

Short communication

Efficient electrochemical oxidation of ethanol to carbon dioxide in a fuel cell at ambient temperature

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Abstract

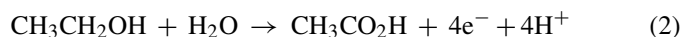
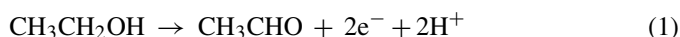
A carbon dioxide monitor has been used to follow the Faradaic yield of CO₂ from the oxidation of ethanol vapour in a direct ethanol PEM fuel cell at ambient temperature. The time resolution of the CO₂ measurements (ca. 15 s at half height for a burst of CO₂) was sufficient to observe stripping of adsorbed CO from the anode, and to monitor CO₂ yields as a function of time during linear sweep and pulse experiments. It has been demonstrated that CO₂ yields can be increased dramatically by pulsing the potential or current such that adsorbed CO is stripped from the electrode and then ethanol is allowed to re-adsorb. Yields of CO₂ as high as 80% have been sustained for as long as 50 s under current pulsing conditions. An average CO₂ yield of 45% was obtained during 600 s of pulsing the current between 0 and 4 mA cm⁻² at 1 Hz.

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1. Introduction

There is currently an enormous worldwide effort to develop fuel cells for environmentally sustainable power production [1–3]. From an environmental perspective, ethanol is the most attractive fuel because it is a renewable resource. Growth of the biomass used to produce it consumes CO₂, mitigating greenhouse gas levels. However, the development of ethanol fuel cells lags that of hydrogen and methanol cells by a huge margin because the main products of electrochemical ethanol oxidation are acetic acid and acetaldehyde (reactions (1) and (2) below) [4–6]. This makes the process very inefficient for power generation, and disposal of these products would be a serious problem. For ethanol fuel cells to have widespread utility, and to be useful in a renewable energy strategy, the anode reaction must produce CO₂ (reaction (3)) almost exclusively. The CO₂ produced would be released into the environment, but reabsorbed in the production of the biomass used to produce ethanol. Net CO₂ production would be minimized by the high efficiency of the fuel cell (e.g. relative to an internal combustion engine).



The attractiveness of ethanol fuel cells has prompted a recent rise in studies of the electrochemical oxidation of ethanol, and there have been a rapidly growing number of reports on direct ethanol cells (reviewed in Refs. [4–6]). Pt based catalysts have been used exclusively for work in acidic media, the test conditions most relevant to proton exchange membrane (PEM) fuel cells. Many binary and ternary alloy catalysts have also been evaluated [5]. Arico et al. [7] have reported a direct ethanol fuel cell, operating at 145 °C, that produces a peak power of 110 mW cm⁻² with 96% conversion of ethanol to CO₂. Under the same conditions, methanol provided a peak power of 240 mW cm⁻². A PtRu catalyst was used in both cases. These results suggest that only a twofold improvement in anode catalyst activity is needed to make ethanol fuel cells competitive with methanol cells, although it is important to note that the durability of the fuel cell would be insufficient at the high temperature employed. At sustainable temperatures (<100 °C), the best reported yield of CO₂ is only 20% [8]. Zhou et al. [9] have reported a peak power density of 62 mW cm⁻² at 90 °C with a Pt_{0.67}Sn_{0.33} anode, while Vigier et al. [10] obtained 45 mW cm⁻² at the same temperature with Pt_{0.83}Sn_{0.17}. PtSn

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was found to give the best fuel cell performance when compared with PtRu, PtPd, PtW, PtRuSn, PtRuW, and PtRuMo [11]. Although conflicting results have been reported, it appears clear now that Sn, which produces the most active catalysts, lowers the yield of CO₂ [5,8].

Monitoring of products from the electrochemical oxidation of ethanol has most commonly been performed by differential electrochemical mass spectrometry (DEMS) [12–16], while FTIR spectroscopy has provided important complementary and mechanistic information [4,17,18]. Gas chromatography [7] and liquid chromatography [8] have been used to analyse products from DEFCs, although there have been a very limited number of reports of quantitative data.

Mechanistic studies by DEMS [12,13,16] and FTIR spectroscopy [4,17] have shown that ethanol adsorbs on Pt and Pt alloys at quite low potentials, and that CO₂ production is primarily a result of the oxidation of adsorbed CO produced in this process. If the potential is insufficient to oxidize this CO, further ethanol adsorption is blocked, direct oxidation of ethanol to acetaldehyde and acetic acid predominates, and the yield of CO₂ is very low. At potentials high enough to oxidize the adsorbed CO, the rates of acetaldehyde and acetic acid production become high relative to the rate of dissociative ethanol adsorption, and so the yield of CO₂ remains low. A possible solution to this dilemma is to vary the potential in such a way that the adsorbed CO is repeatedly stripped from the electrode as CO₂ and ethanol is allowed to re-adsorb onto the catalyst between stripping cycles. A similar strategy has been used to reactivate the anodes of fuel cell operated on reformat [19] and more recently methanol [20].

We report here on a proof of concept for this strategy and demonstrate that very high CO₂ yields can be obtained. The experimental results were obtained by using conventional PEM fuel cell hardware, but the experiments were unconventional in order to provide better insight into the kinetics of the adsorption and stripping processes. Thus hydrogen was passed through the cathode compartment to provide a stable reference potential, and ethanol plus water vapour in a N₂ stream was passed through the anode compartment to facilitate real time analysis of the CO₂ yield. CO₂ in the anode exhaust gas was monitored with a commercial CO₂ sensor as previously reported [21].

2. Experimental

2.1. Membrane and electrode assembly (MEA)

Electrodes consisting of 4 mg cm⁻² Pt black on PTFE treated carbon fibre paper were donated by Ballard Power Systems. Two identical 5 cm² electrodes were bonded to a Nafion 115 membrane at 200 kg cm⁻² and 135 °C for 180 s to prepare the MEA.

2.2. Fuel cell experiments

A commercial 5 cm² active area fuel cell (ElectroChem) was used with dry H₂ at ca. 5 mL min⁻¹ passing through the cathode, which was used as both the counter and reference electrode. N₂ at 27 mL min⁻¹ was bubbled through a 1 M solution of ethanol

in water (to maintain hydration of the membrane) at ambient temperature, through the anode compartment of the cell, and then into a Telaire 7001 CO₂ detector. The accuracy of the CO₂ detector was confirmed by injecting pure CO₂ at a constant rate (syringe pump) into the N₂ stream at a point between the ethanol solution and the cell, with the cell at open circuit. Baseline corrections were not applied because calibration of the detector indicated that this decreased its accuracy. Although CO₂ levels close to the background (typically ca. 0.12 ppt) are unlikely to be very accurate, such readings have little influence on the average yields that are reported, and no influence on the peak yields.

2.3. Instrumentation

The voltage or current of the fuel cell was controlled with a Solartron 1286 potentiostat/galvanostat by using custom software. Current pulses were applied via the POL I/V input by using a Hokuto Denko HB-104 Function Generator. Cell voltage and CO₂ parts per thousand (ppt) data were collected with a data-logger and laptop computer. It should be noted that the slow response of the CO₂ detector (<60 s for 90% of step change) and peak broadening (ca. 15 s at half height for a burst of CO₂) prevent accurate correlation of the CO₂ with the current or potential. However, the time scales of the electrochemical and CO₂ concentration plots have been aligned as accurately as possible by shifting the CO₂ data on the time axis to account for the time required for CO₂ to reach the detector (17 s).

3. Results

3.1. Linear sweep experiments

Stripping of CO from the anode was investigated by applying a linear potential sweep while monitoring CO₂ generation. Representative data are shown in Fig. 1. Based on the known stripping behaviour of CO on Pt, the sharp rise in current at ca. 0.8 V in the voltammogram can be attributed to oxidation of adsorbed CO to CO₂, and this is confirmed by the burst of CO₂ production recorded by the detector. Although the slow response of the CO₂ detector and peak broadening prevent accurate correlation of the CO₂ with the current, and average Faradaic yield of CO₂ can be calculated based on the voltammetric charge and the integral of the CO₂ signal. Integration of the charge from 0.3 V to prevent inclusion of the H-desorption wave between 0.1 and 0.3 V, gave a yield of 52% based on six electrons per molecule ($n=6$; an assumption that is discussed below). This is much higher than the best yields of 13% [15] and 20% [8], respectively, previously reported for ethanol oxidation at ambient temperature and 80 °C.

3.2. Constant potential experiments

Fig. 2 shows current and CO₂ concentration as a function of time following a 0.40 to 0.85 V potential step on the fuel cell. Following a charging spike, the current dropped to a minimum of 36 mA, and then rose to a broad peak of 111 mA at ca. 45 s. This was followed by a slow decline in current. The CO₂ signal

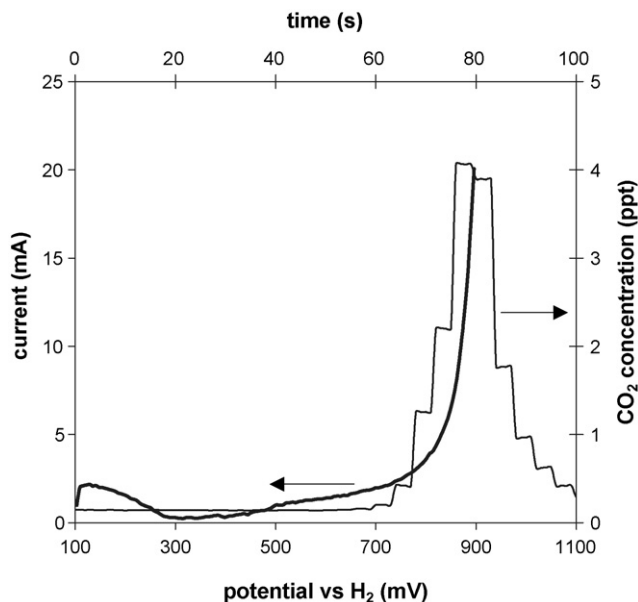


Fig. 1. Current vs. potential (bold) and CO₂ concentration vs. time (light) curves for linear sweep voltammetry on a fuel cell with two Pt black electrodes and a Nafion 115 membrane. H₂ was passed through the cathode and N₂ containing ethanol and water vapour was passed through the anode.

rose sharply to a peak of 4.07 ppt and then declined as the current continued to rise. This response is consistent with the initial current being predominantly due to CO oxidation, while the rising current and current after the 45 s peak became dominated by oxidation of ethanol to acetaldehyde and acetic acid. The average CO₂ yield for the full 200 s experiment was only 19%, while the peak in the CO₂ response corresponds to a CO₂ yield of 81% based on the average current during the first 20 s (and again based on $n=6$). The rising current during this period was presumably due to the exposure of free Pt sites as CO was stripped from the electrode. These sites are clearly active for full oxidation of ethanol to CO₂, since CO₂ production remained significant until the electrode was returned to open circuit. However the low

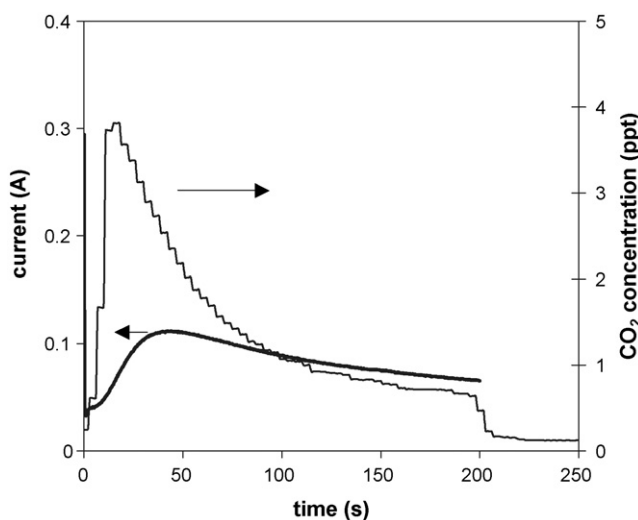


Fig. 2. Current (bold) and CO₂ concentration (light) vs. time curves following a 0.40–0.85 V potential step on the cell described for Fig. 1.

yield of CO₂, which was only 11% for the final 20 s, indicates that the electrode became much more efficient for the oxidation of ethanol to acetaldehyde and acetic acid. This is consistent with the established understanding of steady state oxidation of ethanol on Pt [4,5,18].

It is clear from the above discussion that high transient yields of CO₂ can be achieved by stripping CO from the electrode, but for this to be of practical use ethanol must reabsorb quickly while its oxidation to acetaldehyde and acetic acid must be suppressed. This could be done by pulsing the potential to lower values, but then accurate accounting of the cathodic current during these pulses would be problematic. A better approach is to periodically allow the potential to go to open circuit. Then, all of the charge is anodic and can be attributed to net ethanol oxidation. The tricky questions of how many electrons are needed to produce each CO₂ molecule and how to accurately account for the charging current are avoided because ethanol adsorption and the consequent formation of adsorbed hydrogen atoms and adsorbed CO causes the potential to drift lower, effectively storing four electrons per CO as the adsorbed hydrogen is oxidized to H⁺. This charge is recovered as the charging current when the potential is reapplied.

Representative results for this type of experiment are shown in Figs. 3 and 4. For Fig. 3, a potential of 0.82 V was applied in two 2 s pulses, with 30 s at open circuit before each pulse. Although the current versus time profiles were similar for both pulses, and the charges passed were the same (0.22 C), the yield of CO₂ was much greater for the second pulse. Based on the integrated currents and CO₂ readings, the yields were 34 and 60%, respectively. Although the reason for this difference is not entirely clear, it appears to be due to activation of the electrode by CO stripping. The open circuit potential during the first 30 s was 0.42 V, but fell to 0.34 V during the 30 s period between the two pulses. This indicates that there was dissociative adsorption of ethanol on the electrode following stripping.

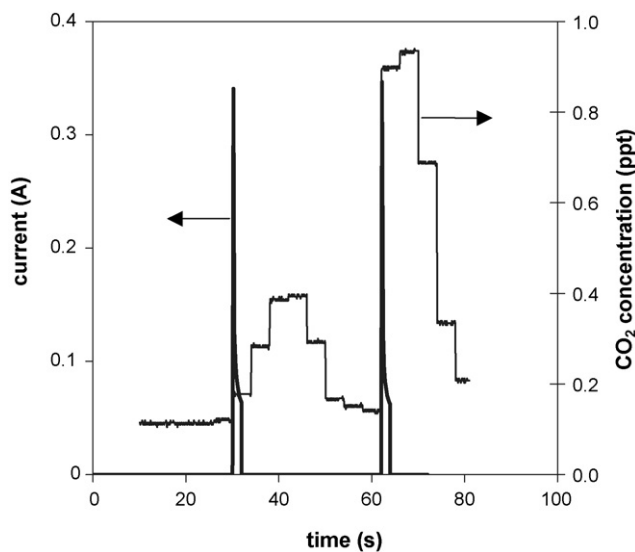


Fig. 3. Current (bold) and CO₂ concentration (light) vs. time curves for potential pulses to 0.82 V applied to the cell described for Fig. 1. The potential was applied in two 2 s pulses, with 30 s at open circuit before each pulse.

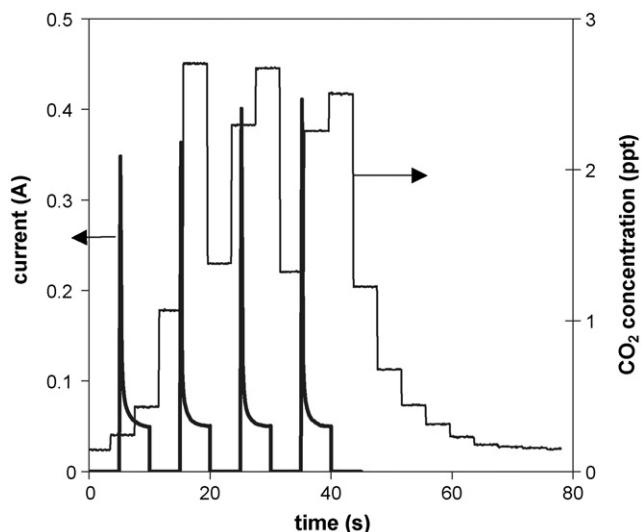


Fig. 4. Current (bold) and CO₂ concentration (light) vs. time curves for potential pulses to 0.82 V applied to the cell described for Fig. 1. The potential was applied in four 5 s pulses, with 5 s at open circuit before each pulse.

The long rest period between pulses in Fig. 3 was employed to clearly differentiate between CO₂ produced during the two pulses, and to allow maximum adsorption of ethanol between pulses. However, for optimal performance the rest period should be as short as necessary to allow formation of an adsorbed monolayer. To this end, data for equal on/off times (5 s) are shown in Fig. 4. The four current transients were very similar, each with a charge of 0.365 ± 0.05 C. Since the CO₂ peaks were not well resolved, particularly for the first two pulses, only an average yield can be calculated, and that was 59%.

3.3. Constant current experiments

Because of difficulties in accurately controlling the timing of rapid changes between an applied voltage and open circuit, further experiments were conducted by using current pulses. This has the added advantage that calculation of the charge passed is trivial, and more accurate than at controlled potential.

Fig. 5 shows the CO₂ yields and potential excursions of the cell when subjected to 50 mA current pulses of 2 s duration with 2 s at zero current between each pulse. The potential rose from an initial open circuit value of 0.44 V to a peak value of 0.77 V at the end of the first pulse. It then fell rapidly to 0.56 V during the subsequent 2 s at zero current. The range of these oscillations increased to ca. 0.52–0.83 V over the next 50 s, and was then stable for the remainder of the 170 s experiment. The CO₂ yield, which was calculated from each CO₂ ppt reading and the average current of 25 mA, rose to 62% following a short delay. It then decayed to a fairly stable value of ca. 33%. The ca. 10 s delay in CO₂ production can be attributed to the time required for the positive potential excursion to become high enough to strip CO from the electrode, since the current for the first few pulses would have been largely consumed by charging of the electrode. The falling yield of CO₂ after the first 25 s of the experiment appears to be correlated with a decrease in the minimum potential reached at zero current on each cycle. Presumably, the decrease in this

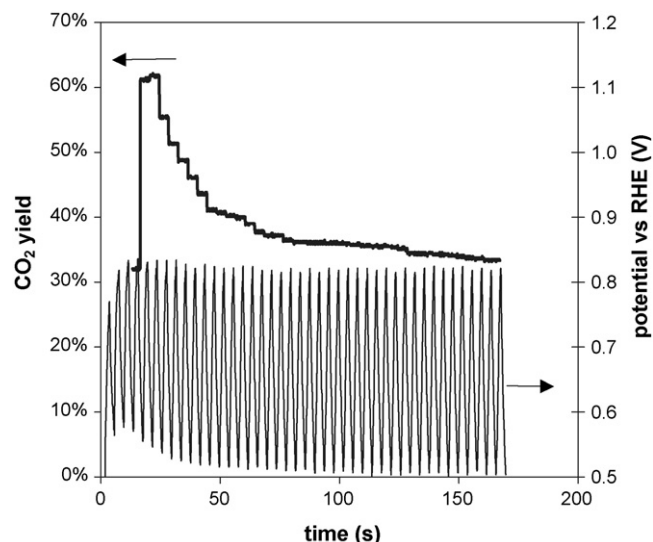


Fig. 5. CO₂ yield (bold) and potential (light) vs. time curves for the cell described for Fig. 1 when subjected to 50 mA current pulses of 2 s duration with 2 s at zero current between each pulse.

potential is due to more rapid adsorption of ethanol on the Pt surface with progressive CO stripping. It can also be expected that the rate of oxidation to acetaldehyde and acetic acid are also accelerated, and this would explain the decreasing CO₂ yield.

The results shown in Fig. 5 suggest that 2 s at zero current is sufficient time for substantial adsorption of ethanol and its conversion to adsorbed CO. In fact, it may be too long for optimum CO₂ production because the electrode potential drops so much that acetaldehyde and acetic acid formation begin to dominate. The use of shorter current pulses was therefore investigated. Results for 20 mA current pulses of 0.5 s duration with 0.5 s at zero current between each pulse are shown in Fig. 6. In this experiment the initial open circuit potential was 0.43 V. Application of the 20 mA pulses produced potential oscillations of ca.

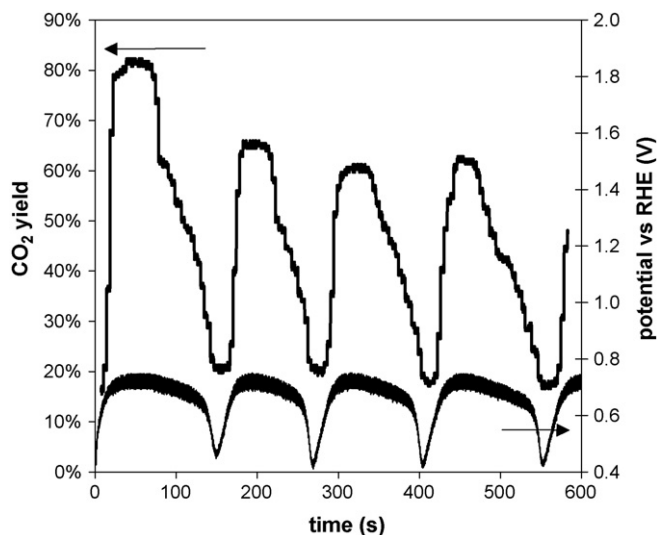


Fig. 6. CO₂ yield (bold) and potential (light; bottom trace) vs. time curves for the cell described for Fig. 1 when subjected to 20 mA current pulses of 0.5 s duration with 0.5 s at zero current between each pulse.

50 mV superimposed on a rising average potential. CO₂ production commenced after ca. 15–20 s, when the electrode potential reached ca. 0.7 V. The yield of CO₂ quickly rose to ca. 80%, where it remained for ca. 50 s. Curiously, the average potential then began to decrease, and the CO₂ yield decreased rapidly. Following a minimum in the potential of ca. 0.45 V, both the average potential and CO₂ yield rose again, went through similar maxima, and then declined. These cycles of potential and CO₂ yield continued with a similar period of ca. 140 s until the experiment was stopped. Such oscillations, but with different periods, were observed with a range of other experimental parameters.

These cycles in potential and CO₂ production can be explained by changes in the average CO coverage on the electrode. Initially, the electrode would have had a high CO coverage, causing the average potential to rise as current was passed. This stripped CO from the electrode, resulting in a burst of CO₂ production. The decreased CO coverage would then allow adsorption of more ethanol during the periods at zero current, resulting in a decrease in the average potential. As the average potential falls, less CO is stripped on each pulse, and so the electrode slowly becomes poisoned. The average potential then begins to rise and another CO stripping cycle begins. Although scientifically interesting, this cycling behaviour would be problematic during operation of a fuel cell, and so would have to be avoided. The most important observation from the data in Fig. 6 is therefore that a 80% yield of CO₂ is shown to be possible, and to be sustainable for at least 50 s. The average CO₂ yield for the whole 600 s experiment was 45%.

4. Discussion

It is clear from the data in Fig. 1 that a large transient of CO₂ can be generated by stripping of adsorbed CO from the electrode following exposure to ethanol at open circuit and/or potentials between 0.1 and 0.5 V versus RHE. This is consistent with DEMS studies [15,16], although the 52% Faradaic yield of CO₂ (based on $n=6$) obtained here is much higher than the 1.7–13% values estimated by DEMS (also based on $n=6$) [15]. This is due in part to the fact that the charge in the DEMS work was calculated for a cyclic scan between 0.05 and 1.15 V, which accentuates the contribution from oxidation of ethanol to acetaldehyde and acetic acid once the CO has been stripped [15]. Another factor may also be the use of ethanol vapour here, which may inhibit these reactions. The presumably lower concentration of ethanol within the anode is also likely to be a factor, since the CO₂ yield from ethanol oxidation has been shown to increase with decreasing concentration [15,18].

The transient formation of CO₂ observed in Fig. 1 is not useful from a practical point of view, unless it can be sustainably repeated by pulsing the current or potential. The results in Figs. 3–6 show that this can be done, although further work is needed to optimize the pulse height and timing. The rapid decreases in open circuit potential between pulses, the higher CO₂ on the second pulse in Fig. 3, and the oscillations in CO₂ production in Fig. 6, all provide evidence that dissociative adsorption of ethanol occurs rapidly between pulses. This is consistent with FTIR results [4], which show a peak in the adsorbed

CO band at 0.60 V versus RHE, and an increasing CO₂ signal at potentials above 0.60 V. The potential oscillations between 0.5 and 0.82 V in Fig. 5 are therefore well suited for sustained generation of CO₂. On the other hand, the shorter rest times employed in Fig. 6 did not allow the potential to fall to low enough values for long enough to allow sufficient dissociative adsorption of ethanol. This results in the creation of long-term stripping-adsorption cycles with similar upper and lower extremes to those seen in Fig. 5.

We have not attempted to optimize the pulsing protocol for the system reported here because it does not fully represent a real fuel cell. Optimization will be performed with an operating fuel cell, with an air or oxygen cathode and a better catalyst for CO oxidation, such as PtRu or PtSn. The results here suggest that operation of the cell with an ethanol + water vapour mix will lead to better efficiency than use of the normal liquid feed.

The yields of CO₂ reported here have all been calculated based on the assumption that six electrons are released per molecule. This is the n value (per CO₂ molecule) for oxidation of ethanol to CO₂ (Eq. (3)), and is the value used in the literature that we have cited. However, formation of CO₂ from adsorbed CO releases only two electrons per molecule, and so it could be argued that $n=2$ should be used for the (unknown) component of CO₂ derived from adsorbed CO. The presence of adsorbed CO on the electrode before the experiment would therefore cause overestimation of the CO₂ yields in this work, as well as the literature values. Although it is very difficult to accurately determine the extent of this overestimation, the data presented in Figs. 3–5 indicate that it is relatively small. In Figs. 3 and 4, the initial potential pulse, which would be expected to be most influenced by pre-adsorbed CO, gave the lowest CO₂ yields. In Fig. 5, the first “cycle” of CO₂ generation (i.e. 0–150 s) did produce more CO₂ than subsequent cycles, suggesting some enhancement by pre-adsorbed CO, but the difference was relatively small.

Acknowledgements

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