



# Measurement of carbon dioxide yields for ethanol oxidation by operation of a direct ethanol fuel cell in crossover mode

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## ABSTRACT

Faradaic yields of carbon dioxide from ethanol oxidation were measured with a non-dispersive CO<sub>2</sub> detector for a direct ethanol fuel cell (DEFC) operating in crossover mode with aqueous ethanol delivered to the cathode and N<sub>2</sub> passing through the anode compartment. Under these conditions, the rate of ethanol oxidation is limited by its rate of diffusion through the Nafion membrane (crossover). It is shown, by comparison with results obtained with methanol and by running the cell normally, that this experimental configuration provides more accurate results by minimizing the effects of CO<sub>2</sub> crossover. The faradaic yield of CO<sub>2</sub> was found to increase significantly with decreasing ethanol concentration, reaching 64% for oxidation of 0.1 M ethanol at 80 °C. However, the highest yield (>68%) was obtained by operating the cell normally.

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## 1. Introduction

Direct ethanol fuel cells (DEFCs) have been receiving rapidly growing attention because they can potentially provide an efficient means of sustainable energy production [1–5]. However, current PEM (proton-exchange membrane) DEFC technology is inadequate because of a combination of high anode overpotentials and inefficient oxidation of ethanol to carbon dioxide. PtSn and PtSnRu anode catalysts have been established as providing the best performances, but overall efficiencies are low because the primary products are acetic acid and acetaldehyde [3,6,7]. Except for one report of work at 145 °C [8], the highest yields of CO<sub>2</sub> in DEFCs have been obtained with pure Pt catalysts [6,7,9], which have low activities. However, an in situ infrared spectrometry (FTIR) study of a PtRhSnO<sub>2</sub>/C catalyst has recently shown close to 50% efficiency for ethanol oxidation to CO<sub>2</sub> [10,11]. Highly selective oxidation of ethanol to CO<sub>2</sub> has also recently been reported for Pt/Ir/Pt multilayer electrodes [12].

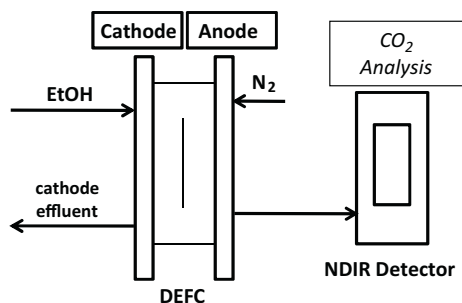
In addition to the development of new anode catalysts, the efficiency of ethanol oxidation to carbon dioxide can be increased by changing the operating parameters and mode of operation of the fuel cell. The yield of CO<sub>2</sub> increases greatly with temperature [7,8,13–15] and can also be dramatically increased by pulsing the potential or current [16]. CO<sub>2</sub> yields have also been found to increase as the ethanol concentration supplied to the cell is decreased [14,17,18] or the fuel flow rate is decreased [14,18],

and decrease as the potential [9,14] or current density [7,15] is increased.

In assessing the efficiency of anode catalysts, and operating conditions, for breaking the C–C bond of ethanol it is crucial to employ reliable and accurate methodology for measuring CO<sub>2</sub> yields. Spectroscopic methods such as in situ FTIR [11,12,19–27] and differential electrochemical mass spectrometry (DEMS) [14,17,22,28–34] are extremely valuable for mechanistic studies, but the results are generally dominated by transient (from adsorbed CO) rather than steady-state CO<sub>2</sub> production. In addition, such experiments do not usually represent fuel cell operating conditions. Measurements on the anode exhaust from DEFCs [6] can provide CO<sub>2</sub> yields averaged over periods of hours, as well as real time monitoring of CO<sub>2</sub> production [7]. However, they suffer from crossover effects [35,36] due to the diffusion of oxygen, ethanol, and its oxidation products across the Nafion<sup>TM</sup> membrane (PEM). It is also possible that the build-up of ethanol oxidation products in the anode flow field can cause product distributions to vary along the length of the flow field.

In order to minimize the effects of CO<sub>2</sub> crossover and variations in concentrations along the flow field on measured CO<sub>2</sub> yields in a DEFC we report here on the effects of controlling the flux of ethanol to the anode, by operating the cell in crossover mode, where the rate of ethanol oxidation is limited by its rate of diffusion through the Nafion<sup>TM</sup> membrane (crossover). The experimental set-up is illustrated schematically in Fig. 1. A conventional PEM fuel cell was used with Pt black electrodes sandwiching a Nafion<sup>TM</sup> 115 membrane. Aqueous ethanol was delivered to the cathode and N<sub>2</sub> was passed through the anode compartment. The CO<sub>2</sub> concentration of

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**Fig. 1.** Schematic diagram of a DEFC operated in crossover mode with CO<sub>2</sub> monitoring of the anode exhaust using a non-dispersive infrared (NDIR) detector.

the anode exhaust gas was continuously monitored with a non-dispersive infrared (NDIR) CO<sub>2</sub> detector. We demonstrate that this configuration virtually eliminates inaccuracies due to crossover effects (ethanol, oxygen, and carbon dioxide) and produces high yields of CO<sub>2</sub>.

## 2. Experimental

### 2.1. Materials

Electrodes consisted of 4 mg cm<sup>-2</sup> Pt black on Toray™ carbon fiber paper. Anhydrous ethanol was obtained from Commercial Alcohols Inc.

### 2.2. The fuel cell

A 5 cm<sup>2</sup> commercial cell (Fuel Cell Technology Inc.) was used. The cathode inlet and outlet were both modified to prevent the ethanol solution from contacting any metal parts of the hardware. Membrane and electrode assemblies were prepared by hot pressing a 5 cm<sup>2</sup> anode and a 5 cm<sup>2</sup> cathode onto a Nafion™ 115 membrane (Ion Power) at a pressure of 200 kg cm<sup>-2</sup> at 135 °C for 90 s. The cell was operated with a cathode feed of 0.10–1.0 mol L<sup>-1</sup> ethanol or methanol solution at 0.50 mL min<sup>-1</sup>. The anode feed was N<sub>2</sub> at 45 or 90 cm<sup>3</sup> min<sup>-1</sup>. Electrochemical measurements were made using a Solartron 1286 potentiostat operated with Corrware software.

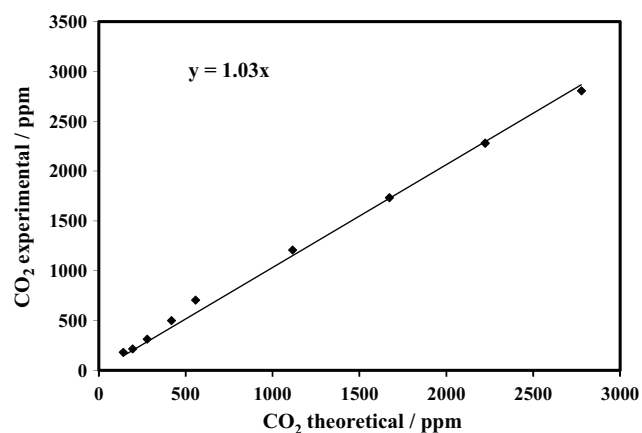
### 2.3. CO<sub>2</sub> analysis

The N<sub>2</sub> exhaust from the fuel cell was passed through a 125 mL flask to collect condensates and then into a Telaire 7001 non-dispersive infrared CO<sub>2</sub> monitor [7]. All CO<sub>2</sub> yields reported in this work are faradaic yields based on the current passed by the fuel cell. Since it was found that the accuracy of the detector deteriorated with time when used in these experiments over long periods (weeks), it was necessary to recalibrate regularly either with known concentrations of CO<sub>2</sub> in N<sub>2</sub> or using methanol in crossover mode and assuming a 100% yield of CO<sub>2</sub> (see below).

## 3. Results and discussion

### 3.1. Testing and calibration of the system with methanol

The accuracy of the system for measuring CO<sub>2</sub> yields was first evaluated using methanol as the fuel, which was expected to give close to a 100% faradaic yield. A 1 M methanol solution was fed through the cathode compartment of the cell at a flow rate of 0.50 mL min<sup>-1</sup>. At the anode, N<sub>2</sub> gas was passed at a rate of 90 mL min<sup>-1</sup>. Methanol crossing through the Nafion 115 membrane was oxidized at the anode, using constant currents ranging from 5 to 80 mA, while the cathode acted as a dynamic hydrogen electrode



**Fig. 2.** Measured CO<sub>2</sub> concentration in the anode exhaust vs. theoretical concentration for a 100% faradaic yield for constant current (5–80 mA) oxidation of methanol crossing through a Nafion 115 membrane ( $T=80^{\circ}\text{C}$ ).

(DHE). As shown in Fig. 2, the CO<sub>2</sub> concentrations measured in these experiments agreed well the calculated concentrations based on a 100% faradaic yield of CO<sub>2</sub>. The slope of the data shown in Fig. 2 was 1.03, indicating that the system provides an accurate measure of the CO<sub>2</sub> yield, and that methanol is almost exclusively oxidized to CO<sub>2</sub> under the conditions employed. Crossover of CO<sub>2</sub> to the cathode must also have been insignificant in these experiments.

Many of the previously reported measurements of CO<sub>2</sub> yields from methanol oxidation have shown yields below 100% due to incomplete oxidation to formaldehyde and formic acid [37,38]. However, since these two intermediates can both be oxidized to CO<sub>2</sub> within the porous structure of a fuel cell electrode [39,40], high CO<sub>2</sub> yields and low levels of formaldehyde and formic acid are achieved in direct methanol fuel cells [41].

In order to assess the effects of CO<sub>2</sub> crossover in conventional measurements (i.e. measuring the CO<sub>2</sub> in the fuel stream exhaust; “normal” mode), the anode and cathode connections in Fig. 1 were reversed. Thus, in these experiments the cathode was flushed with N<sub>2</sub> and acted as a DHE and the anode was supplied with 0.1 M methanol. The CO<sub>2</sub> concentration was measured in the N<sub>2</sub> exiting the cathode chamber and in the 0.1 M methanol exiting the anode chamber (following extraction into an N<sub>2</sub> stream [7]). It was found that at 30 mA, ca. 34% of the measured CO<sub>2</sub> exited the cell in the N<sub>2</sub> stream from the cathode, while 66% exited in the anode exhaust. Clearly, there was a great deal of CO<sub>2</sub> crossover from the anode to the cathode, as would be expected given the high activity of CO<sub>2</sub> at the anode (ca. 0.53 for CO<sub>2</sub> gas saturated with water at 80 °C) and low activity at the cathode (close to 0 for ca. 650 ppm CO<sub>2</sub> in N<sub>2</sub>). These results confirm [35] that conventional measurements of CO<sub>2</sub> yields in direct alcohol fuel cells (i.e. measurement of CO<sub>2</sub> in the anode exhaust only) underestimate the true yield due to crossover. Indeed, such measurements on the DMFC here gave significantly lower CO<sub>2</sub> yields (ca. 70% on average over a 2–30 mA current range) than the measurements reported in Fig. 2.

### 3.2. Ethanol oxidation

The crossover of ethanol through proton exchange membranes in fuel cells has been described in a number of papers [35,42–44]. The effects of oxygen permeation from the cathode compartment of a fuel cell through the membrane have also recently been described [36]. It has been shown that the use of oxygen at the cathode can result in both a misinterpretation of ethanol oxidation products, due to ethanol crossing through the membrane and chemically reacting with oxygen at the cathode [35] and also acetic acid and acetaldehyde formation at the anode due to oxygen permeation

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