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ELECTROCHEMISTRY AT THE MOLECULAR LEVEL(U) SOUTHAMPTON
UNIV (ENGLAND) DEPT OF CHEMISTRY P J HENDRA ET AL.
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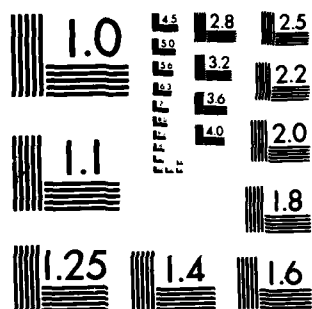
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Department of Chemistry
University of Southampton

Ninth Periodic Report

to

United States Navy
Office of Naval Research

on

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Report on Period 1st December 1982 - 31st October 1983

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P. J. Hendra
M. Fleischmann
A. Bewick
J. Robinson

December 1983

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Final Report to the United States Navy Office of Naval Research on

Contract No. N00014-77-G-006

This report covers work completed at Southampton only during the period January to October 1983. Although it would have been valuable to collect the output under our ONR contract for the whole of its duration, it will be clear from this document that the product of this research programme has been so extensive that it is essential to restrict the scope of this report. It should, therefore, be read with our earlier periodic reports.

The format adopted is one we have used before as follows:

The work covered is included under three distinct, and to some extent unrelated research effort areas, viz:

- A) An exploration of the use of in situ techniques in completing molecular analyses of working electrode-electrolyte systems.
This field embraces:
 - A1. → X-ray measurements (Prof. M. Fleischmann and Dr. J. Robinson)
 - A2. → Raman studies (Prof. M. Fleischmann and Dr. P. Hendra)
 - and ~~and~~ Infrared methods (Dr. A. Bewick).
- B) A long term investigation of the properties of microelectrode systems (Prof. M. Fleischmann), and
- C) A study of the role of molecular entanglement in dictating the properties of polymer solids (Dr. P. Hendra).

cont'd

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In each area considerable progress has been made and we therefore offer as a report a set of abstracts of papers either already published or to appear in the very near future. Many readers will find some of these papers of potential value. Where this is the case would they please write to one of the principal investigators expressing their interest in particular papers and photocopies or reprints as appropriate will be mailed to them promptly.

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RAMAN SPECTROSCOPIC AND X-RAY DIFFRACTION STUDIES OF ELECTRODE-SOLUTION INTERFACES

①
M. FLEISCHMANN, P. GRAVES, I. HILL, A. OLIVER and J. ROBINSON
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(Received 29th July 1982)

A-1 ABSTRACT

Surface-enhanced Raman scattering (SERS) of adsorbed water species has been obtained at roughened silver electrodes; these species are always coadsorbed with anions. The spectra obtained with adsorbed cyanide and iodide ions are used to illustrate this behaviour. For the latter system it is shown that the water molecules seen by SERS are in the solvation shells of the alkali metal counterions. The spectra due to coadsorbed water, chloride and pyridine are reinterpreted and it is shown that the potential dependence of the spectra correlate with changes in the differential capacitance; preliminary data for SERS on palladium electrodes are also given.

It is shown that whereas Raman spectra give information about the short-range order and environment of species adsorbed at electrode-solution interfaces, in situ X-ray diffraction measurements (INSEX) give information about the longer-range order. Measurements are illustrated by the UPD of lead on silver and it is shown that here again the change in structure of the solvent in the interface may be observed.

J. Electroanal. Chem. 119 (1983) JECu6901 (NC)
Elsevier Sequoia S.A. - Lausanne - Printed in The Netherlands

② A RAMAN SPECTROSCOPIC STUDY OF THIIOUREA ADSORBED ON SILVER AND COPPER ELECTRODES

A-2
M. FLEISCHMANN, I. R. HILL and G. SUNDHOLM *
Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)
(Received 26th January 1983)

ABSTRACT

The adsorption of thiourea to silver and copper electrodes has been studied using surface enhanced Raman scattering. The results show that thiourea is adsorbed via sulphur, at low pH values the adsorbed thiourea remains unprotonated but the spectral intensity is appreciably higher and additional bands arising from polysulphate anions are observed.

③

A RAMAN SPECTROSCOPIC INVESTIGATION OF THE ELECTROPOLYMERIZATION OF PHENOL ON SILVER ELECTRODES

A-2

M. FLEISCHMANN¹, I. R. HILL¹, G. MENGOLI² and M. M. MUSIANI²

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(Received 22 February 1983)

Abstract—The characterization of the electropolymerization of phenols on silver (both in the presence and absence of amines) shows that the process is closely similar to that observed on iron. Raman spectroscopy shows that amines displace phenoxide ions which are adsorbed flat on the substrate. This displacement of phenoxide by amine explains the formation of thick protective films.

Volume 97, number 4,5

CHEMICAL PHYSICS LETTERS

27 May 1983

④

SURFACE-ENHANCED RAMAN SCATTERING FROM SILVER ELECTRODES: POTENTIAL AND CATION DEPENDENCES OF THE VERY-LOW-FREQUENCY MODE

A-2

M. FLEISCHMANN, I.R. HILL and J. ROBINSON

Department of Chemistry, The University, Southampton SO9 5NH, UK

Received 13 February 1983; in final form 25 March 1983

The very-low-frequency mode observed in SERS experiments near 8 cm^{-1} is shown to shift both with the nature of the cation and with potential. The assignment of this mode to acoustic vibrations in the metal is discussed with respect to the chemical specificity of the shifts.

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A-2

THE SYNERGETIC EFFECT OF BENZYLAMINE ON THE CORROSION INHIBITION OF COPPER BY BENZOTRIAZOLE

M. FLEISCHMANN, I. R. HILL

Department of Chemistry, The University, Southampton SO9 5NH, U.K.

G. MENGOLI and M. M. MUSIANI

Istituto di Polarografia ed Elettrochimica Preparativa del CNR, Corso Stati Uniti, 35100 Padova, Italy

(Received 16 December 1982)

Abstract—Passivating films, formed by the anodization of copper in alkaline benzotriazole (BTA) solutions, have been investigated. Addition of benzylamine to the anodizing solution was found to lead to much faster passivation and greater corrosion resistance in aqueous chloride. These passivating films appear to consist mainly of a $[\text{Cu(II)BTA}_2]_n$ polymeric network.

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A-2

A RAMAN SPECTROSCOPIC STUDY OF QUINOLINE AND ISOQUINOLINE ADSORBED ON COPPER AND SILVER ELECTRODES

M. FLEISCHMANN I.R. HILL and G. SUNDHOLM *

Department of Chemistry, University of Southampton, Southampton SO9 5NH (Great Britain)

(Received 19th January 1983; in revised form 6th April 1983)

ABSTRACT

The adsorption of quinoline and isoquinoline, examples of one class of organic additives with possible applications in copper refining, on silver and copper electrodes in 0.2 M K_2SO_4 and 2 M H_2SO_4 has been studied using in situ Raman spectroscopy and electrochemical measurements.

The results show that the adsorption of the quinolines in K_2SO_4 solution depends on the potential with respect to the p.z.c. of the metal. The effects noted are more pronounced in the case of isoquinoline.

In 2 M H_2SO_4 the results show that the quinoline ions form ion pairs at the electrode surface. The changes in the SERS spectra on addition of Cl^- to the solution clearly indicate a displacement of SO_4^{2-} by Cl^- to leave a quinolinium-chloride surface complex. It is concluded that additives of the type studied are likely to be adsorbed as ion pairs in acidic plating baths.

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**SURFACE ENHANCED RAMAN SCATTERING FROM SILVER
ELECTRODES: FORMATION AND PHOTOLYSIS OF CHEMISORBED
PYRIDINE SPECIES**

M. FLEISCHMANN and I.R. HILL

Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)

(Received 26th July 1982; in revised form 12th October 1982)

ABSTRACT

An investigation of the nature of the adsorbed species at a silver electrode surface in aqueous alkali halide solutions containing pyridine has shown that both strongly bound Lewis acid coordinated (chemisorbed) pyridine and weakly bound (physisorbed) pyridine are adsorbed at the interface; the conditions for the formation and destruction of the chemisorbed species have been defined. In the presence of specifically adsorbed halide the physisorbed pyridine has been found to be in equilibrium with an adsorbed form of water.

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**THE OBSERVATION OF SOLVATED METAL IONS IN THE DOUBLE
LAYER REGION AT SILVER ELECTRODES USING SURFACE ENHANCED
RAMAN SCATTERING**

M. FLEISCHMANN and I.R. HILL

Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)

(Received 2nd August 1982)

ABSTRACT

The SERS spectra of water observed when halide ions are adsorbed to roughened silver electrodes is shown to be dependent upon the nature of the supporting electrolyte cation. This cation dependence as well as the potential dependence for any given cation are interpreted as being due to the progressive desolvation of cations with increasing radius and with increasingly negative potentials, the cations being adsorbed as solvent separated ion pairs.

A-2

A-2

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A-2

The effect of Triton* on the electropolymerisation of phenol; an investigation of the adhesion of coatings using surface enhanced Raman scattering(SERS)

G. Mengoli, M.M. Musiani and B. Pelli,
Istituto di Polarografia ed Electrochimica Preparativa
del CNR, Corso Stati Uniti, 35100 Padova, Italy.

M. Fleischmann and I.R. Hill, Department of Chemistry,
The University, Southampton SO9 5NH, U.K.

(Electrochim. Acta. in press)

Abstract

The physical properties and adhesion of protective amine-modified polyoxyphenylene coatings, electroformed in-situ onto metal substrates, have been found to be greatly improved by the addition of small quantities of the surfactant Triton to the electrolyte. The rôle of Triton is investigated using infrared and Raman spectroscopic techniques. Triton is found to be present both at the metal substrate surface and dispersed throughout the polymer, becoming chemically bonded to the polymer after curing in air.

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A-2

J Electroanalytical Chem (In Press)

An Investigation of Cu^I Acetylide Films on Cu Electrodes:

I. Electrochemical and Raman Spectroscopic Analysis of the Film Formation

by

L.M. Abrantes*, M. Fleischmann, I.R. Hill and L.M. Peter,
Department of Chemistry, The University, Southampton SO9 5NH,
Great Britain

and

M. Mengoli and G. Zotti,
Istituto di Polarografia ed Electrochimica Preparativa del CNR,
Corso Stati Uniti, 35100 Padova, Italy.

Abstract

The synthesis of copper (I) phenylacetylide films directly onto a copper substrate from solution is described. Films of controlled thickness may be grown electrochemically. Raman spectra of adsorbed phenylacetylene (surface enhanced) and of the film (resonance enhanced) are also reported.

A-2 Submitted to Chem Phys Letters.

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Simultaneous Raman Spectroscopic and Differential
Double Layer Capacitance Measurements of Pyridine
Adsorbed on Roughened Silver Electrodes

by M. Fleischmann, P.R. Graves, I.R. Hill and J. Robinson
Department of Chemistry, The University, Southampton SO9 5N

Abstract

It is shown that differential double layer capacitance data can be obtained simultaneously with the recording of the Raman spectra of adsorbates at a roughened silver microelectrode. The use of such data to provide information about the structure of the silver electrode/aqueous KCl(0.1M)/ pyridine(0.1M) interface is demonstrated.

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B

Submitted to J. Phys. Chem.

The Use of Platinum Microelectrodes for Electrochemical
Investigations in Low Temperature Solution-Solid Eutectic
Mixtures and Glasses of Non-aqueous Solvents.

A.M. Bond*, M. Fleischmann and J. Robinson.

Department of Chemistry, The University,
Southampton SO9 5NH, England.

* On leave from Division of Chemical and Physical Sciences,
Deakin University, Waurn Ponds,
Victoria 3217, Australia.

ABSTRACT

Platinum microelectrodes of radius less than 1 μm enable steady state voltammetric measurements to be made at temperatures down to the freezing point of the solvent (eutectic mixtures) even in the absence of supporting electrolyte. At lower temperatures, where the "glass" phase is formed, voltammetric measurements can still be made in the absence of electrolyte. The possibility of making such measurements using a two electrode configuration results from the very low Ohmic iR drop associated with the use of platinum microelectrodes of such small radius. Data are presented for oxidation of ferrocene in acetonitrile at temperatures from 25°C to the temperature of the solution-solid eutectic mixtures and in an acetonitrile "glass" at -78°C. Measurements on the same oxidation process down to the temperature of the acetone and dichloromethane eutectics are also presented. The combination of electrode radius $\leq 1 \mu\text{m}$ and low temperature glasses should facilitate studies in electron transfer unhindered by chemical reactions following the charge transfer

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Submitted to J. Electroanal. Chem.

Voltammetric measurements using microelectrodes in highly dilute

B

electrolyte solutions: theoretical considerations

A.M. Bond*, M. Fleischmann and J. Robinson.

Department of Chemistry, The University, Southampton SO9 5NH, England

*On leave from Division of Chemical and Physical Sciences,

Deakin University, Waurin Ponds,

Victoria 3217, Australia.

Abstract

It is shown that the steady state voltammetric behaviour of uncharged substrates for the unusual conditions of highly dilute support electrolyte can be simply determined by using spherical microelectrodes. Ohmic losses are small and calculable so that simple two-electrode cells can be used. The reverse process of the discharge of an ion of the dilute electrolyte is not symmetric with respect to the voltammetry of uncharged substrates (due to migration effects) but again leads to simple voltammograms. The use of electrodes of small dimensions therefore opens the way for the study of a wide range of new systems.

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A-2

**RAMAN SPECTROSCOPY OF PYRIDINE ADSORBED
ON ROUGHENED β PALLADIUM HYDRIDE ELECTRODES**

M. FLEISCHMANN, P.R. GRAVES, I.R. HILL and J. ROBINSON

Department of Chemistry, The University, Southampton SO9 5NH, UK

Received 8 December 1982

SERS spectra of pyridine and CO adsorbed on roughened β PdH electrodes have been obtained. The potential dependence is shown to be similar to that at a silver electrode. The method for obtaining the roughened electrodes is shown to require chemical control of the redeposition of palladium metal.

Submitted to J. Electroanal. Chem.

The Application of Microelectrodes to the Study of Homogeneous
Processes Coupled to Electrode Reactions. Part 1. EC' and CE
Reactions

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Southampton SO9 5NH, England.

* J. Robinson, Department of Physics,

Warwick University, Coventry CV4 7AL

15

B

Abstract

A new technique for the determination of the kinetics of fast first order, or pseudo first order, homogeneous chemical reactions coupled to heterogeneous electron transfer reactions at electrodes is presented. This technique involves the recording of steady state current voltage curves at finite disk microelectrodes and an analysis of the limiting current in terms of a spherical diffusion field. To demonstrate this approach, platinum microelectrodes of radii in the range 0.3 μ m to 25 μ m have been used in a simple two electrode configuration to study a ce reaction, hydrogen evolution from aqueous acetic acid solutions, and an ec' reaction, the oxidation of ferrocyanide in the presence of amidopyrine. In both cases the derived rate constants agreed closely with those obtained by other more conventional means.

15A

B

Submitted to J. Am. Chem. Soc.

Electrochemistry without a supporting electrolyte in non-aqueous solvents using platinum microelectrodes.

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². Department of Chemistry, The University,
Southampton SO9 5NH, England.

¹. Division of Chemical and Physical Sciences,
Deakin University, Waurn Ponds, Victoria 3217, Australia.

ABSTRACT

Restrictions placed on applications of electrochemistry by the perceived need to add an electrolyte may be overcome in the case of neutral molecules by the use of microelectrodes. In this work the oxidation of ferrocene to the ferrocenium cation at platinum microelectrodes of radius 25 to 0.3 μm is reported under steady state conditions in acetonitrile without a supporting electrolyte. A two electrode rather than potential-stated three electrode measuring system must be used to minimize problems associated with noise. With an electrode radius of 25 μm and 10^{-3}M ferrocene concentrations, the diffusion controlled limiting current is essentially the same (slight change in diffusion coefficient) as in the presence of electrolyte. However, the shape is distorted by ohmic IR drop. With radii less than 1 μm and/or at lower concentrations of ferrocene, IR drop effects are greatly minimized and conventional electrochemical data are obtained in the absence of any deliberately added electrolyte. In principle this oxidation process should be studied under conditions of the theoretically interesting one-ion problem, but secondary chemical reactions with traces of water, other impurities, or the solvent itself, are believed to produce conditions equivalent to the presence of an extremely dilute supporting electrolyte. The proposed methodology based on the use of microelectrodes should lead to applications of electrochemistry in fields such as monitoring of chemical reactions in high resistance organic solvents, measurement of diffusion coefficients and other data at zero ionic strength, and an ability in analytical applications to use electrochemical detection after normal phase and chromatographic separations.

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**A STUDY BY ELECTROCHEMICALLY MODULATED INFRARED
REFLECTANCE SPECTROSCOPY OF THE ELECTROSORPTION OF
FORMIC ACID AT A PLATINUM ELECTRODE**

A-3

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(Received 31st August 1982; in revised form 24th November 1982)

ABSTRACT

EMIRS is a new spectroscopic technique which has been shown to be very useful for the "in situ" identification of adsorbed species at the electrode-electrolyte interface.

This work is a first attempt to compare the qualitative results given by EMIRS to the quantitative determination of the adsorbed layer, as obtained by conventional electrochemistry.

Systematic investigations of the influence of the electrochemical parameters on the spectral characteristics have shown that the so-called CO species, which are detected by EMIRS during the chemisorption of formic acid on a Pt electrode, are the dominant species over a large potential range during which the coverage reaches a maximum and constant value.

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**A COMPARATIVE STUDY OF FORMIC ACID ADSORPTION ON A
PLATINUM ELECTRODE BY BOTH ELECTROCHEMICAL AND EMIRS
TECHNIQUES**

A-3

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(Received 16th August 1982; in revised form 3rd January 1983)

ABSTRACT

In order to make the IR reflectance spectroscopy quantitative, the variation of the electrochemically modulated infrared reflectance spectrum characteristics with the electrode potential is explored, comparatively to the variation of the degree of coverage of a Pt electrode by adsorbed intermediates, as determined by conventional electrochemical method.

An Infrared Study of the Electrosorption of

Isotopic Mixtures of CO on Pt

A-3

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J. W. Russell
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Abstract

Infrared spectra of ^{12}CO - ^{13}CO mixtures adsorbed on polycrystalline platinum electrodes from 1M H_2SO_4 solutions have been obtained by EMIRS, electrochemically modulated infrared spectroscopy. Spectra for variable ^{12}CO - ^{13}CO ratios at constant saturation coverage and for fixed ^{12}CO - ^{13}CO ratios at high coverage show a single bipolar EMIRS band indicative of a highly coupled system. Lower coverage mixed isotopic samples with greater than 30% ^{13}CO produced spectra with two bipolar bands. A simple three parameter model for calculation of infrared band contours was used to determine whether dipole-dipole coupling or through-metal vibrational coupling is more important. The observed spectra were best explained by a model with coverage independent force constants; thus contributions from through-metal vibrational coupling appear less important than dipole-dipole coupling. The essential differences between the coverage dependence and the potential dependence of the spectra supports this conclusion.

J. Electroanal. Chem., in press.

19 A COMPARATIVE STUDY OF FORMIC ACID ADSORPTION ON
A PLATINUM ELECTRODE BY BOTH ELECTROCHEMICAL AND
E.M.I.R.S. TECHNIQUES.

A-3

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**Chemistry Department, The University, SOUTHAMPTON SO9 5NH (Great Britain)

ABSTRACT

In order to make the IR Reflectance Spectroscopy quantitative, the variation of the E.M.I.R. Spectrum characteristics with the electrode potential is explored, comparatively to the variation of the degree of coverage of a Pt electrode by adsorbed intermediates, as determined by conventional electrochemical method.

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Infrared Spectrum of CO on a Platinum Electrode in Acidic Solution

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and Alan Bewick

Department of Chemistry, Southampton University, Southampton, England (Received May 17, 1982; In Final Form June 9, 1982)

A-3

Polarization-modulated infrared reflection absorption spectroscopy has been used to measure the spectrum of adsorbed CO on a platinum electrode in both 1 M H₂SO₄ and 1 M HClO₄ saturated with CO gas. This is the first direct measurement of the infrared band of adsorbed CO on an active electrode and definitively establishes the dependence of the band wavenumber on electrode potential as the primary source of the unusual bisignate band previously observed with electrode-modulated infrared spectroscopy.

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On the nature of reduced CO_2 an IR

Spectroscopic Investigation

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A-3

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AUT

IN-SITU INFRARED SPECTROSCOPY OF THE ELECTRODE/ELECTROLYTE SOLUTION INTERPHASE

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(Received 27th October 1982)

A-3

INTRODUCTION

The spectacular progress made in recent years in studies of the structure of and adsorption at the metal/vacuum interface using structure-sensitive, spectroscopic methods is now beginning to be matched for the electrode/electrolyte solution interphase by the development of in-situ spectroscopy methods to complement the ex-situ, high vacuum techniques. The achievements of Surface Enhanced Raman Spectroscopy, SERS [1], are well known and now external specular reflectance infrared spectroscopy is firmly established. Thus, interaction between electrochemistry and other areas of surface science is possible at a level which provides the greatest progress to the understanding of the structure and orientation of, and bonding in, adsorbed species as well as their interactions with the surface and with one another. An advantage unique to electrochemistry, the ability to use the electrode potential to "fine-tune" the electronic properties of the atoms in the metal surface, can be of considerable assistance in unravelling problems connected with surface/adsorbate and adsorbate/adsorbate interactions and helps to compensate for the special problems presented by electrochemical systems.

Infrared Spectrum of CO Adsorbed on a Platinum Electrode

23

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Department of Chemistry, Southampton University, Southampton, England (Received August 16, 1982;
In Final Form, September 20, 1982)

A-3

Polarization-modulated infrared reflection-absorption spectroscopy has been used to measure directly the infrared spectrum of CO adsorbed on the surface of a platinum electrode in the presence of an electrolyte, either 1 M H₂SO₄ or 1 M HClO₄. The band due to the CO-stretching vibration has been found to shift with applied potential moving to higher wavenumber as the electrode potential is made more positive. The band shape and the band area remain essentially unchanged when the potential is changed over the range 15–650 mV (NHE). The results are interpreted as evidence that, in the case of CO on Pt, there is a significant contribution to coverage-dependent shifts from electrochemical interactions between substrate and adsorbate.

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INFRARED STUDY OF ADSORBED SPECIES ON ELECTRODES: ADSORPTION OF CARBON MONOXIDE ON Pt, Rh AND Au

A-3

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(Received 28th May 1982)

ABSTRACT

Infrared spectra of adsorbed species at the solid–aqueous electrolyte interface are reported following the adsorption of CO on platinum, rhodium and gold electrodes using *in situ* electrochemically modulated IR spectroscopy. Similarities exist with the corresponding solid–gas interfaces, i.e.

(1) a linearly bonded species is formed absorbing near 2060 cm⁻¹ on Pt, 2030 cm⁻¹ on Rh and 2120 cm⁻¹ on Au.

(2) bridged bonded or multibonded CO species are also present and detected at 1860 cm⁻¹ (Pt), 1800 cm⁻¹ (Rh) and 1930 cm⁻¹ (Au).

(3) CO₂ produced by CO oxidation is detected near 2360 cm⁻¹ at potentials as low as 0.35 V (vs SHE).

Electrosorption of CO on Pd in acid solution:
a study using in situ IR spectroscopy

A. Bewick and T. Solomon

Department of Chemistry
The University of Southampton
Southampton, SO9 5NH
England.

Abstract

In situ IR spectra of CO adsorbed onto a polycrystalline

Pd electrode were obtained as a function of surface coverage

using 1M HClO₄ and 0.5M H₂SO₄ electrolytes. The surface

coverages were measured by direct electrochemical oxidation

of the adsorbed CO. At low coverages a single, broad absorption

band was observed at a vibrational frequency attributed to CO

in a three-coordinate surface site. The spectra showed a sudden

change in the state of the adsorbed layer over a narrow range of

coverage to a well defined structure with the adsorbed CO occupying

two-coordinate sites. This layer coexisted with an increasing

amount of linearly bonded CO as the coverage was increased further.

EMIRS STUDY OF ADSORBATE BONDING IN THE ELECTRODE SOLUTION INTERFACIAL REGION

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¹Department of Chemistry, Southampton University, Southampton SO9 5NH, ENGLAND

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ABSTRACT

EMIRS spectra for ¹²C₁₃-CO mixtures on platinum, HSO₄⁻ and acrylonitrile on gold and water on silver are discussed. These examples illustrate the adsorbate identification, bonding, and orientation information which EMIRS data offer to complement electrochemical Raman data and infrared reflection absorption and EELS results. The advantages of experimental fine control of the electronegativity of the metal are shown with application to studies of coupling mechanisms between adsorbed species.

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INVESTIGATIONS OF ADSORBED SPECIES IN ELECTROCATALYTIC
OXIDATIONS USING IN-SITU IR SPECTROSCOPY

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Abstract

In situ infrared reflectance spectroscopy has been used to identify the strongly adsorbed species formed from the electroreduction of small organic molecules such as CH₃OH, HCHO and HCOOH on catalytic electrodes of Pt, Rh and Pd in acidic electrolytes. A number of differently bonded (CO) species were identified according to the vibration frequency of the CO stretch. These poisoning species could also be formed by reduction of CO₂. The presence of sub-monolayer amounts of adsorbed Pb on the electrode surface was seen to inhibit their formation. Even under extreme conditions a species such as ! COH could not be observed and it is presumed not to play a role in these systems. These measurements are contrasted with those for adsorption of HCOOH on Au, which does not show the poisoning effect, and for which an adsorbed, intact formate species is seen.

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Chain Branching in high pressure polymerised polyethylene II

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Abstract

In a paper of 6 years ago, we reported on the detailed molecular structure of lamellar crystalline high pressure polymerised polyethylenes rich in branching. We showed that the crystalline cores contained few ethyl and butyl side-branches but did contain long side chains. In this paper, we exploit recent developments in technique to refine our observations, improve their rigour and to extend them to commercially significant high-pressure polymerised polyethylenes of modest side-branch content. We also study and report on some common ethylene olefin copolymers. We conclude that our earlier conclusions were correct, that the side-branches are bunched rather than being randomly situated along the backbones and that most of the branches, and particularly the branched branches, become concentrated in the inter-core regions on melt crystallisation.

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The effect of cooling rate upon the morphology of quenched melts of isotactic polypropylenes

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Abstract

Experimental data are provided on the molecular structure of paracrystalline samples of quenched melts (glasses). We propose that rods of helical molecules are present in the 'glasses', their length being sensitive to the temperature of the melt from which the 'glass' is produced, the amount of time held in the melt and the rate of quenching.

A comparison is made between samples crystallised from the melt and those crystallised via the glassy phase. By measuring the lamellar thickness, from Raman spectroscopy, and calculating the absorbance ratios A_{1220}^{998} and A_{1256}^{973} from infrared spectroscopy, longer helical sequences were shown to exist to a greater extent in the samples crystallised from the melt. Samples crystallised from the glassy phase contained shorter helical sequences.

In investigating the effect of the surrounding temperature on solid polypropylenes, we have shown that the density of the material can be related to the temperature of storage. We comment on the relevance of this observation to dimensional stability in mouldings.

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STRUCTURE AND PROPERTIES OF LINEAR POLYETHYLENE
CRYSTALLIZED BY RAPID COOLING OF MELTS III THE EFFECT
OF SHEAR

J. Vile, P. J. Hendra and H. A. Willis

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INTRODUCTION

Injection moulding is an important fabrication method for producing a variety of thermoplastic articles and sections. Although the process of moulding is reasonably well understood for the commercially important polymers, it is often found that for a given thermoplastic, apparently constant and reproducible moulding conditions do not necessarily produce mouldings having equivalent mechanical properties. This discrepancy may be due to subtle variations in the processing equipment and/or changes in the conditions of operating control. However, the most important factor to consider is the nature of the polymer itself. Properties of most polymers such as softening or melting ranges, heats of fusion, variation of viscosity with temperature, chemical stability, etc., are well characterized in each case but homogeneity may be relatively poorly controlled. The whole problem of the performance of polymeric mouldings is further complicated by a lack of precision in our understanding of the process occurring during melting, flow mould filling and subsequent solidification.

It is generally recognized that the final properties of injection mouldings are strongly dependent on the morphology and orientation of the material throughout the article^(1,2,3). Examination for various polymers reveals that injection mouldings possess a skin of highly oriented molecules. The molecules being oriented along the flow direction immediately prior to quenching. The central bulk region, or core, is frequently found to be completely unoriented. This morphology has been

observed in both glassy and semicrystalline polymers. The high degree of molecular orientation in the skin is thought to cause dimensional instability and premature fracture under impact and flexure^(1, 2).

In an attempt to produce a solid specimen under conditions which are as fully as possible controlled and understood, we have devised a laboratory experiment where a polymer is flowed under well controlled conditions through a cylindrical capillary die then solidified by cooling in a reproducible manner.

This paper describes the effect of polymer melt temperature, injection pressure, and shear at the wall of a capillary mould on the overall morphology and consequent properties of linear polyethylene.

We will later discuss the effect of the skin-core structure by flow processes and temperature gradients in the mould^(1, 2).

STRESS - INDUCED CHAIN RUPTURE IN LINEAR POLYETHYLENE:-
AN INFRA-RED STUDY.

Sub to Polymer

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Abstract:-

The scission of polyethylene molecules under stress in a polymer film was studied. It is proposed that the rupture of such molecular chains may be investigated utilising infra-red spectroscopy, since the radical initiated reaction of rupture in polymer chains may terminate via the production of stable unsaturated end groups, mainly in the form of carbonyl species.

Increases in the carbonyl absorption were detected and the trends, with respect to sample thickness, the atmosphere in which the samples were drawn, and the effect of the actual extent of drawing were evaluated.

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