

Performance of dimethoxymethane and trimethoxymethane in liquid-feed direct oxidation fuel cells

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Abstract

The present study involves the evaluation of dimethoxymethane (DMM) (formaldehyde dimethyl acetal, or methylal) and trimethoxymethane (TMM) (trimethyl orthoformate) in direct oxidation liquid-feed fuel cells as novel oxygenated fuels. We have demonstrated that sustained oxidation of TMM at high current densities can be achieved in half-cells and liquid-feed polymer electrolyte fuel cells [1–3]. In the present study, the performance of dimethoxymethane and trimethoxymethane was compared with that of methanol in 2" × 2" (25 cm² electrode area) and 4" × 6" (160 cm² electrode area) direct oxidation fuel cells. The impact of various parameters upon cell performance, such as cell temperature, anode fuel concentration, cathode fuel pressure and flow (O₂ and air), was investigated. Fuel crossover rates in operating fuel cells were also measured for methanol, DMM, and TMM and characterized in terms of concentration and temperature effects. Although DMM and more particularly TMM may present some logistical advantages over that of methanol, such as possessing a higher boiling point, higher flash point, and lower toxicity, the overall performance was observed to be inferior to that of methanol under typical fuel cell operating conditions.
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1. Introduction

Direct oxidation fuel cells that are designed with liquid-feed systems and operate at low temperatures (60–100 °C) are becoming increasingly attractive for both stationary and mobile applications. The direct methanol liquid-feed fuel cell has recently been demonstrated [4–6] to have several advantages over the SOA H₂/O₂ fuel cell for certain applications, such as being able to operate at lower temperatures, requiring no humidification of the gas stream, and fewer safety concerns associated with transportation and handling of the fuel. The viability of the technology has also been independently verified by a number of groups [7,8]. In addition to methanol, a number of organic fuels have been investigated in the context of low temperature, PEM-based, liquid-feed direct oxidation fuel cells,

such as dimethyl ether [9,10], formic acid [11–15], ethyl formate [16], ethanol [17–20], ethylene glycol [21–24], dimethyl oxalate [21,25], 1-methoxy-2-propanol [26], and L-ascorbic acid [27].

Although methanol logistically is a very attractive fuel, it would be advantageous to identify novel high-energy organic fuels that have increased safety and performance. In addition, it would be beneficial to identify any alternative fuels that display low crossover rates across the proton exchange membranes. The present study involves the evaluation of dimethoxymethane (DMM) and trimethoxymethane (TMM) (trimethyl orthoformate) in direct oxidation liquid-feed fuel cells as novel oxygenated fuels. We have previously demonstrated that sustained oxidation of TMM at high current densities can be achieved in half-cells and liquid-feed polymer electrolyte fuel cells. [1–3] Since then, a number of groups have also investigated the electro-oxidation of trimethoxymethane and other aliphatic ether compounds in fuel cell-related research [28–32]. In the present study, the performance of dimethoxymethane and trimethoxymethane was compared with that of methanol in

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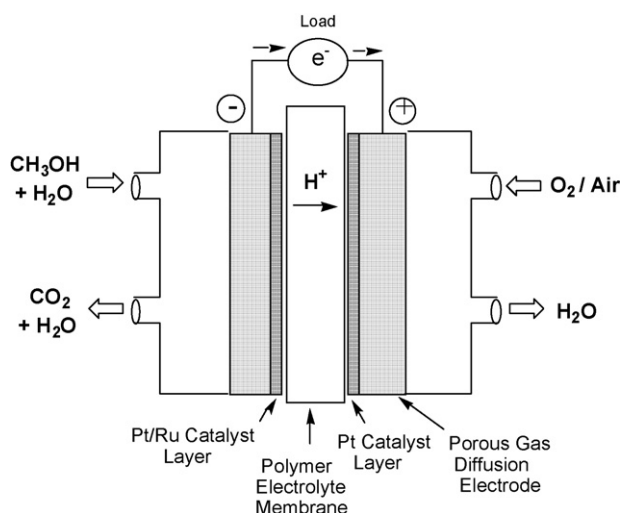
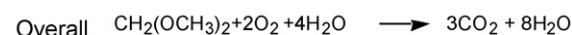
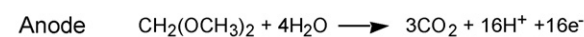


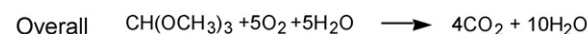
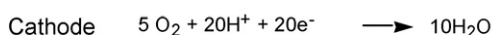
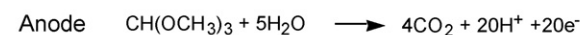
Fig. 1. Schematic diagram of liquid-fed direct oxidation fuel cell shown with methanol as the anodic fuel.

2" × 2" (25 cm² electrode area) and 4" × 6" (160 cm² electrode area) direct oxidation fuel cells, a schematic of which is shown in Fig. 1. The cell reactions of these three oxygenated compounds, assuming that they are completely electro-oxidized to CO₂, are shown in Scheme 1. However, while considering probable mechanisms of electro-oxidation of these compounds, the possibility of acid catalyzed decomposition (and hydrolysis) occurring and producing byproducts that are subsequently oxidized must also be considered. It has been demonstrated that TMM is readily hydrolyzed to methyl formate and methanol in aqueous solution at ambient temperatures [32]. In addition, DMM has been shown to be unstable in acidic solutions and at elevated temperatures, resulting in the generation of methanol and formaldehyde [32]. Thus, the electrical performance of TMM and DMM in direct oxidation fuel cells is fundamentally influenced by the oxidation of the hydrolyzed species, which can be generated in the bulk solution and/or in the acidic electrocatalytic layer. In this

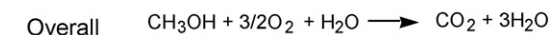
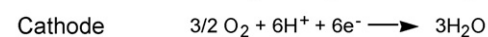
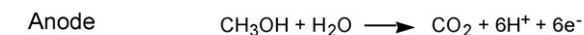
Anodic Oxidation of Dimethoxymethane (DMM)



Anodic Oxidation of Trimethoxymethane (TMM)



Anodic Oxidation of Methanol



Scheme 1. Cell reactions for trimethoxymethane (TMM), dimethoxymethane (DMM), and methanol.

study, the impact of various parameters upon cell performance, such as cell temperature, anode fuel concentration, cathode fuel pressure and flow (O₂ and air), will be described. Fuel crossover rates in operating fuel cells were also measured for methanol, DMM, and TMM and characterized in terms of concentration and temperature effects.

2. Experimental

Solutions of DMM, TMM and methanol were evaluated in single cells and in a 5-cell stack supplied by Giner, Inc. (Newton, MA). The cells were operated at temperatures ranging from 25 to 90 °C and were heated at both the cell block and the anode fuel reservoir, which was equipped with a condenser to prevent evaporation, but allow CO₂ rejection from the system. In the present study, the membrane-electrode assembly (manufactured by Giner, Inc.) consisted of electrocatalytic Pt–Ru (50/50 at.%) on the anode and Pt fine metal powders (surface area 30–70 m² g⁻¹) on the cathode bonded to either side of a Nafion[®]-117 polymer electrolyte membrane. The organic fuel was typically prepared in solutions of concentrations ranging from 0.25 to 3.0 M and circulated at flow rates of 1 L min⁻¹ or greater. The cathode compartment was pressurized with 20–30 psig oxygen, or air, and regulated with a valve located on the cathode exit stream. Flow rates of oxygen ranged from 1.0 to 5.0 L min⁻¹ and were measured on the inlet stream. The cells were operated at current densities in the range of 1–600 mA cm⁻².

The methanol (fuel) crossover rates in operating fuel cells were measured by analyzing the CO₂ content present in the cathode exit stream. This was accomplished by utilizing an on-line analyzer, which measures the CO₂ volume percent in the cathode stream. Before each measurement, the instrument was calibrated with gases of known CO₂ content.

3. Results and discussion

3.1. Electrical performance of TMM, DMM, and methanol

The current–voltage response of a 2" × 2" direct oxidation liquid-fed fuel cell operated with TMM and methanol, investigated over a range of concentrations, under similar conditions, is compared and illustrated in Fig. 2. As evident from the current–voltage response, the 1.0 M solution of methanol delivered better performance at low current densities compared with all concentrations of TMM studied at 90 °C. However, at very high current densities (>750 mA cm⁻²) the 0.5 and 1.0 M solutions of TMM shows improved performance with respect to methanol. This type of behavior was observed at a number of different cell operating temperatures. When the effect of TMM concentration upon cell performance was investigated, it was observed that at low current densities the solutions of low fuel concentration showed less polarization, whereas at higher current densities solutions of higher concentrations showed better performance. This trend in performance is due to fuel crossover effects that dominate at low current densities and mass transfer limitations at higher current densities. A significant feature of

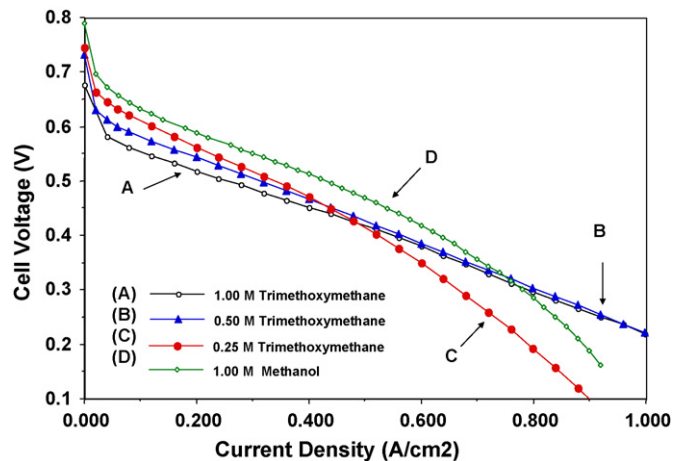


Fig. 2. Performance of trimethoxymethane (TMM) at different concentrations (0.25, 0.50, and 1.0 M solutions) compared with methanol (1.0 M) in a 2'' × 2'' liquid-feed direct oxidation fuel cell at 90 °C.

the performance of 0.50 M TMM is that voltages in excess of 0.50 V are delivered at 300 mA cm⁻² and high current densities can also be sustained (~0.300 V at 800 mA cm⁻²).

When the performance of TMM is compared with methanol in terms of the power densities delivered in operating cells at 90 °C, as shown in Fig. 3, at lower current densities methanol possesses superior performance. However, at current densities exceeding 750 mA cm⁻², solutions of trimethoxymethane displayed higher power densities compared to 1.0 M methanol with greater than 200 mW cm⁻² realized at 1 A cm⁻².

The current–voltage response of a 2'' × 2'' direct oxidation liquid-feed fuel cell operating with dimethoxymethane, investigated as a function of cell operating temperature, is illustrated in Fig. 4. At low temperatures (i.e., 60 °C) and low current densities (i.e., <200 mA cm⁻²), DMM performs in a similar manner compared with TMM and methanol in terms of the current–voltage response. However, when DMM was evaluated at 90 °C the performance was surprising in its inability to sustain high current densities. Presumably, a contributing factor causing the cell polarization is due to the mass transfer limitations introduced

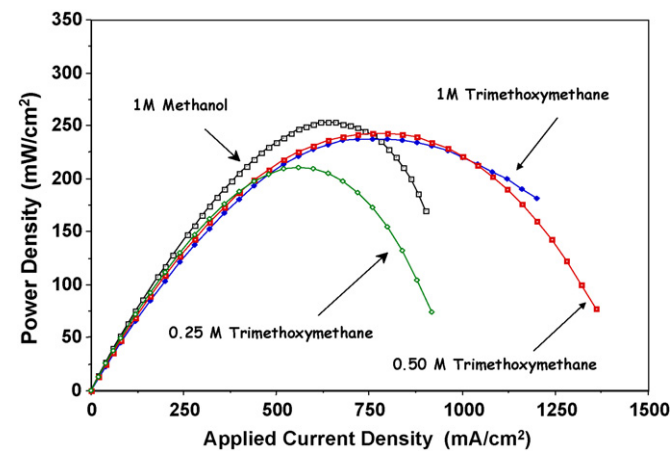


Fig. 3. Comparison of the power densities delivered with 0.25, 0.50 and 1.0 M solutions of TMM and 1.0 M methanol in a liquid-feed direct oxidation fuel cell at 90 °C.

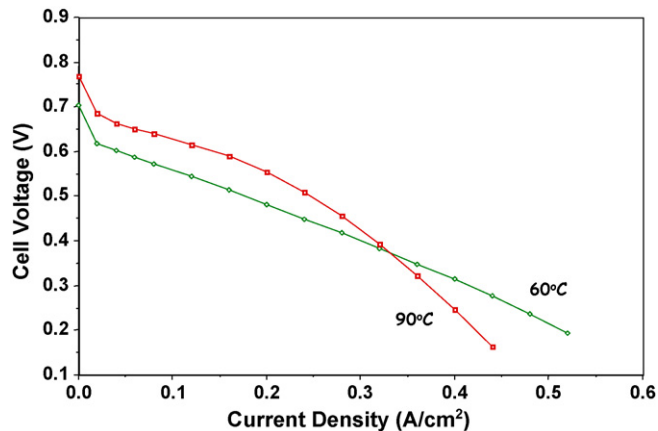


Fig. 4. Performance of 0.50 M DMM at different temperatures (60 and 90 °C) in a 2'' × 2'' liquid-feed direct oxidation fuel cell.

by the volatile nature of DMM (b.p. = 41–42 °C) dominating the vapor phase [33], the vapors resulting in lower concentration at the electrode. Furthermore, presuming that DMM can be hydrolyzed at higher temperatures, other volatile species are generated, such as formaldehyde (b.p. = -21 °C), which in turn can lead to the formation of methylene glycol (HO(CH₂O)H) and poly(oxyethylene) glycols (HO(CH₂O)_nH, where *n* > 1) when in contact with water [34].

A comparison of the current–voltage response for the three fuels investigated is shown in Fig. 5. Since both trimethoxymethane and dimethoxymethane behave in a similar manner to concentrated solutions of methanol, the comparison of fuels was made using less concentrated solution of TMM and DMM compared with the standard 1.0 M methanol solution. In addition, since the Faradaic inefficiency resulting from the parasitic reactions which occur at the cathode due to fuel crossover in the process of the species of oxidation, the more energetic fuels were prepared in less concentrated solutions to compare with methanol. As shown in Fig. 5, dimethoxymethane performed almost identically at low current densities (<150 mA cm⁻² at 90 °C) with methanol. At higher current densities, the methanol shows the best performance with TMM displaying cell volt-

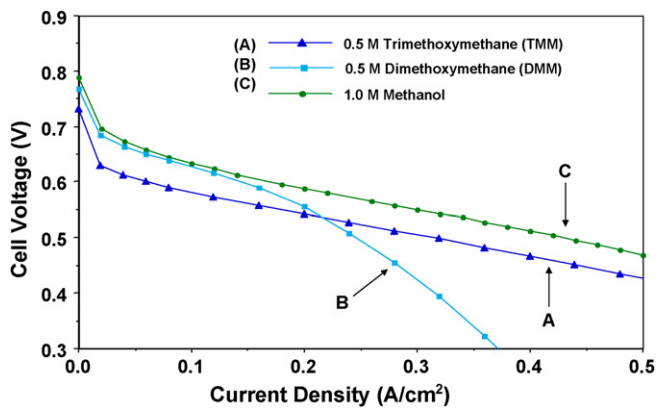


Fig. 5. Comparison of the electrical performance of trimethoxymethane (0.5 M), dimethoxymethane (0.50 M), and methanol (1.0 M) in a liquid-feed direct oxidation fuel cell at 90 °C.

ages typically 50 mV lower over a range of current densities while DMM shows dramatic decrease in cell performance above 150 mA cm^{-2} current density at 90°C .

3.2. Fuel crossover rates of TMM, DMM, and methanol in direct oxidation fuel cells

One of the attractive features of using TMM and DMM as fuels for liquid-feed direct oxidation fuel cells compared to that of methanol is that they are physically much larger, thus, are expected to display lower low fuel crossover rates in operating fuel cells. Thus, one of the objectives of the current study was to determine the fuel crossover rates of TMM, DMM, and methanol in operating cells under similar conditions as a function of current density. The amount of fuel crossover was determined by measuring the carbon dioxide content in the cathodic stream, which assumes that the anodic fuel that permeates through the membrane and anode structure is completely oxidized at the high electro-reduction potentials of oxygen. Thus, for each mole of methanol which permeates to the cathode 1 mol of carbon dioxide will be produced, whereas, each mole of DMM and TMM will produce 3 and 4 mol of carbon dioxide at the cathode, respectively. It is probable that the direct electro-oxidation of DMM and TMM involves multiple steps producing methanol as an intermediate byproduct that is subsequently oxidized. Alternatively, hydrolysis reactions of TMM and DMM can occur under acidic conditions that can result in the formation of intermediate products, such as methyl formate, methanol, formic acid, and formaldehyde. Earlier studies resulted in no detection of any byproducts in the case of TMM and DMM besides methanol, which suggests that if these intermediate byproducts are formed they are oxidized with facility at the electrode, leaving no soluble products in solution. The interpretation of the crossover data in operating fuel cells, however, does not depend on whether hydrolysis or other multiple electro-oxidation steps are occurring, since both mechanisms result in the same amount of carbon dioxide generated at the cathode.

The amount of trimethoxymethane crossover in a 25 cm^2 direct oxidation fuel cell was measured under different conditions and compared with that of other fuels. When the effect of concentration was studied, the expected trend was displayed, in that a nearly linear decrease in the crossover rates were observed with decreasing concentration, expressed in molar concentrations in Fig. 6 and expressed as fuel crossover current densities in Fig. 7. In the case of the cell operated with 1.0 M TMM, crossover rates in the range of $4 \times 10^{-4} \text{ mol min}^{-1}$ were detected at the cathode. As the current density increases, there is a noticeable decline in the amount of fuel crossover due to consumption of the fuel at the anode; however, at much higher current densities the extent of fuel crossover slightly increases. This type of behavior at high current densities is indicative that other transport mechanisms dominate, such as electro-osmotic drag. This type of behavior at high current densities, however, is not observed with the lower concentrations of TMM investigated, such as 0.25 and 0.50 M solutions, suggesting that consumption of the fuel at the anode dominates in these cases.

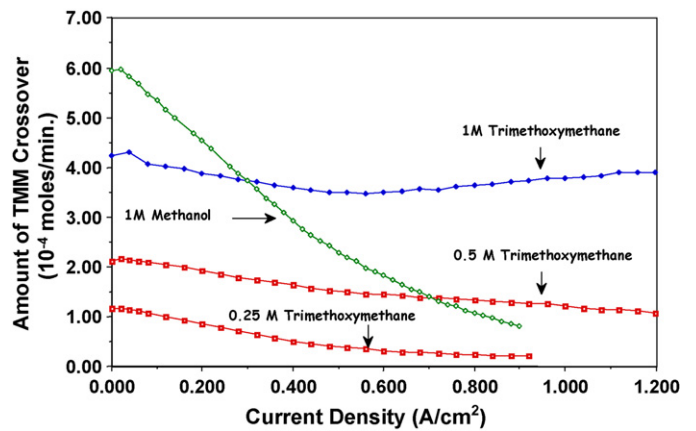


Fig. 6. Comparison of the crossover rates (molar basis as function of applied current) as a function of TMM concentration (0.25, 0.50, and 1.0 M solutions) compared with methanol (1.0 M) in a liquid-feed direct oxidation fuel cell at 90°C .

When the molar crossover rates of trimethoxymethane and methanol are compared in operating fuel cells, as shown in Fig. 6, it is evident that the TMM permeation rate is less than that of methanol. Under open circuit conditions, solutions of TMM displays 30% lower crossover rates than that observed with a similar concentration of methanol. However, at high current densities ($>300 \text{ mA cm}^{-2}$) the methanol permeation sharply decreases, displaying as low as half the molar amount of TMM (or its byproducts) detected, at the cathode at 600 mA cm^{-2} . These results support the understanding that the observed fuel crossover in operating fuel cells under load is due to a number of factors including (i) the permeation rate of the fuel through the membrane-electrode assembly, (ii) the rate of fuel consumption at the anode under load, and the (iii) the effect of electroosmotic drag. One feature of note illustrated in Fig. 6 is that solutions of 0.25 and 0.50 M TMM have much lower molar crossover rates compared with 1.0 M methanol. This fact is significant since the electrical performance of the lower concentration TMM solutions were somewhat comparable.

When the crossover of DMM was investigated in direct oxidation fuel cells, low crossover rates were observed at both 60

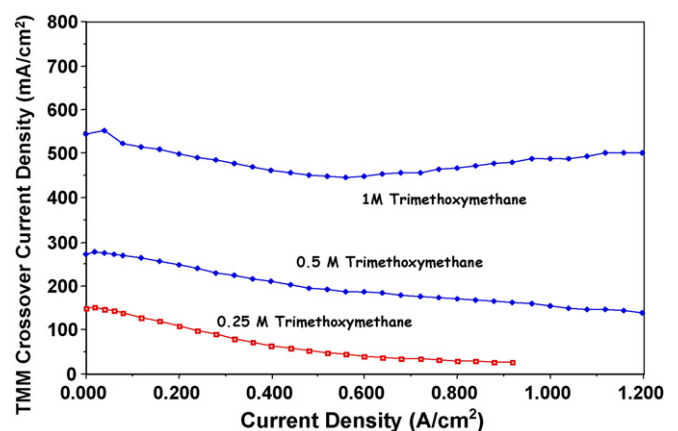


Fig. 7. Crossover current density of trimethoxymethane as a function of concentration (0.25, 0.50, and 1.0 M solutions) in liquid-feed direct oxidation fuel cells at 90°C .

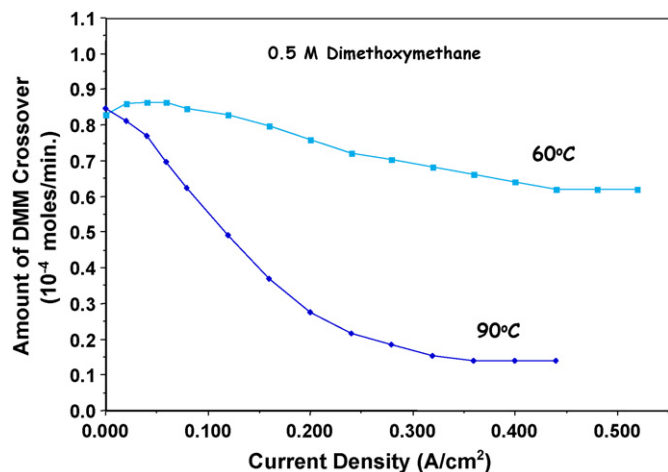


Fig. 8. Crossover rates (mol min^{-1}) of dimethoxymethane at different temperatures (60 and 90 °C) in a liquid-feed direct oxidation fuel cell at 90 °C.

and 90 °C, as shown in Fig. 8. Surprisingly, the values were much lower at the higher temperature and sharply declined as a function of current density. This behavior, however, is consistent with the electrical performance in that the cell could not sustain high current densities and become strongly polarized. This reason for this type of behavior might be due to the fact that DMM is a relatively volatile fuel, and at temperatures as high as 90 °C the fuel feed might contain a vapor phase rich in DMM and depleted aqueous phase, reducing the effective concentration of fuel at the anode. Furthermore, DMM has the propensity to hydrolyze under acidic conditions to produce formaldehyde and methanol at high temperature [32]. These effects must contribute to produce conditions that result in mass transfer limitations at the anode. Thus, the amount of fuel available for participation in transport across the membrane to the cathode will be decreased, explaining the sharp decline in the crossover rate as a function of current density. In contrast, the crossover current densities observed as a function of temperature for TMM follow a similar behavior as that seen for methanol, in which higher crossover rates are observed at high temperatures due to higher diffusion rates through the membrane [6,35].

In order to evaluate the impact of the relative amount of fuel crossover upon the cathode performance and the overall cell voltage, it is necessary to compare the crossover current densities, rather than on molar crossover fluxes. When the crossover rates in terms of parasitic current density experienced at the cathode are considered, the values observed for TMM are more than double than that of methanol for equimolar solutions under open circuit conditions. The observed crossover current densities at the cathode for different concentrations of TMM, DMM and methanol are shown in Fig. 9. Since the electro-oxidation of TMM and DMM involve 20 electron and 16 electron processes, respectively, each molecule that permeates across to the cathode has a proportionately higher contribution in terms of current density than methanol. When the behavior of TMM is contrasted with that of methanol, it is apparent that a 1.0 M methanol solution displays similar crossover characteristics compared with a ~0.3 M solution of trimethoxymethane. This trend is under-

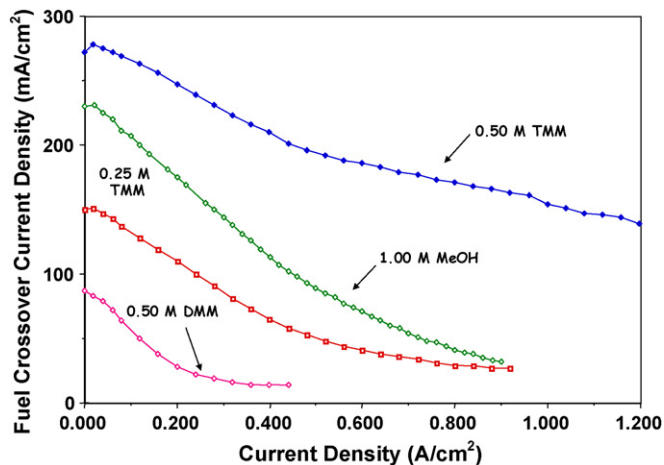


Fig. 9. Comparison of the crossover current densities of dimethoxymethane (DMM), trimethoxymethane (TMM) and methanol in direct oxidation fuel cells under applied load at 90 °C.

standable in that one trimethoxymethane molecule is converted to four carbon dioxide molecule in an overall 20 electron electro-oxidative process, which is equivalent in the number of electrons to the oxidation of three and one-third moles of methanol to CO₂. When DMM is compared with methanol, it is apparent that at 90 °C the crossover rates are significantly lower than that of 1.0 M methanol, with a 0.5 M DMM solution displaying approximately one tenth the crossover observed with 1.0 M methanol at high current densities (>250 mA cm⁻²).

3.3. Fuel and fuel cell efficiencies of TMM, DMM, and methanol

Since the extent of methanol crossover occurring in the fuel cell was measured under operating conditions, it is possible to generate fuel efficiency plots. Using such an *in situ* technique, the fuel efficiency of methanol has been compared with that of fuel cell operating with trimethoxymethane. As shown in Fig. 10, when equimolar solutions of methanol and trimethoxymethane are compared at 90 °C in terms of the fuel efficiency in operat-

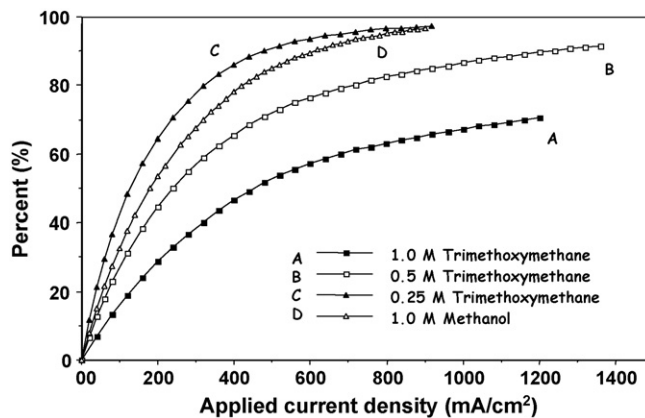


Fig. 10. Comparison of fuel efficiency as a function of trimethoxymethane concentration (0.25, 0.5, and 1.0 M solutions) compared with methanol (1.0 M) in a 2'' × 2'' liquid-feed direct oxidation fuel cell at 90 °C.

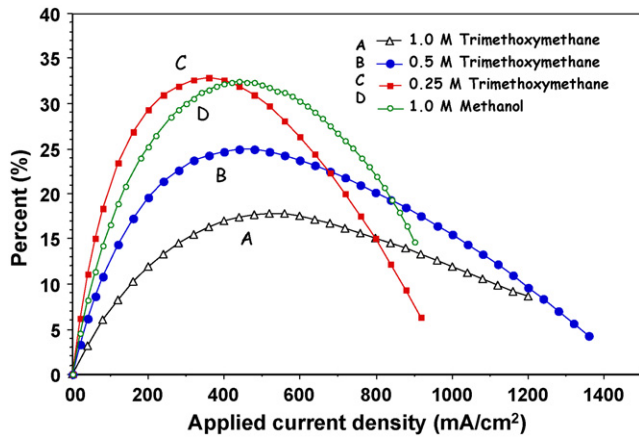


Fig. 11. Comparison of fuel cell efficiency as a function of trimethoxymethane concentration (0.25, 0.50, and 1.0 M solutions) compared with methanol (1.0 M) in liquid-feed direct oxidation fuel cells at 90 °C.

ing cells, the methanol solution was shown to have dramatically higher efficiency at all current densities. However, less concentrated solutions of trimethoxymethane solution (0.25 M) yielded higher fuel efficiency due to the fact that the extent of fuel crossover is less and the dilute solution results in mass transfer limitations decreasing the amount of fuel available for transport across the membrane. It is interesting to note that a 1.0 M solution of methanol behaves in a manner similar to that of a 0.25–0.40 M solution of trimethoxymethane which correlates well with the energetic content of the fuels (a 6 electron and 20 electron oxidation process, respectively) and suggests that one molecule of trimethoxymethane behaves in a similar fashion to approximately three molecules of methanol. In the case of both 1.0 M methanol and 0.25 M trimethoxymethane, greater than 90% fuel efficiency was observed at 600 mA cm⁻².

In addition to calculating the fuel efficiencies, the fuel cell efficiencies were calculated (as shown below) and compared for solutions of trimethoxymethane and methanol, as shown in Fig. 11. It is evident that the peak fuel cell efficiency value for a fuel cell operating on 1.0 M methanol is within the range of 350–550 mA cm⁻², corresponding to ~32%. In the low current density region, fuel crossover characteristics dominate and adversely affect the efficiency values,

$$\text{Efficiency} = \left(\frac{\text{Voltage}}{1.24 \text{ V}} \right) \left(\frac{i_{\text{applied}}}{i_{\text{crossover}} + i_{\text{applied}}} \right)$$

whereas as at higher current densities the overall efficiency is dictated by the voltage efficiency, which steadily drops as polarization effects become more significant. When the dilute solution of trimethoxymethane (0.50 M) is compared with that of 1.0 M methanol, it is evident that that the fuel cell efficiency is slightly higher at its peak and surpasses 30% efficiency at a much lower current density. However, the high fuel cell efficiency cannot be sustained as successfully when compared at the higher current densities. These results are consistent with a use of a dilute fuel stream in which there is lower crossover and larger mass transfer limitations at high current densities. The more concentrated solutions of trimethoxymethane suffered from high fuel

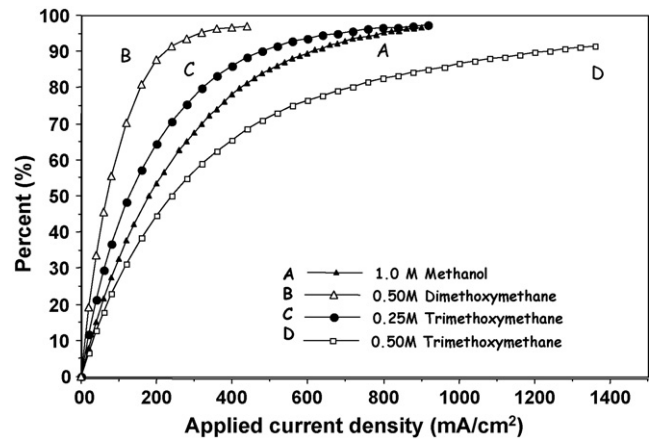


Fig. 12. Comparison of fuel efficiencies of trimethoxymethane (0.50 and 0.25 M solutions), dimethoxymethane (0.5 M), and methanol (1.0 M) in liquid-feed direct oxidation fuel cells at 90 °C.

crossover rates and were unable to attain efficiencies greater than 25%. However, at very high current densities (>850 mA cm⁻²) the 0.50 M solution of trimethoxymethane displayed higher fuel cell efficiencies than that of 1.0 M solution methanol due to the diminished impact of fuel crossover.

When the behavior of dimethoxymethane was considered with respect to fuel and fuel cell efficiency at 90 °C with that of trimethoxymethane and methanol, it was interesting to note that very high efficiency values were obtained at low current densities (200–400 mA cm⁻²). As shown in Fig. 12, fuel efficiency values approaching 90% were observed at current densities as low as 200 mA cm⁻² in the case of a fuel cell run with 0.50 M DMM solution at 90 °C. When the fuel cell efficiency values were computed for these same current–voltage curves, as illustrated in Fig. 13, over 39% fuel cell efficiency was observed at 90 °C at current densities of ~200 mA cm⁻² with 0.50 M solutions of DMM. A possible explanation for the high fuel and fuel cell efficiencies observed with solutions of DMM in fuel cells run at high temperatures is that the fuel is likely hydrolyzed (either in the bulk solution and/or at the electrocatalytic reaction

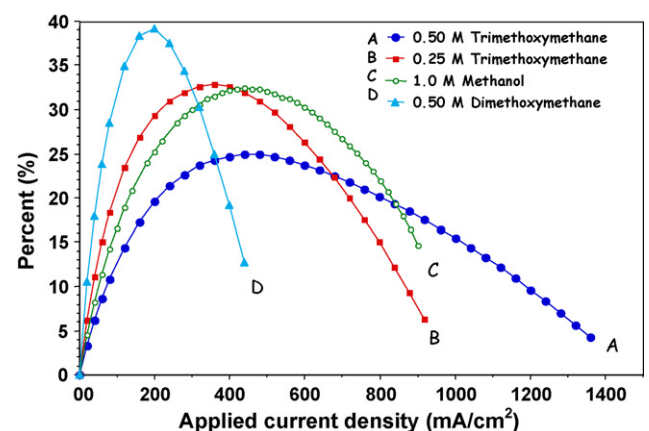


Fig. 13. Comparison of fuel cell efficiencies of trimethoxymethane (0.50 and 0.25 M solutions), dimethoxymethane (0.5 M), and methanol (1.0 M) in liquid-feed direct oxidation fuel cells at 90 °C.

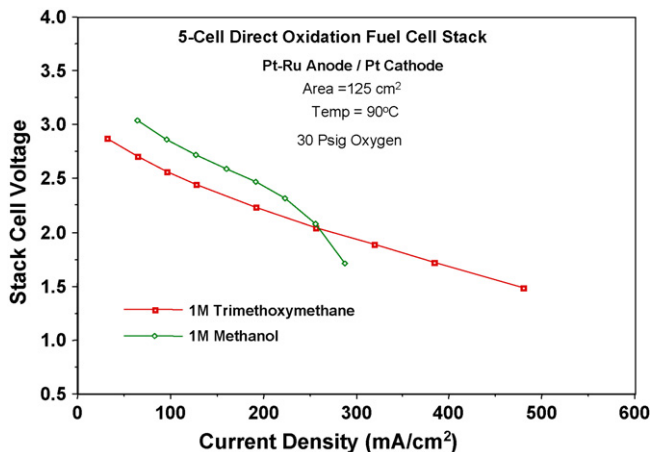


Fig. 14. Performance of trimethoxymethane and methanol in a liquid-feed direct oxidation 5-cell stack.

zone), to produce volatile, reactive species, such as formaldehyde, which are rapidly oxidized at the anode or evaporate from the anode stream.

3.4. Stack performance

The performance of TMM was also evaluated on a 5-cell stack and compared with that of methanol, as shown in Fig. 14. When 1.0 M solutions were evaluated, TMM showed superior performance to that of MeOH at high current densities. An interesting feature is that a 1.0 M TMM solution shows similar characteristics to the performance of a 3.0 M MeOH solution. Additionally, a 3.0 M methanol solution showed better performance than that observed with a 1.0 M methanol solution over the range of current densities. Further investigations revealed that the stack design was very sensitive to fuel concentrations. This type of behavior is not seen in single cells where the higher concentrated solutions tend to perform poorly at low current densities.

4. Conclusion

The performance of dimethoxymethane and trimethoxymethane were compared with that of methanol in $2'' \times 2''$ (25 cm^2 electrode area) and $4'' \times 6''$ (160 cm^2 electrode area) direct oxidation fuel cells. The impact of various parameters upon cell performance, such as cell temperature and anode fuel concentration, was investigated. As evident from the current–voltage response 1.0 M solutions of methanol delivered better performance at low current densities compared with all concentrations of TMM studied at 90°C . However, at very high current densities ($>750 \text{ mA cm}^{-2}$) 0.5 and 1.0 M solutions of TMM shows improved performance with respect to methanol. At low temperatures (i.e., 60°C) and low current densities (i.e., $>200 \text{ mA cm}^{-2}$), DMM performs like TMM and methanol in terms of the current–voltage response. However, when DMM was evaluated at 90°C the performance was surprising in its inability to sustain high current densities. Fuel crossover rates in operating fuel cells were also measured for methanol, DMM,

and TMM and characterized in terms of concentration and temperature effects. It was interesting to note that a 1.0 M solution of methanol behaves in a manner similar to that of a 0.25–0.40 M solution of trimethoxymethane, which correlates well with the energy content of the fuels, and suggests that TMM (and DMM), are hydrolyzed to smaller molecules during the operation of the fuel cells. In summary, DMM and TMM have been observed to provide good electrical performance in direct oxidation fuel cells, however, the overall performance was observed to be inferior to that of methanol under desirable operating conditions. Thus, any advantage of utilizing these fuels, especially TMM, hinges upon the expectation that they can be handled and transported more safely, due to more favorable physical properties and lower toxicity.

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References

- [1] S.R. Narayanan, E. Vamos, S. Surampudi, H. Frank, G. Halpert, R. Knieler, M. Smart, G.K.S. Prakash, G.A. Olah, Ext. Abst. 187th Meeting of the Electrochemical Society, 95-1, 1995, p. 722.
- [2] M.C. Smart, G.K.S. Prakash, G.A. Olah, S.R. Narayanan, H. Frank, S. Surampudi, G. Halpert, J. Kosek, C. Cropley, Ext. Abs. 190th Meeting of the Electrochemical Society (Abs.# 789), vol. 96-2, San Antonio, Texas, 1996.
- [3] S.R. Narayanan, E. Vamos, S. Surampudi, H. Frank, G. Halpert, G.K. Surya Prakash, M.C. Smart, R. Knieler, G.A. Olah, J. Kosek, C. Cropley, J. Electrochem. Soc. 144 (1997) 4195.
- [4] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. Laconti, J. Kosek, G.K.S. Prakash, G.A. Olah, J. Power Sources 47 (1994) 377.
- [5] S.R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M. Smart, S. Surampudi, G. Halpert, Electrochem. Soc. Proc. 95–123 (1995) 261.
- [6] S.R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M.C. Smart, T.I. Valdez, S. Surampudi, G. Halpert, J. Kosek, C. Cropley, Proceedings of the IEEE 11th Annual Battery Conference on Applications and Advances, Long Beach, CA, 1996, p. 113.
- [7] (a) X. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) L13; (b) X. Ren, M.S. Wilson, S. Gottesfeld, Electrochem. Soc. Proc. PV, 95-23, Pennington, 1995.
- [8] A.K. Shukla, P.A. Christensen, M. Hamnett, M. Hogarth, J. Power Sources 55 (1995) 87.
- [9] M.M. Mench, H.M. Chance, C.Y. Wang, J. Electrochem. Soc. 151 (2004) A144–A150.
- [10] J.T. Muller, P.M. Urban, W.F. Holderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, J. Electrochem. Soc. 147 (11) (2000) 4058–4060.
- [11] C. Rice, R.I. Ha, R.I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, J. Power Sources 111 (1) (2002) 83–89.
- [12] M. Baldauf, D.M. Kolb, J. Phys. Chem. 100 (27) (1996) 11375–11381.
- [13] M. Weber, J.T. Wang, S. Wasmus, R.F. Savinell, J. Electrochem. Soc. 143 (7) (1996) L158–L160.
- [14] S. Ha, C. Rice, R.I. Masel, A. Wieckowski, J. Power Sources 112 (2) (2002) 655–659.
- [15] C. Rice, S. Ha, R.I. Masel, A. Wickowski, J. Power Sources 115 (2) (2003) 229–235.

- [16] K.Y. Chen, A.C.C. Tseung, *J. Electroanal. Chem.* 451 (1/2) (1998) 1–4.
- [17] F. Delime, J.M. Leger, C. Lamy, *J. Appl. Electrochem.* 28 (1) (1998) 27–35.
- [18] J.T. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 142 (12) (1995) 4218–4224.
- [19] A.S. Arico, P. Creti, P.L. Antonucci, V. Antonucci, *Electrochem. Solid State Lett.* 1 (2) (1998) 66–68.
- [20] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.M. Leger, *J. Power Sources* 105 (2) (2002) 283–296.
- [21] E. Peled, T. Duvdevani, A. Aharon, A. Melman, *Electrochem. Solid State Lett.* 4 (4) (2001) A38–A41.
- [22] E. Peled, V. Livshits, T. Duvdevani, *J. Power Sources* 106 (1/2) (2002) 245–248.
- [23] Z. Ogumi, K. Matsuoka, S. Chiba, M. Matsuoka, Y. Iriyama, T. Abe, M. Inaba, *Electrochemistry* 70 (12) (2002) 980–983.
- [24] R.B. de Lima, V. Paganin, T. Iwasita, W. Vielstich, *Electrochim. Acta* 49 (1) (2003) 85–91.
- [25] S. Suarez, S.H. Chung, S. Greenbaum, S. Bajue, E. Peled, T. Duvdevani, *Electrochim. Acta* 48 (14–16) (2003) 2187–2193.
- [26] Z.G. Qi, A. Kaufman, *J. Power Sources* 110 (1) (2002) 65–72.
- [27] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, T. Kobayashi, *Electrochem. Solid State Lett.* 6 (12) (2003) A257–A259.
- [28] J.T. Wang, W.F. Lin, M. Weber, S. Wasmus, R.F. Savinell, *Electrochim. Acta* 43 (24) (1998) 3821–3828.
- [29] O. Savadogo, X. Yang, *J. Appl. Electrochem.* 31 (7) (2001) 787–792.
- [30] O. Savadogo, X. Yang, *J. New Mater. Electrochem. Syst.* 5 (1) (2002) 9–13.
- [31] Y. Tsutsumi, Y. Nakano, S. Kajitani, S. Yamasita, *Electrochemistry* 70 (12) (2002) 984–987.
- [32] N. Wakabayashi, K. Takeuchi, H. Uchida, M. Watanabe, *J. Electrochem. Soc.* 151 (10) (2004) A1636–A1640.
- [33] C. Kuhnert, M. Albert, S. Breyer, I. Hahnenstein, H. Hasse, G. Maurer, *Ind. Eng. Chem. Res.* 45 (2006) 5155–5164.
- [34] R. Peschla, B.C. Garcia, M. Albert, C. Kreiter, G. Maurer, *Ind. Eng. Chem. Res.* 42 (2003) 1508–1516.
- [35] Y. Wu, T.A. Zowodinski, M.C. Smart, G.K.S. Prakash, G.A. Olah, S. Greenbaum, *Materials Research Society Symposium Proceedings on Materials for Electrochemical Energy Storage and Conversion II*, Boston, MA, December 1997.