Product analysis of the ethanol oxidation reaction on palladium-based catalysts in an anion-exchange membrane fuel cell environment

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ABSTRACT
We report a quantitative product analysis of the oxidation of ethanol in an anion-exchange membrane direct ethanol fuel cell (AEM DEFC) that consists of a Pd/C (or Pd2Ni3/C) anode, an AEM, and a Fe–Co cathode. The effects of the operating conditions including temperature, discharging current density, and fuel concentration, on the selectivity of each product of ethanol oxidation are investigated. It is found that incomplete ethanol oxidation to acetate prevails over complete oxidation to CO2 in the range of testing conditions. Experimental results show that the change in the anode catalyst from Pd/C to Pd2Ni3/C leads to a significant increase in the cell performance, but does not help improve the CO2 selectivity of ethanol oxidation. It is also shown that among the operating conditions tested, the operating temperature is the most significant parameter that affects the CO2 selectivity: increasing the temperature from 60 to 100 °C enables the CO2 current efficiency to increase from 6.0% to 30.6% with the Pd/C anode.

1. Introduction
Direct ethanol fuel cells (DEFCs), promising to be a clean and efficient energy production technology, have attracted worldwide attention over the past decade [1–3], not only because ethanol is a carbon-neutral, sustainable fuel that can be produced in great quantity through the fermentation of agricultural products or biomass, but also because it possesses many unique properties including high energy density, low toxicity, and ease in handling and transportation. Based on electrolyte membranes used, DEFCs can be divided into two types: proton-exchange membrane (PEM) DEFCs and anion-exchange membrane (AEM) DEFCs. Over the past decade, although tremendous efforts have been made to the development of PEM DEFCs, the performance remains unsatisfactory even at relatively high operating temperatures, and the state-of-the-art peak power density is 79.5 mW cm⁻² at 90 °C [4]. On the other hand, AEM DEFCs have recently received increasing attention because the kinetics of both the ethanol oxidation reaction (EOR) and oxygen reduction reaction (ORR) in alkaline media is much faster than that in acidic media, making it possible to use non-platinum or low-cost metal catalysts, and thus the cost of the fuel cell technology can be greatly reduced [5–9]. It has been demonstrated that with a non-Pt catalyst, the peak power density of an AEM DEFC can be as high as 185 mW cm⁻² at 60 °C [10].

The electro-oxidation of ethanol is believed to be a complex multi-step reaction through both the C1- and C2-pathway, and to be involved with an active intermediate CH3CHO_{ads} and a poisoning intermediate CO_{ads}. The reaction
products are supposed to include the complete oxidation product, i.e., CO$_2$ and the incomplete oxidation products, such as acetaldehyde and acetic acid:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} & \rightarrow \text{CH}_3\text{CHO}_{\text{ads}} \\
\text{CH}_3\text{CHO}_{\text{ads}} & \rightarrow \text{CH}_3\text{COOH} \text{ or acetate (alkaline)} \\
\text{CH}_3\text{CHO} & \rightarrow \text{CO}_2 \text{ or carbonate (alkaline)}
\end{align*}
\]

Unlike the complete oxidation of ethanol to CO$_2$ that yields 12 electrons per ethanol molecule, the incomplete oxidation of ethanol to acetaldehyde and acetic acid liberates only 2 and 4 electrons, respectively, which greatly reduces the Faradic efficiency of the fuel cell [2,6].

In PEM DEFCs, the products of the EOR on the Pt/C, PtRu/C, and PtSn/C catalysts have been proved to be a mixture of acetaldehyde, acetic acid and CO$_2$ [11–13]. In alkaline media, the mechanism of the EOR on the state-of-the-art Pd catalyst has also been investigated by the electrochemical methods, including cyclic voltammetry (CV) and chronopotentiometry (CA) combined with in situ Fourier transform infrared spectroscopy (FTIR) or high performance liquid chromatography (HPLC) [14–17]. It is generally agreed that unlike the EOR in acidic media, acetaldehyde is an active intermediate rather than the final product; on the Pd catalyst, ethanol is selectively oxidized to acetate through a 4-electron pathway and this means compared to the complete oxidation of ethanol to CO$_2$ that releases 12 electrons, the loss of the Faradic efficiency of the fuel cell is as high as 66.7%. Hence, the complete oxidation of ethanol to CO$_2$ remains a challenging issue.

Previous efforts have mainly been made to the product analysis of ethanol oxidation in a CV environment. But the work dealing with the quantitative product analysis of the EOR in an AEM fuel cell environment is scarce [18,19], and the effect of fuel cell operating conditions on the selectivity of each product has not been investigated. The present study aims to reveal the product distribution of the EOR in an AEM DEFC that consists of a Pd/C (or Pd$_2$Ni$_3$/C) anode, an AEM and a Fe–Co Hypermec™ K14 cathode. To form the anode electrode, an anode ink was first prepared by mixing the Pd/C (or Pd$_2$Ni$_3$/C) catalyst with PTFE emulsion as a binder in ethanol, then the catalyst ink was well dispersed by the ultrasonic process and brushed onto a nickel foam (Hohsen Corp., Japan), which served as the backing layer of the anode electrode [21]. The content of PTFE in the anode catalyst layer was maintained at about 5 wt.%, and the Pd loading was 1.0 mg cm$^{-2}$. An in-house fabricated AEM DEFC was composed of a MEA with an active area of 1.0 cm $\times$ 1.0 cm, sandwiched between two fixture plates. Both the two plates were made of stainless steel and a single serpentine flow-field, having 1.0 mm rib width, 0.5 mm channel depth, and 1.0 mm channel width, was machined onto each fixture plate [22].

\[\text{Ethanol} + 13/2 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}\]

\[\text{Complete oxidation of ethanol to CO}_2\]

2.2. Catalyst synthesis and characterization

Carbon supported Pd (Pd/C) and PdNi catalysts with a Pd: Ni atomic ratio of 2:3 (Pd$_2$Ni$_3$/C) were synthesized by the simultaneous reduction method [20], and used as the anode catalyst in the AEM DEFC. The primary process was described as follows: the metal precursors of PdCl$_2$ and NiCl$_2$•6H$_2$O were first dissolved in DI water, and potassium citrate was added as the complexing agent and stabilizer. Then, carbon powders were suspended into the resulting solution to form a homogeneous suspension under vigorous stirring. Finally, a solution of 2 wt.% NaBH$_4$ was added into the mixture under steady stirring, and the resulting precipitate was collected by filtration, washed several times with DI water and dried at 70 °C in an oven. Both the Pd/C and Pd$_2$Ni$_3$/C catalysts were guaranteed with a 20 wt.% Pd loading. The morphologies of the obtained Pd/C and Pd$_2$Ni$_3$/C catalysts were characterized by transmission electron microscopy (TEM) using a high-resolution JEOL 2010F TEM system operating with a LaB$_6$ filament at 200 kV. The TEM images of the Pd/C and Pd$_2$Ni$_3$/C catalysts are shown in Fig. 1a and b, respectively.

2.3. Membrane electrode assembly and fuel cell setup

The membrane electrode assembly (MEA) used during the experiments consisted of a Pd/C (or Pd$_2$Ni$_3$/C) anode, an AEM (A201) and a Fe–Co Hypermec™ K14 cathode. To form the anode electrode, an anode ink was first prepared by mixing the Pd/C (or Pd$_2$Ni$_3$/C) catalyst with PTFE emulsion as a binder in ethanol, then the catalyst ink was well dispersed by the ultrasonic process and brushed onto a nickel foam (Hohsen Corp., Japan), which served as the backing layer of the anode electrode [21]. The content of PTFE in the anode catalyst layer was maintained at about 5 wt.%, and the Pd loading was 1.0 mg cm$^{-2}$. An in-house fabricated AEM DEFC was composed of a MEA with an active area of 1.0 cm $\times$ 1.0 cm, sandwiched between two fixture plates. Both the two plates were made of stainless steel and a single serpentine flow-field, having 1.0 mm rib width, 0.5 mm channel depth, and 1.0 mm channel width, was machined onto each fixture plate [22].

2.4. Experimental apparatus and test conditions

The schematic illustration of the experimental apparatus for product analysis is shown in Fig. 2. At the cathode, dry pure oxygen at ambient pressure was supplied by a mass flow controller (Omega FMA-765A and FMA-767A), along with a multiple-channel indicator (Omega FMA-78P4). At the anode, the fresh fuel solution with different ethanol and KOH concentrations was fed by a peristaltic pump. Before operation, the fuel cell was purged with nitrogen for 20 min. Fuel solution was preheated to the desired operating temperature before being routed to the fuel cell. The cell operating temperature was measured with a thermocouple installed in the anode fixture plate; two electrical heating
rods were installed in the fixture to control the operating temperature. An Arbin BT2000 electric load interfaced to a computer was employed to control the condition of discharging and record the performance curves. During the constant-current discharging tests, the product solution from the anode outlet of the AEM DEFC was trapped in a nitrogen-purged bottle, and analyzed by the product analysis system: the Agilent 6890N gas chromatography (GC) equipped with the Agilent DB-WAX 7033 capillary column was used to quantify the produced acetaldehyde, and the Metrohm 883 basic ionic chromatography (IC) equipped with the Metrosep Organic Acids 250/7.8 column was used to quantify acetate and CO₂ that existed as carbonate in alkaline media. To eliminate the influence of the dead volume of the experimental apparatus, the collection of the product solution from the anode outlet of the AEM DEFC started after 20-min constant-current discharging and lasted for 40 min. Then, aliquots of the product solution were, respectively, analyzed by GC and IC, and at each condition, the analysis of the products was conducted for four times, and the average value was obtained. To conduct the product analysis, the selectivity of each product is characterized by the corresponding current efficiency, including acetaldehyde current efficiency, acetate current efficiency (ACE) and CO₂ current efficiency (CCE) according to the following equations:

\[
X_{\text{CH}_3\text{CHO}} = \frac{C_{\text{CH}_3\text{CHO}} \times 2}{C_{\text{CH}_3\text{CHO}} \times 4 + C_{\text{CH}_3\text{CHO}} \times 2 + C_{\text{CO}_2} \times 6} \tag{1}
\]

\[
X_{\text{CH}_3\text{COO}^-} = \frac{C_{\text{CH}_3\text{COO}^-} \times 4}{C_{\text{CH}_3\text{COO}^-} \times 4 + C_{\text{CH}_3\text{CHO}} \times 2 + C_{\text{CO}_2} \times 6} \tag{2}
\]

and

\[
X_{\text{CO}_2} = \frac{C_{\text{CO}_2} \times 6}{C_{\text{CH}_3\text{CHO}} \times 4 + C_{\text{CH}_3\text{CHO}} \times 2 + C_{\text{CO}_2} \times 6} \tag{3}
\]

where \(X\) represents the current efficiency contributed by each product; \(C\) is the concentration of each product obtained from the GC or IC; 2, 4 or 6 are, respectively, the number of electrons needed for the formation of one molecule of CH₃CHO, CH₃COOH or CO₂ from the CH₃CH₂OH molecule. It is noted that the blank experiments was conducted at the open-circuit voltage (OCV), and no carbonate was detected, suggesting that the present experimental apparatus can effectively eliminate the carbonation of fuel solution caused by the atmospheric CO₂.

3. Results and discussion

3.1. Cell performance of the AEM DEFC with the Pd/C anode

Fig. 3 shows the polarization and power density curves of the AEM DEFC with the Pd/C anode at 60, 70, 80, 90 and 100 °C. The fuel solution containing 1.0 M ethanol and 1.0 M KOH was pumped to the anode at a rate of 1.0 ml min⁻¹, and the dry pure oxygen at a flow rate of 100 standard cubic centimeters per minute (sccm) was fed to the cathode. It is noticed that the highest operating temperature tested here is 100 °C, which is limited by the normal boiling point of fuel solution and by the thermal stability of the membrane. As shown in Fig. 3, both the OCV and power density increase significantly with the temperature. The OCV and the power density of the fuel cell increase, respectively, from 0.666 to 0.812 V and from 18 to
40 mW cm$^{-2}$ when the temperature is increased from 60 to 100 °C. The increased performance can be attributed to the improved kinetics of the reactions on both the anode and cathode at higher temperatures.

To study the effects of operating temperature and current density on the selectivity of each product of ethanol oxidation, the constant-current discharging tests were carried out by varying the temperature from 60 to 100 °C and the current density from 20 to 80 mA cm$^{-2}$; the results are shown in Fig. 4.

It can be observed that at the same temperature, the cell voltage of the fuel cell decreases with the current density; for instance, at 60 °C, the cell voltage decreases from 0.355 to 0.175 V when the current density is increased from 20 to 80 mA cm$^{-2}$. This is because as the current density increases, the overpotential on both the anode and cathode becomes larger, resulting in a decrease in the cell voltage. It is also seen from Fig. 4 that, at the same current density, the cell voltage of the fuel cell increases with the temperature, which is consistent with the trend in Fig. 3; for instance, at the current density of 20 mA cm$^{-2}$, the cell voltage increases from 0.355 to 0.478 V when the temperature is increased from 60 to 100 °C. Note that at each condition in Fig. 4, the fluctuation of the cell voltage is smaller than 15 mV during the 40-min product collection, indicating that there is no change in the reaction mechanism during the constant-current discharging. Hence, the change in the selectivity of each product can be attributed to the operating conditions only.

3.2. Effect of the operating temperature on the product selectivity

Similar to the results reported elsewhere [18,19], under all the conditions tested in this work, the concentration of acetaldehyde is negligibly low and its current efficiency is lower than 1%. In addition, no aldol condensation product [17], which is caused by acetaldehyde in alkaline media, is detected. Hence, the current efficiency of acetate and CO$_2$, defined by Eqs. 2 and 3, can be reduced to:

$$X_{\text{CH}_3\text{COO}} = \frac{C_{\text{CH}_3\text{COO}} \times 4}{C_{\text{CH}_3\text{COO}} \times 4 + C_{\text{CO}_2} \times 6}$$  (4)

and

$$X_{\text{CO}_2} = \frac{C_{\text{CO}_2} \times 6}{C_{\text{CH}_3\text{COO}} \times 4 + C_{\text{CO}_2} \times 6}$$  (5)

Fig. 5 shows the effect of the operating temperature on the ACE and CCE at different current densities (20, 40, 60 and 80 mA cm$^{-2}$). At each condition, incomplete ethanol oxidation to acetate prevails over complete oxidation to CO$_2$, which is consistent with the electrochemical studies reported earlier [14–17]. In addition, it is clear from Fig. 5 that at each current density, the CCE increases with the temperature, especially in the temperature range from 80 to 100 °C; at the current density of 20 mA cm$^{-2}$, the CCE increases from 6% to 9.5%, 20% and 30.6%, respectively, when the temperature is increased from 60 to 80, 90 and 100 °C. This suggests that the CO$_2$ selectivity of the EOR can be improved on the thermally activated catalyst.
surface [23,24]. On one hand, as the temperature is increased, the oxygen-containing species is more easily formed on the Pd catalyst, facilitating the oxidation of the strongly adsorbed poisoning intermediate CO_ads to CO_2. On the other hand, an increase in the temperature leads to an increased activation for the dissociative adsorption of ethanol, and the capability of the Pd catalyst for breaking the C–C bond is greatly enhanced on the thermally activated catalyst surface.

3.3. Effect of the discharging current density on the product selectivity

Fig. 6 shows the effect of the current density on the ACE and CCE at different temperatures (60, 70, 80, 90 and 100 °C). As can be seen, unlike the effect of temperature, the current density shows a much less significant effect on the CO_2 selectivity of ethanol oxidation. At each temperature, changing the current density in the range from 20 to 80 mA cm^{-2} only leads to an increase in the CCE by less than 6%. In Fig. 6, it is also found that the CCE first decreases with the current density increasing from 20 to 60 mA cm^{-2}, and then increases with a further increase in the current density to 80 mA cm^{-2}. It is noted that the increase in the CCE caused by changing the current density from 60 to 80 mA cm^{-2} is smaller at higher temperatures (90 and 100 °C) than that at lower temperatures (60, 70 and 80 °C). For the EOR, the dissociative adsorption of ethanol usually occurs at low potentials, resulting in the formation of both the adsorbed CO_ads and CH_x species. At low potentials, the formation of CO_2 results mainly from the oxidation of the adsorbed CO_ads species [25,26]. At the constant-current discharging, a lower current density corresponds to a higher cell voltage and thus a lower anode potential, and vice versa. Consequently, at the same temperature, the CCE decreases with the current density increasing from 20 to 60 mA cm^{-2}. As far as the relative high CCE at the current density of 80 mA cm^{-2}, it can be attributed to both the oxidation of the adsorbed CH_x species [27,28] and bulk oxidation of ethanol on the kinetically activated catalyst surface at the much higher potentials [15,16].

3.4. Effect of the fuel concentration on the product selectivity

The effect of the fuel concentration on the product selectivity was also studied, including both ethanol and KOH concentrations. The effect of ethanol concentration was investigated by varying the concentration of ethanol from 0.2, 0.5 to 1.0 M while fixing the concentration of KOH at 1.0 M. In a similar manner, the effect of KOH concentration was studied by varying the concentration of KOH from 0.2, 0.5 to 1.0 M while fixing the concentration of ethanol at 1.0 M. Fig. 7 shows the transient cell voltage of the AEM DEFC at the constant current density of 20 and 40 mA cm^{-2}. The operating temperature is 80 °C. As shown in Fig. 7, among the fuel concentrations tested, the fuel solution containing 1.0 M ethanol and 1.0 M KOH gives the highest and most stable performance, and the cell voltage decreases and fluctuates as the ethanol and KOH concentrations are reduced. This is attributed to the fact that in alkaline media, the performance of the EOR depends on not only the local concentrations of ethanol and OH^- ions but also the balance of the competing adsorption between ethanol and the OH_ads species.

Fig. 8 shows the effect of the fuel concentration on the ACE and CCE at the current density of 20 and 40 mA cm^{-2}. It is seen that the CCE remains almost the same with decreasing the ethanol concentration from 1.0 to 0.2 M at the both current densities, indicating that the ethanol concentration has little effect on the CO_2 selectivity of the EOR. For instance, at the current density of 40 mA cm^{-2}, decreasing the KOH concentration from 1.0 to 0.2 M enables the CCE to increase from 6.9% to 10.5%. It is worth mentioning that when either of ethanol or KOH concentrations was lower than 0.2 M, the operation of
the present fuel cell system became unstable. Although measurements could not be made when the concentration of either ethanol or KOH was lower than 0.2 M, it is believed that the CO₂ selectivity of the EOR will be higher based on previous studies in a CV environment. For instance, Fang et al. [15] studied the effect of the NaOH concentration on the CO₂ selectivity of the EOR in alkaline media, and demonstrated that the breaking of the C–C bond was favored when the concentration of NaOH was lower than 0.1 M.

3.5. Effect of the anode catalyst on the product selectivity

Fig. 9 shows the transient cell voltage of the AEM DEFC with the Pd₂Ni₃/C anode at different temperatures (60, 70, 80, 90 and 100 °C) and different current densities (60 and 80 mA cm⁻²). As can be seen, the change in the anode catalyst from Pd/C to Pd₂Ni₃/C leads to a significant increase in the cell performance; for instance, at the current density of 60 mA cm⁻², after the 40-min product collection, the cell voltages of the AEM DEFC with the Pd₂Ni₃/C anode at 60, 70, 80, 90 and 100 °C are 0.304, 0.322, 0.347, 0.374 and 0.386 V, which are, respectively, 80, 70, 77, 60 and 34 mV higher than that with the Pd/C anode. This also confirms that the addition of Ni to Pd can greatly improve the electrode kinetics of the EOR in alkaline media [29].

Fig. 10 shows the effect of the anode catalyst on ACE and CCE at different temperatures and different current densities.

4. Conclusions

In this work, we have investigated the product distribution of the EOR in an AEM fuel cell environment that is composed of a Pd/C (or Pd₂Ni₃/C) anode, an AEM and a Fe–Co cathode by regulation of the operating conditions including temperature, discharging current density, and fuel concentration. The findings are summarized as follows:

**Fig. 8** – Effect of the fuel concentration on the ACE and CCE at different current densities.

**Fig. 9** – Transient cell voltage of the AEM DEFC with the Pd₂Ni₃/C anode at different temperatures and different current densities (Anode: 1.0 M ethanol and 1.0 M KOH aqueous solution, 1.0 ml min⁻¹; Cathode: dry pure oxygen, 100 sccm).

**Fig. 10** – Effect of the anode catalyst on the ACE and CCE at different temperatures and different current densities.
(1) In general, in an AEM fuel cell environment, incomplete ethanol oxidation to acetate prevails over complete oxidation to CO2 in the range of testing conditions. This finding is consistent with that in a CV environment reported in the literature.

(2) Experimental results showed that the change in the anode catalyst from Pd/C to Pd3Sn/C led to a significant increase in the cell performance, but did not help improve the CO2 selectivity of ethanol oxidation.

(3) Among the operating conditions tested, the operating temperature was the most significant parameter that affected the CO2 selectivity: increasing the temperature from 60 to 100 °C enabled the CO2 current efficiency to increase from 6.0% with the Pd/C anode. This suggests that the CO2 selectivity of the EOR can be greatly improved on the thermally activated catalyst surface.

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REFERENCES


