

# 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 cm<sup>2</sup> electrode area) and 4" × 6" (160 cm<sup>2</sup> 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 (O<sub>2</sub> 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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**Keywords:** Direct oxidation fuel cell; Dimethoxymethane; Trimethoxymethane; Methanol

## 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 H<sub>2</sub>/O<sub>2</sub> 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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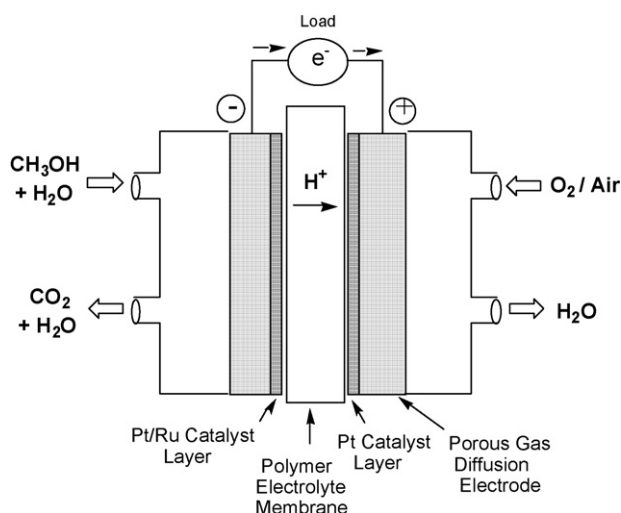
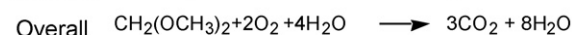
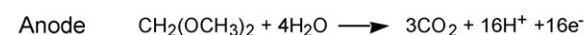


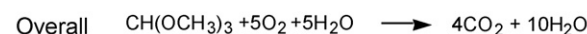
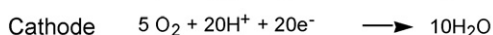
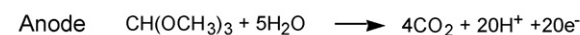
Fig. 1. Schematic diagram of liquid-fed direct oxidation fuel cell shown with methanol as the anodic fuel.

2" × 2" (25 cm<sup>2</sup> electrode area) and 4" × 6" (160 cm<sup>2</sup> 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 CO<sub>2</sub>, 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

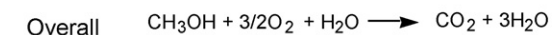
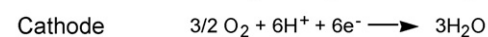
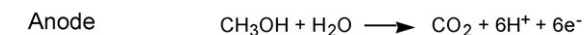
#### Anodic Oxidation of Dimethoxymethane (DMM)



#### 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 (O<sub>2</sub> 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 CO<sub>2</sub> 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 m<sup>2</sup> g<sup>-1</sup>) on the cathode bonded to either side of a Nafion<sup>®</sup>-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<sup>-1</sup> 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<sup>-1</sup> and were measured on the inlet stream. The cells were operated at current densities in the range of 1–600 mA cm<sup>-2</sup>.

The methanol (fuel) crossover rates in operating fuel cells were measured by analyzing the CO<sub>2</sub> content present in the cathode exit stream. This was accomplished by utilizing an on-line analyzer, which measures the CO<sub>2</sub> volume percent in the cathode stream. Before each measurement, the instrument was calibrated with gases of known CO<sub>2</sub> 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<sup>-2</sup>) 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

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