Modelling the In Situ Infrared Reflection-Absorption Spectra of the Diffuse Layer

by

P.W. Faguy, S. McCullough and W.R. Fawcett

Prepared for Presentation

at

The Electrochemical Society Meeting
Los Angeles, CA, May 1989

May 1, 1989

Reproduction in whole or in part is permitted for any purpose of the United States Government

"This document has been approved for public release and sale; its distribution is unlimited"
Modelling the In Situ Infrared Reflection-Absorption Spectra of the Diffuse Layer

P.W. Faguy, S. McCullough and W.R. Fawcett

In the double layer region for aprotic, organic electrolytes on gold electrodes.

Keywords: Infrared spectroscopy; Electrode/electrolyte interface; Electrochemistry (etc.)

Prepared for Presentation at: The Electrochemical Society Meeting, Los Angeles, CA, May 1989

Using a stratified medium model for the electrochemical interface and Gouy-Chapman-Stern theory of the double layer, a method to model infrared reflection-absorption spectra of the diffuse layer is developed. This method is applied to spectra obtained in the double layer region for aprotic, organic electrolytes on gold electrodes.
In Situ Techniques for Electrochemistry

Using a stratified medium model for the electrochemical interface and Gouy-Chapman-Stern theory of the double layer a method to model infrared reflection-absorption spectra of the diffuse layer is developed. This method is applied to spectra obtained in the double layer region for aprotic, organic electrolytes on gold electrodes.
Modelling the In Situ Infrared Reflection-Absorption Spectra of the Diffuse Double Layer.

P.W. Faguy, S. McCullough, W.R. Fawcett
Department of Chemistry, University of California, Davis, CA 95616-0395

The sensitivity of in situ IRRAS techniques such as EMIRS and SNIFTIRS to molecular structure at the electrode/electrolyte interface arises from the coupling of two physical phenomena: the local increase in the electric field strength for parallel polarized light reflect at the surface of the electrode and the potential drop across the double layer. In the EMIRS or SNIFTIRS experiment there is enhanced sensitivity to species present within a few wavelengths of the IR radiation from the electrode surface and only to those species which change due to the applied electrochemical potential. As the diffuse layer is typically 10-100 Å for these experiments and as the large electromagnetic field at the metal surface decays over much longer distances, the resultant in situ spectra will be a function of the product of these two effects integrated over the complete diffuse layer. Thus with such techniques the diffuse layer is probed to almost the same extent as the electrode surface.

This paper presents a method for calculating the in situ infrared reflection-absorption spectra for species present in the diffuse layer based on a stratified media model of the electrode/electrolyte interface, Gouy-Chapman-Stern theory and the attenuated total reflection IR spectra of the electrolyte solutions.

In order to calculate reflection-absorption spectra it is necessary to construct an optical model of the interface. Figure 1 is a schematic drawing showing an N layer system consisting of a non-absorbing semi-infinite initial phase, N-2 planar finite strata and an absorbing semi-infinite final phase. This approach assumes that the media are isotropic, homogeneous, linear and that the dielectric constant is independent of position within an individual layer.

In this treatment, the matrix formalism developed by Hansen for the N layer system will be applied to a stratified medium where the 3rd through N-2 components represent the diffuse layer as shown in Figure 1. Each of these N-4 strata will have a dielectric constant and characteristic thickness associated with it, obtained from bulk solution and solvent values and GSC theory. The real and the imaginary components of the dielectric constants are calculated using ATR measurements of the bulk components and the appropriate Fresnel equations.

The modelled and measured spectra for gold electrodes, using alkali perchlorate salts in dimethylformamide and acetonitrile solutions will be presented.

References


Figure 1. Multiple layer optical model of the electrode/electrolyte interface.