



Short communication

Online analysis of carbon dioxide from a direct ethanol fuel cell

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ABSTRACT

Carbon dioxide yields from a direct ethanol fuel cell have been monitored by using a commercial infrared CO₂ monitor. The time dependence is reported as a function of temperature, current density, and anode catalyst (Pt vs. PtRu). Yields increased strongly with temperature, with a Faradaic yield of 76% being obtained at 100 °C with a Pt black anode. PtRu gave lower yields than Pt by a factor of ca. 3 at 80 and 100 °C, but higher yields than Pt at ambient temperature. The superior ability of PtRu to strip adsorbed CO is important at low temperatures, but not a key factor at 100 °C.

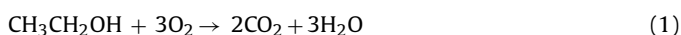
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1. Introduction

Over the past decade, the study of electro-oxidation of ethanol in fuel cells has attracted growing attention due to the development of ethanol as an alternative fuel [1–4]. Fuel cells offer efficiency advantages over conventional power sources, and as a fuel ethanol is advantageous compared to methanol due to its low toxicity. Moreover it has a comparable theoretical mass energy density (8.0 kWh kg⁻¹) to gasoline, and is renewable.

The slow kinetics for ethanol oxidation at temperatures compatible with proton exchange membrane fuel cell (PEMFC) technology and low selectivity for total oxidation to CO₂ are major challenges in the practical application of direct ethanol fuel cells (DEFCs). Much effort has therefore been devoted to finding a suitable catalyst that can improve cell performance and increase the yield of CO₂, while keeping the parallel reactions to acetaldehyde and acetic acid to a minimum [2].

Platinum and Pt promoted by ruthenium and tin have been reported as the most promising catalysts [2]. Activation of ethanol is more challenging compared to methanol as ethanol contains two covalently bonded carbon atoms. To achieve maximum electrical energy, it is necessary to break the C–C bond to form CO₂ as the sole reaction product according to following equation for the cell reaction:



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This total oxidation reaction of ethanol involves the transfer of 12 electrons. However, this is not the sole reaction occurring at Pt catalysts under the acidic conditions of a PEMFC. Reactions forming partial oxidation products, almost exclusively acetic acid and acetaldehyde, have been reported to occur in preference to CO₂ formation [5,6]. Much effort had been devoted to identifying adsorbed intermediates and reaction mechanisms using a combination of electrochemical and spectroscopic techniques, such as differential electrochemical mass spectroscopy (DEMS) [7–16] and Fourier transform infrared (FTIR) spectroscopy [14,17–26].

Only a few publications have reported product distributions from DEFCs [5,6,27–30]. An integrated system for HPLC analysis of CO₂, acetaldehyde and acetic acid from a fuel cell has been described by Lamy et al. [6,22] and used by others in a modified form [30]. Use of a commercial CO₂ detector for continuous monitoring of CO₂ from ethanol oxidation in a conventional liquid electrolyte cell [31] and a fuel cell fed with ethanol vapor [32] has recently been reported. This methodology has been adapted here for use with a conventional liquid feed DEFC operated at both ambient and elevated temperatures.

The goals of this work were primarily to investigate the dependence of the CO₂ yield from the DEFC on temperature and other cell operating conditions for Pt and PtRu catalysts. The focus on temperature stems from a report [27] of a 96% chemical yield (99% Faradaic yield) of CO₂ from a DEFC operating at 145 °C. This temperature is not sustainable for the Nafion-based membrane that was employed, and so it is important to measure and improve yields at sustainable temperatures. The focus here is on the CO₂ yield because this is what determines the practical feasibility of a DEFC. Yields of CO₂ have to be close to 100% for acceptable efficiency, and to minimize the need for destruction or collection of byproducts. Analysis of

acetic acid, acetaldehyde and other products from the DEFC is of secondary importance and much more difficult to perform accurately because of fuel and product crossover. These issues will be addressed elsewhere.

2. Experimental

2.1. Materials and apparatus

Electrodes used in this work consisted of 4 mg cm^{-2} Pt black on TorayTM carbon fiber paper (donated by Ballard Power Systems), and 5.5 mg cm^{-2} PtRu (1:1) black on carbon fiber paper (donated by the former H Power Corp.). Anhydrous ethanol was obtained from Commercial Alcohols Inc.

2.2. MEA preparation

The Nafion 115 membranes were cleaned at 80°C with 3% H_2O_2 , 1 M H_2SO_4 (aq) and deionized water, and stored in deionized water. Membrane and electrode assemblies (MEA) were prepared by hot pressing a 5 cm^2 anode and a 5 cm^2 cathode (4 mg cm^{-2} Pt black) onto a Nafion 115 membrane at 200 kg cm^{-2} and 135°C for 90 s.

2.3. Fuel cell operation and CO_2 analysis

A 5 cm^2 commercial (Fuel Cell Technology Inc.) fuel cell was operated with an anode feed of 0.5 or 1.0 mol L^{-1} ethanol solution at flow rates ranging from 0.2 to 1.6 mL min^{-1} . The cathode feed was either O_2 at 30 mL min^{-1} or N_2 at 16 mL min^{-1} (to provide a dynamic hydrogen electrode). For operation of the cell at elevated temperatures, the fuel was preheated to 80°C for 80°C operation or 120°C for 100°C operation. The high preheating temperature at 100°C was to ensure that the cell was fed with an ethanol plus water vapor.

Electrochemical measurements were made using a Solartron 1286 electrochemical interface. Carbon dioxide produced in the cell was measured by using a Telaire 7001 CO_2 monitor based on non-dispersive infrared (NDIR) technology. For operation of the cell at ambient temperature, the ethanol plus products solution from the anode outlet of the fuel cell was passed into a N_2 gas (16 mL min^{-1}) stream. Transfer of the dissolved carbon dioxide into the nitrogen flow was facilitated by passing the two-phase mixture through a glass coil. A T-junction then directed the nitrogen flow to the CO_2 monitor and the liquid waste to a beaker.

The higher levels of CO_2 produced at elevated temperatures (80 and 100°C were used) caused wide fluctuations in the CO_2 readings if the CO_2 was separated from the liquid anode exhaust with the glass coil. In order to dampen these fluctuations, the coil was not used for high temperature operation of the cell. Instead, the exhaust was collected in a 100 mL round flask that was continuously flushed with N_2 at 90 mL min^{-1} , which was then passed through the CO_2 detector.

All yields reported in this work are Faradaic yields based on the charge generated by the fuel cell. Thus, the yield of CO_2 ($n=6$) is calculated as:

$$\text{CO}_2 \text{ yield} = \left(\frac{6 \times \text{moles of CO}_2}{\text{moles of electrons}} \right) \times 100\%$$

3. Results

3.1. Operation of the DEFC at ambient temperature

Carbon dioxide levels exiting the anode of the DEFC were monitored by using a commercial IR-based detector. This method has been previously used to measure CO_2 produced in a conventional

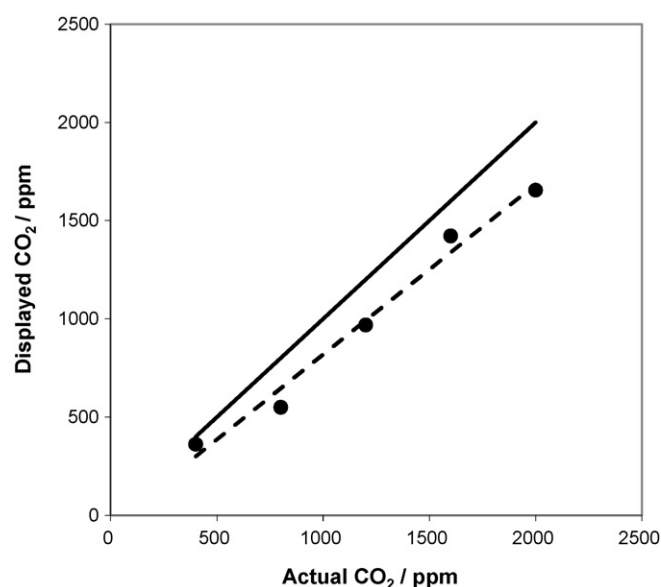


Fig. 1. Calibration plot for dissolved carbon dioxide.

electrochemical cell [31], by monitoring CO_2 levels in the purge gas, and CO_2 levels exiting a vapor fed DEFC [32]. The difference here is that the CO_2 had to be extracted from the liquid exhaust from the fuel cell into a nitrogen gas stream for measurement with the CO_2 detector. The carbon dioxide measurement was found to be dependent on a number of factors, such as the nitrogen gas flow rate that is used to control the concentration of the CO_2 , and the mixing time between nitrogen gas and liquid (controlled by the length of mixing coils). It was found that a nitrogen flow of 16 mL min^{-1} gave a suitable balance between the CO_2 readings, which should be maximized, and the background CO_2 reading, which should be minimized. A 100 cm coil length provided a suitable balance between efficiency and response time.

The system was initially calibrated to correct for the extraction efficiency. Calibration solutions were prepared by dissolving known amounts of CO_2 gas in deionized water. The CO_2 detector was calibrated by passing CO_2 solutions of known concentrations through the system (without the fuel cell). The results are presented in Fig. 1. For 100% extraction of the carbon dioxide into the nitrogen stream, the slope would be 1 and the plot would pass through the origin, as indicated by the solid line. The experimental values for carbon dioxide were all slightly lower than the expected values indicating that the extraction had an efficiency of only ca. 83%. All CO_2 readings from the fuel cell when operated at ambient temperature with the separation coils were corrected for this extraction efficiency.

Correction for the background reading (at zero current) due to diffusion of atmospheric CO_2 into the detector was not applied because linear regression of the calibration plot (Fig. 1) gave a zero intercept, within experimental error. The explanation for this is that the effect of atmospheric CO_2 decreases as the CO_2 level in the sample increases. Over the range covered in Fig. 1, it is clearly insignificant.

Initial experiments focused on operation of the DEFC at ambient temperature since ultimately it would be desirable to develop low temperature DEFCs for consumer products. The only CO_2 yield data currently available for low temperatures ($<80^\circ\text{C}$) is for pulse operation with an impractical vapor feed [32], and for liquid electrolyte cells. Pt and PtRu catalysts were used here since PtRu is well known to be a more effective anode catalyst for DEFCs than Pt in terms of the current and power densities that can be produced, but it is not clear how the presence of Ru influences the efficiency in terms of CO_2 production.

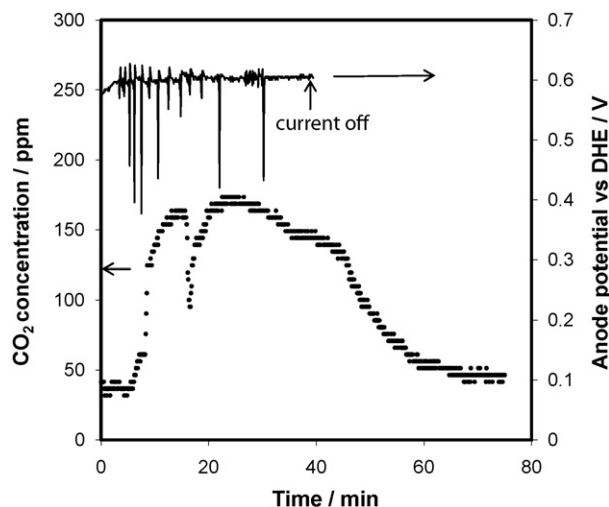


Fig. 2. CO₂ concentration and anode potential vs. time at 40 mA for a DEFC with a Pt anode. The cell was operated at ambient temperature with 1 M ethanol at 0.4 mL min⁻¹ and dry N₂ at 16 mL min⁻¹.

Fig. 2 shows a CO₂ concentration vs. time plot for operation of the cell at a current density of 8 mA cm⁻² with a Pt anode. After a ca. 5 min delay due to the dead volume of the detection system, the CO₂ reading rose to a maximum of 173 ppm. There was a slight decrease in the CO₂ level after ca. 25 min, and then a decay to the baseline reading after the current was terminated. The peak Faradaic yield of CO₂ in this experiment was 3.3%, with an average of 3.0% from 10 to 40 min. During the experiment, the anode potential was steady at ca. 0.60 V vs. DHE.

Fig. 3 shows a CO₂ concentration vs. time plot for operation of the cell at a current density of 8 mA cm⁻² with a PtRu anode. There are significant differences relative to the data in Fig. 2 for the Pt anode. The CO₂ readings rose much more rapidly and reached a much higher level (398 ppm vs. 173 ppm) than at the Pt anode, but then decayed much more rapidly. The peak CO₂ yield was 7.6%, with an average from 3 to 20 min of 4.7%. At 20 min, the CO₂ yield at the PtRu anode (3.0%) was close to the average for the Pt anode.

The increased initial CO₂ yield at the PtRu anode is most likely due to more efficient stripping of adsorbed CO that had accumulated on the electrode, by adsorption and dissociation of ethanol

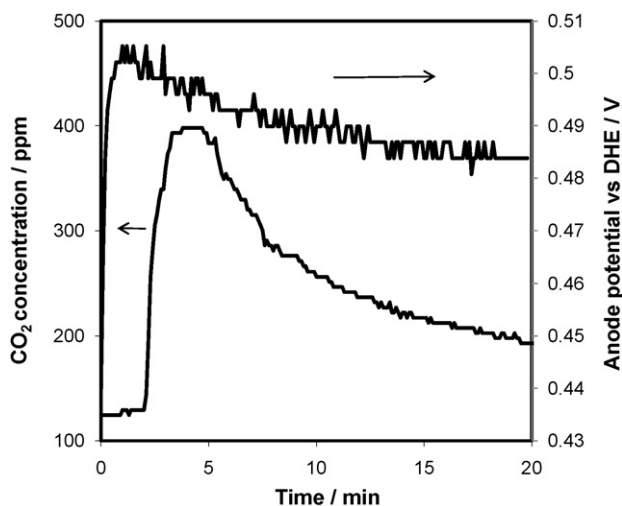


Fig. 3. CO₂ concentration and anode potential vs. time at 40 mA for a DEFC with a PtRu anode. The cell was operated at ambient temperature with 1 M ethanol at 0.4 mL min⁻¹ and dry N₂ at 16 mL min⁻¹.

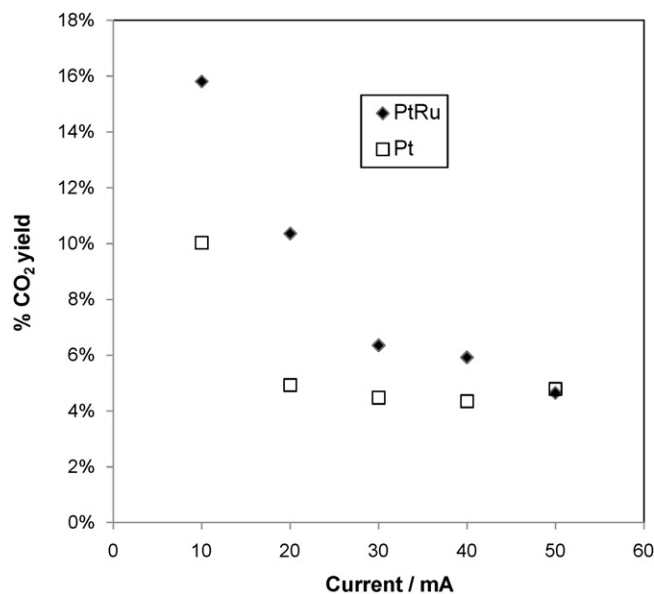


Fig. 4. Comparison of CO₂ yields vs. current density for ambient temperature DEFCs with Pt and PtRu catalysts.

[1], before the current was initiated. PtRu is well known as an effective bi-functional catalyst for CO stripping at lower potentials than on Pt. It can be seen from the potential traces in Figs. 2 and 3 that the anode potential was significantly lower for the PtRu electrode (ca. 0.49 vs. 0.60 V), which supports this hypothesis.

CO₂ yields were monitored over a range of current densities for both catalysts. The results are summarized in Fig. 4, which shows yields averaged over the best 10 min. The CO₂ vs. time profiles were generally similar to those shown in Figs. 2 and 3, and so a 10 min time window provides a suitable balance between peak and long-term performances. Yields of CO₂ at PtRu peaked quickly (within 5 min) and then decayed as seen in Fig. 3. Both the peak yield and average yield over the best 10 min fell sharply with increasing current. This is consistent with the peak in CO₂ production being due to stripping of adsorbed CO. At higher currents, the adsorbed CO would be oxidized to CO₂ more rapidly and produce higher peak CO₂ readings. However, the anode potential would be higher and this would cause faster oxidation of ethanol to acetaldehyde and acetic acid, decreasing the yield of CO₂ if the potential dependence is stronger. Since the amount of CO initially on the electrode is fixed, its oxidation would contribute less at higher currents to the average over a fixed time.

At the Pt electrode, peak yields were lower than for PtRu at all currents, but yields decayed more slowly. In several cases (20 and 50 mA), peak yields were reached after more than 25 min. The average yield over the best 10 min was higher at 10 mA than at higher currents, but then became independent of current. This suggests that there is a smaller contribution from CO stripping.

3.2. Operation of the DEFC at elevated temperatures

Fig. 5 shows CO₂ yields and cell voltages as a function of time for operation of a DEFC with a Pt black anode at a constant current of 200 mA at two different cell temperatures. At 80 °C, the average yield of CO₂ was ca. 15%, which is much higher than the 4.8% seen at 50 mA at ambient temperature (Fig. 4). Increasing the cell temperature to 100 °C, produced an even greater increase in CO₂ yield, with an average of 76% obtained over 55 min of operation. This increase in yield appears to be due in part to the fact that at 100 °C the cell was operating on a mixed water + ethanol vapor, since higher yields were obtained at 80 °C by use of a vapor feed. This is illustrated in

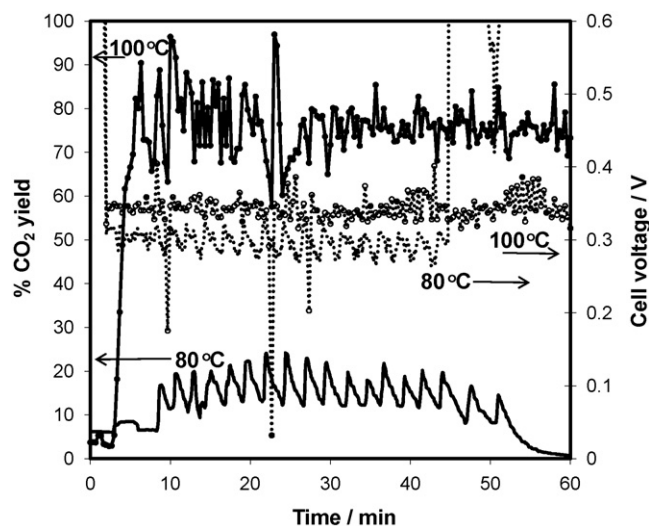


Fig. 5. CO₂ yield and cell potential vs. time at 200 mA for a DEFC with a Pt anode. The cell was operated at 80 or 100 °C, as specified, with 0.5 M ethanol at 0.2 mL min⁻¹ and dry O₂ at 30 mL min⁻¹.

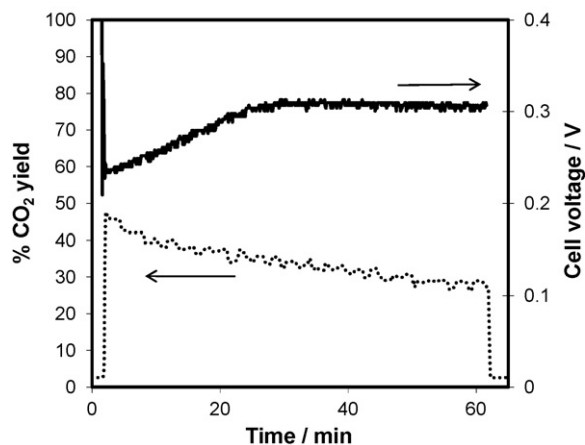


Fig. 6. CO₂ yield and cell potential vs. time at 200 mA for a DEFC with a Pt anode. The cell was operated at 80 °C with an ethanol/water/N₂ gas mixture and dry O₂ at 30 mL min⁻¹. The ethanol/water/N₂ mixture was generated by passing N₂ at 60 mL min⁻¹ through 0.5 M ethanol at 80 °C.

Fig. 6, where an average CO₂ yield of 34% over 1 h was obtained at 80 °C with ethanol and water vapor in N₂ fed to the anode.

Repetition of the experiment at 100 °C with different MEAs gave significant variations in the average CO₂ over 1 h, with a range of 51–81% for 5 experiments. Operation of the cell at temperatures above 100 °C (at ambient pressure) resulted in decreased CO₂ yields and a decay in the cell voltage, probably due to dehydration of the MEA. Operation of the cell with backpressure was not attempted.

Operation temperature had a much less pronounced effect on the CO₂ yield when PtRu was used as the anode catalyst. Results at 100 °C are shown in Fig. 7. The average CO₂ yield was only 25%. Furthermore, at this temperature the performance of the cell was not significantly better with the PtRu catalyst relative to Pt (compare the cell voltage traces in Figs. 5 and 7).

4. Discussion

Table 1 summarizes results from this work and the literature on the analysis of CO₂ levels from DEFCs. Results for a conventional fuel cell at ambient temperature are reported here for the first time.

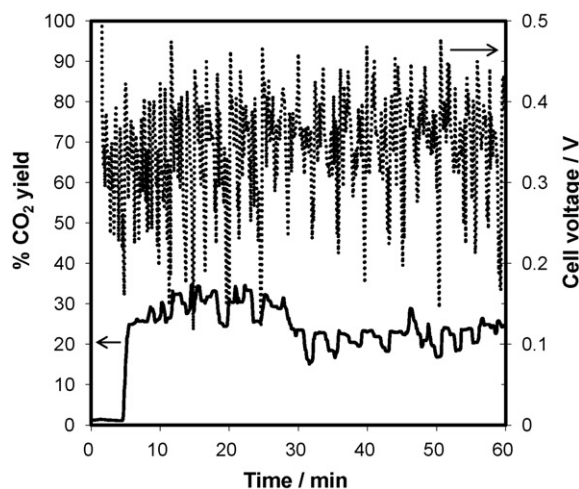


Fig. 7. CO₂ yield and cell potential vs. time at 200 mA for a DEFC with a PtRu anode. The cell was operated at 80 °C with 0.5 M ethanol at 0.2 mL min⁻¹ and dry O₂ at 38 mL min⁻¹.

The CO₂ yields of 4–6% indicate that the C–C bond of ethanol can be broken at a significant rate at ambient temperature. CO₂ production at short times and low currents is dominated by stripping of CO from the anode surface, as previously observed [10,32], but sustained CO₂ production of ca. 3–4% was observed for at least 1 h with a Pt anode. The results at ambient temperature are consistent with the 3–7% range reported for ethanol oxidation in conventional liquid electrolyte cells [10,14,31]. Much higher CO₂ yields at ambient temperature have been reported for a vapor fed DEFC under current or potential pulsing conditions [32].

At 80 °C, there is now a useful amount of CO₂ yield data available (Table 1). It is clear that Pt provides the best yields, although there is a significant discrepancy between the two values (15% and 35%) that are available. This may be due to the difference in current density employed, and is also likely to be influenced by differences in electrode history as well as differences in the electrode structure and composition employed. The effects of electrode history on CO₂ yields are illustrated in Figs. 5 and 7. The CO₂ yield vs. time at 80 °C in Fig. 5 shows that the average yield of 15% encompasses significant variations with time. Although the regular fluctuations due to CO₂ bubbles can be assumed to average out, it is clear from this and other results (e.g. Fig. 7) that the average yield can mask significant changes with time. One of the advantages of the continuous monitoring of CO₂ over a batch process is that variations with time can be identified. Further work is necessary to explore how yields vary

Table 1
Summary of Faradaic yields for ethanol oxidation in DEFCs.

Catalyst	Temperature/°C	Current density/mA cm ⁻²	% CO ₂	Reference
Pt	~20	4–12.5	4.6	This work
PtRu	~20	10	5.9	This work
Pt	80	40	15	This work
Pt	80	8	35 ^a	[6]
PtRu	80	40	4.0	This work
PtRu	80	20–60	6.2–6.7	[29]
PtSn	80	30–60	9.0–9.4	[29]
PtSn	80	32	12 ^a	[6]
PtRuSn	80	32	15 ^a	[6]
PtRu	90	~150	2.08	[30]
PtSn	90	~175	0.87	[30]
Pt	100	40	76	This work
PtRu	100	40	25	This work
PtRu	145	300	99 ^a	[27]

^a Faradaic yields have been calculated from the reported chemical yields (mol of product/total mol of products [27] or mol product/mol ethanol [6]).

with the operating history of the cell, but this is clearly an issue that needs to be addressed.

Although PtRu and PtSn are well known to provide better DEFC performances than Pt, it is clear from Table 1 that they lower the yield of CO₂ and are therefore less attractive than Pt for practical applications. The yield of 4% from this work for PtRu at 80 °C is reasonably consistent with our previous results of 5.6–6.7% [29] and a recent result of 2.08% at 90 °C [30], given the typical variations observed with time and history. PtSn appears to give higher CO₂ yields than PtRu at 80 °C, although probably not consistently so [30], and PtRuSn appears to be slightly better too.

The superiority of Pt over PtRu is maintained at 100 °C, and the performance advantage of PtRu diminishes. The high yields of CO₂ at 100 °C (76% for Pt; 25% for PtRu) appear to be due in part to use of a vapor feed, and this conclusion is supported by the high yields previously obtained [32] at ambient temperature with a vapor feed (in N₂).

A very high yield (99%), even with a PtRu catalyst and liquid feed, has been obtained at 145 °C [27]. However, durability of the membrane and catalysts are serious issues at this temperature and even at 100 °C. Significant progress in catalyst development is therefore needed to bring CO₂ yields at sustainable temperatures to the level needed for a practical DEFC. It appears that co-catalysts other than Ru and Sn will be required, although further work with PtSn is needed to determine whether it can provide sufficiently high CO₂ yields under appropriate operating conditions.

5. Conclusions

An online CO₂ monitoring system has been used to follow the time dependence of CO₂ yields from a DEFC under a range of operating conditions. Evidence is provided for sustained CO₂ production at ambient temperature. CO₂ yields rise rapidly with increasing temperature and are strongly influenced by the catalyst (Pt vs. PtRu) and the state of the fuel (liquid vs. vapor). The highest yield of 76% was obtained at 100 °C with a Pt catalyst and vapor feed of ethanol and water.

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