Electrochemical and Solid-State Letters, **4** (4) A38-A41 (2001)
1099-0062/2001/4(4)/A38/4/$7.00 © The Electrochemical Society, Inc.

New Fuels as Alternatives to Methanol for Direct Oxidation Fuel Cells

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Hydrocarbons and aliphatic alcohols are difficult to electro-oxidize. Even at 190°C the oxidation of ethanol is incomplete (less than 40% CO_2). We report here, for the first time, on the complete electro-oxidation of two molecules having C-C bonds; ethylene glycol (EG) and dimethyl oxalate (DMO). Both are less prone to pass through the membrane, and, as a result, have up to 94-95% fuel utilization, 9-10% higher than that of methanol. EG is well known in the automobile industry and, in contrast to methanol, its distribution infrastructure already exists, making it a promising candidate for practical electric vehicles. DMO is a solid that has limited solubility in water, thus it may be added directly to the anode compartment with no need of a separate fuel tank and monitoring and feeding systems. It is projected that a flat dimethyl oxalate fuel cell will deliver up to 600 Wh/kg, five to ten times the specific energy of the lithium-ion battery in small portable devices. However, methanol does have some advantages over EG and DMO, its theoretical capacity is 20 to 40% higher and so far it has higher energy conversion efficiency.
[DOI: 10.1149/1.1355036]

Manuscript submitted November 10, 2000; revised manuscript received January 5, 2001. Available electronically February 14, 2001.

Fuel cells (FC) are electrochemical devices that convert, with high efficiency, the chemical energy of a fuel-oxidation reaction directly into electrical energy. Fuel cells employing organic fuels are extremely attractive as power sources for electric vehicles, and for both stationary and portable applications. A direct oxidation fuel cell (DOFC) is a device in which the organic fuel is fed directly into the fuel cell without any previous chemical modification. Inside the cell, the fuel is oxidized at the anode and oxygen is reduced to water at the cathode. Hence, DOFCs offer a considerable weight and volume advantage over indirect fuel cells, in which the fuel is reformed into hydrogen prior to use.

Until now, methanol has been considered the ''best'' fuel.[1-9] It has a low cost and happens to be more efficiently oxidized, at certain conditions, than other alcohols and aqueous hydrocarbons. However, the use of methanol as a fuel presents several problems: methanol is toxic, highly flammable, has a low boiling point (65°C), and is highly prone to pass through the polymer-electrolyte membrane (high crossover). Fuel crossover lowers the operating potential of the oxygen electrode and results in the consumption of fuel and generation of heat without the production of useful electrical energy. Hence, it is obviously desirable to minimize the rate of fuel crossover. Hydrocarbons and aliphatic alcohols are difficult to electro-oxidize completely,[10,11] the main products of aliphatic alcohols being aldehydes or ketones, CO_2, and acids or esters. Even at 190°C, in a polymer-electrolyte membrane (PEM) FC, the oxidation of ethanol is incomplete, the main oxidation product (over 60%) is ethanal and not CO_2 (less than 40%).[11] There has been no report on the complete electro-oxidation of a molecule with a C-C bond, except for oxalic acid.[12] An appropriate fuel would be one that is oxidized completely to CO_2 with no or only minor side products.

Our initial guideline, in searching for new fuels, was the complete electro-oxidation reported for oxalic acid.[12] After confirming that this is possible in our DOFC, with very high conversion (91%, Table I), we successfully electro-oxidized dimethyl oxalate (DMO) and ethylene glycol (EG).

These fuels are more efficient, safer, and have a capacity density (in terms of Ah/g) 20-40% lower than that of methanol (Table I). EG is well known in the automobile industry, and, as opposed to methanol, its distribution infrastructure already exists, thus it is a promising candidate for practical electric vehicles and for mobile and stationary applications. The use of solid fuels, like DMO, trioxane[13] (or polyethylene oxalate (PolyEO), which we have yet to examine), in small liquid-feed fuel cells (LFFC) has several advantages over the use of liquid fuels like methanol. These include simplification in the logistics, storage, and transport of the solid fuels[13] and a smaller fuel-crossover current due to the larger size and the limited solubility of the solid fuel. The solubility of DMO at 20°C, is only 6 g/100 g of water[14] while methanol is completely miscible. However, we found that in a few days the solubility of DMO increases, probably as a result of partial hydrolysis to methanol, monomethyl oxalate, and oxalic acid. Because of its infinite solubility, methanol must be diluted to 3-6% before being fed into the DMFC. In contrast, as a result of its limited solubility, solid DMO (and possibly PolyEO or its oligomers) may be fed directly into the anode compartment (which serves as a fuel tank) thus removing the need for a separate fuel tank, fuel monitoring, and feeding systems. This configuration is obviously advantageous for small, portable applications like cellular phones, mobile internet systems, and computers.

We recently reported the development of a new nanoporous proton-conducting membrane (NP-PCM) and have applied it in a DMFC.[15,16] The use of the NP-PCM in the DMFC offers several advantages over the Nafion-based DMFC; lower membrane cost (by more than two orders of magnitude), smaller pores (by a factor of two), lower methanol crossover (by up to an order of magnitude) leading to much higher fuel utilization, and higher conductivity (by up to a factor of four). The ionic conductivity of the NP-PCM, unlike Nafion, is not affected by heavy-metal impurities. Thus it permits the use of cheaper catalysts and hardware materials. The maximum power density achieved so far, at 80°C and at ambient oxygen pressure, is 85 mW/cm^2 (obtained at 0.35 A/cm^2). Other ramifications of using aqueous sulfuric acid in DOFC are presented in Ref. 15.

We report here the characterization of EG and DMO as new fuels in DOFCs on the basis of our new NP PCM.[15]

Experimental

We used the same FC setup described in Ref. 16. Our test vehicle was a 7 cm^2 DOFC operating at ambient oxygen pressure. The fuel-cell housing was built from synthetic graphite blocks provided by Globetech Inc., in which flow fields were engraved, one for the organic fuel solution and the other for oxygen or air. The membrane/electrode assembly consisted of 240 μm thick NP-PCM[15] (composition 24% (v/v) polyvinylidene fluoride (PVDF), 16% SiO_2, and 60% void volume, conductivity 0.2 S/cm at 25°C for 3 M sulfuric acid) hot pressed between two Toray papers coated with catalyst layers. The anode catalyst layer (6 mg/cm^2 Pt loading) consisted of 91 wt % platinum-ruthenium (1:1 atomic) nanopowder (Johnson-Matthey) and 9% Kynar 2801 PVDF. The cathode consisted of Pt nanopowder (Johnson-Matthey) catalyst layer (4 mg/cm^2 loading) spread on a diffusion layer. The fuels tested were oxalic acid, dimethyl oxalate, and ethylene glycol, in the concentration range of

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Table I. Utilization comparison of different fuels.

	Number of elecrons	Theoretical capacity [Ah/g]	Utilization at 0.4 V[a] [%]		Utilization at 0.2 V[a] [%]	
			Experimental	Corrected	Experimental	Corrected
Oxalic acid	2	0.43			91	
Methanol	6	5.03	79	81	82	85
Ethylene glycol	10	4.32	83	89	89	94
Dimethyl oxalate	14	3.18	64	67	93	95

[a] An average of at least two tests.

0.1-1.0 M. During operation, an aqueous solution of 3 M sulfuric acid and a fuel was circulated past the anode (using a Masterflex L/S Cole-Parmer Instrument Co. peristaltic pump) at flow rates of from 4 to 15 mL/min. Oxygen was fed into the cathode compartment directly or through a water bubbler at ambient pressure and at a rate of 7 to 40 mL/min.

The fuel utilization was determined by performing electrochemical titrations on 50 mL of fuel solution at constant voltage until the current dropped to 3 mA. It is estimated that at this current only a small percentage of the fuel remained. The utilization was calculated by comparing the experimental capacity with the theoretical value. A further correction was made by extrapolation of the titration curves to zero current. This correction increases the utilization values by 3 to 6% (Table I). Measurements of fuel crossover were carried out at several temperatures by feeding nitrogen instead of oxygen into the cathode compartment (at ambient pressure) and feeding organic fuel-acid solution into the anode compartment. Cell voltage was reversed; hydrogen was evolved at the fuel electrode while fuel that crossed over to the cathode side was oxidized. The current that flows at 1 V was found to be the limiting current for fuel oxidation.[16,17]

Results and Discussion

Oxidation of DMO may proceed by two parallel paths; the first involves a preceding chemical step of hydrolysis of the ester to monomethyl oxalate or oxalic acid and two methanol molecules, followed by the oxidation of the products. The second path involves the oxidation of DMO itself. Similar mechanisms were suggested for dimethyl orthoformate.[13] Fuel utilization at 0.2 V is 95% for DMO and 94% for EG and is lower (85%) for methanol (Table I). At the more practical voltage of 0.4 V fuel utilization is 89% for EG, 67% for DMO, and 81% for methanol. At the lower voltage, the current density is higher, the fuel concentration at the PCM/anode interface is lower, and the titration time is shorter, therefore the fuel crossover is smaller (for DMO the initial current is 0.4 and 0.1 A at 0.2 and 0.4 V, respectively). These high utilization values (Table I) prove almost total oxidation of the new fuels. Note that some of the fuel is consumed in the crossover process. No attempt to determine the distribution of products was made. The most important result is the proof of two-electron transfer for oxalic acid ($C_2O_4H_2$) oxidation, 14 for DMO ($C_4O_4H_6$), and 10 electrons for ethylene glycol ($C_2O_2H_6$)

$$C_2O_4H_2 \rightarrow 2CO_2 + 2H^+ + 2e^- \quad [1]$$

$$C_4O_4H_6 + 4H_2O \rightarrow 4CO_2 + 14H^+ + 14e^- \quad [2]$$

$$C_2O_2H_6 + 2H_2O \rightarrow 2CO_2 + 10H^+ + 10e^- \quad [3]$$

Measurements of fuel crossover were carried out at several temperatures. Table II summarizes the test results. The crossover current density depends on fuel permeability, temperature, concentration, and the total number of electrons involved in the oxidation. The crossover current density for 1 M methanol (at 80°C) is double that of 1 M EG and that of 0.25 M DMO. However, when the number of electrons is taken into account and the fuel flux in terms of mol s^{-1} cm^{-2} (at 80°C and under diffusion-controlled conditions) is normalized to 1 M fuel, it can be seen that the permeability (flux) of EG is one-third that of methanol while that of DMO is only a little smaller.

In this paper, we report preliminary results obtained with nonoptimized Pt-Ru catalysts used for methanol. It is not clear whether the methanol catalyst is the best choice of EG and DMO electrooxidation. We are sure that much better performance can be achieved following dedicated catalyst development and after cell optimization.

Figure 1 shows polarization curves for several fuels in 3 M H_2SO_4 fed into an NP-PCM fuel cell at 80°C. The operating voltage of EG and DMO are lower than that of methanol. With the use of a reference electrode it was found that the voltage losses at both the DMO and EG electrodes and at the oxygen electrodes are larger than in the case of methanol (Fig. 2). This means that both EG and DMO, which cross to the cathode side, slow or deactivate oxygen reduction. As the permeability of EG is smaller than that of DMO, its cell voltage is higher, especially at high current densities. It is important, in addition to developing better catalysts, to lower the crossover of both EG and DMO. The use of lower fuel concentra-

Table II. Crossover of different fuels.

Fuel	Crossover test			
	Temperature [°C]	Concentration [M]	Crossover current density [A/cm^2]	Fuel flux[a] [mol s^{-1} cm^{-2}] 1×10^{-8}
Dimethyl oxalate	60	0.10	0.009	6.7
	60	0.25	0.025	7.4
	80	0.25	0.038	11
Ethylene glycol	80	0.5	0.019	3.9
	80	1.0	0.041	4.2
Methanol	80	1.0	0.076	13

[a] Normalized to 1 M.

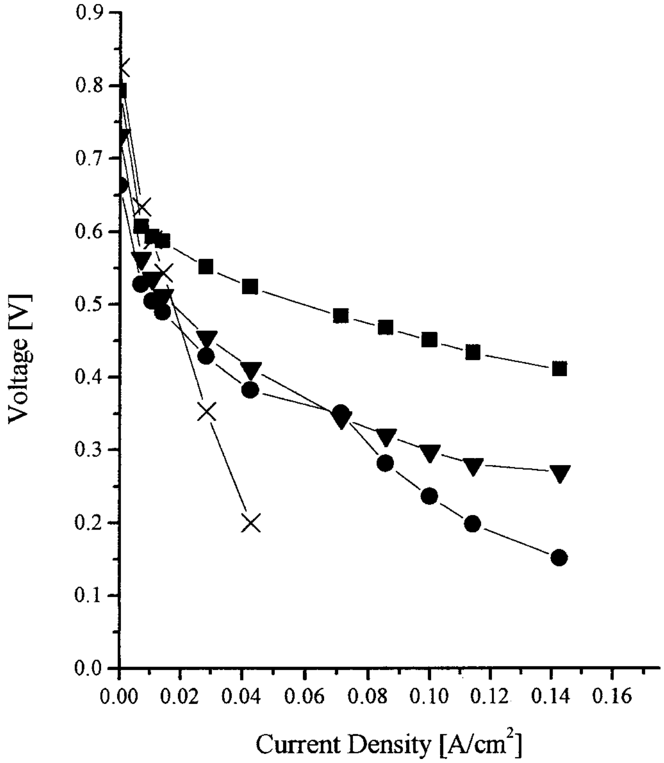

Figure 1. Polarization curves for several fuels in 3 M H_2SO_4 fed into NP-PCM fuel cell at 80°C -■- 1.0 M MeOH; - ●- 0.25 M dimethyl oxalate; -×- 1.0 M oxalic acid; -▼- 0.5 M ethylene glycol.

tions (0.25 M DMO and 0.5 M EG) can cause mass-transport problems at higher current densities (Fig. 1). This cell worked with different fuels for over 3500 h at 60 to 95°C.

Figure 3 shows an 8 mm thick flat 7 cm^2 DMO DOFC with a transparent acrylic house. The DMO tank is an integral part of the anode compartment, and the amount of solid DMO fuel can be seen at the back of the FC. The thickness of the fuel tank is about 4 mm. It has the same membrane electrode assembly (MEA) as has the previous cell. Figure 4 presents its polarization curve in air.

DMO is a solid with limited solubility in water and so may be added directly (in the form of tablets, granules, particles, etc.) to a fuel tank attached to the back of the anode; there is thus no need of a separate fuel tank and feeding system. Two flat DMO fuel cells in series combination together with a dc/dc converter (which can start working from 0.7 V) is an excellent power system candidate for small portable devices (cellular phones, mobile internet devices, and computers). In applications where current pulses are needed, a small high-power rechargeable battery can be added. These flat cells can be mounted either on the cover or at the bottom of the electronic device. It is much simpler than the stack type FC that requires a separate fuel tank, fuel monitoring, and feeding systems. One gram of DMO supplies 1.272 Wh at 0.4 V. As a result, a 10 mm thick, flat, single-cell DMO DOFC (which is charged with about 0.6 g DMO per cm^2 of electrode area), can provide 600 Wh/kg, five to ten times more energy per weight than the best lithium-ion battery in small portable devices. In addition to DMO, other solid and liquid fuels can be considered for DOFC applications. These include the EG esters of formic, glyoxalic, and oxalic acids and the methyl ester of glyoxalic acid. Methanol has some advantages over EG and DMO: its theoretical capacity is 20 to 40% higher and so far it has higher energy conversion efficiency. Better catalysts for the new fuels are needed.

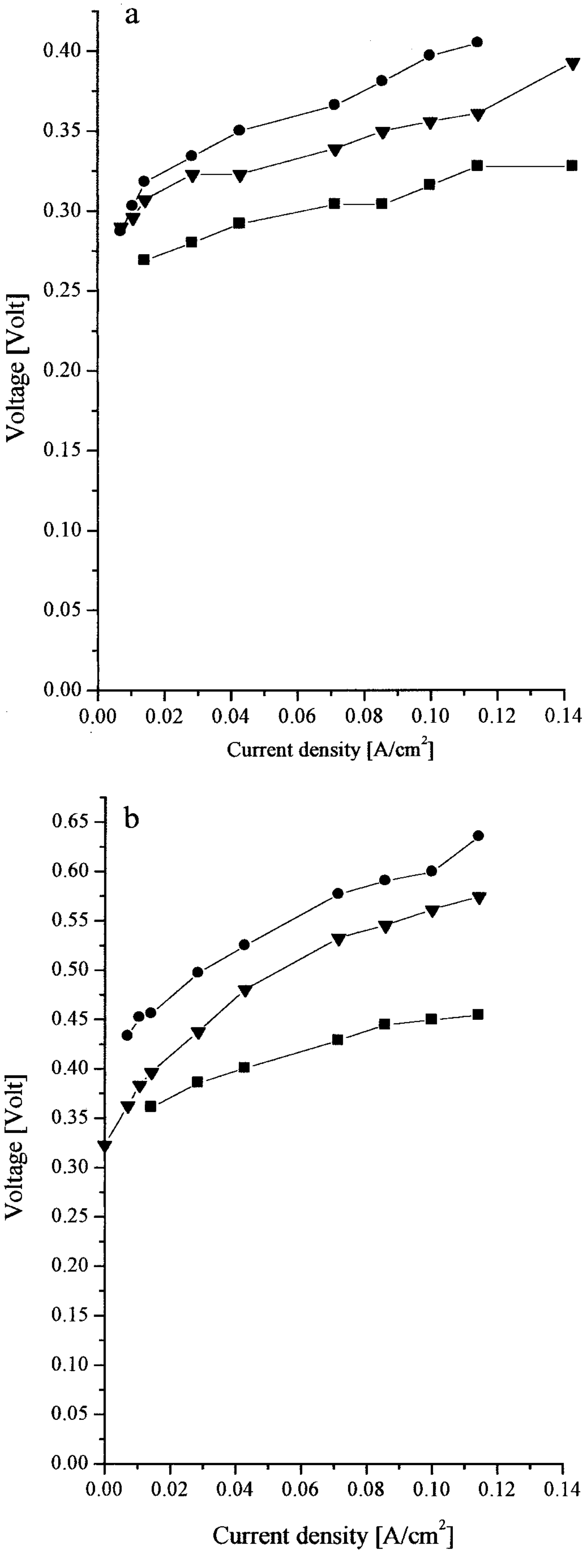

Figure 2. (a) Anodic and (b) cathodic overpotentials at 80°C, -▼- 0.5 M EG; -■- 1 M MeOH; -●- 0.5 M DMO.

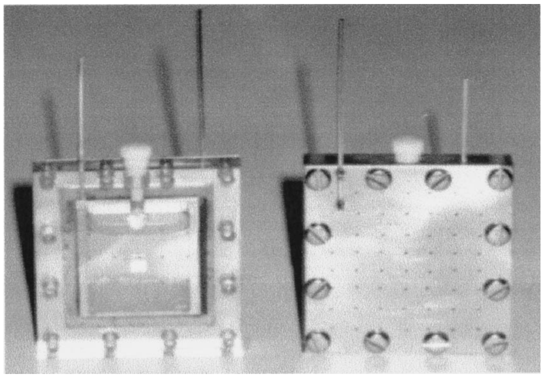

Figure 3. A flat 7 cm^2 acrylic house fuel cell; fuel side (left) and air side (right).

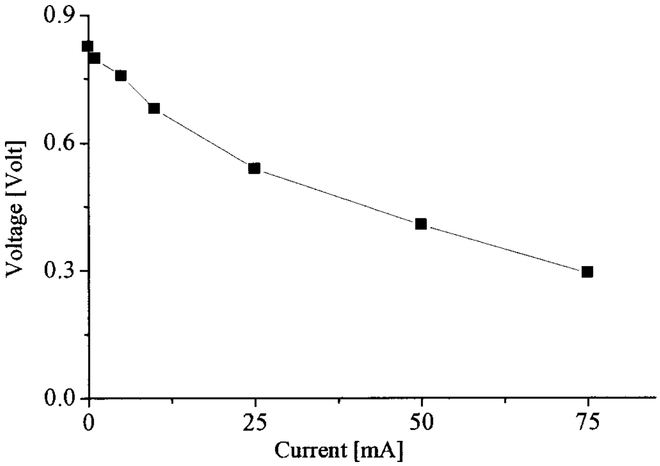

Figure 4. Polarization curve of the flat 7 cm^2 acrylic house cell with 0.25 M DMO and 0.5 M H_2SO_4 at 28°C.

Acknowledgment

We thank Degussa for supplying silica samples and ELF Autochem for supplying Kynar (PVDF) samples. This research was supported in part by the Israel Science Foundation founded by the Israel Academy of Sciences & Humanities.

Tel Aviv University assisted in meeting the publication costs of this article.

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