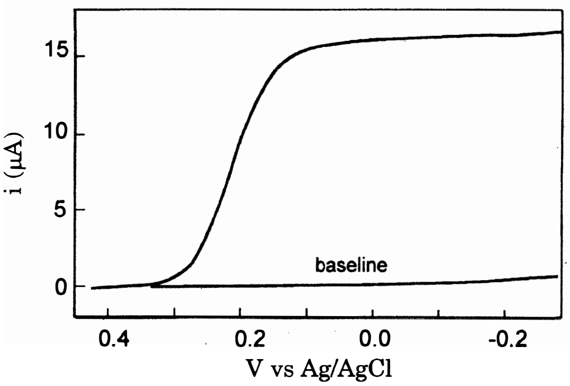

Figure 4. Hydrodynamic voltammogram of 4 mM potassium ferricyanide in 0.1 M KCl. Parameters are given in the text.

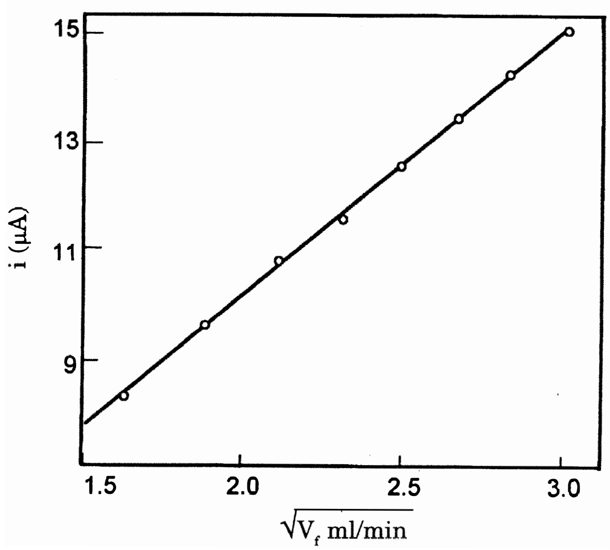

Figure 5. Effect of the solution flow rate on the limiting current in the wall-tube electrode.

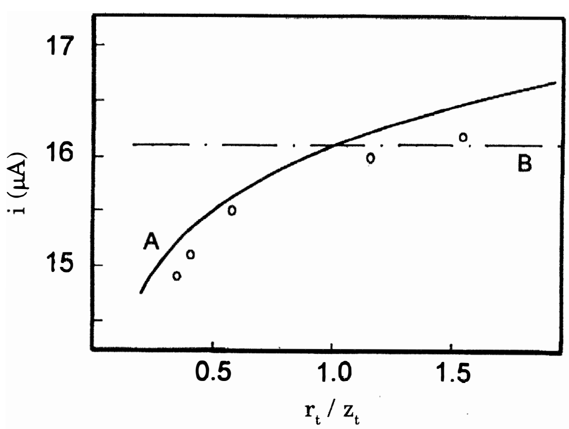

Figure 6. Effect of tube-to-electrode distance. Small circles are experimental points. Solid line is calculated taking this term into account in the CTAB equation and the dashed line is calculated assuming that this term is unity.

Modulated Hydrodynamic Voltammetry

Sinusoidal and other wave-form modulation of the flow rate. Figure 7 shows the output current from the working electrode (A) when the hydraulic head is varied with a square wave which is changed midway into a sine wave of the same frequency (B). Note the slight delay in the response current as flow rate is changed, a consequence of the slow electrode reaction of the ferricyanide. The voltage is kept at 0.0 V vs Ag/AgCl to assure that the current is the maximum (plateau) value.

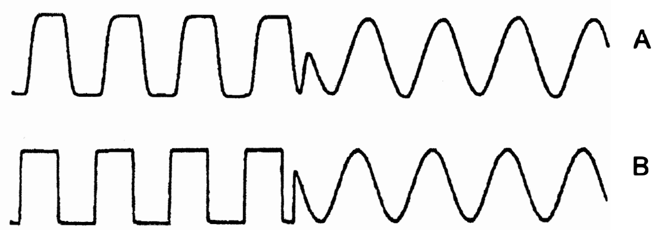

Figure 7. Square wave and sine wave modulation of the flow rate (B) and the resulting change in the current through the working electrode in the wall-tube cell (A), plotted on the same time base. The flow rate is modulated by the varying the hydraulic head, which is the actual parameter that is plotted in B as a function of time.

A modulated rotational rate system was described by Miller and Bruckenstein (5) for the RDE.

Pulse modulated hydrodynamic voltammetry. Figure 8 shows the modulated current which results as the modulating frequency is changed. At 1.0 Hz or below, the peak-to-peak modulation current of a 4 mM solution of potassium ferricyanide in 0.1 M KCl remains constant but starts to taper down above this value. It is therefore possible to determine the concentration of an active species from its pulse modulated voltammogram as long as the modulation frequency is kept below that which will attenuate the modulated current. Figure 9 shows the linear plot of concentration vs modulation current for millimolar concentration of ferricyanide. The linearity is carried down to micromolar concentrations as shown in Figure 10.

In these experiments with the square wave or pulse modulation of the flow at 0.8 Hz, the amplitude of the modulation is such as to change the resulting current by ± 11%.

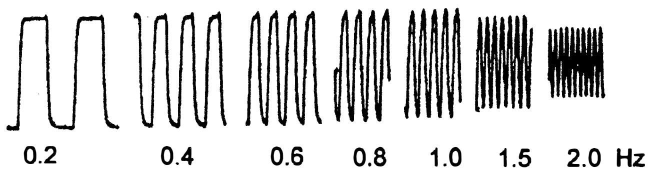

Figure 8. Square wave or pulse modulationg of the same solution in Figure 7, showing the effect of increasing the pulse rate. the small spike apparent just before the current rises or falls is an artifact of the pinch valve operation.

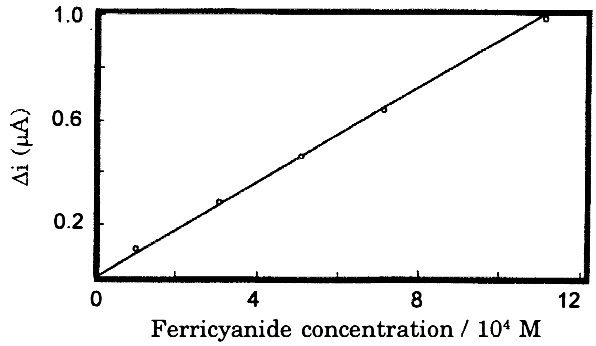

Figure 9. Pulse modulated voltammetry of millimolar concentrations of potassium ferricyanide in 0.1 M KCl. Pulse modulation is 0.8 Hz.

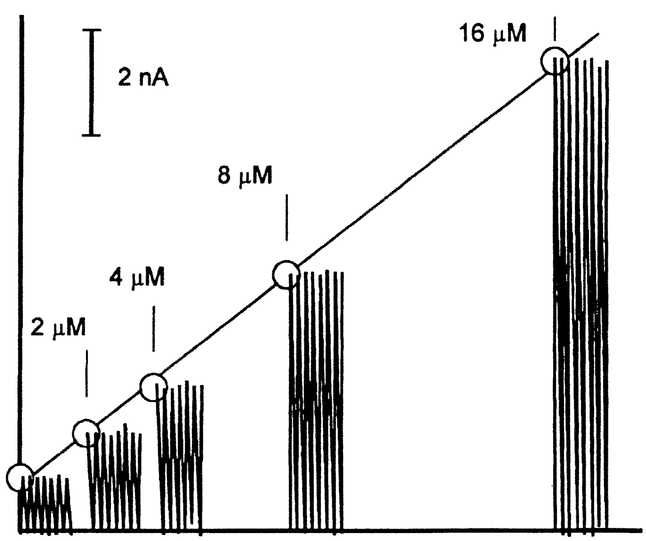

Figure 10. Pulse modulated voltammograms of micromolar concentrations of potassium ferricyanide in 0.1 M KCl showing linear relation between concentration and modulation current. Modulation is 0.8 Hz. A small residual due to an unidentified contaminant is present.

Conclusion

The wall-tube electrode behaves in a completely predictable manner and follows the equations developed for it. As Albery and Bruckenstein point out (2), it behaves very much like a rotating disc electrode in which a flow rate parameter substitutes for the rotational rate. It is an ideal electrode system to try in various application that call for an RDE.

References

1. Chin,D.T. and Tsang, C.H., *J. Electrochem. Soc. 125*, 1461, (1978).
2. Albery, W.J. and Bruckenstein, S., *J. Electroanal. Chem. 144*, 105 (1983).
3. Bard, A.J. and Faulkner, L.R., *Electrochemical Methods*, p.288 (John Wiley and Sons, 1980).
4. Sawyer, D.T. and Roberts, J.L., *Experimental Electrochemistry for Chemists*, p.77 (John Wiley and Sons, 1974).
5. Miller, B. and Bruckenstein, S., *Anal. Chem. 46*, 2026 (1974).