

Fig 2. SNIFTIRS spectra taken off the Au electrode immersed in O₂-saturated 0.7 M KOH at (a) 780 mV/RHE and (b) 280 mV/RHE. Spectra were taken at various times after the admission of the O₂ solution and normalised to the reference spectrum taken at 1.11 V/RHE of the N₂-saturated 0.7 M KOH solution immediately prior to admission.

IN SITU INFRARED REFLECTANCE SPECTROSCOPY OF FORMALDEHYDE ADSORPTION ON POLYCRYSTALLINE PLATINUM ELECTRODES IN ALKALINE MEDIUM

P. OLIVI and L. O. S. BULHÕES

LIEC - Depto. de Química - Univ. Federal de São Carlos
13560 - São Carlos - SP - BRASIL

B. BEDEN, F. HAHN, J-M. LEGER and C. LAMY

Laboratoire de Chimie 1, Electrochimie et Interactions
URA au C.N.R.S. n° 350, Université de Poitiers
40, Av. du Recteur Pineau, 86022 - Poitiers - FRANCE

ABSTRACT

The oxidation of formaldehyde at platinum polycrystalline electrodes in alkaline solutions was investigated by Electrochemically Modulated Infrared Reflectance Spectroscopy (EMIRS). From the assignment of the IR absorption bands, adsorbed species were identified as linearly and bridge-bonded CO (poisoning intermediates), and as formate (reaction product).

INTRODUCTION

On the basis of cyclic voltammetry experiments, it was recently demonstrated that the oxidation of formaldehyde on platinum electrodes in alkaline solutions can occur through different processes, depending on potential, and that there is strong adsorption of intermediates in the hydrogen region (1,2). These strongly adsorbed species are oxidised in the potential range where a Pt(OH)_{ads} layer is formed. The determination of the number of electrons per site, N_{eps} , shows that these species can be identified as CO species both in the linear and bridge-bonded forms, characterized by N_{eps} of 2 and 1, respectively.

Furthermore, in aqueous solutions, formaldehyde is present as methylene glycolate, its hydrated form, the equilibrium constant of the dehydration reaction being about 10^{-3} (3). This shows that two active species are always in equilibrium in solution, and that the adsorption of methylene glycolate or its derivated forms onto the electrode surface must be considered. In this work some

preliminary spectroscopic results are presented, using Electrochemically Modulated Infrared Reflectance Spectroscopy (EMIRS), which has been demonstrated to be powerful a technique for the "in situ" observation of the vibrational spectra of adsorbed species.

EXPERIMENTAL

The supporting electrolyte solutions were prepared from ultrapure water obtained with a Millipore Milli Q system and NaOH suprapur Merck. Formaldehyde solutions were prepared by refluxing paraformaldehyde during at least 4 hours. The cell, as well as the technique used in the EMIRS experiments, were described and discussed elsewhere (4). A systematic investigation of the 1000-2700 cm^{-1} wavenumber range was carried out, using an EMIRS III spectrometer (Hi-Tek Instruments), under various modulations conditions and formaldehyde concentrations.

RESULTS AND DISCUSSION

Using 200 mV amplitude modulation signals at a 13.5 Hz frequency and a mean potential $\bar{E} = -0.85$ V vs Hg/HgO, EMIR spectra were obtained, all of them being similar to the one given in Figure 1, provided that the potential limits were kept in the hydrogen adsorption region. The two IR absorption bands at ca. 1830 and 2000 cm^{-1} result from the well known bridge and linearly-bonded CO species, respectively. These results are in agreement with a mean N_{eps} value of 1.4, which was found after long adsorption times ($t_{\text{ads}} > 300$ s), through cyclic voltammetry (2). No bands related to the methylene glycolate species were detected at around 1050 cm^{-1} . However at wavenumbers lower than 1800 cm^{-1} one peak is seen at 1700 cm^{-1} , which can be attributed to the C=O stretching vibrations of the formyl group of adsorbed formaldehyde or of one of its adsorbed reaction products.

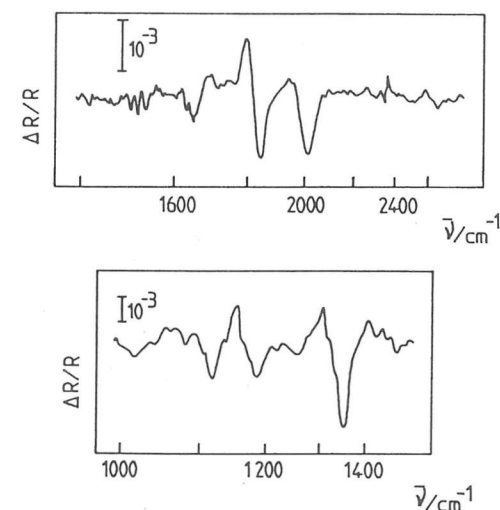


Fig. 1 - EMIR spectra of a Platinum electrode in a 1.25 M NaOH + 5 mM HCHO solution. $\bar{E} = -0.85$ V vs Hg/HgO. $\delta E = 200$ mV and $f = 13.5$ Hz.

Another band at 1350 cm^{-1} and a complex band with two negatives and one positive lobes in the 1100-1200 cm^{-1} range are also clearly seen in the spectrum. These bands are very similar to those observed with formic acid in solution (5) and therefore could result from the oxidation of methylene glycolate in the potential range of the first voltammetric peak. Such a formation of formic acid (or formate) from the oxidation of formaldehyde in alkaline medium on platinum electrodes has already been postulated by several authors (6).

Similar spectra were obtained with 0.1 M formaldehyde solutions, under the same conditions of potential modulation. Only the band intensities vary, showing more production of carbon monoxide.

Beside, it is interesting to note that the evolution of spectra with time during spectral accumulation, shows that the formation of the CO layer is much slower with formaldehyde, than with CH_3OH (7) or HCOOH (8). The

dehydrated HCHO form can be taken as responsible for the formation of the CO layer. Thus the equilibrium between the hydrated and dehydrated forms, which certainly changes with time in the vicinity of the surface, controls probably the concentration of fresh formaldehyde for the CO layer formation.

ACKNOWLEDGEMENTS

One of the authors (P.O.) thanks CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for a fellowship.

REFERENCES

- 1- P. OLIVI and L. O. S. BULHÕES, Resúmenes de la VIII Reunión Latinoamericana de Electroquímica y Corrosión, Argentina (1988) 86.
- 2- P. OLIVI and L. O. S. BULHÕES, Anais do VII Simposio Brasileiro de Eletroquímica e Eletroanalítica, vol. II, Brasil (1990) 476.
- 3- L. C. GRUEN and P. T. MCTIGUE, J. Chem. Soc. (1963) 5217.
- 4- B. BEDEN and C. LAMY in R. J. GALE (Ed.), Spectroelectrochemistry, Theory and Practice, Plenum Press, New York, 1988, chap. 5, p. 189
- 5- R. MECKE and F. LANGENBUCHER, Infrared Spectra of Selected Chemical Compounds, Heyden and Son Ltd. Spectrum House, London (1965).
- 6- a) R. PARSONS and T. VANDERNOOT, J. Electroanal. Chem., 257 (1988) 9. b) J. E. A. M. VAN DEN MEERAKKER, J. Appl. Electrochem., 11 (1981) 387. c) S. SIBILLE, J. MOIROUX, J. C. MAROT and S. DEYCARD, J. Electroanal. Chem., 88 (1978) 105.
- 7- M. I. S. LOPES, F. HAHN, B. BEDEN, J-M. LEGER and C. LAMY, J. Electroanal. Chem., accepted.
- 8- M. CHOY de MARTINEZ, F. HAHN, B. BEDEN and C. LAMY, J. Electron Spectroscopy and Related Phenomena, 45 (1987), 153.

SOCIEDADE PORTUGUESA DE ELECTROQUÍMICA PORTUGUESE ELECTROCHEMICAL SOCIETY

Society officers

- Prof. CÉSAR A. N. VIANA, President
Instituto Bento da Rocha Cabral
Calçada Bento da Rocha Cabral, 14
1200 LISBOA
- Prof. ARMANDO J. L. O. POMBEIRO, Vice-President
Complexo I
Instituto Superior Técnico
1096 LISBOA Codex
- Prof. CARLOS A. S. PALITEIRO, Secretary
Chemistry Department
Faculty of Sciences and Technology
University of Coimbra
3000 COIMBRA
- Prof. MARIA MANUEL P. M. NETO, Treasurer
Instituto Bento da Rocha Cabral
Calçada Bento da Rocha Cabral, 14
1200 LISBOA
- Prof. JOÃO E. SIMÃO, Director of Publications
Chemistry Department
University of Aveiro
3800 AVEIRO

Membership fees: individual members Esc. 2.500\$00
collective members Esc. 15.000\$00

Those interested in membership of the Society should fill in the overleaf and send it to the Secretary.

Destacar pelo picotado

PORTUGALÆ ELECTROCHIMICA ACTA is published quarterly by the Portuguese Electrochemical Society.

The address for the editorial office is

Prof. J. E. Simão
Department of Chemistry
University of Aveiro
3800 AVEIRO
PORTUGAL

Subscription free to members of the Portuguese Electrochemical Society. Subscription to non members Esc. 2.500\$00.

Those interested in the journal should fill in the overleaf form and send it to the above address.