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Voltammetry at electrodes decorated with an insulating porous film: Understanding the effects of adsorption

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Abstract

Recent literature has evinced a keen interest in porous electrodes. Numerous applications have been discussed and some aspects of the voltammetry investigated, a theoretical description of adsorption- and desorption processes though remains largely absent. The present study fills this important gap and provides a detailed analysis of the impact of adsorption on voltammetric electrode responses in porous materials. It is shown that in some cases, adsorption- and desorption processes may aid the detection of analytes while in other cases a planar unmodified electrode is superior in performance. Finally practical conclusions are drawn for the design of future experimental systems.

Keywords

Porous electrodes, adsorption processes, nanoelectrochemistry.

1 Introduction

Recent years have seen a broad interest in porous electrodes¹⁻⁸ in electrochemistry that is due to advantages offered in various applications: The vast increase in surface area drastically advances the electrode capacitance and hence the performance of supercapacitors, porous layers are often easier to functionalise in biosensing- and biological studies than their planar equivalents, and thin-layer diffusion effects may be exploited in electroanalytical measurements to just name a few.

The greater surface area of porous electrodes may however lead to significant adsorption of reactants in electrochemical sensing, which certainly affects the outcome of the measurement. This effect may be exploited straightforwardly at fully *electrochemically-active* electrodes in anodic stripping experiments but may also be highly beneficial to electrodes decorated with a porous *electrochemically-inactive* film, which we address in the following. Many chemical sensors are deliberately designed to incorporate an electrochemically-inactive porous layer on the surface of an electrode in which analyte pre-concentration is used to amplify the signals recorded amperometrically. This work investigates the extent to which such adsorption effects can be helpful in such sensing applications and, where yes, how they can be exploited. To this end, we develop a simple representative model and conduct a detailed parameter study of experimentally-relevant parameter ranges. Our results reveal direct implications for experimental studies and provide useful guidance to experimentalists.

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