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In situ spectroscopy studies of ethanol oxidation reaction using a single fuel cell/ATR-FTIR setup

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ARTICLE INFO

Article history:

Received 5 March 2013

Received in revised form

6 June 2013

Accepted 7 June 2013

Available online 12 July 2013

Keywords:

EOR

Electrocatalysis

Pt/C

ATR-FTIR

DEFC

ABSTRACT

This work presents a new method to study the ethanol oxidation reaction in a functional fuel cell adapting the single cell on an ATR-FTIR accessory. Using this configuration it was possible to observe the formation of the main products — acetaldehyde and acetic acid — and also measure the decay of the ethanol concentration at various temperatures. Furthermore, it was ascertained that the increment of power density with the temperature increase in the Pt/C anode fuel cell favors the acetaldehyde production. The proposed setup is a very promising characterization technique for studies of *in situ* electrochemical oxidation of small organic molecules.

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1. Introduction

According to an extrapolation calculated by the International Energy Agency (IEA), the growing demand for oil is spearheaded by the need for fuel transportation in the nearest future. Considering also that just a few countries produce oil and that is questionable how long the oil producers can satisfy the growing demand [1], nowadays there is a great interest in the use of renewable fuels as ethanol and more efficient power sources such as direct alcohol fuel cells (DAFC) [2–4]. Moreover, ethanol has been proposed as a fuel for this cell because it is produced in large quantities from biomass, it has higher energy density (8.01 kWh kg^{-1}) and is less volatile and toxic than methanol [5,6], the most studied alcohol for polymer electrolyte membrane fuel cells [7].

However, the strength of the C–C bond of the ethanol molecule make it extremely stable and, therefore, difficult to break at low temperature. Thus, ethanol complete oxidation to CO_2 is still a great challenge and, many studies about ethanol oxidation reaction (EOR) have been performed [8–13].

Studies of EOR in electrochemical cells using IR spectroscopy demonstrated that the major soluble products formed are acetaldehyde, acetic acid and carbon dioxide [14,15]. The intermediates species and products of EOR have usually been identified by *in situ* FTIR spectroscopy [16–19], differential electrochemical mass spectrometry (DEMS) [20–22], gas or liquid chromatography [23–25], and others.

Another approach to the study of EOR was made by Melke et al. [26,27], that used an X-ray absorption spectroscopy (XAS) to identify the species covering the catalytic sites of the Pt or Pt

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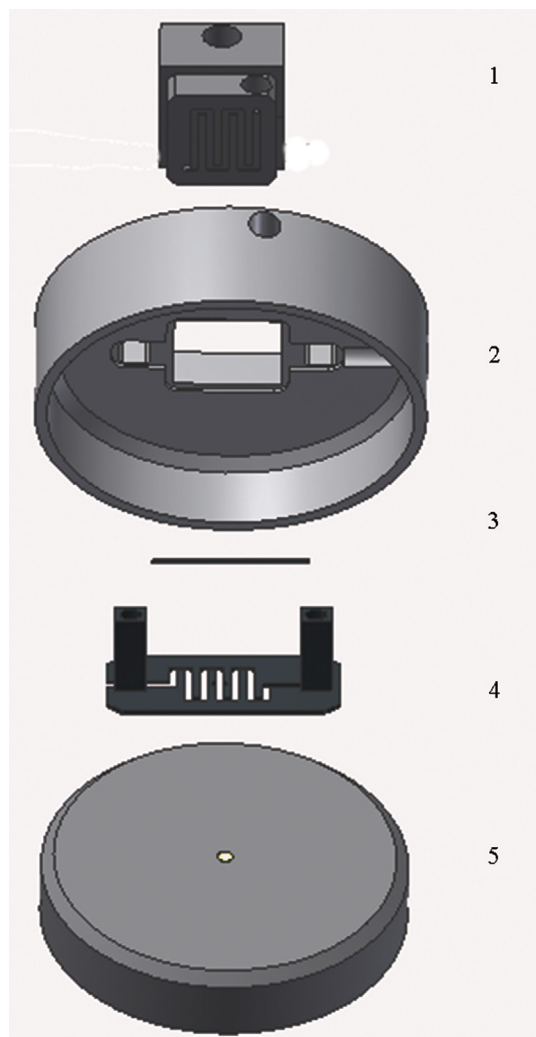


Fig. 1 – Single Cell/ATR-FTIR setup (1) cathode plate, (2) assembler, (3) MEA, (4) anode plate and (5) ATR plate.

based electrocatalysts during chronoamperometric experiments using half cell.

Most of the identification of intermediates species and products using FTIR, DEMS and gas or liquid chromatography techniques were done on electrochemical half cells, which do not really reproduce the conditions of a DAFC because it is not possible to detect the intermediates and products in real-time inside a cell.

An example that the results in half cells cannot reproduce a DAFC is the study of De Souza et al. [10]. In this work the authors used Attenuated Total Reflection – Fourier Transformed Infra Red spectroscopy (ATR-FTIR) to study Pt/C deposited on different supports (gold, glass carbon, and carbon cloth) and reported that acetaldehyde, acetic acid and CO₂ formed during the EOR have the onset formation potential shifted in function of these support, indicating that the extrapolation of the results obtained in electrochemical experiments cannot be true, considering what occurs inside a fuel cell.

ATR-FTIR Spectroscopy uses a high refractive index crystal, thereby permitting radiation to reflect in the crystal one or more times independent of the sample reflectance [11,28,29]. These characteristics make this technique very interesting to be coupled on a single fuel cell and to study the oxidation of small organic molecules. Using this technique it is possible to analyze the real intermediate species and products in EOR.

Taking into account that the development of new tools for *in situ* studies on single fuel cells represent an important step to understand the mechanism of the reactions in real time and conditions, this work, presents a single fuel cell adapted on ATR accessory for EOR. The influence of the temperature for EOR was also considered.

2. Material and methods

Single direct ethanol cell tests were carried out using Pt/C BASF (20 wt.%) electrocatalysts as the anode and cathode in the gas diffusion electrodes. The electrocatalyst was painted over the gas diffusion layer (GDL – Carbon Paper Teflon

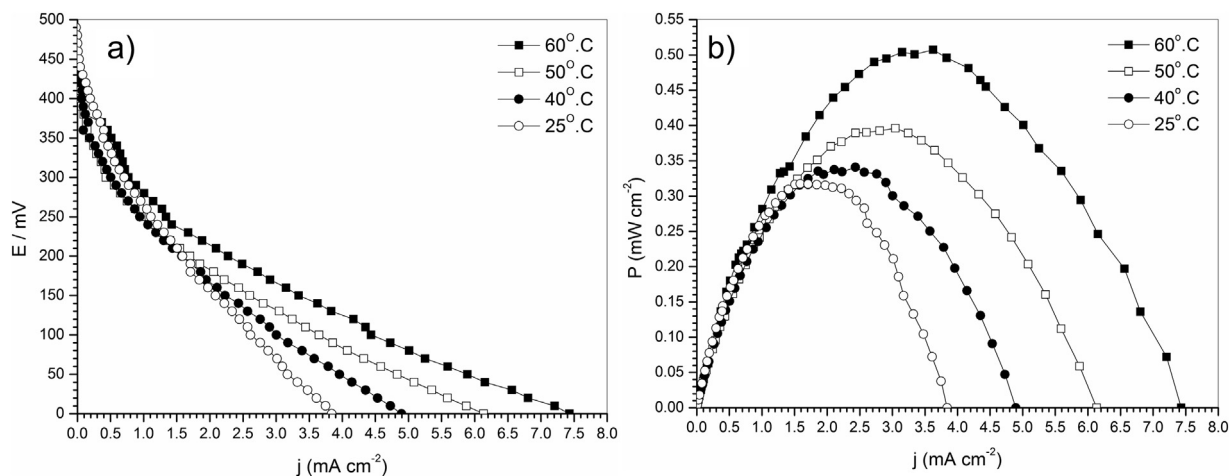


Fig. 2 – Polarization curves (a) and power density curves (b) in 1 cm² DEFC using 20 wt.% Pt/C Basf electrocatalyst in anode and cathode (1 mg_{Pt} cm⁻²). Nafion® 117 was used as the membrane. 2 mol L⁻¹ Ethanol with 0.8 mL min⁻¹ flux.

treated and Electrochem EC-TP1-060T) in order to obtain a homogeneous dispersion made with Nafion[®] solution (5 wt.%, Aldrich) and isopropanol (J.T. Baker).

All electrodes were constructed with 1 mg Pt cm⁻² in the anode and cathode. After preparation, the electrodes were hot pressed on both sides of a Nafion[®] 117 membrane at 100 °C for 2 min under a pressure of 225 kgf cm⁻². Prior to use, the membranes were exposed to 3 wt.% H₂O₂, washed with distilled water and treated with 0.5 mol L⁻¹ H₂SO₄.

The performance and ATR-FTIR *in situ* spectroscopy of the ethanol fuel cell was investigated using a special single cell (Fig. 1) with a geometric area of 1 cm², adapted in an ATR accessory (MIRacle with a Diamond/ZnSe Crystal Plate Pike[®])

installed on a Nicolet[®] 6700 FT-IR spectrometer equipped with a MCT detector cooled with liquid N₂. The temperature was set to 25, 40, 50, and 60 °C for the fuel cell and 80 °C for the oxygen humidifier. The fuel (2 mol L⁻¹ ethanol aqueous solutions) was delivered at approximately 0.8 mL min⁻¹ and the oxygen flow was set to 150 mL min⁻¹ under pressure of 2 bar.

The polarization curves were obtained using an Autolab PGSTAT 302N Potentiostat. Absorbance spectra were collected as the ratio (R/R₀) where R represents a spectrum at a given potential and R₀ is the spectrum collected at an open-circuit voltage (OCV). Negative and positive bands represent the consumption and production of substances, respectively.

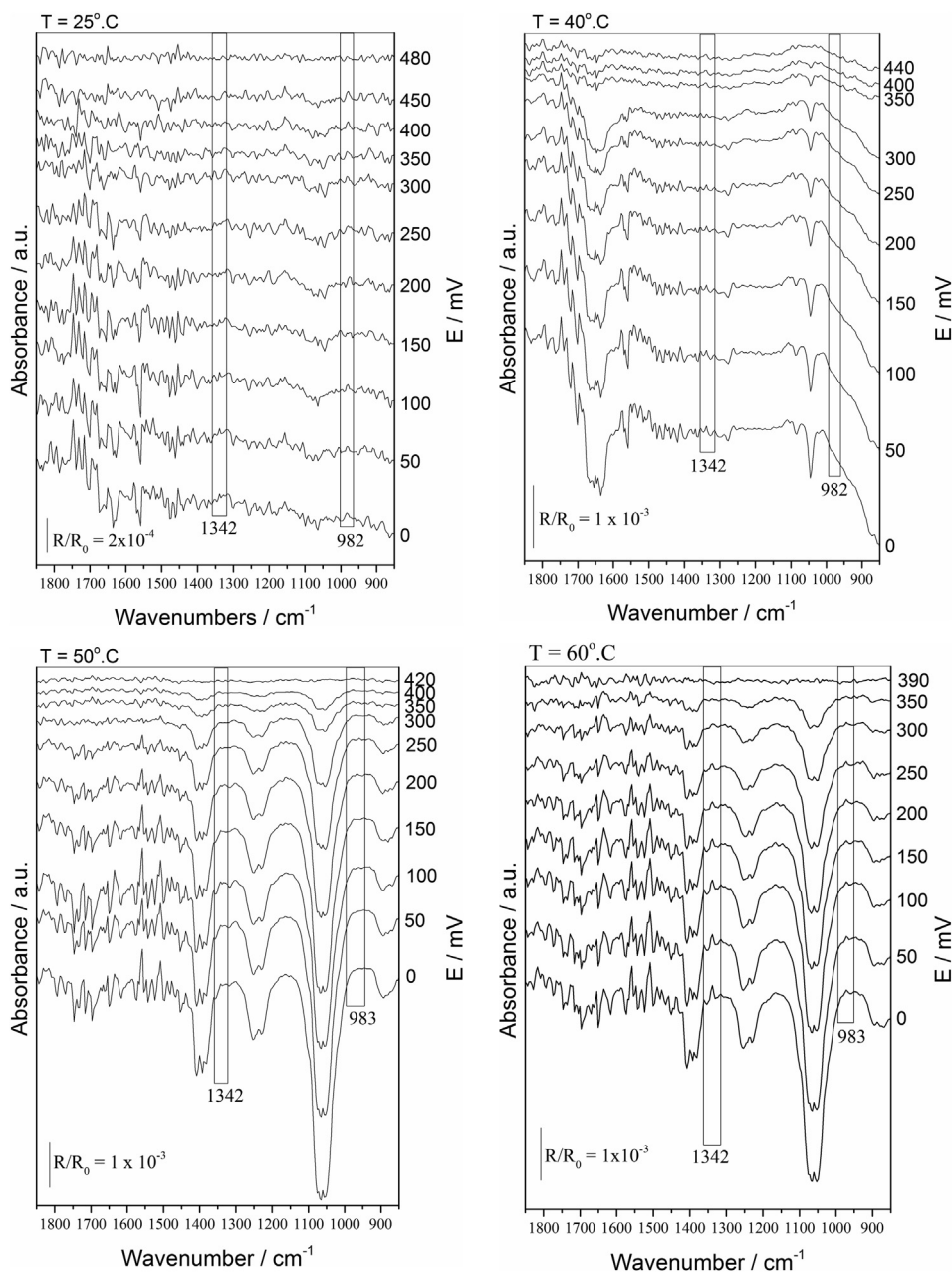


Fig. 3 – *In situ* ATR-FTIR spectra taken at OCV to 0 V in 1 cm² DEFC using 20 wt.% Pt/C Basf electrocatalyst in anode and cathode (1 mg_{Pt} cm⁻²). Nafion[®] 117 was used as the membrane. 2 mol L⁻¹ Ethanol with 0.8 mL s⁻¹ flux. The backgrounds were collected at OCV.

3. Results and discussion

The performance of a single cell adapted in an ATR setup at different temperatures (25, 40, 50, and 60 °C) and with O₂ as the cathodic oxidant is present in Fig. 2. The OCV of the DEFC is about 480 mV at 25 °C and decreases while increase the temperature 440 mV at 40 °C, 420 mV at 50 °C, and 390 mV at 60 °C. However, the maximum power increases with the temperature due to electrode kinetics, membrane conductivity and mass transfer properties that are thermally activated resulting in a performance enhancement [30,31].

OCV and the power density values obtained using this single fuel cell is smaller than the ones described in the literature [32]. Perhaps this could be explained by the electrical resistances, the diffusion of the reactants and other factors [28–31] occurring in the single fuel cell due to the device construction.

The ATR-FTIR spectra (Fig. 3) were acquired during the experiments of polarization curves (Fig. 2) on the anode side of the single fuel operating with ethanol solution at different temperatures. These spectra correspond to solved species in the fuel solution and it is possible to observe the decrease of the ethanol bands (1053, 1075, 1090, 1228, 1242, 1252, 1392 and 1405 cm⁻¹) [33] with the decrease of the potential, and consequently, an increase of the bands resulting from acetaldehyde (1342 cm⁻¹) [34] and acetic acid (≈983 cm⁻¹) formation

[35]. CO₂ signal (2343 cm⁻¹) [36] was not detected in these spectra.

Tayal et al. [37] analyzed the liquid effluent of the ethanol electro-oxidation and determined that acetaldehyde and acetic acid were formed in higher amounts, while the concentration of CO₂ was very low. The FTIR spectra obtained for all temperatures did not suggest the occurrence of additional pathways of oxidation. Using this technique it was possible to observe the same products already described in the literature [9,18,36,38], acetic acid (983 cm⁻¹) and acetaldehyde (1342 cm⁻¹) were chosen to analyze this bands because they correspond to the major products found during the oxidation of ethanol.

Thus, the discussion was focused on those species even though low intensity suffer minor interference with peaks near the regions where they are. The bands in the region of 1050 cm⁻¹, 1550 cm⁻¹ and 1650 cm⁻¹ cited by reviewer as a most significant modifications do not bring indications of selectivity for a particular product according to increase of temperature. The band in the region of 1650 cm⁻¹ is associated water [38] and with the C=O bond [39], for both aldehydes and carboxylic acids. Thus it was not possible to separate the contribution of acetic acid and acetaldehyde. The band around 1550 cm⁻¹ can be attributed to acetic acid [40,41], however both bands are strongly influenced by the absorption of water (around 1598 cm⁻¹) [38,42]. Then, infer something about the variation of these concentration bands

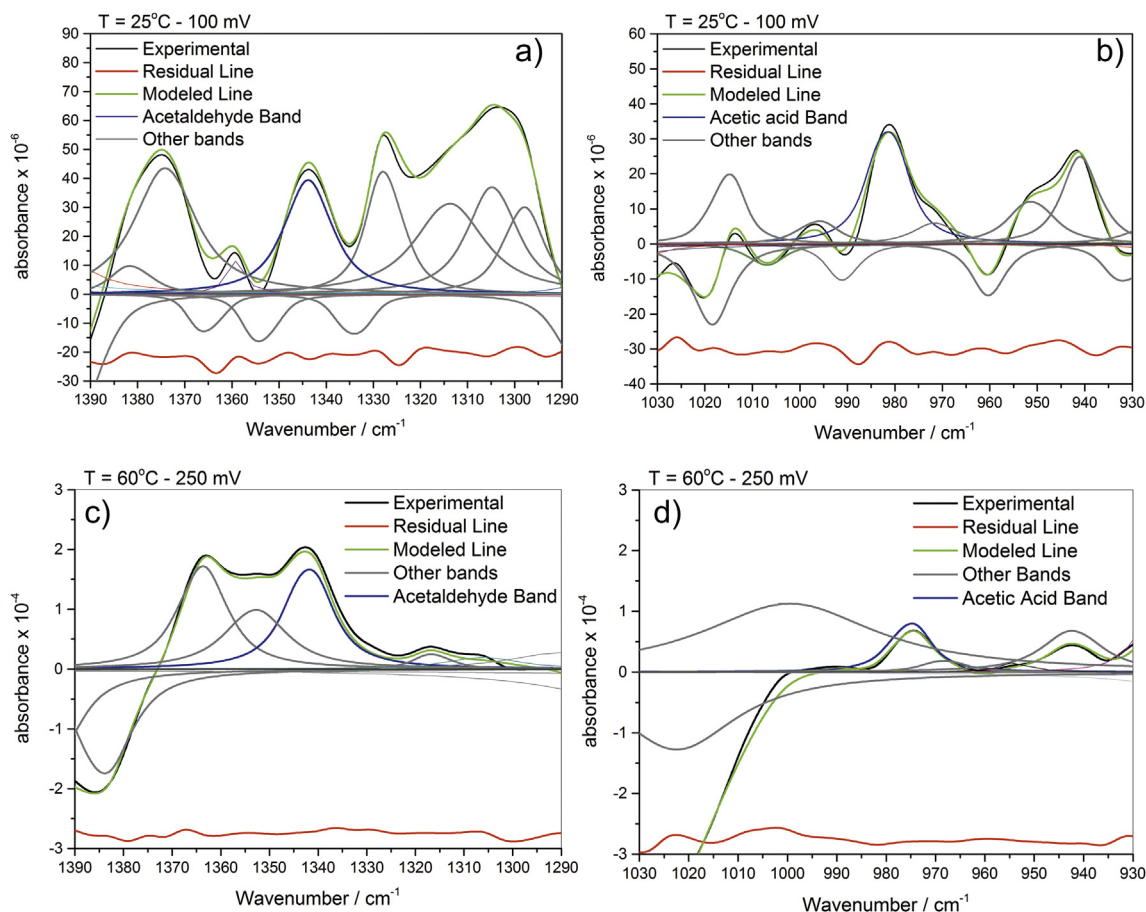


Fig. 4 – Deconvolution in Lorentzian line forms of spectra at (i) 25 °C and 100 mV; (ii) 60 °C and 250 mV.

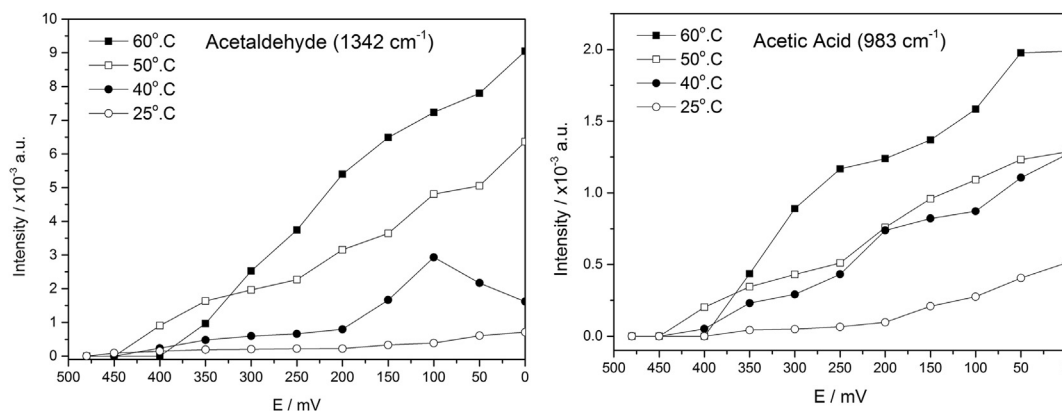


Fig. 5 – Acetaldehyde and acetic acid integrated intensities bands as a function of the potential for temperatures. Data extracted from Fig. 3.

in aqueous solution flow in a fuel cell could cause some error.

During the fuel cell experiments, as the temperature increases there was an increase in the ethanol consumption (negative bands) and consequently there was also an increase in the power density that is a result of the electro-oxidation of ethanol to acetaldehyde and acetic acid. In order to evaluate the temperature effect in the products with the application of different potentials, all bands were deconvoluted to Lorentzian line forms [43] (illustrated in Fig. 4).

Using the deconvolution, the intensity and the width line of each band can be individually analyzed. From Fig. 4 it is possible to observe the acetaldehyde and the acetic acid bands at 25 °C and 60 °C at potential of 100 mV and 250 mV. Considering the region about 1390 cm⁻¹ and 1290 cm⁻¹, both conditions, as well as in all other spectra, only one positive band remains approximately at the same position (1343 cm⁻¹), this band can be associated to CH₃ s-deform of acetaldehyde [34]. Two other bands can also be seen at the spectra, a band at 1365 cm⁻¹ and other at 1381 cm⁻¹, corresponding to acetic acid CH₃ s-deform [35]. It is important to stress that, the acetic

acid center band is shifted, due to the ethanol consumption band at 1392 [33].

Considering the other region about 1030 cm⁻¹ and 930 cm⁻¹, for both conditions, it was also noticed that acetic acid band CH₃ rock centered in 983 cm⁻¹ almost does not suffer interference from other peaks and noise present in this region. Because of this explanation, these bands are chosen to study the acetaldehyde and acetic acid production. Fig. 5 presents the integrated intensities of the acetic acid and acetaldehyde bands.

Taking into account the deconvolution results, it was possible to observe that the onset potential for acetaldehyde and acetic acid production are simultaneous and really close to the OCV for each temperature. This may indicate that the formation of these products can be followed by parallel mechanisms. Giz et al. [36] reported that the production of acetic acid follows two parallel pathways; one of them requires the presence of acetaldehyde as intermediate while in the other one, acetic acid seems to be produced by some mechanism that is still not envisaged at this stage.

To obtain a comparative relation between the power density and the products distribution, the integrated band intensity ratio for the acetic acid and acetaldehyde was plotted at 150 mV. This value corresponds to the maximum power density. Fig. 6 was constructed as function of temperature.

Based on the profiles shown in Fig. 5 it is possible to infer that the increase in the temperature in the range of 25–60 °C results in an increment of power density favoring the production of acetaldehyde on the Pt/C electrode under a fuel cell operating conditions. The power density increase could be explained by the temperature enhancement and increase of the molecular movement, favoring the hydrogen removal from ethanol molecule by the catalyst and then forming acetaldehyde that maintains the alcohol adsorbed to oxidizes it to acetic acid or CO₂.

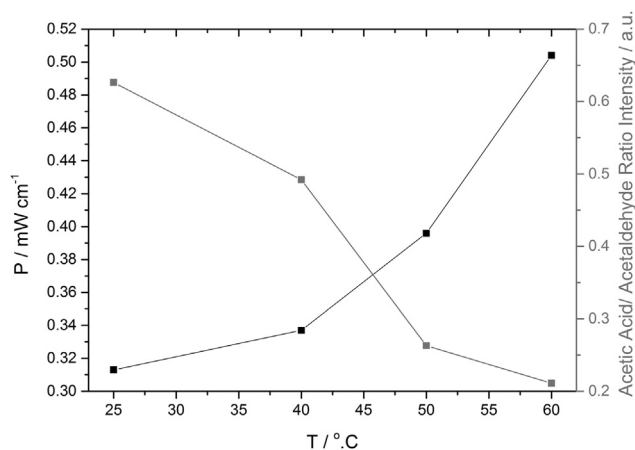


Fig. 6 – Acetic acid/acetaldehyde band intensity ratios at 150 mV (data extracted of Fig. 4), and maximum power density (data extracted of Fig. 2) as a function of the temperature.

4. Conclusion

To our knowledge, this is the first report employing a single fuel cell adapted in an ATR-FTIR spectroscopy setup. The

development proposed permits the study of the ethanol electro-oxidation inside of a DEFC. Using this technique it was possible to investigate the formation of the main species produced during the fuel cell operation, namely acetic acid and acetaldehyde. Therefore, it was also possible to detect the ethanol consumption by the negative bands.

Using a Pt/C electrode it was concluded that there is an increment of power density with the increase of the fuel cell temperature what favors the acetaldehyde production. This single fuel cell adapted on ATR-FTIR approach seems to be a very promising technique for *in situ* fuel cell studies.

Acknowledgments

The authors thank FAPESP (2011/18246-0, 2012/03516-5) and CNPq (150639/2013-9) for financial support.

REFERENCES

- [1] Friedl J, Stimming U. Model catalyst studies on hydrogen and ethanol oxidation for fuel cells. *Electrochim Acta* 2013;101:41–58.
- [2] Antolini E. Catalysts for direct ethanol fuel cells. *J Power Sources* 2007;170:1–12.
- [3] Silva JCM, De Souza RFB, Parreira LS, Neto ET, Calegari ML, Santos MC. Ethanol oxidation reactions using $\text{SnO}_2/\text{Pt/C}$ as an electrocatalyst. *Appl Catal B* 2010;99:265–71.
- [4] Zhu M, Sun G, Xin Q. Effect of alloying degree in PtSn catalyst on the catalytic behavior for ethanol electro-oxidation. *Electrochim Acta* 2009;54:1511–8.
- [5] Xu C, Shen PK. Electrochemical oxidation of ethanol on Pt-CeO₂/C catalysts. *J Power Sources* 2005;142:27–9.
- [6] Pramanik H, Basu S. Modeling and experimental validation of overpotentials of a direct ethanol fuel cell. *Chem Eng Process Process Intensif* 2010;49:635–42.
- [7] Kadirgan F, Beyhan S, Atilan T. Preparation and characterization of nano-sized Pt–Pd/C catalysts and comparison of their electro-activity toward methanol and ethanol oxidation. *Int J Hydrogen Energy* 2009;34:4312–20.
- [8] Antolini E, Perez J. The use of rare earth-based materials in low-temperature fuel cells. *Int J Hydrogen Energy* 2011;36:15752–65.
- [9] De Souza RFB, Parreira LS, Silva JCM, Simões FC, Calegari ML, Giz MJ, et al. PtSnCe/C electrocatalysts for ethanol oxidation: DEFC and FTIR “in-situ” studies. *Int J Hydrogen Energy* 2011;36:11519–27.
- [10] Song S, He C, Liu J, Wang Y, Brouzgou A, Tsiakaras P. Two-step sequence for synthesis of efficient PtSn/Rh/C catalyst for oxidizing ethanol and intermediate products. *Appl Catal B* 2012;119–120:227–33.
- [11] De Souza RFB, Silva JCM, Simões FC, Calegari ML, Neto AO, Santos MC. New approaches for the ethanol oxidation reaction of Pt/C on carbon cloth using ATR-FTIR. *Int J Electrochem Sci* 2012;7:5356–66.
- [12] Henrique RS, De Souza RFB, Silva JCM, Ayoub JMS, Piasentin RM, Linardi M, et al. Preparation of Pt/C-In₂O₃.SnO₂ electrocatalysts by borohydride reduction process for ethanol electro-oxidation. *Int J Electrochem Sci* 2012;7:2036–46.
- [13] Jablonski A, Lewera A. Electrochemical oxidation of ethanol on Pt, Pt-Ru and Pt-Sn nanoparticles in polymer electrolyte membrane fuel cell—role of oxygen permeation. *Appl Catal B* 2012;115–116:25–30.
- [14] Del Colle V, Souza-Garcia J, Tremiliosi-Filho G, Herrero E, Feliu JM. Electrochemical and spectroscopic studies of ethanol oxidation on Pt stepped surfaces modified by tin adatoms. *Phys Chem Chem Phys* 2011;13:12163–72.
- [15] Chang SC, Leung LWH, Weaver MJ. Metal crystallinity effects in electrocatalysis as probed by real-time FTIR spectroscopy – electrooxidation of formic-acid, methanol, and ethanol on ordered low-index platinum surfaces. *J Phys Chem* 1990;94:6013–21.
- [16] Li J-T, Chen Q-S, Sun S-G. In situ microscope FTIR studies of methanol adsorption and oxidation on an individually addressable array of nanostructured Pt microelectrodes. *Electrochim Acta* 2007;52:5725–32.
- [17] Pacheco Santos V, Del Colle V, de Lima RB, Tremiliosi-Filho G. In situ FTIR studies of the catalytic oxidation of ethanol on Pt(1 1 1) modified by bi-dimensional osmium nanoislands. *Electrochim Acta* 2007;52:2376–85.
- [18] Camara GA, de Lima RB, Iwasita T. The influence of PtRu atomic composition on the yields of ethanol oxidation: a study by in situ FTIR spectroscopy. *J Electroanal Chem* 2005;585:128–31.
- [19] Ribeiro J, dos Anjos DM, Kokoh KB, Coutanceau C, Léger JM, Olivi P, et al. Carbon-supported ternary PtSnIr catalysts for direct ethanol fuel cell. *Electrochim Acta* 2007;52:6997–7006.
- [20] Barranco J, Pierna AR. Bifunctional amorphous alloys more tolerant to carbon monoxide. *J Power Sources* 2007;169:71–6.
- [21] Seiler T, Savinova ER, Friedrich KA, Stimming U. Poisoning of PtRu/C catalysts in the anode of a direct methanol fuel cell: a DEMS study. *Electrochim Acta* 2004;49:3927–36.
- [22] Wang H, Jusys Z, Behm RJ. Ethanol electro-oxidation on carbon-supported Pt, PtRu and Pt3Sn catalysts: a quantitative DEMS study. *J Power Sources* 2006;154:351–9.
- [23] James DD, Bennett DV, Li G, Ghumman A, Helleur RJ, Pickup PG. Online analysis of products from a direct ethanol fuel cell. *Electrochem Commun* 2009;11:1877–80.
- [24] Song SQ, Zhou WJ, Zhou ZH, Jiang LH, Sun GQ, Xin Q, et al. Direct ethanol PEM fuel cells: the case of platinum based anodes. *Int J Hydrogen Energy* 2005;30:995–1001.
- [25] Rousseau S, Coutanceau C, Lamy C, Léger JM. Direct ethanol fuel cell (DEFC): electrical performances and reaction products distribution under operating conditions with different platinum-based anodes. *J Power Sources* 2006;158:18–24.
- [26] Melke J, Schoekel A, Gerteisen D, Dixon D, Ettingshausen F, Cremers C, et al. Electrooxidation of ethanol on Pt. An in situ and time-resolved XANES study. *J Phys Chem C* 2012;116:2838–49.
- [27] Melke J, Schoekel A, Dixon D, Cremers C, Ramaker DE, Roth C. Ethanol oxidation on carbon-supported Pt, PtRu, and PtSn catalysts studied by operando X-ray absorption spectroscopy. *J Phys Chem C* 2010;114:5914–25.
- [28] Hind AR, Bhargava SK, McKinnon A. At the solid/liquid interface: FTIR/ATR – the tool of choice. *Adv Colloid Interface Sci* 2001;93:91–114.
- [29] Fringeli UP. ATR and reflectance IR spectroscopy, applications. In: John L, editor. *Encyclopedia of spectroscopy and spectrometry*. Oxford: Academic Press; 1999. p. 94–109.
- [30] Antolini E, Colmati F, Gonzalez ER. Ethanol oxidation on carbon supported (PtSn)alloy/SnO₂ and (PtSnPd)alloy/SnO₂ catalysts with a fixed Pt/SnO₂ atomic ratio: effect of the alloy phase characteristics. *J Power Sources* 2009;193:555–61.
- [31] Alzate V, Fatih K, Wang H. Effect of operating parameters and anode diffusion layer on the direct ethanol fuel cell performance. *J Power Sources* 2011;196:10625–31.
- [32] Song S, Wang Y, Shen P. Thermodynamic and kinetic considerations for ethanol electrooxidation in direct ethanol fuel cells. *Chin J Catal* 2007;28:752–4.

- [33] National Institute of Standards and Technology, NIST. <http://webbook.nist.gov/cgi/cbook.cgi?Name%3dethanol%26Units%3dSI>.
- [34] Hauchecorne B, Terrens D, Verbruggen S, Martens JA, Van Langenhove H, Demeestere K, et al. Elucidating the photocatalytic degradation pathway of acetaldehyde: an FTIR in situ study under atmospheric conditions. *Appl Catal B* 2011;106:630–8.
- [35] National Institute of Standards and Technology, NIST. <http://webbook.nist.gov/cgi/cbook.cgi?Name%3dacetic+acid%26Units%3dSI>.
- [36] Giz MJ, Camara GA. The ethanol electrooxidation reaction at Pt (1 1 1): the effect of ethanol concentration. *J Electroanal Chem* 2009;625:117–22.
- [37] Tayal J, Rawat B, Basu S. Bi-metallic and tri-metallic Pt–Sn/C, Pt–Ir/C, Pt–Ir–Sn/C catalysts for electro-oxidation of ethanol in direct ethanol fuel cell. *Int J Hydrogen Energy* 2011;36:14884–97.
- [38] Simões FC, dos Anjos DM, Vigier F, Léger JM, Hahn F, Coutanceau C, et al. Electroactivity of tin modified platinum electrodes for ethanol electrooxidation. *J Power Sources* 2007;167:1–10.
- [39] Li M, Kowal A, Sasaki K, Marinkovic N, Su D, Korach E, et al. Ethanol oxidation on the ternary Pt–Rh–SnO₂/C electrocatalysts with varied Pt:Rh:Sn ratios. *Electrochim Acta* 2010;55:4331–8.
- [40] Duarte de Farias AM, Barandas APMG, Perez RF, Fraga MA. Water-gas shift reaction over magnesia-modified Pt/CeO₂ catalysts. *J Power Sources* 2007;165:854–60.
- [41] Ho C-H, Shieh C-Y, Tseng C-L, Chen Y-K, Lin J-L. Decomposition pathways of glycolic acid on titanium dioxide. *J Catal* 2009;261:150–7.
- [42] Léger JM, Rousseau S, Coutanceau C, Hahn F, Lamy C. How bimetallic electrocatalysts does work for reactions involved in fuel cells?: example of ethanol oxidation and comparison to methanol. *Electrochim Acta* 2005;50:5118–25.
- [43] Silva JCM, Parreira LS, De Souza RFB, Calegari ML, Spinacé EV, Neto AO, et al. PtSn/C alloyed and non-alloyed materials: differences in the ethanol electro-oxidation reaction pathways. *Appl Catal B* 2011;110:141–7.