

E1-06: Theoretical study on the diffusion-controlled current density at a cylindrical wire-microelectrode

K Premaratne¹, R M G Rajapakse²

(¹Dept of Physics, ²Dept of Chemistry, Univ of Peradeniya)

In electrochemical reactions, the study of transient behaviour of current due to application of a potential step is useful in understanding the diffusion-controlled processes in relation to the shape of the electrodes. Eventhough theoretical information on planer and spherical electrodes is available, relatively less work has been done on cylindrical electrodes. Among electrodes, wires made of metals, alloys, semiconductors and even conducting polymers have cylindrical shapes and they have very promising practical applications. We obtained an expression for the diffusion-controlled current density by solving the diffusion equation for a cylindrical system:

$$\frac{\partial C(r,t)}{\partial t} = D \left[\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{1}{r} \frac{\partial C(r,t)}{\partial r} \right]$$

where C and D are the concentration and diffusion coefficient respectively for electroactive species, r is the radial distance from the axis of the electrode and t is the time. It was assumed: that the volume of the electrolyte solution was very large compared to that of the electrode, so that any passage of current through the solution did not alter the bulk concentration of the electroactive species. It was also assumed that the transport of current through the solution was predominantly by the ions of the inert background electrode present in excess, compared to the concentration of electroactive species. The solution yields an expression for the current density I(t,a) as

$$I(t,a) = A \frac{nFD}{a} e^{-\frac{BDt}{a^2}}$$

where a is the electrode radius and A and B are two parameters independent of t and a and the other symbols have their usual meanings. Strong dependence of current density on electrode radius and its exponential variation with time are two important conclusions that can be drawn from this study.