

Advances in the Theory of Electrochemical Methods
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Abstract

This thesis is concerned with dynamic electrochemistry experiments in which faradaic processes are driven by the application of potential to an electrode immersed in an electrolyte solution. In particular, experimental methods are considered which could be used to study electrochemical systems in a more informative way if the processes occurring at the electrode were better understood. The work develops the theoretical models which describe these experiments, and details the approximations made in each model and the conditions under which they are appropriate. Numerical simulations are reported which demonstrate how the models can be used to infer quantitative details of chemical behaviour from experimentally recorded data.

The first system studied in detail is linear sweep voltammetry at a microband electrode array. The diffusional behaviour of an electroactive species is shown to depend on the configuration of the microband array and on the potential scan rate used. Details are given on how experimental conditions can be optimised for the study of electrochemical systems.

The next area of work develops the theory of nanoparticle-modified electrodes. Experiments are considered in which an electron transfer reaction is catalysed only at the site of the nanoparticles, whilst the supporting planar electrode remains electrochemically inert. Numerical simulations show how the current measured at these modified electrodes depends on the size and shape of the particles, on the distribution of the particles on the electrode surface, and on the timescale of the experiment.

The final theme of work is on electrochemical experiments in poorly conducting solutions. A theoretical model is developed which takes into account the effects of an electric field on the mass transport of electroactive species and on the charge transfer kinetics at the electrode. The model is then used to rationalise the unusual current behaviour that is observed in the anodic stripping of thallium from an amalgam.