

3rd LAMNET Workshop – Brazil 2002**The Electrocatalysis of Ethanol Oxidation**

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ABSTRACT

In this paper, the main characteristics of ethanol electrooxidation are presented and the results of electrochemical and spectroscopic methods are discussed. The total oxidation reaction should produce 12 e⁻/molecule. However, on Pt catalysts, the reaction follows parallel pathways forming acetaldehyde, acetic acid and carbon dioxide as soluble products. Thus much lower yields of charge per ethanol molecule are obtained. An increase of the CO₂ production is observed at PtRu electrodeposits. Further research looking for more effective catalysts to produce the total oxidation is necessary.

INTRODUCTION**Electrocatalysis as a heterogeneous process**

Small organic molecules (methanol, formaldehyde, formic acid, ethanol) are considered candidate materials for operating at the anode of a Fuel Cell (FC). The primary goal of electrocatalysis of FC reactions is finding electrode materials where such reactions occur at potentials as close as possible to their thermodynamic equilibrium potential. This has to be so, in order to have the highest possible potential difference between anode and cathode. However, this is a difficult task since even the simplest alcohol molecules (e.g., CH₃OH) present bonds that have to be stretched, broken or modified in order to convert the molecule into CO₂. Such processes have usually very high activation energies and can therefore occur, at appropriate rates, only in the presence of a catalyst.

From studies of heterogeneous catalysis in the gas phase, it is well known that Pt is a good material to adsorb organic molecules and break intermolecular bonds. Through this process the molecule is broken in particles, which may remain at the catalyst surface as adsorbed radicals, or forms minor stable products which can pass to the gas phase. Similar processes can occur in an electrochemical cell if a Pt sheet is used as an electrode in the presence of an aqueous electrolytic solution of the organic species. However, in the electrochemical cell the catalyst is also an electrode at a given potential. Therefore, the species formed can exchange electrons and become oxidized (or reduced). During the oxidation, water provides, if necessary, oxygen atoms to convert the adsorbed species into CO₂. The role of Pt as catalyst, water as oxygen donor, and the electrode potential as responsible for the electron transfer is displayed in the following scheme representing the electrooxidation reaction of methanol:

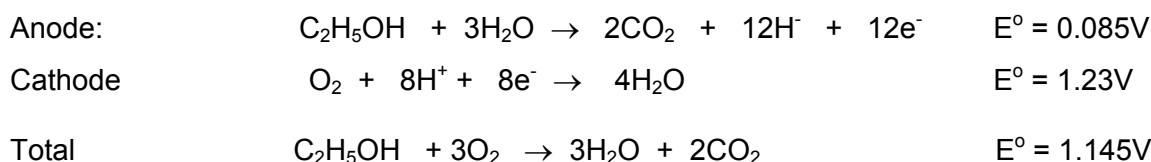
- 1) $\text{Pt}(\text{H}_2\text{O})_{\text{ad}} + \text{CH}_3\text{OH} \rightarrow \text{Pt}(\text{CH}_3\text{OH})_{\text{ad}} + \text{H}_2\text{O}$ (methanol adsorption),
- 2) $\text{Pt}(\text{CH}_3\text{OH})_{\text{ad}} \rightarrow \text{Pt}(\text{CO})_{\text{ad}} + 4\text{H}^+ + 4\text{e}^-$ (methanol dissociation, e⁻ exch.),
- 3) $\text{Pt}(\text{OH}_2)_{\text{ad}} \rightarrow \text{Pt}(\text{OH})_{\text{ad}} + \text{H}^+ + \text{e}^-$ (water dissociation, e⁻ exch.),
- 4) $\text{Pt}(\text{CO})_{\text{ad}} + \text{Pt}(\text{OH})_{\text{ad}} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^-$ (CO₂ formation, e⁻ exch.).

It should be noted that methanol dissociation (Eq. 2) occurs in several steps, but for simplicity, it has been written here as a one step process.

Any of the above processes may be too slow and limit the total rate of reaction. The steps involving electrons can be accelerated by increasing the electrode potential and thus, some energy is lost when current flows through the cell. The increase in potential in order to produce a given current is called overpotential. The nature of the electrode material is a deciding factor determining the overpotential required for a given current level because organic molecules can be adsorbed and dissociated only on metals presenting an appropriate electronic structure. For this purpose, metals having d-orbitals vacancies have shown to be good substrates for adsorbing and dissociating hydrogen. Correspondingly, high current densities for H₂ oxidation occur at relatively low overpotentials and therefore the H₂/O₂ fuel cell can present an optimum performance. However, organic species are much more complex than H₂ molecules and organic oxidations present, in general, serious kinetic limitations due to their complex oxidation mechanism. This is exemplified above (Eqs. 1-4) for methanol and will be shown in the next sections for ethanol.

Ethanol as a candidate fuel for FC

The desired reactions in an ethanol FC can be formulated as follows:



For each reaction, the thermodynamic standard potentials (vs. the standard hydrogen electrode) and the equilibrium potential difference are also given. The cell voltage under standard conditions, 1.145V, is the value for the reversibly working cell, producing CO₂ and delivering 12 electrons per ethanol molecule. Accordingly, ethanol would be very appreciated candidate substance for driving a fuel cell. However, thermodynamic potentials have no useful meaning since no practical system operates under reversible conditions! As explained in the previous section, in order to obtain measurable currents from ethanol oxidation at platinum electrodes, very high overpotentials (>0.4V, i.e., well above the standard value of 0.085V.) are necessary. This can be observed in Fig. 1, where the cyclic voltammogram (CV) during the oxidation of 1 mol L⁻¹ C₂H₅OH on a monocrystalline Pt(111) electrode is shown. In a CV experiment, the potential is first increased at a constant rate, from 0.05V up to 1.6V and then decreased back to the initial value. In doing this, the current grows and decreases forming peaks at the potentials at which different electrode processes take place.

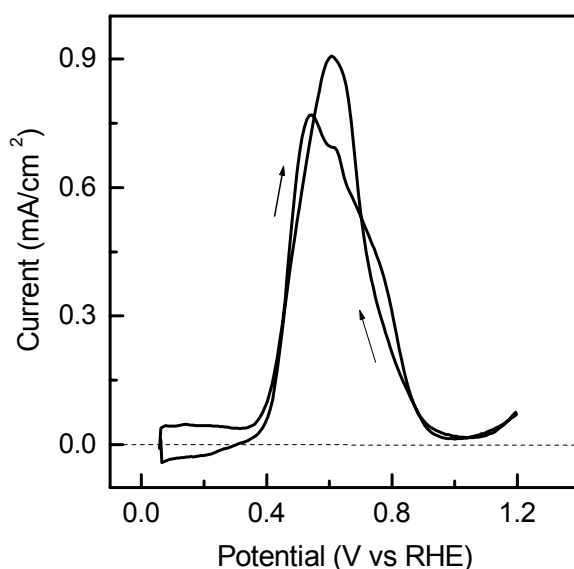


Figure 1: Cyclic Voltammogram for a Pt(111) electrode in 1 mol L⁻¹ C₂H₅OH + 0.1 mol L⁻¹ HClO₄ solution. Sweep rate: 50 mV/s. Room temperature (25 °C).

Obviously, without the help of additional methods, it would be very difficult to establish the nature of the processes that are occurring under the peaks of the voltammogram. Therefore, useful analytical tools have been developed for this purpose, thus allowing to establish the nature of the reaction products and intermediates [1] as a function of the applied potential. On-line mass spectrometry, also called DEMS and in situ Fourier transform infrared spectroscopy (FTIRS) are successfully used in electrocatalysis. These methods are briefly described in the next section.

Use of spectroscopic methods to study ethanol electrocatalysis

On line mass spectrometry

This method uses a mass spectrometer connected directly to the working electrode of a cell, which has been specially designed for this purpose (Fig. 2). The cell has the working electrode assembly at the bottom (see details in the enlargement). This consists of a PTFE membrane covered with the catalyst (porous Pt deposit), which is placed on a porous steel disc. This assembly is the interface between the liquid in the cell and the vacuum at the entrance of the MS. Due to the porous nature of both electrode and membrane, all volatile substances produced on the electrode can enter the MS being immediately detected. Details on the MS construction have been described elsewhere [2]. The most important characteristic of the MS is the very fast entrance and elimination of the analyzed species. Due to this property, the masses can be detected during the application of any potential program as, e.g., a cyclic voltammogram and the responses follow the time dependence of the applied program. This is illustrated in Fig. 3, for the electrooxidation of D-labeled ethanol on a Pt porous electrode. We observe the typical current CV for a polycrystalline Pt electrode (a) and the mass CV for the oxidation products detected through the mass signal $m/z = 44$ for CO_2 (b) and $m/z = 47$ for acetaldehyde (c). It is clear, that the current in the CV represents the overlapping of at least two processes: one leading to CO_2 and another one producing acetaldehyde. Thus, this experiment demonstrates that ethanol oxidation on polycrystalline Pt is not complete, leading to a partial oxidation product, acetaldehyde. Moreover, the experiment shows that during the negative-going sweep of the voltammogram, acetaldehyde prevails, only minor quantities of CO_2 being formed.

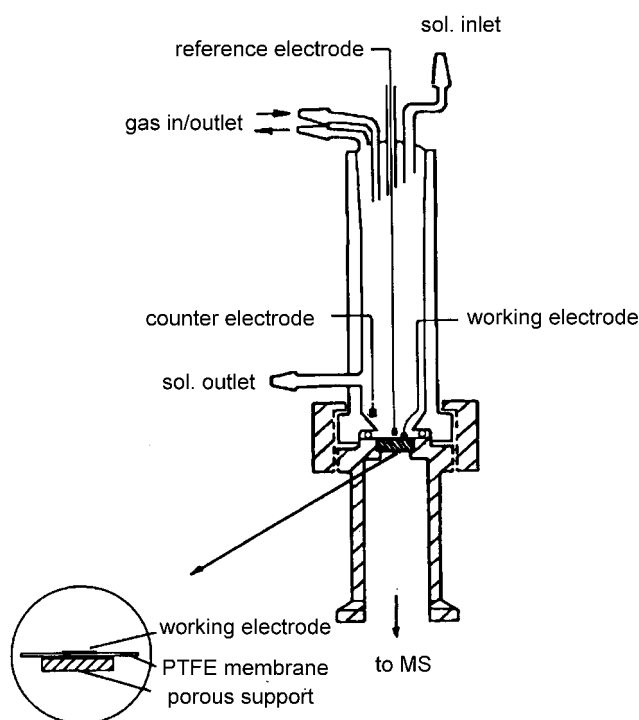


Figure 2: Electrochemical cell for on-line mass spectrometry experiments (DEMS).

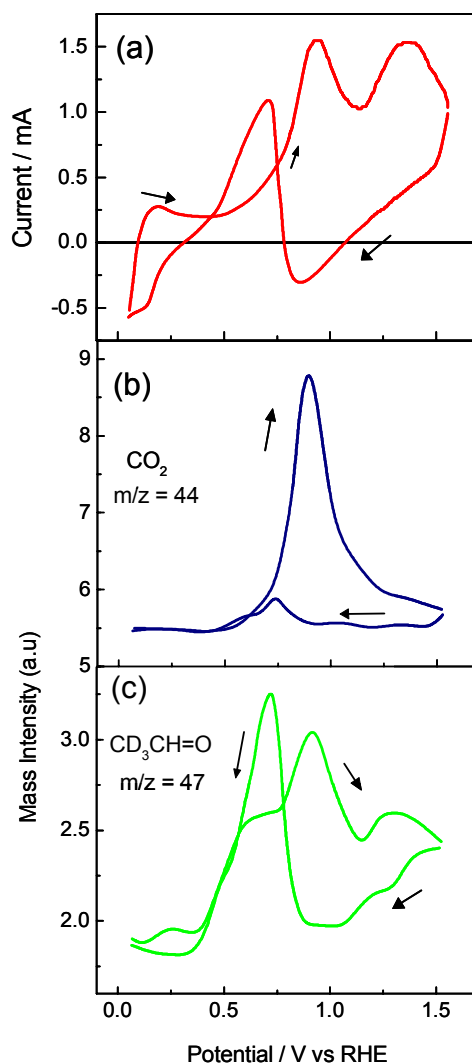


Figure 3: On-line MS experiment for ethanol oxidation. During a cyclic voltammogram at 10 mV/s the current (a) and the mass signals for CO₂ (b) and acetaldehyde (c) were simultaneously recorded. Electrolyte: 0.05 mol L⁻¹ C₂D₅OD + 0.05 mol L⁻¹ H₂SO₄.

In situ FTIR Spectroscopy

In this method, the electrochemical cell (Fig. 4a) is mounted in the path of the IR beam. A mirror-polished disc is used as a working electrode. It is placed against the IR window, at the bottom of the cell letting in between a thin layer of electrolyte (1-10 μm) (Fig. 4b). The use of this thin layer configuration minimizes the absorption of IR light by the solvent. Spectra are calculated as the ratio of two single beam spectra obtained at two different potentials. The spectrum at one of these potentials is used as a reference. Preferentially, a potential where no reaction occurs is taken for this purpose. So, the changes occurring at the second potential are monitored. Since the solution is confined in the thin layer cavity between electrode and IR-window, soluble species need very long time to diffuse into and away from the cavity and thus, spectral features will be observed due to formation and consumption of species. More details on the method are given elsewhere [3].

Fig. 5 shows spectra obtained during the application of a series of potentials at a Pt(100) electrode in the presence of ethanol [4]. A spectrum at 0.05V was used as a reference. The negative bands refer to substances formed at the indicated potentials, while the positive bands are due to ethanol consumed during its oxidation.

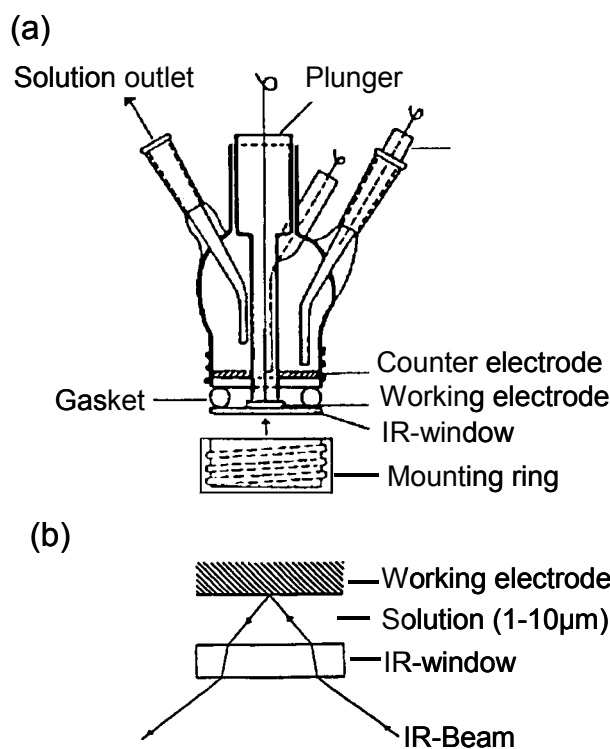


Figure 4: (a) Electrochemical cell for FTIR measurements. (b) Schematic representation (not to scale), of the thin-layer configuration for in situ IR measurements.

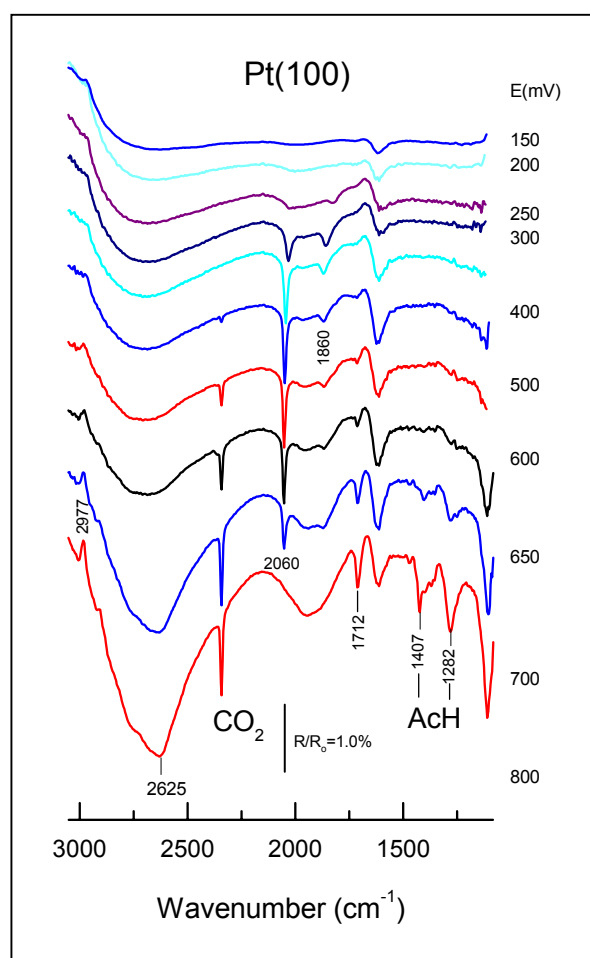


Figure 5: In situ FTIR spectra (256 scans, 8 cm⁻¹ resolution) at Pt(100) in 0.1 M CH₃CH₂OH + 0.1 M HClO₄. The reference spectrum was collected at 50 mV and the sample spectra were measured after applying potential steps towards more positive potentials as indicated in the figure [4].

The negative bands observed are due to the products CO₂, acetic acid and acetaldehyde. Band assignments are given in Table 1. Also, two bands due to linearly and bridge bonded CO as adsorbed reaction intermediate are observed at ca. 2050 cm⁻¹ and 1850 cm⁻¹. Another adsorbed molecule fragments containing C-H bonds have been reported from IR and on-line MS experiments on polycrystalline Pt [7]. However, such intermediates are finally oxidized to CO₂, at very high potentials.

Wavenumber / cm ⁻¹	Functional group or chemical species	Mode, comments, refs.
2977	CH ₃ , CH ₂	C-H str. [5]
2625 (broad)	COOH	O-H str. [5]
2341	CO ₂	C-O asym. str. [5]
2055-2060	adsorbed CO	linearly bonded
1860	adsorbed CO	bridge bonded
1712	COOH or CHO	C=O str., carbonyl [5]
1412	CH	C-H deformation
1370/1281	COOH	coupl. C-O str.- OH def. [5]
1100	ClO ₄ ⁻	Cl-O str. (F) [6]

TABLE 1: Assignment of some of the fundamental bands in the spectra of Fig. 5

Parallel pathways of ethanol oxidation

The results presented in the preceding sections show that ethanol oxidation undergoes parallel pathways leading to different soluble products as shown in the scheme of Fig. 6. We observe, that depending on the final product, 2, 4, or 12 electrons can be delivered per ethanol molecule. This scheme describes in a synthetic manner, one of the main problems of ethanol electrooxidation, (1) a considerable loss of the available energy occurs when the ethanol molecule is oxidized to acetaldehyde or acetic acid and (2) acetaldehyde is an undesirable, highly volatile substance.

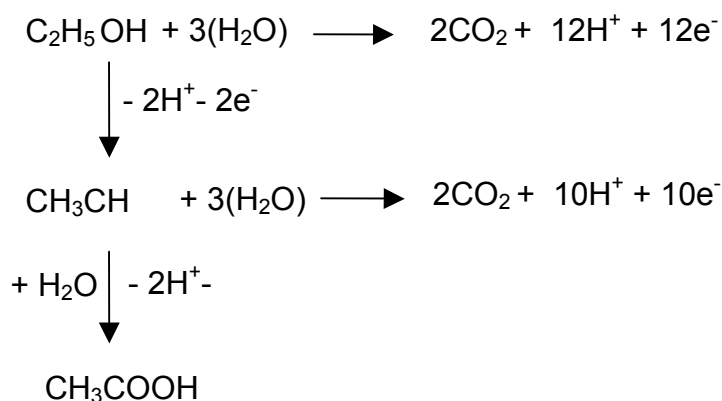


Figure 6: Parallel pathways during ethanol oxidation at Pt electrodes in acid solutions.

Use of a binary PtRu catalysts for ethanol electrooxidation

It is well known that PtRu materials are good catalysts for methanol oxidation [8]. The benefits of Ru has been assigned to the promotion of water dissociation (see Eq. 3). Ru is able to dissociate water at potentials as low as 0.2V, lowering in this way the potential for the oxidation of the methanol intermediate CO (see Eq. 4). A similar effect should be expected for ethanol oxidation, since also in this case CO is formed as a reaction intermediate in the pathway producing CO₂ (Fig. 6). Thus, infrared results showing an increase of CO₂ production in the presence of Ru, have been reported [9]. In Fig. 7 FTIR spectra for ethanol oxidation at two different PtRu materials are shown, both of identical atom composition Pt:Ru = 50:50. One is a smooth alloy and the other, an deposit of Pt and Ru on Au, prepared through electrolysis in a solution containing equal molar concentration of Pt and Ru. The resulting deposit contains approximately the same atom ratio of Pt and Ru. It can be clearly seen that the latter produces a higher ratio of CO₂ to acetic acid than the former. With other words, the surface structure of the catalyst plays an important role in determining the yields of products.

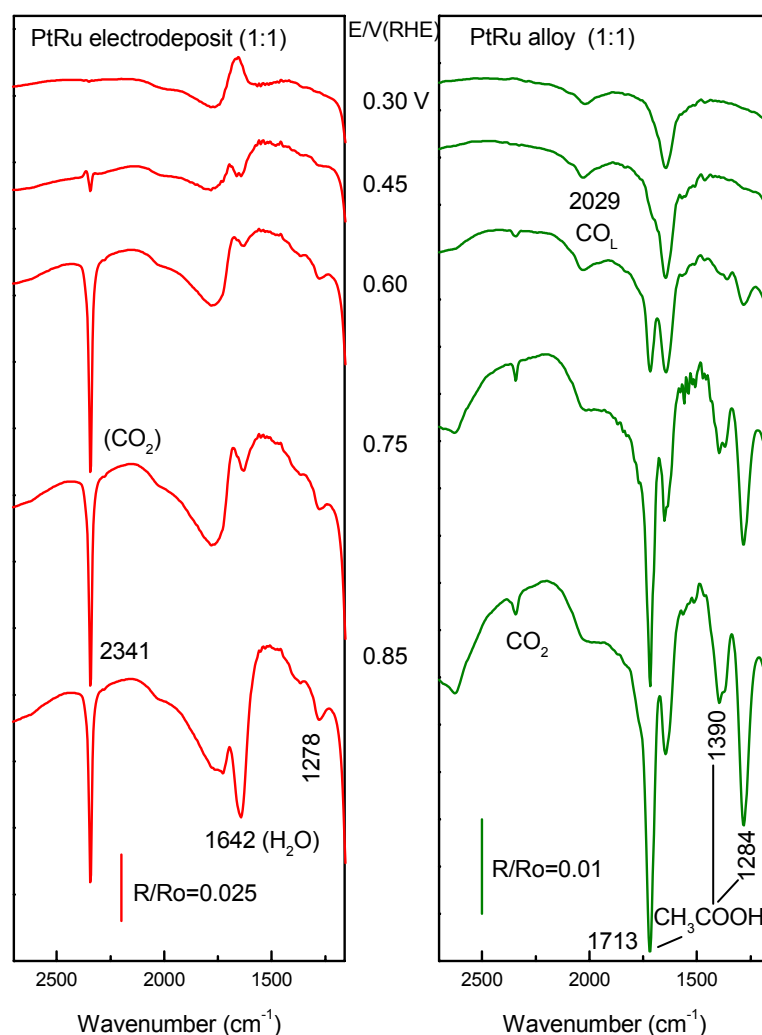


Figure 7: FTIR reflectance spectra during oxidation of 0.1M C₂H₅OH in 0.1M HClO₄, using a (1:1) Pt Ru electrodeposit on a gold substrate and a (1:1) PtRu alloy. Note the differences in the ratio of the bands for CO₂ (2341 cm⁻¹) and acetic acid (bands at 1284 cm⁻¹, 1390 cm⁻¹ and 1717 cm⁻¹).

Outlook

The results above show the complexity of the ethanol electrocatalysis. The main difficulty lies in the finding of a catalyst being able to break the C-C bond, forming small molecule fragments, which should be able to be oxidized at relatively low potentials. Preliminary experiments using PtRu electrodeposits indicate an enhanced activity of this catalyst towards the total oxidation reaction. This result shows the directions that can be followed in the search for more appropriate catalysts for the reaction.

REFERENCES

1. T. Iwasita, in *Advances in Electrochemical Science and Engineering*, H. Gerischer, Ch. Tobias (Eds.), Verlag Chemie: Weinheim, 1990, Vol. 1, p. 127.
2. B. Bittins-Cattáneo, E. Cattáneo, W. Vielstich, P. Königshoven, in *Electroanal. Chem.*, A. Bard (Ed.), vol 17, p. 181, Marcel Dekker, New York 1991.
3. T. Iwasita and F. C. Nart, in H. Gerischer and Ch. Tobias (eds), *Advances in Electrochemical Science and Engineering*, vol. 4, p. 123, Verlag Chemie, (1995)
4. X. H. Xia, H. D. Ließ and T. Iwasita, *J. Electroanal. Chem.*, 437 (1997) 233
5. G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, New York, 1966
Physics of Electrocatalysis
6. K. Nakamoto, *Infrared and Raman spectra of inorganic and Coordination Compounds*, John Wiley, New York, 1986
7. T. Iwasita and E. Pastor, *Electrochim. Acta*, 39 (1994) 351
8. T. Iwasita, *Electrochim. Acta*, 47 (2002) 3663; *ibid.* 48 (2002) 289
9. J. P. I. Souza, F. J. B. Rabelo, I. R. de Moraes, F. C. Nart, *J. Electroanal. Chem* 420 (1997) 17

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