Setup, sensitivity and application of thin electrolyte layer ATR-FTIR spectroscopy

Moon, S.-M.; Bock, C.; MacDougall, B.

National Research Council Canada   Conseil national de recherches Canada

Canada

THIS IS NOT AN INVOICE / CECI N'EST PAS UNE FACTURE

MARIA CLANCY
DGO
INST FOR CHEM PROCESS & ENVIR TECH
NATIONAL RESEARCH COUNCIL CANADA
M-12, ROOM 141, 1200 MONTREAL RD.
OTTAWA, ON K1A 0R6
CANADA

ORDER NUMBER:	**CI-07843420-5**
Account Number:	WR001844
Delivery Mode:	XLB
Delivery Address:	
Submitted:	2009/04/24 11:06:45
Received:	2009/04/24 11:06:45
Printed:	2009/04/27 13:03:24

Extended	Periodical	Virtual Lib. Blank	CANADA
		form	

Client Number:	MARIA E. CLANCY
Title:	**JOURNAL OF ELECTROANALYTICAL CHEMISTRY**
Vol./Issue:	568/12
Date:	2004
Pages:	225–233
Article Title:	SETUP, SENSITIVITY AND APPLICATION OF THIN ELECTROLYTE LAYER ATR–FTIR SPECTROSCOPY
Article Author:	MOON, S.–M.; BOCK, C.; MACDOUGALL, B.

INSTRUCTIONS: NEEDED BY: 11 MAY 2009

Estimated cost for this 9 page document: $0 document supply fee + $0 copyright = $0

Setup, sensitivity and application of thin electrolyte layer ATR-FTIR spectroscopy

S.-M. Moon, C. Bock *, B. MacDougall

National Research Council of Canada, ICPET, 1200 Montreal Road, Ottawa, ON, Canada K1A 0R6

Abstract

A new setup of an attenuated total reflection-Fourier transform infrared (ATR-FTIR) method involving a thin electrolyte layer was developed for the in situ investigation of electrode processes. The applicability of the approach was tested in 0.5 M H_2SO_4 by studying the oxidation of adsorbed CO using polycrystalline Pt and Pt particles supported on high surface area carbon black. The sensitivity of this new ATR–FTIR method appears to be better than found for previously reported results obtained using external reflection–absorption FTIR. High sensitivity was obtained by making a very good contact between the electrode surface and the ATR crystal, which was achieved by using a spring, a micrometer and X- and Y-position controllers. This new thin electrolyte layer ATR-FTIR technique was also successfully applied to the in situ study of surface species adsorbed on an IR non-reflecting porous electrode.
© 2004 Elsevier B.V. All rights reserved.

Keywords: In situ ATR-FTIR; CO adsorption/desorption; Porous electrode; IR non-reflecting electrode; Fuel cell catalysts

1. Introduction

In situ Fourier transform infrared (FTIR) techniques are widely applied in electrochemistry to obtain information of the electrode|electrolyte interface [1,2]. In situ FTIR techniques can be classified into two categories, namely transmission and reflection FTIR. Most in situ FTIR studies are performed using reflection FTIR, which can also be divided into two groups: external and internal reflection spectroscopy. External reflection FTIR involves specular IR reflection at a mirror-like electrode surface that is pushed against an IR transparent window leaving an electrolyte layer in the gap of 1–6 μm [1]. Internal reflection FTIR relies on an internal reflection element within which the IR beam is internally reflected if the incident angle of IR is higher than the critical angle [1,3]. Attenuated total reflection (ATR) crystals are typically used as internal reflection elements

and hence internal reflection methods are referred to as ATR-FTIR spectroscopy.

In situ ATR-FTIR spectroscopy has been developed using two different configurations: the Kretschmann and the Otto configurations [1,4,5]. The Kretschmann configuration employs a thin film electrode deposited on an ATR crystal where an evanescent wave (a form of standing wave generated at the reflected position) passes through the thin film electrode and interacts with the species on the electrode surface. This configuration is termed as thin film electrode ATR-FTIR. In the Otto configuration, a bulk electrode is pushed against the ATR crystal, i.e., involving a similar principle as used in external reflection spectroscopy. This method does not require that the IR beam is reflected on the electrode surface, as it is reflected internally at the ATR crystal|solution interface. This ATR configuration is designated as a thin electrolyte layer ATR-FTIR in the present paper.

External reflection FTIR spectroscopy is the most commonly used method to study electrochemical surface processes [6,7]. However, its requirement of using smooth and IR reflecting electrode surfaces greatly

---

* Corresponding author. Tel: +613-990-2252; fax: +613-941-2529.
E-mail address: christina.bock@nrc.ca (C. Bock).

limits the choice of electrode materials, i.e., it cannot be applied to IR non-reflecting and porous electrodes. The thin film electrode ATR technique has also been widely applied to obtain in situ electrochemical information. However, the limitations of this method are the need for thin working electrodes deposited onto the ATR crystal and therefore, the difficult preparation and exchange of the working electrode material. The thin electrolyte layer ATR-FTIR method discussed in this work has no such limitations of electrode properties, and is expected to be applicable to a wide range of electrode materials including IR non-reflecting and porous electrodes. The optical configuration of the thin electrolyte layer ATR-FTIR technique has been well known [4,5] and has been tested theoretically by Brooksby and Fawcett [5] and experimentally by Faguy and Marinkovic [4]. However, the experimental setup by Faguy and Marinkovic [4] cannot be assigned as a pure ATR technique because it included both external and internal reflections. At present, the feasibility of the thin electrolyte layer ATR-FTIR method for in situ investigation of the metallic or IR non-reflecting porous electrode surfaces has not been explored successfully.

In this work, a new setup of a thin electrolyte layer ATR-FTIR technique has been designed using commercially available ATR crystals. The sensitivity of the technique has been investigated in H_2SO_4 by studying the electrochemical oxidation reaction of adsorbed CO. Polycrystalline Pt and Pt particles supported on high surface area carbon black are used as working electrodes.

2. Experimental

2.1. Electrodes

Polycrystalline platinum wires (1.5 or 2 mm diameter, 99.95% purity, Alfa Aesar) were used as working electrodes. Pt particles supported on carbon black (Pt/C) that were deposited on a glassy carbon rod (3 mm diameter) were also used. The Pt wire and the glassy carbon rod were partly mounted in an epoxy block, as follows: the end surfaces of the Pt wire and glassy carbon rod were abraded flat using SiC emery papers and then polished on wet cloth with alumina powders up to 0.3 μm. The polished electrodes were then washed in distilled water and their side walls were wrapped with Teflon tape leaving only the top surface free. The Pt electrode was spot welded to a Cu wire. Sticky carbon paper was used to attach a Cu wire to the glassy carbon rod. The electrodes were then mounted into a glass tube using epoxy, which was connected to another inner glass tube using a steel spring, as shown in Fig. 1(a). The spring allows a soft and controlled contact to be made between the electrode and the ATR crystal, thus minimizing mechanical damage. The spring was surrounded with an outer glass tube to avoid contact with the electrolyte solution.

The Pt/C electrode was prepared by applying Pt/C powder (20 wt% Pt on C, Electrochem, Inc.) in the form of an ink to the glassy carbon surface. The ink was formed by sonicating 13 mg of the Pt/C powder with 1 ml of water and 0.3 ml of Nafion® solution (5 wt%
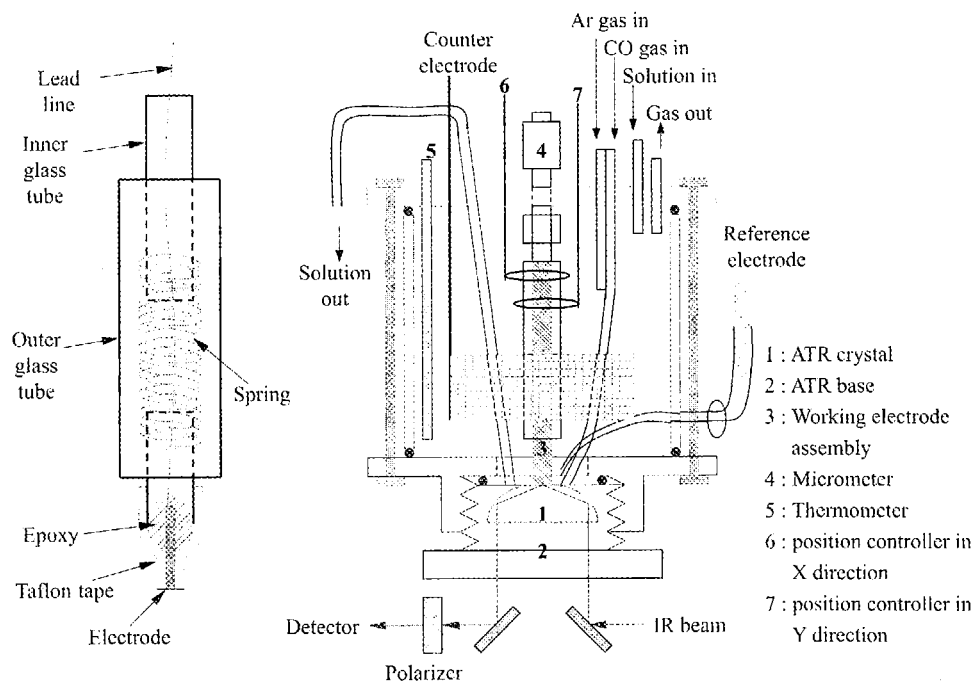

Fig. 1. Schematic representation of the experimental setup of the in situ thin electrolyte layer ATR-FTIR technique: (a) electrode assembly; (b) electrochemical cell, electrode and ATR crystal assembly.

Nafion® dissolved in lower alcohols, Sigma Aldrich) for 30 min. Ca. 15 µl of the ink was applied to the glassy carbon surface and dried overnight in air at room temperature.

A high surface area Pt gauze served as the counter electrode and a mercurous sulfate electrode (MSE, 1 M H_2SO_4) was used as the reference electrode. All potentials are referred to the MSE (0.68 V vs. SHE) in this work.

2.2. Electrochemical cell

Fig. 1(b) shows a schematic diagram of the spectro-electrochemical cell designed in this work for the thin electrolyte layer ATR-FTIR studies. The working electrode assembly was mounted onto a micrometer located at the center of the cell. The micrometer was used to push the electrode against the ATR crystal. The spring and the controllers in X- and Y-directions assisted in positioning the electrode on the ATR crystal, as discussed in Section 3.

The cell was mounted to an ATR base assembly (PIKE Technologies) and sealed with a rubber ring for the in situ experiments. The cell was equipped with two gas inlets to allow for argon or CO purging over and into the electrolyte solution. The exchange of electrolyte was controlled using the argon gas pressure and a mercury thermometer was positioned in the electrolyte to monitor the electrolyte temperature.

2.3. In situ electrochemical studies

0.5 M H_2SO_4, which was deaerated prior to the experiments by argon purging in a separate chamber, was used as the electrolyte in this work. The 0.5 M H_2SO_4 was flushed into the in situ FTIR cell and the Pt based working electrodes were cleaned by cycling the potential between −0.65 and 0.8 V at a rate of 100 mV s^{-1} until the typical characteristics for clean Pt were observed. Immediately afterwards, the solution was exchanged with new and deaerated 0.5 M H_2SO_4. Cyclic voltammograms (CVs) were obtained at 100 mV s^{-1} between −0.65 and 0.8 V when the electrode and crystal were well separated (i.e., under non-contact conditions) and when the electrode was in close contact with the crystal (i.e., under contact conditions). For the electrochemical CO adsorption/desorption experiments, the electrode potential was maintained at −0.65 V immediately after the surface cleaning process and gaseous CO was bubbled through the electrolyte for 20 min. The CO gas dissolved in the electrolyte was then removed by Ar bubbling for another 20 min. All experiments were conducted at room temperature.

High purity argon (Air Products) and CO (Matheson) gases were used. All chemicals used were ACS grade and high purity water (18 MΩ) was used.

2.4. Instrumentation, IR spectra collection and data treatment

A Bruker IFS 66/S FTIR spectrometer equipped with a global IR source and a narrow-band mercury–cadmium–telluride (MCT) detector was used. The latter was cooled using liquid nitrogen. Single reflection MIRacle Si and AMTIR ATR crystals with 2 mm diameter of exposed area (PIKE Technologies) were used in this work. The Si ATR crystal produced by PIKE is designed to have an incident angle of around 43°, which is slightly higher than the critical angle of ca. 40° of the Si|water interface. Single beam spectra were obtained by averaging 32 scans collected for about 20 s with a 4 cm^{-1} resolution and a scan speed of 20 kHz. For the adsorbed CO oxidation experiments, the electrode potential was increased in 50 mV steps starting at −0.65 V. The potential was applied for 180 s and single beam spectra were recorded after 150 s at each potential.

The absorbance spectra were calculated automatically using an OPUS software program (Bruker) that uses the following relationship:

$$\text{Absorbance} = -\log(R/R_0) \times x/1000. \tag{1}$$

In Eq. (1), R is the intensity of the sample spectrum, R_0 is the intensity of the reference spectrum, and x represents the wavenumber. The penetration depth of IR light into the sample depends on the wavenumber, and hence, $x/1000$ is used to compensate for the contribution of the different penetration depths with the wave number. In order to compare the sensitivity of the thin electrolyte layer ATR-FTIR technique with those of thin film electrolyte layer ATR-FTIR and external reflection FTIR techniques, the FTIR spectra are also presented in the form of the normalized change of reflectance, i.e., $-(R-R_0)/R_0$.

An EG&G 273A potentiostat/galvanostat was used for the electrochemical experiments. The instrument was computer controlled and was driven by Corrware software (Scribner Associates). A gold wire-grid polarizer (Perkin–Elmer) was positioned just before the detector.

3. Results and discussion

3.1. Contact between the working electrode and the ATR crystal

The interferograms obtained by measuring p- or s-polarized components of IR light in 0.5 M H_2SO_4 at open circuit showed that the magnitude of the main peaks decreases upon contact of the electrode with the Si ATR crystal, compared with that obtained under non-contact conditions. This reduction in IR intensity is clearly recognizable in the single beam spectra obtained by Fourier transformation of the interferograms, as

presented in Fig. 2. The IR intensity is seen to decrease over the entire wavenumber range upon contact. External reflection of IR light by the Pt electrode surface, which is a good mirror, is expected to result in an increased IR intensity upon contact, as the reflected IR beam would contribute to the IR intensity detected [4]. It is, therefore, concluded that the observed decrease of the IR intensity is an indication of the total internal reflection condition.

It is also seen in Fig. 2 that the amount of reduction of the IR intensity by the contact between the Pt electrode and the Si ATR crystal depends on the wavenumber, and the dependence is different with different polarization states of the IR light. The p-polarized IR beam, which has an electric field parallel to the incident plane, showed a significant decrease of IR intensity in the regions around 3400 and 1600 cm^{-1}, i.e., at wavenumbers

typical for H_2O stretching and bending, respectively, while only small decreases in the other wavenumber regions are observed. In contrast, the s-polarized IR beam, which has an electric field perpendicular to the incident plane, showed a very low change of IR intensity in the wavenumber regions of the H_2O stretching and bending, while a large decrease of IR intensity appeared in the other wavenumber regions. The different IR absorption behavior with the polarization states of IR light is very clearly seen in the absorbance spectra shown in Fig. 3. The IR absorption particularly by the water molecules is seen to be greatly enhanced with electrode pressing for p-polarized IR, presented as positive bands in Fig. 3(a). In contrast, the absorption of s-polarized IR by water molecules was observed to decrease with electrode pressing, indicated by negative bands in Fig. 3(b). The positive and negative water bands for p- and s-polarized
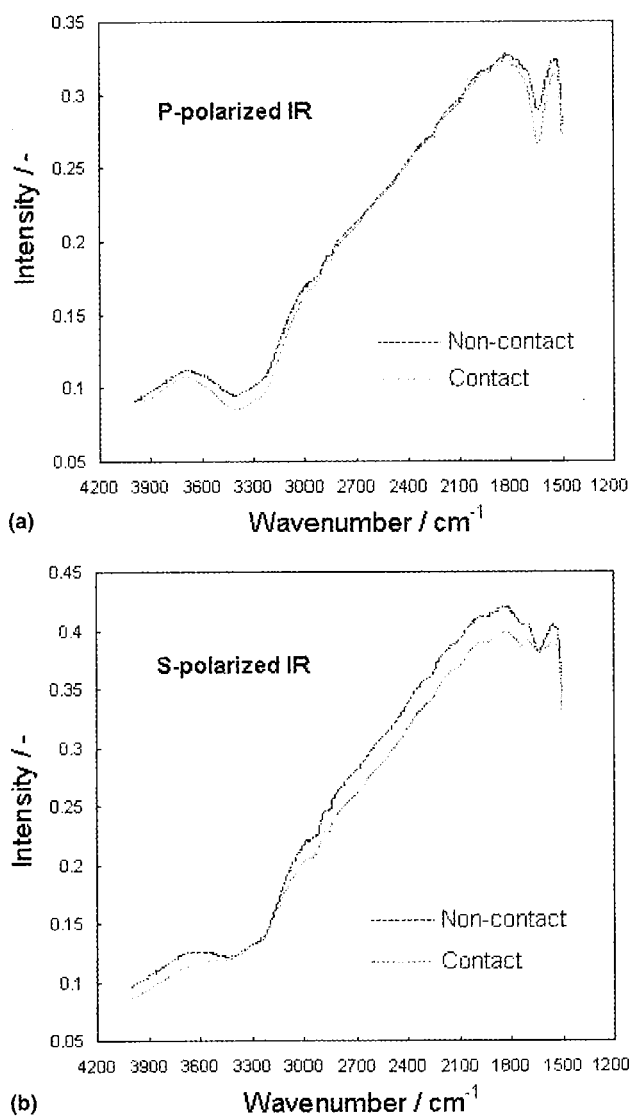
Fig. 2. Single beam spectra collected for: (a) p- and (b) s-polarizations of IR under non-contact and contact conditions of the Pt electrode with the Si ATR crystal in 0.5 M sulfuric acid solution.
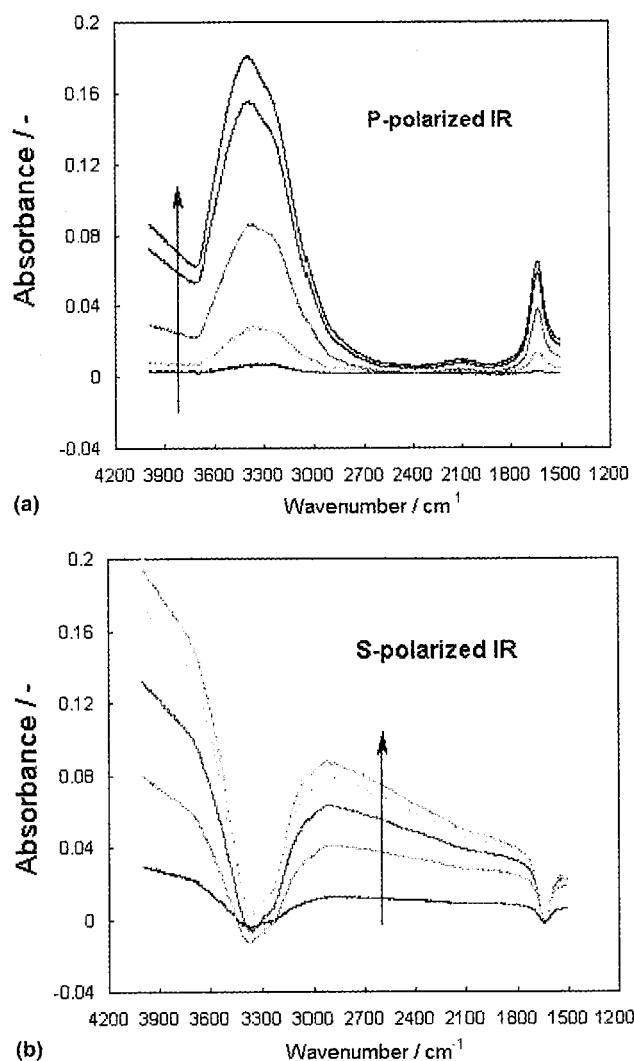
Fig. 3. Absorbance FTIR spectra recorded for different degrees of pressing of the Pt electrode against the Si ATR crystal in 0.5 M H_2SO_4 for: (a) p- and (b) s-polarizations of IR. The background spectra were collected under non-contact conditions.

IR represent more and less absorption of p- and s-polarized IR by water, respectively, indicating that the parallel component of OH stretching bonds of water to the incident plane increases while their perpendicular component decreases with the pressing of the electrode. These may be explained by an increased contribution of water dipoles in the double layer region with the electrode pressing where OH stretching bonds of water are aligned more in the normal direction to the electrode surface as compared to water in bulk solution.

It should be noted that IR absorption was seen to occur at all wavenumbers upon contact of the Pt electrode with the Si ATR crystal in the H_2SO_4 solution (Fig. 3). Its extent increases and then reaches a saturated value as the electrode is pressed against the ATR crystal. The enhanced IR absorption is also observed in an argon atmosphere, as indicated by the arrows in Fig. 4. The increased IR absorption upon contact can be readily understood by ohmic heating of the Pt electrode by transfer of IR energy to free electrons on the elec-

trode. A metallic wire-grid polarizer uses the same principle of IR absorption by ohmic heating but in only one direction by metallic wires. The IR absorption by the electrode should be considered also in the external reflection FTIR and the Kretschmann ATR configuration where IR touches the metallic electrode directly.

The IR absorption by the electrode in the Otto configuration can occur only when the electrode surface approaches very closely to the ATR crystal surface within the penetration depth of the evanescent wave. Thus, the IR absorption achieved by pressing of the electrode against the ATR crystal can be used as an indication of good contact between the Pt electrode and the ATR crystal, i.e., the higher the IR absorption, the better the contact between the electrode and the ATR crystal.

The establishment of good contact between the electrode and ATR crystal is a crucial experimental factor, as it determines the sensitivity of the in situ ATR-FTIR technique. In order to investigate the relationship between the degree of electrode contact with the ATR crystal and the sensitivity of the ATR-FTIR technique for detecting species on the electrode surface, the absorbance spectra of CO adsorbed (CO_{ads}) on the Pt electrode surface were collected with pressing of the electrode against the Si ATR crystal at −0.65 V in 0.5 M H_2SO_4, as described in Section 2. Fig. 5 shows the absorbance spectra (recorded at −0.65 V) with different degrees of electrode pressing against the ATR crystal. The absorption peak observed at 2070 cm^{-1} is due to linearly adsorbed CO on the Pt surface [1]. Both the peak intensity of CO_{ads} and the IR absorption by the Pt electrode are seen to increase with pressing for both p- and s-polarizations, as indicated by the arrows in Fig. 5(a) and (b). This shows that a good contact between the Pt electrode and the ATR crystal increases the sensitivity of the in situ ATR-FTIR technique.

It is interesting to note that CO_{ads} can absorb not only p- but also s-polarizations although the absorbed amount of s-polarization is very small, only one tenth of p-polarization. The IR absorption of s-polarization can be explained by assuming that the CO_{ads} is not perfectly aligned normal to the electrode surface and/or by surface roughness which makes different orientations of CO_{ads} molecules to the incident beam plane.

In Fig. 6, the peak height of CO_{ads} is plotted vs. the decreased amount of ADC counts obtained with pressing of the Pt electrode against the ATR crystal. The ADC counts were recorded just before taking sample spectra at various pressing distances. It is clear that the more the amount of ADC counts is decreased by the contact, the higher is the CO_{ads} peak intensity. Since the electromagnetic field strength of the evanescent wave decreases exponentially with the distance from the ATR crystal surface, it is evident that the positioning of the electrode surface closer to the ATR crystal surface can
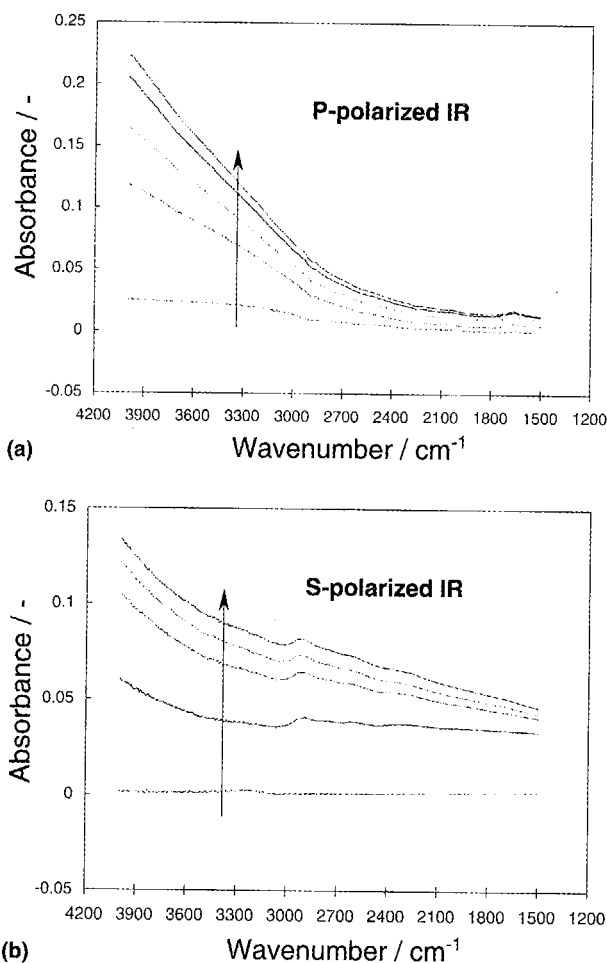

Fig. 4. Absorbance FTIR spectra recorded for different degrees of pressing of the Pt electrode against the Si ATR crystal in an argon atmosphere for: (a) p- and (b) s-polarizations of IR. The background spectra were collected under non-contact conditions.
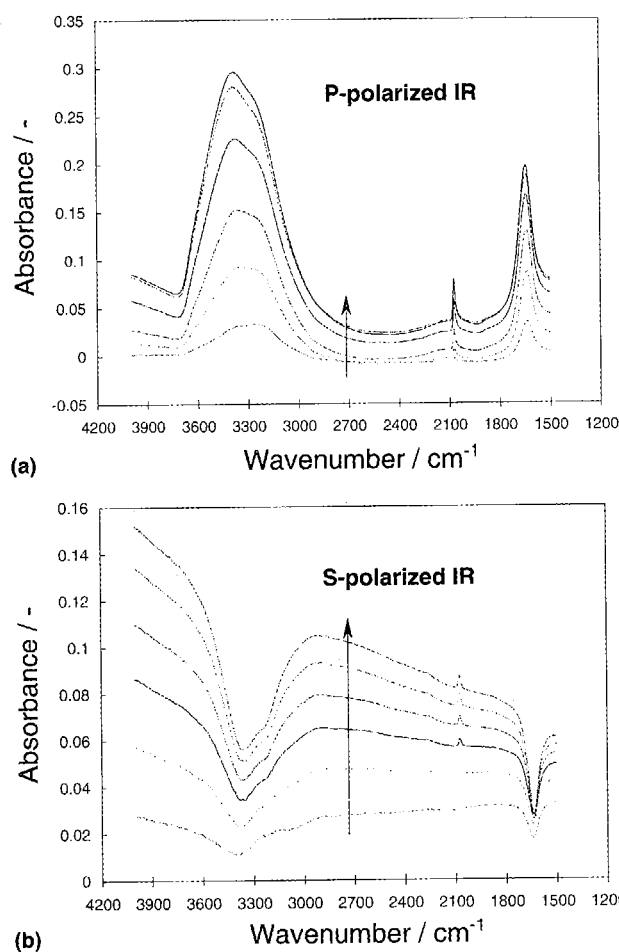
(a)

(b)

Fig. 5. Absorbance FTIR spectra of CO adsorbed on polycrystalline Pt electrode in 0.5 M H₂SO₄. The spectra were collected under contact conditions for: (a) p- and (b) s-polarizations of IR. The background spectra were collected under non-contact conditions.
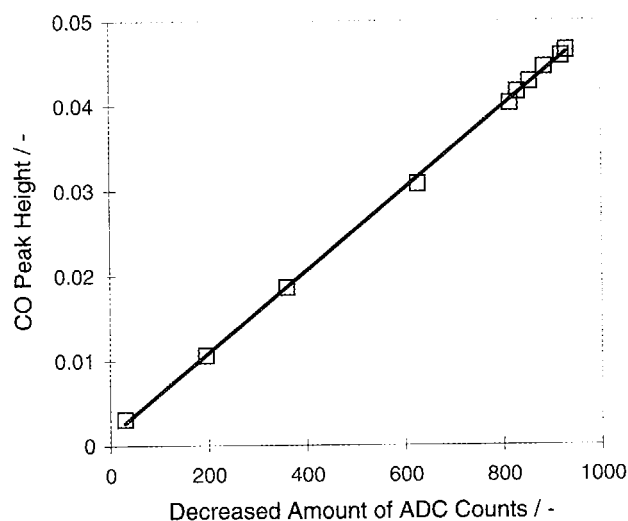

Fig. 6. Plots of the dependence of the CO peak height on the decreased amount of ADC counts. The spectra were recorded at −0.65 V vs. MSE in 0.5 M H₂SO₄. The CO peak height was obtained from Fig. 5(a) and ADC counts were recorded just before the sample spectra were collected.

produce more absorption of IR energy by the species adsorbed on the electrode surface. Thus, the decreased amount of ADC counts with the electrode pressing in thin electrolyte layer ATR-FTIR spectroscopy can be used as a measure of good electrode–crystal contact (i.e., good sensitivity).

3.2. Sensitivity of the thin electrolyte layer ATR-FTIR method

The sensitivity of an in situ FTIR technique determines its applicability for electrochemical studies and a number of methods have been tested by researchers to increase the sensitivity of in situ FTIR techniques [1]. In this section, the sensitivity of the ATR-FTIR technique presented in this work is compared to external reflec-
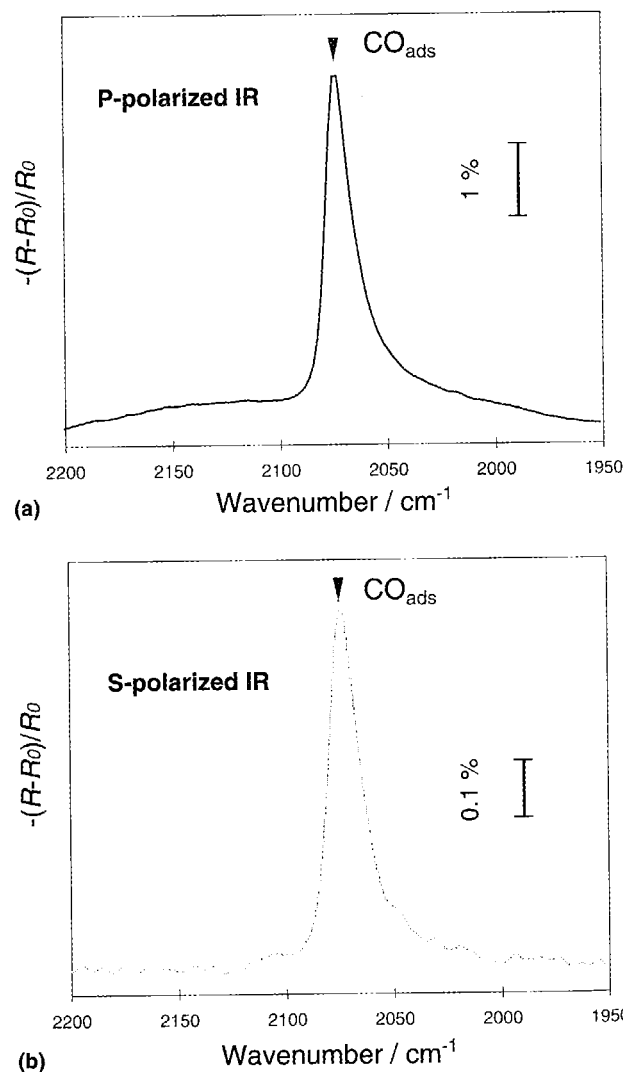

(a)

(b)

Fig. 7. $-(R-R_0)/R_0$ spectra of linearly adsorbed CO on polycrystalline Pt in 0.5 M H₂SO₄. The data were collected under contact conditions for: (a) p- and (b) s-polarizations of IR at −0.65 V vs. MSE. The background spectra were obtained after complete removal of the CO$_{ads}$ by electro-oxidation at 0.1 V vs. MSE.

tion–absorption FTIR and thin film electrode ATR-FTIR methods. Therefore, the normalized change of reflectance, $-(R–R_0)/R_0$, is calculated and presented in Fig. 7. The peak height of the CO_{ads} (at ca. 2070 cm^{-1}) represents the percentage of IR light absorbed by this molecule. It is seen that ca. 5 and 0.5% of the IR light energy at 2070 cm^{-1} is absorbed by CO_{ads} for the p- and s-polarizations, respectively. The highest IR absorption by CO_{ads} reported in the literature is ca. 4% which was obtained using an external reflection technique based on a polarization modulation and dispersive infrared spectroscopy [8]. The IR absorption by CO_{ads} using FTIR spectroscopy is normally between 0.1 and 2% for both the external reflection [1,9–12] and the thin film electrode ATR-FTIR techniques [13,14]. Recently, Zheng and Sun [12] reported a significant enhancement of IR light absorption by CO adsorbed on a nanometer-scale thin Ru film using an external reflection method. However, they reported an IR absorption by the CO_{ads} of less than 2%. Therefore, it can be said that the sensitivity of the thin electrolyte layer ATR-FTIR setup discussed in this work is better than the sensitivity of the external reflection and thin film electrode ATR-FTIR methods. Additionally, the experimental error of the Otto ATR set-up introduced here is extremely low provided that the degree of contact between the electrode surface and crystal is controlled, as described in this work.

3.3. Applications of the new setup of in situ thin electrolyte layer ATR-FTIR method

Fig. 8 shows typical normalized differential FTIR reflectance spectra collected during the oxidation of CO_{ads} on the Pt electrode in 0.5 M H_2SO_4 as a function of the applied potential. The intensity of the CO_{ads} peak is seen to decrease as the potential is made more positive, and the peak representing the oxidation product, i.e., CO_2, appears at 2043 cm^{-1}. The CO_2 peak disappears rapidly with time, indicating that the removal of CO_2 (which takes place by diffusion) is not as slow as reported using different cell set-ups. The fast diffusion from the gap between the Pt electrode and Si ATR crystal to the bulk electrolyte is explained by the small contacting area, ca. 0.0314 cm^2, used in this work. This is much smaller than the ca. 0.8 cm^2 area commonly employed for in situ external reflection FTIR methods [11,15].

It should be stressed that the in situ thin electrolyte layer ATR-FTIR technique discussed in this work does not require any IR reflectivity by the electrode surface, unlike the external reflection FTIR technique. Therefore, this technique potentially allows the study of electrochemical processes using a wide range of electrodes. In order to confirm the applicability of this technique to the study of IR non-reflecting electrodes,
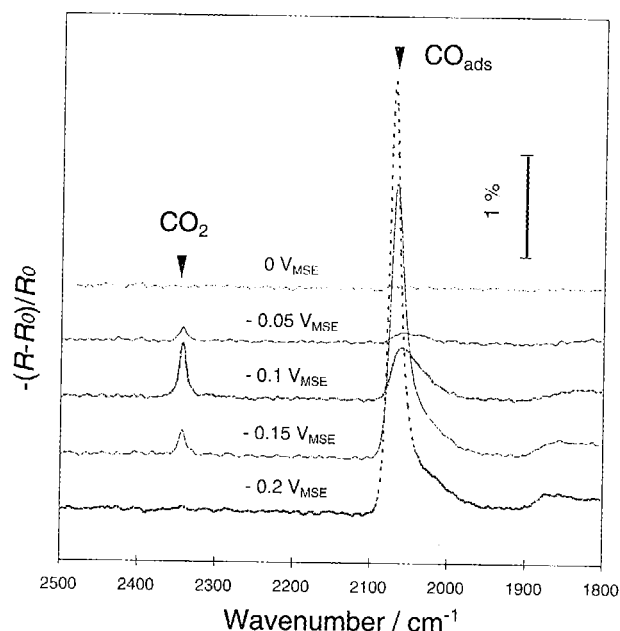

Fig. 8. $-(R–R_0)/R_0$ spectra of linearly adsorbed CO on polycrystalline Pt in 0.5 M H_2SO_4 as a function of potential. The data were collected under contact conditions for: (a) p- and (b) s-polarizations of IR. The background spectrum was obtained after complete removal of the CO_{ads} by electro-oxidation to CO_2 at 0.1 V vs. MSE.

electrochemical CO_{ads} oxidation studies were conducted using Pt/C particles dispersed on the glassy carbon electrode. The results are shown in Fig. 9. At more negative potentials, the peak for linearly bonded CO_{ads}
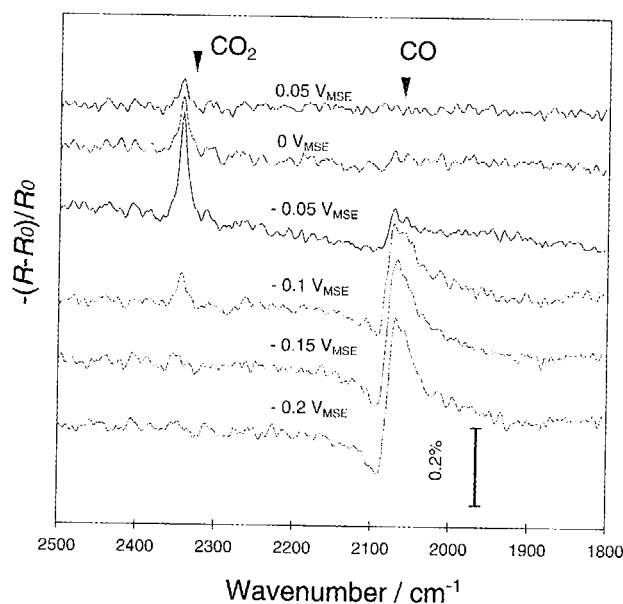

Fig. 9. $-(R–R_0)/R_0$ spectra of linearly adsorbed CO on a Pt/C catalyst deposited on a glassy carbon electrode as a function of potential. 0.5 M H_2SO_4 was used as electrolyte solution. The spectra were recorded under contact conditions for p-polarization of IR. The background spectrum was collected after complete removal of the CO_{ads} by electro-oxidation to CO_2 at 0.1 V vs. MSE.

is clearly observed ca. 2050 cm^{-1}. As expected, the intensity of the CO$_{ads}$ peak decreases with increasing potential and the CO$_2$ peak appears at ca. 2043 cm^{-1} as the CO$_{ads}$ is oxidized. The application of in situ FTIR techniques to powder-dispersed porous electrode systems is very important because they represent real (fuel cell) catalyst systems. Pt particles supported on carbon black have been examined using an external reflection technique. However, a highly IR reflecting metallic electrode such as gold is needed for the study and only a thin catalyst layer can be applied to the substrate to attain a high sensitivity [16,17]. Another successful study of a carbon supported PtRu (40 wt% Pt + 20 wt% Ru) catalyst deposited on a glassy carbon electrode was conducted by Munk et al. [18] using the external reflection technique. However, the IR absorption by CO$_{ads}$ on the Pt and Ru catalyst sites was poor. In fact, the IR absorption was only ca. 0.06%, i.e., much smaller than the ca. 0.3% found in this work for a 20 wt% Pt/C catalyst. This significantly improved sensitivity of our thin electrolyte layer ATR method is attributed to the fact that the IR intensity for internal reflection conditions is not as strongly dependent on the IR absorption or scattering by the electrode surface as observed for external reflection methods. However, the CO$_{ads}$ band is seen to be distorted. The origin of this distortion needs to be investigated in future work.

3.4. Electrochemical inertness of Si and AMTIR ATR crystals in 0.5 M H$_2$SO$_4$

The ATR crystal used for in situ electrochemical IR studies needs to be inert, i.e., the crystal cannot be involved in or altered by electrochemical reactions. In this section, CV experiments are used to discuss the inertness of a Si and an AMTIR ATR crystal in 0.5 M H$_2$SO$_4$ and the results are shown in Fig. 10(a) and (b), respectively. Close contact of the Pt electrode with the Si crystal is seen not to alter the typical Pt CV characteristics indicating that the Si crystal is inert. However, contact of the Pt electrode with the AMTIR ATR crystal is seen to result in two new peaks in the Pt double layer and Pt oxide formation region. Furthermore, the magnitude of the hydrogen adsorption/desorption charge is significantly reduced upon contact. These results show that the AMTIR crystal is not stable for in situ experiment in strong sulfuric acid solution. Therefore, the AMTIR (that is a glass consisting of Ge, As and Se) crystal is not recommended for in situ FTIR work in the strong sulfuric acid solution. This is unfortunate, as the penetration depth of the evanescent wave out of the AMTIR crystal is almost twice the penetration depth of the Si ATR crystal, and this would result in an increased intensity of the signal of IR active species adsorbed on the electrode surface.
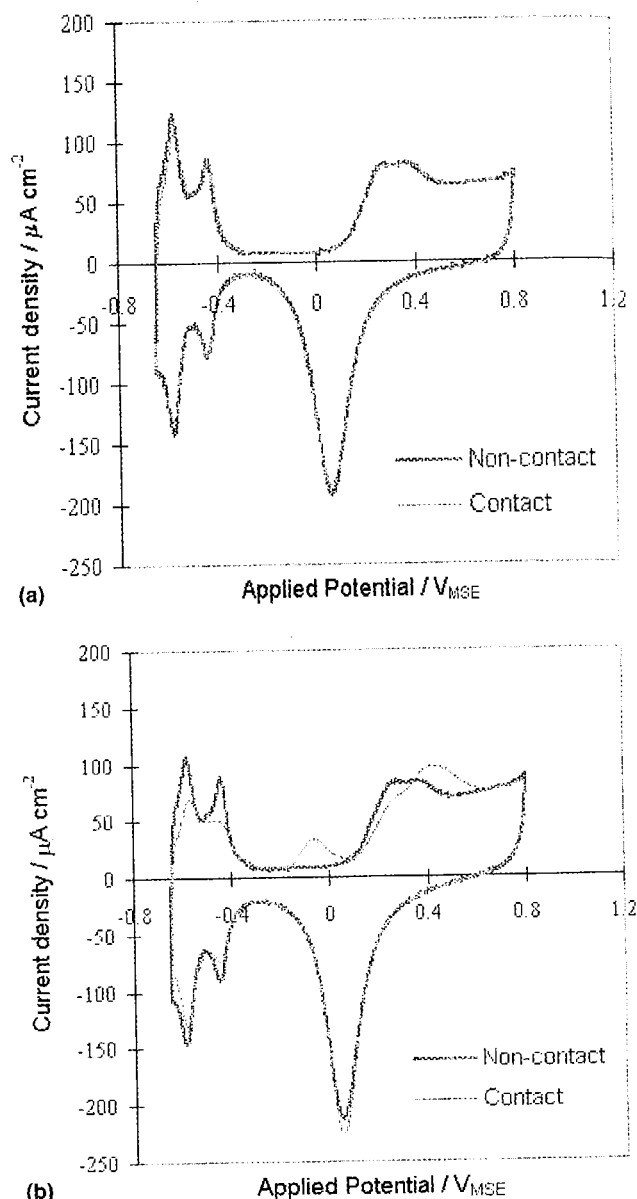

Fig. 10. Typical CVs for a polycrystalline Pt electrode recorded at 100 mV s^{-1} under non-contact and contact conditions in 0.5 M H$_2$SO$_4$. (a) Si and (b) AMTIR ATR crystals were used.

It is generally known that the electrochemical reaction rates are limited (seen in distorted CV characteristics) by a high resistance in the thin gap between the electrode and the IR transparent window in situ external reflection FTIR methods [1]. In this work, the CV characteristics are seen to be not influenced by the resistance of the electrolyte in the gap. This is attributed to the small contact area of 0.0314 cm^2, which is much smaller than the contact area of ca. 0.8 cm^2 normally employed in external reflection methods [11,15]. The small contact area, and hence small current, is an advantage of the commercial ATR crystal assembly used in this work, as it results in negligible voltage (IR) drops.

4. Conclusions

A new experimental setup of a thin electrolyte layer ATR-FTIR method has been developed and tested for the in situ investigation of electrode processes in 0.5 M H_2SO_4. Controlled and close contact between the electrode and ATR crystal surface was achieved using a micrometer, a spring and X-, Y-position controllers. The IR intensity was found to decrease over the entire wavenumber range tested as the contact between the electrode and the ATR crystal was improved. The sensitivity of the new setup was determined using the typical signal observed for linearly adsorbed CO (CO_{ads}) on polycrystalline Pt electrodes and was found to be proportional to the amount of the IR intensity decreased by the contact. The decrease of the IR intensity with increasing electrode–crystal contact results from the IR absorption by free electrons on the Pt electrode and is an indication of the total internal reflection condition. It was, therefore, used as a measurement of good contact between the electrode and ATR crystal.

The sensitivity of the new thin electrolyte layer ATR-FTIR setup appears to be better than found using external reflection and thin film electrode ATR-FTIR methods. Furthermore, the new in situ thin electrolyte layer ATR-FTIR technique was successfully applied to detect IR active species on an IR non-reflecting porous electrode.

The stability of the ATR crystal is obviously an important factor for the successful study of electrode processes. In this work, it was found that a commercially available Si ATR crystal is inert during electrochemical studies carried out in 0.5 M H_2SO_4. Furthermore, the CV characteristics, recorded when the electrodes were in contact with the Si crystal, were found to be not distorted by possible electrolyte resistance effects, as is typically observed in external reflection FTIR experiments. The fact that voltage drops are essentially not observed in this work is due to the small electrode area (resulting in small currents) used in this work.

The objectives of the present work were to describe a new set-up of an in-situ ATR-FTIR technique and to show its applicability to examine surface species adsorbed on smooth as well as IR non-reflecting and rough surfaces. A full interpretation of the results presented will require theoretical calculations involving the Fresnel equations.

References

[1] B. Beden, C. Lamy, in: R.J. Gale (Ed.), Spectroelectrochemistry: Theory and Practice, Plenum Press, New York, 1988 (Chapter 5).
[2] N.M. Marković, P.N. Ross Jr., Surf. Sci. Rep. 45 (2002) 117.
[3] A.R. Hind, S.K. Bhargava, A. McKinnon, Adv. Colloid Interf. Sci. 93 (2001) 91.
[4] P.W. Faguy, N.S. Marinkovic, Anal. Chem. 67 (1995) 2791.
[5] P.A. Brooksby, W.R. Fawcett, Anal. Chem. 73 (2001) 1155.
[6] A. Bewick, K. Kunimatsu, B.S. Pons, Electrochim. Acta 25 (1980) 465.
[7] B. Beden, C. Lamy, A. Bewick, K. Kunimatsu, J. Electroanal. Chem. 121 (1981) 343.
[8] K. Kunimatsu, J. Electroanal. Chem. 213 (1986) 149.
[9] D.S. Corrigan, M.J. Weaver, J. Electroanal. Chem. 241 (1988) 143.
[10] Y. Morimoto, E.B. Yeager, J. Electroanal. Chem. 441 (1998) 77.
[11] W.F. Lin, T. Iwasita, W. Vielstich, J. Phys. Chem. B 103 (1999) 3250.
[12] M.-S. Zheng, S.-G. Sun, J. Electroanal. Chem. 500 (2001) 223.
[13] Y. Zhu, H. Uchida, M. Watanabe, Langmuir 15 (1999) 8757.
[14] Y. Zhu, H. Uchida, T. Yajima, M. Watanabe, Langmuir 17 (2001) 146.
[15] K.A. Friedrich, F. Henglein, U. Stimming, W. Unkauf, Colloids Surf. A 134 (1998) 193.
[16] K.A. Friedrich, F. Henglein, U. Stimming, W. Unkauf, Electrochim. Acta 47 (2001) 689.
[17] S. Park, Y. Tong, A. Wieckowski, M.J. Weaver, Electrochem. Commun. 3 (2001) 509.
[18] J. Munk, P.A. Christensen, A. Hamnett, E. Skou, J. Electroanal. Chem. 401 (1996) 215.