

Short communication

Continuous monitoring of CO₂ yields from electrochemical oxidation of ethanol: Catalyst, current density and temperature effects

Azra Ghumman*, Christina Vink,
Omar Yopez, Peter G. Pickup

*Department of Chemistry, Memorial University of Newfoundland,
Elizabeth Avenue, St. John's, Newfoundland, Canada A1B 3X7*

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Abstract

A very simple method for continuous quantification of carbon dioxide yields from electrochemical processes, using a commercial CO₂ detector, is presented. Application of this method to electrochemical oxidation of ethanol greatly decreases the time needed to evaluate catalyst behaviours and allows for efficient elucidation of the factors that influence CO₂ yields. A systematic study of the effects of current density and temperature on the performances of Pt and PtRu anode catalysts has been carried out. The amount of CO₂ produced at each current and temperature has been measured in real time. Yields of CO₂, the product of total oxidation of ethanol, are compared with the limited results reported in the literature for direct ethanol fuel cells.

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1. Introduction

In recent years, direct ethanol fuel cells have received growing attention for their possible use as power sources for mobile applications [1–3]. With its theoretical mass energy density comparable to gasoline (ca. 8.0 kWh kg⁻¹), ethanol can be the fuel of the future as it is renewable and can be produced in large quantities from fermentation of biomass and agricultural products [4]. It can be classified as a green fuel because the emitted carbon dioxide from direct ethanol fuel cells (DEFC) will be consumed by biomass growth without disturbing the environmental CO₂ balance.

Previous research has shown that the performances of DEFCs are quite promising. Ethanol oxidation at a variety of different catalysts and temperatures has been reported. Platinum, and Pt-based catalysts promoted mainly by Ru and Sn have been reported as the most promising catalytic systems. Wang et al. [5]

reported that the performance of a DEFC using a Pt/Ru catalyst was close to that of a direct methanol fuel cell at a temperature of 170 °C. Arico et al. [6] reported a maximum power density of 110 mW cm⁻² using a Pt/Ru catalyst at 145 °C.

Low-temperature operation of DEFCs with various catalysts has been reported in many recent publications [e.g. 7–11]. Using pure oxygen as the oxidant with a Pt/Sn catalyst at 60 °C [10] and 90 °C [7–9,11], maximum power densities of ca. 30 mW cm⁻² and 50–60 mW cm⁻² have been obtained, respectively.

Despite these very promising performances, DEFCs remain impractical for almost all applications because of the products they produce. In their study of the effect of ethanol concentration and temperature on the electro-oxidation of ethanol (ranging from 0.001 to 0.5 mol L⁻¹ and 23 to 60 °C) with a commercial carbon supported Pt catalyst, Wang et al. reported that the total oxidation of ethanol to CO₂ occurred with only 2–13% current efficiency [12]. They found that acetaldehyde and acetic acid were the other major products of the reaction. Several studies have been devoted to identifying the adsorbed intermediates and reaction mechanism of electro-oxidation of ethanol by means of various techniques such as differential electrochemical mass

* Corresponding author. Tel.: +1 709 737 8904; fax: +1 709 737 3702.
E-mail address: aghumman@mun.ca (A. Ghumman).

spectrometry (DEMS), in situ Fourier transform infrared spectroscopy (FTIRS) and electrochemical thermal desorption mass spectroscopy (ECTDMS) [13]. In a recent review, Antolini [13] reported the globally accepted oxidation mechanism of ethanol in acid solution as a scheme of parallel reactions leading to CO₂ as a total oxidation product and acetic acid via acetaldehyde as final partial oxidation products. There are still disagreements however regarding the nature of adsorbed species and on whether acetic acid is a primary product of the partial oxidation or is formed through acetaldehyde.

Regardless of these unresolved issues though, it is clear that the main reaction products are acetaldehyde, acetic acid and CO₂. The product distribution is reported to vary over different catalytic materials and there are inconsistencies between results for similar catalysts. Alloying Pt with other metals such as Ru [14,15], Sn [16–18], Os and Mo has been shown to increase its activity for ethanol oxidation, but selectivity for CO₂ production is generally lower. On the other hand, alloying with Rh increases the selectivity for CO₂ formation but decreases overall activity [19].

There are a relatively small number of reports on product analysis and some are conflicting. Arico et al. [6] have reported a 96% conversion of ethanol to CO₂ for a direct ethanol fuel cell operating at 145 °C. In contrast Wang et al. [5] have reported yields of only 20–40% CO₂ with Pt and PtRu catalysts at 150–190 °C. Pt was found to give slightly higher CO₂ yields than PtRu under most conditions studied.

In a study using GC analysis, Song et al. [11] measured 95:5 and 73:27 acetic acid:acetaldehyde ratios, respectively at PtSn/C and PtRu/C anodes, with only “quite small” amounts of CO₂ detected. Rousseau et al. [18] used HPLC analysis for the product distribution of electro-oxidation of ethanol at 80 °C with Pt/C, PtSn/C and PtSnRu/C anodes. They have reported 20%, 7.7% and 9.8% yields of CO₂, respectively, with acetic acid and acetaldehyde being the other major products of the reaction. Some publications have reported minor amounts of other products like ethyl acetate [5,8,11] and methane [20].

Achieving high CO₂ yields is now one of the main aims of research on the electro-oxidation of ethanol. However, without a clear understanding of mechanisms and the factors that determine the CO₂ yield, the rational design of catalysts remains impractical. The limited results presented in the literature, and the many different catalysts and operating conditions employed, make it difficult to judge what factors might be important. There is therefore a need for systematic studies and for more efficient analytical methods for determining product distributions. Lamy and coworkers [18] have made an important step in this direction with an integrated system for HPLC analysis of CO₂, acetaldehyde and acetic acid from a fuel cell, but this is still a relatively slow batch process. We are therefore developing a flow-through system for continuous monitoring of these products. As a first step, CO₂ monitoring is reported here.

In order to demonstrate the characteristics and value of the CO₂ monitoring system, a systematic study of the effects of varying current density and temperature on the CO₂ yield for electro-oxidation of ethanol at both Pt black and RuPt black catalysts has been carried out. The amount of CO₂ evolved at

each current and temperature in real time has been measured using a low-cost commercial portable CO₂ monitor.

2. Experimental

2.1. Materials

Electrodes used in this work consisted of 4 mg cm⁻² Pt black on TorayTM carbon fibre paper (these electrodes were donated by Ballard Power Systems) and 4.5 mg cm⁻² Pt/Ru (1:1) black on carbon fibre paper (donated by H. Power Corp.). Strips of these electrodes with approximate dimensions of 0.6 cm × 3.5 cm were connected to a home-made Ti clip in a gas-tight fitting that screwed into the body of the electrochemical cell. An area of ca. 1.7 cm² was typically immersed in the electrolyte solution.

2.2. Electrochemical cell

The electrochemical oxidation of ethanol was carried out at constant current with a HA-301 potentiostat/galvanostat (HOKUTO DENKO Ltd.) in a conventional three-compartment glass cell fitted with a condenser to prevent solvent and ethanol loss at elevated temperatures. A platinum wire was used as the counter electrode. An Ag/AgCl reference electrode (0.2224 V vs. SHE) in a Luggin capillary was used to monitor the potential of the working electrode during electrolyses. Before the measurements, the electrolyte solution (1.0 mol L⁻¹ ethanol + 1.0 mol L⁻¹ H₂SO₄) was purged with pure N₂ gas to expel dissolved oxygen gas and then the N₂ flow was maintained during measurements to keep the environment oxygen free and flush the CO₂ produced through the CO₂ monitor. A nitrogen flow rate of 27 mL min⁻¹ was used in all experiments. For experiments at elevated temperatures, the cell was heated with a thermostatically controlled heating mantle. The cell solution was stirred continuously with a magnetic stirrer during all experiments.

2.3. CO₂ monitoring

A Telaire 7001 CO₂ monitor was used for measuring the CO₂ produced in the cell. This CO₂ monitor, which is based on NDIR (nondispersive infrared) technology, has an inlet port for flow-through monitoring. The nitrogen exiting the electrochemical cell was passed through a water (5 mL) trap to remove acetaldehyde for GC analysis before entering into the sample chamber of the CO₂ monitor. The concentration of CO₂ was displayed in ppm on the carbon dioxide detector display window, and could be recorded as a function of time with the monitor's HOBO data collection system. However, because of the limited resolution of the HOBO and the low levels of CO₂ produced, all data reported here were collected manually from the monitor's display. The detector exhibits a significant baseline response (typically 80–90 ppm at 27 mL min⁻¹) due to atmospheric CO₂ that can be minimized by sealing the diffusion vents. However, this was found not to significantly influence the accuracy of the measurements.

2.4. Calibration of the CO₂ detector

To calibrate the CO₂ detector, known amounts of NaHCO₃ were added to the cell solution (1.0 mol L⁻¹ ethanol + 1.0 mol L⁻¹ H₂SO₄ solution) and the evolved CO₂ (ppm) was measured with the detector. A plot of the measured moles of CO₂, based on integration of the CO₂ detected before the readings returned to baseline, against the moles of NaHCO₃ added had a slope of 1.04 ($R^2 = 0.995$) indicating that the factory calibration of the instrument was accurate, and that all of the CO₂ produced in the cell could be detected. At the low CO₂ levels being monitored (10⁻⁷ to 10⁻⁵ mol), the uncertainty determined in these experiments and the electrolysis experiments, was better than the manufacturers specification of ± 50 ppm. This is presumably a result of integrating the individual CO₂ readings over a number of minutes (typically 10 min) and the background subtraction.

3. Results

3.1. Effect of varying current on the rate of CO₂ formation at Pt and PtRu

The electro-oxidation of ethanol (1.0 mol L⁻¹ ethanol in 1.0 mol L⁻¹ H₂SO₄) was carried out at room temperature with the applied current varied from 10 mA to 50 mA (ca. 6–30 mA cm⁻²). Before passing current, the cell solution was purged with N₂ flow for 15–20 min. Once the CO₂ ppm reading became steady (background ppm), a selected current was allowed to pass through the electrolyte solution. Evolved CO₂ (ppm) was recorded at 1 min intervals. Once a constant or maximum value of CO₂ ppm was obtained the current was switched off allowing the CO₂ ppm to return to the baseline. Baseline values were subtracted from each set of experimental data to get the actual values. Fig. 1 shows typical uncorrected data for a series of experiments at different currents. The amount of CO₂ (ppm) detected in the nitrogen stream exiting the electrochem-

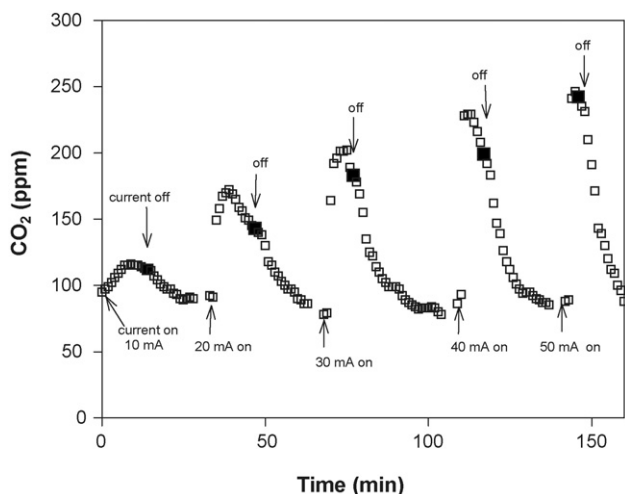


Fig. 1. CO₂ concentrations detected during electro-oxidation of 1.0 mol L⁻¹ ethanol in 1.0 mol L⁻¹ H₂SO₄ at a Pt/Ru electrode at 25 °C.

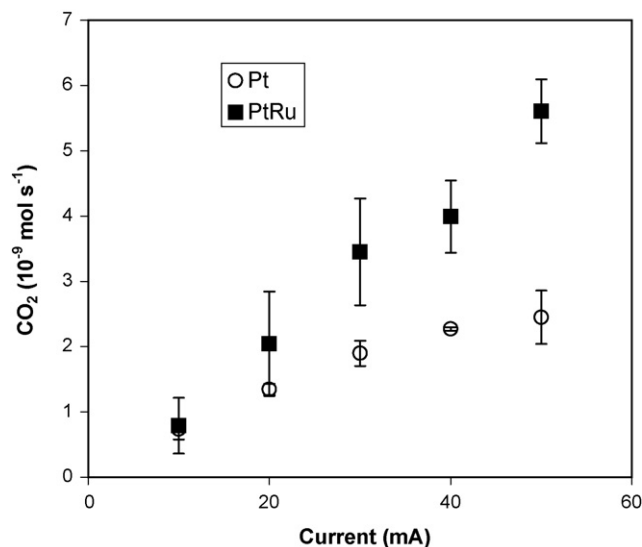


Fig. 2. Effect of varying current on the rate of formation of CO₂ during the electro-oxidation of ethanol (1.0 mol L⁻¹ ethanol in 1.0 mol L⁻¹ H₂SO₄ at 25 °C) at Pt and PtRu electrodes. Error bars are standard deviations for two (Pt) and three (PtRu) electrodes.

ical cells is plotted versus time. The potential of the working electrode during these electrolyses rose from ca. 0.3–0.4 V versus Ag/AgCl at 10 mA to ca. 0.6–0.7 V at 50 mA for both types of electrode.

Average rates of CO₂ formation over the duration of each electrolysis were calculated using the integral of the CO₂ ppm readings, the electrolysis time, and the nitrogen flow rate (27 cm³ min⁻¹ at NTP). Fig. 2 shows a comparison of rates of CO₂ formation at varying currents at Pt and PtRu electrodes. To check the reliability of the data, the experimental runs were repeated with new electrodes and averages and standard deviations are shown in Fig. 2. With the same catalytic material the results showed the same trend for each run with only minor irregularities.

The rate of CO₂ formation at Pt increased almost linearly with increasing current from 10 to 30 mA and thereafter at 40 and 50 mA the increases were smaller, with little change between 40 and 50 mA, showing that the activity of the catalyst for total oxidation was dropping, presumably due to poisoning of the active sites.

The rate of CO₂ formation at the PtRu catalyst increased linearly with increasing current over the full range investigated. Rates of CO₂ production were higher at current densities >10 mA than at Pt, with the difference increasing with increasing current. This suggests that ruthenium enhances the rate of CO₂ formation by oxidation of strongly bound CO as reported by Fujiwara et al. [15].

Average yields of CO₂ from the data in Fig. 2 are presented with relative standard deviations in Table 1. At Pt, the yield of CO₂ dropped significantly with increasing current, while it increased at the PtRu over the same current range. Consequently, the yield at 50 mA at the PtRu electrode was more than double that at the Pt electrode.

Table 1

Average CO₂ % yields and standard deviations obtained from two runs with Pt and three runs with PtRu catalyst under same reaction conditions (room temperature)

Current (mA)	Pt % CO ₂	Pt/Ru % CO ₂
10	4.28 ± 0.93	4.6 ± 2.5
20	3.90 ± 0.25	5.9 ± 2.3
30	3.66 ± 0.37	6.7 ± 1.6
40	3.28 ± 0.39	5.78 ± 0.80
50	2.81 ± 0.45	6.49 ± 0.57

3.2. Effect of varying temperature on the rate of CO₂ formation at Pt and PtRu electrodes

The effect of varying temperature on the rate of CO₂ formation was studied over a range of temperatures (25–95 °C) keeping the current constant at 10 mA. Electrode potentials ranged from 0.28 to 0.36 V versus Ag/AgCl for Pt and 0.25 to 0.42 V versus Ag/AgCl for PtRu. Fig. 3 shows the average % yield of CO₂ produced at each temperature for two different Pt and PtRu electrodes. Standard deviations are high for these data because of the small amounts of CO₂ produced at 10 mA.

The CO₂ yield at the Pt catalyst increased approximately linearly with increasing temperature, from ca. 4 to 13% while the yield at PtRu remained constant at 6–7%.

3.3. Time dependence of CO₂ yields

Fig. 4 shows CO₂ yields for multiple electrolyses using the same electrode. In each experiment, the current was applied until

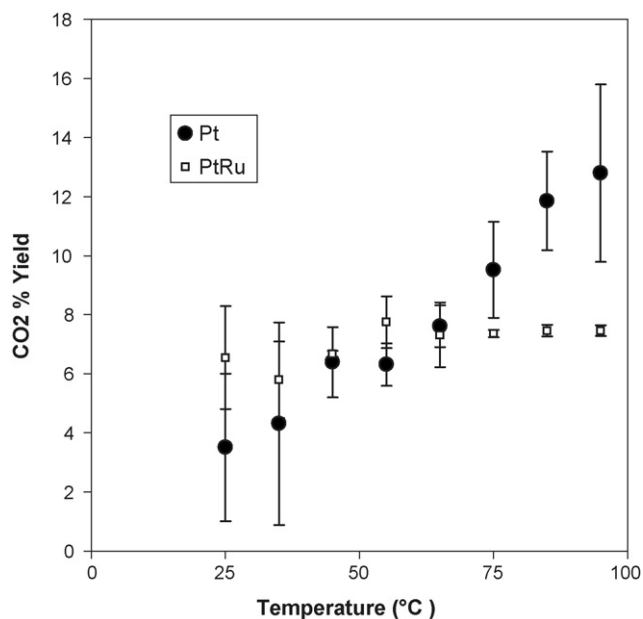


Fig. 3. Comparison of % yields of CO₂ from the electro-oxidation of 1.0 mol L⁻¹ ethanol in 1.0 mol L⁻¹ H₂SO₄ at Pt and PtRu (1:1) at varying temperature and constant current (10 mA). Averages and standard deviations for two electrodes of each type tested under same reaction conditions are shown.

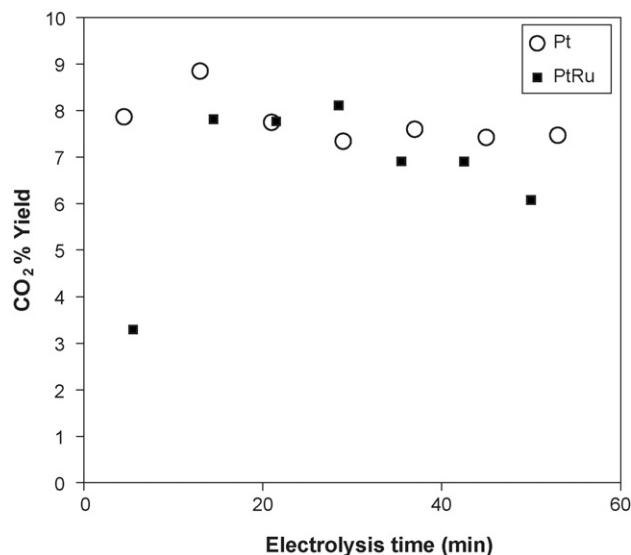


Fig. 4. CO₂ yields for multiple electrolyses (50 mA and 95 °C) using the same electrode.

a steady CO₂ reading was obtained (7–11 min), turned off until the CO₂ level returned to background, and then reapplied. Seven consecutive electrolyses were performed with each electrode. The time axis in Fig. 4 shows the cumulative electrolysis time, with the average CO₂ yield for each electrolysis plotted at the mid point of that electrolysis.

The data in Fig. 4 shows that under the conditions used (50 mA and 95 °C), the yield of CO₂ was fairly constant at ca. 7–8% for both the Pt and PtRu electrodes, except for an anomalously low yield in the first electrolysis at the PtRu electrode. This low reading illustrates an activation process that was commonly observed with new electrodes, and this effect is also seen to a small extent in the data for the Pt electrode in Fig. 4. Both electrodes also exhibited a slight decrease in yield with time, following the initial activation.

4. Discussion

The CO₂ yields reported in the literature for ethanol oxidation at 80 °C are compared with the results from this work in Table 2. All of the literature results in Table 2 were obtained by analysis of products from a DEFC with a polymer (Nafion) electrolyte, and are therefore not directly comparable with ours, which were obtained by electrolysis of ethanol in a liquid electrolyte (1 M H₂SO₄(aq)). Nevertheless, the yields that we have obtained are similar to the literature values, and we see the same qualitative difference between pure Pt and the PtRu alloy. Specifically, the literature yield for CO₂ at Pt is 20% [18,22], while PtRu is reported to produce only 6.7% CO₂ [4] under similar conditions. The difference between Pt and PtRu is somewhat smaller in this work (13% vs. 7%), and this may be due to adsorption of SO₄²⁻ on the Pt electrode in the H₂SO₄ electrolyte. The lower yields of CO₂ at alloy electrodes have been attributed to a decrease in the average Pt cluster size on the catalyst surface due to the presence of the foreign atoms [18], and SO₄²⁻ could play a similar role.

Table 2
Summary of yields of CO₂ from electrochemical oxidation of ethanol at Pt-based catalysts

Catalyst (alloy atom ratio)	Temperature (°C)	CO ₂ (% yield)	Reference
60% Pt on C	80	20 ^a	[22]
60% Pt–Sn on C (9:1)		8 ^a	
60% Pt on C	80	20 ^b	[18]
60% Pt–Sn on C (9:1)		7.7 ^b	
60% Pt–Sn–Ru (86:10:4)		9.8 ^b	
Pt–Ru on C (1:1)	80	6.7	[4]
Pt–Sn on C (4:1)		8.4	
Pt	85	13 (11.85) ^c	This work
Pt–Ru (1:1)	85	7.32 (7.29) ^c	This work

^a $I = 8$ and 32 mA cm^{-2} for Pt and Pt–Sn, respectively.

^b $E = 0.30$ for Pt, and 0.45 – 0.55 V for Pt–Sn and Pt–Sn–Ru.

^c Average of %Y at 75 and 85 °C; current = 10 mA; $E = 0.4$ – 0.45 V (Pt) and 0.20 – 0.30 V (PtRu).

At lower temperatures the difference between Pt and PtRu reverses (Fig. 3), particularly at higher current densities (Table 1). This is due to a decreasing CO₂ yield at Pt with decreasing temperature, while the yield at PtRu remains constant. Since increasing temperature promotes CO desorption from the electrode, these results suggest that adsorbed CO blocks the total oxidation of ethanol to a greater extent on Pt than PtRu, and this is consistent with the well-known ability of Ru to release CO from Pt-based catalysts at low potentials by the so-called bifunctional mechanism. The decreasing yield of CO₂ with increasing current density at Pt (Table 1) is also consistent with the rate of total oxidation of ethanol at Pt being limited by the CO coverage (rather than the current). For PtRu, the CO₂ yield is independent of both current and temperature, indicating that the rates of all ethanol oxidation pathways are affected similarly by these parameters.

The above observations are fully consistent with the hypothesis [21] that foreign atoms (Ru in this case) in/on the Pt surface inhibit ethanol adsorption by reducing the number of neighbouring active sites. Thus the benefit of Ru for oxidizing adsorbed CO is important at lower temperatures, whereas for temperatures at which thermal CO desorption becomes more important, the inhibiting effect on ethanol adsorption becomes more important.

Finally, it is important to comment on the precision of the CO₂ measurements reported here. The relative standard deviations for replicate measurements on the same electrode for Fig. 4 (discounting the first point for PtRu) are 6.2% for Pt and 10.6% for PtRu. The added uncertainty for PtRu is clearly due in part to a systematic decrease in CO₂ yield, and so the precision of the measurement technique can be estimated to be ca. 6% under the conditions of these experiments. The results in Table 1 include additional errors due to variations between electrodes, which will include differences in the amounts of active material on each strip of carbon paper and variations in the extent and rate of poisoning. These variations appear to be much greater for the PtRu electrodes, which were from a different source than the Pt electrodes, and

also show more variation with time (Fig. 4). It is also clear from the data in Table 1 that relative errors in the CO₂ measurements are highest at low currents when the rate of CO₂ formation is lower, as would be expected. More precise results at low currents can be obtained by using longer data collection periods, and sealing the detector to decrease the background signal.

The CO₂ detector described here has also been used to successfully monitor CO₂ production from a direct ethanol fuel cell, with acetic acid and acetaldehyde analysis by gas chromatography. The results of this work will be reported shortly.

5. Conclusions

A commercial CO₂ detector has been shown to provide accurate and precise measurement of CO₂ from electrochemical ethanol oxidation in real time by a simple and efficient procedure. This methodology is well suited for screening of catalytic materials, determining the factors that determine CO₂ yields and investigating changes with time. Its use will greatly simplify and speed-up the development of catalysts that provide high CO₂ yields and therefore high efficiencies in direct ethanol fuel cells.

Acknowledgements

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