

Direct Methanol Fuel Cells (DMFCs) in Transportation and its Applications in India

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ABSTRACT

The direct methanol fuel cell (DMFC) has been considered as the ideal fuel cell system since it produces electric power by the direct conversion of the methanol fuel at the fuel cell anode. This is more attractive than the conventional hydrogen fuelled cells, particularly for transportation applications, which rely on bulky and often unresponsive reformer systems to convert methanol, or other hydrocarbon fuels, to hydrogen. However, commercialisation of the DMFC has been impeded by its poor performance compared with hydrogen/air systems, the major limitation being the anode performance which requires highly efficient methanol oxidation catalysts. Such catalyst materials have been sought, and it appears that only platinum-based materials show reasonable activity and the required stability. The recent application of proton exchange membrane electrolyte materials has extended the operational temperature of DMFCs beyond those attainable with traditional liquid electrolytes, and this has led to major improvements in performance over the last five years. This article describes some key work tackling the above limitations and suggests that the DMFC is approaching the stage where it may become a commercially viable alternative to hydrogen/air systems.

INTRODUCTION

Drivers for a long-term secure and sustainable energy supply are: (1) security of energy supply, (2) reduction of CO₂ (Kyoto) emissions and (3) pollution abatement. In particular security of oil

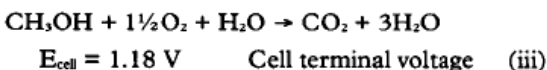
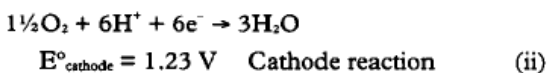
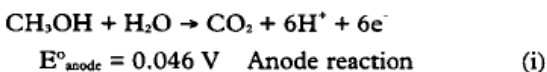
supply is a key issue as the share of oil in the final energy supply of the EU is 45.7%. The European oil supply depends for nearly 80% on the imported oil, of which a large and increasing part originates from the unstable middle east (where 65.4% of the global oil reserves are located); in particular transport is very vulnerable. Global oil reserves are sufficient for around 40 years with the current level of oil production [1] (Fig. 1). However, the global GDP is rapidly increasing with a subsequent increase in oil consumption. In a report by Goldman Sachs [2] (Fig. 2), it is expected that the GDP of the EU, the US and four major developing “BRIC” countries (Brazil, Russia, India and China) will have increased by a factor 7 in 2050. Oil reserves will therefore be exhausted in a much shorter time period.

We have come to the end of oil discoveries. During the decade 1990–2000 new oil discoveries amounted to only 25% of those during the period 1950–1960 [3] (Fig. 3). Today for every four barrels we consume one new barrel is discovered. We have used a bit less than half of the available oil and new cheap fields are not likely to be found. In a publication in The Economist of 8/12/2001 [4] it is stated that where oil demand is continuously increasing, oil production has reached its maximum in 2003 and has started to decrease. It is expected that by 2020 there will be a gap between demand and supply of 65 million barrels/day and that the oil produced will come for nearly 100% from the Middle East. Increased oil recovery from existing wells will only marginally improve this situation. Development

of new fields will be expensive (e.g. deep sea drilling down to 2000m in 2010) and the required investments for the next decade have been estimated by the IEA to be US\$ 1 trillion. The key question is whether these investments, needed to develop new and more expensive oil wells, will be made in time. If this process is too slow, this will lead to shortages, high prices and unfriendly competition. In the long-term oil reserves will last much shorter than 40 years due to a strongly increasing demand in particular from emerging countries, such as India and China.

PRINCIPLES OF THE DMFC

A schematic of a DMFC is shown in Figure. Methanol and water react electrochemically (methanol being oxidised) at the anode to produce carbon dioxide, protons and electrons as shown in Equation (i). The DMFC must contain an acidic electrolyte to aid carbon dioxide rejection, since insoluble carbonates form in alkaline electrolytes. The protons produced at the anode migrate through the polymer electrolyte to the cathode where they react with **oxygen** (usually from the air) to produce water, as shown in Equation (ii).



The electrons produced at the anode carry the free energy change of the chemical reaction and travel **through** the external circuit where they can be made to do useful work, such as power an electric motor. The overall cell reaction, as shown in Equation (iii), is therefore the reaction of methanol and **oxygen** to produce water and carbon dioxide. In a practical system, these reactions are promoted by the incorporation of platinum-based electro catalyst materials in the

electrodes. In principle, methanol should be oxidized spontaneously when the anode potential is above 0.046 V, with respect to the reversible hydrogen electrode (RHE). Similarly, oxygen should be reduced spontaneously when the cathode assumes a potential below 1.23 V. In reality, and in common with all fuel cell types, poor electrode kinetics (kinetic losses) cause the electrode reactions to deviate from their ideal thermodynamic values so as to incur a practical reduction of the extremely high theoretical efficiency possible from the cell.

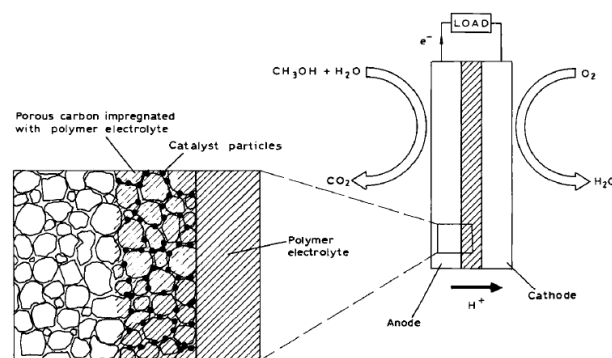


Fig. 1 A DMFC employing an acidic solid polymer electrolyte such as Du Pont's Nafion[®] and finely dispersed platinum electrocatalyst supported on porous carbon electrodes

The real behavior of the individual electrodes in the DMFC system is shown in Figure 2. In practice, a far more positive potential is required at the anode and a more negative potential at the cathode to accelerate the reactions to a reasonable rate. Besides kinetic losses, there are ohmic losses deriving from the internal resistance of the fuel cell. Hence, the output of a real DMFC is substantially lower than that of the ideal cell.

Kinetic Limitations

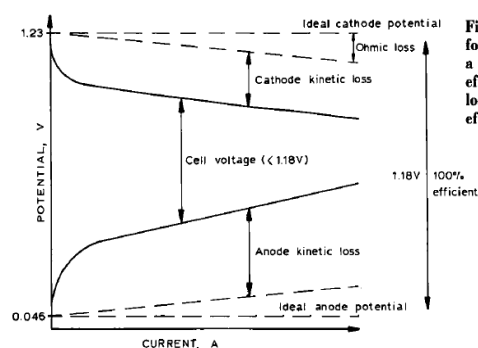


Fig. 2 Current/potential curves for the anode and cathode of a DMFC demonstrating the effects of the kinetic and ohmic losses which greatly reduce the efficiency of the cell

The poor electrode kinetics at the anode and cathode result from the electrochemical processes being much more complex than Equations (i) and (ii) suggest. Each oxygen molecule requires the transfer of four electrons for complete reduction. The simultaneous transfer of these electrons is difficult to achieve, and in fact only partial electron transfer takes place, leading to the formation of surface intermediates, such as superoxide.

Using a platinum electro catalyst allows the stabilisation of these intermediates and permits the reaction to proceed at a reasonable and useful rate. The catalyst may also accelerate the reaction by opening up new reaction pathways. The picture is even less clear for the methanol reaction and the electro-oxidation of methanol again only occurs at a useful rate in the presence of platinum or a platinum-based electro catalyst. Therefore this reaction has remained an active focus of research, and substantial studies into this process are present in the literature. The discrepancies between sets of experimental data may be due to the wide range of experimental conditions.

The electro-oxidation of methanol to carbon dioxide requires the transfer of six electrons, but it is highly unlikely that these electrons will transfer simultaneously. It is also unlikely that partial electron transfer will lead to the formation of a range of stable solution intermediates.

Clearly, there must be surface adsorbed species present on the surface of the platinum electro catalyst across its useful potential range, and it is these species which are responsible for the poor catalytic activity of platinum towards Methanol electro-oxidation. The postulated mechanisms for methanol electro-oxidation were reviewed by Parsons and Vandernoot (2), and can be summarised as:

Step 1 : Electrosorption of methanol onto the substrate to form carbon-containing intermediates.

Step 2: Addition of oxygen (from water) to the adsorbed carbon-containing intermediates to generate carbon dioxide.

COMPARATIVE STUDY

From the resources cited above it is clear that both hydrogen and methanol show a great potential for efficiency improvements in spark-ignition engines. The achievable level of improvement depends on whether the engine is designed to run on hydrogen or methanol only (dedicated engine) or should also be able to burn gasoline (flex-fuel engine). For dedicated hydrogen and methanol engine, peak brake thermal efficiencies of respectively 45% and 42% have been reported, compared to 36% and 42% for modern gasoline and diesel engines respectively. In part-load operating conditions the ability to use high compression ratios and throttle less load control enables increases in efficiency of 10-20% relative to throttled gasoline operation. Since dedicated engines are not designed to run on gasoline, a direct comparison on the same engine is not possible. Figures published by Ford Motor Company suggest, however, that the mean brake thermal efficiency of their dedicated hydrogen P2000 vehicle over a metro cycle is up to 17.9% higher than a similar gasoline vehicle. For flex-fuel vehicles, the efficiency improvements are more modest. Qualitative load control allows improvements of 15-20% relative to gasoline for hydrogen flex-fuel vehicles in part-load. Methanol flex-fuel vehicles can have the advantage of faster flames speeds in combination with reduced cooling and flow losses when running on methanol. Methanol shows a prosperous market for its low price and easy obtainment. Coal is comparatively richer than petroleum and natural gas in China. It plays 70% role of annual energy balance. These years, its production is about 1.5 billion tons. Because it is easy and economical to be liquefied to methanol, more attentions are paid to the application in SI engines. The advantages and disadvantages can

be summarized as following:

- (1) LHV of Stoichiometric mixture is similar as gasoline, so the engine power can be remained. However, to keep engine power, more fuel should be delivered, because of lower LHV of methanol. Experiments showed that, if the engine was fueled with low fraction methanol/gasoline blends, it runs stably and successfully.
- (2) With k-closed loop control of ECU, the engine can automatically keep the value of k near unit accordingly to 14.7. So actually, the reduction of CO and HC emissions are due to the leaner mixture to some extent. Also, the lower of HC and CO emissions was due to the oxygen content of the fuel blends.
- (3) Higher RON, even if it is blended with gasoline, the octane number of the fuel blend can be increased. Therefore, engine CR can be increased so that engine thermal efficiency and power can be improved. However, the engine CR was remained in this study to make the engine retrofit easily.
- (4) Thought the latent heat of methanol is higher, measures are not necessary for the mixture preparing due to lower fraction, while it may increase engine volumetric efficiency and thus increase engine power.
- (5) Methanol has a higher laminar flame propagation speed, which may make combustion process finish earlier and thus improve engine thermal efficiency.
- (6) Uncertainty of potential poisons of formaldehyde emission, corrosion to some materials like rubber and some aluminum alloys.

Experimental set-up

A Volvo four-cylinder sixteen valve naturally aspirated gasoline engine with a total swept volume of 1783 cc and a compression ratio of 10.3:1 with maximum power output 88 kW (120 HP) at 5800 rpm and maximum torque 170 Nm at 4000 rpm was converted to tri-fuel operation by mounting an additional fuel rail supplying gaseous fuel (in this case, hydrogen) to 8

Teleflex GSI gas injectors (2 per cylinder), mounted on the intake manifold.

Table 1
Comparison of fuel properties

	Methanol	Ethanol	Gasoline
Molecular formula	CH ₃ OH	C ₂ H ₅ OH	–
Molecular weight	32	46	95–120
Oxygen content (%)	50%	34.8%	0
Density (kg/m ³)	792	785	740
LHV (MJ/kg)	20.0	26.9	44.3
Octane number	111	108	>90
Auto-ignition temperature (°C)	465	425	228–470
Stoichiometric A/F ratio	6.47	9.00	14.8
Latent heat (kJ/kg)	1103	840	305
LHV of stoi-mixture (MJ/m ³)	3906	3864	3810

Additional adjustments to allow reliable operation on hydrogen are described in. Liquid fuel injectors with increased flow capacity and stainless steel fuel lines and fuel rail were installed to ensure methanol compatibility. The standard spark plugs were replaced by colder ones to avoid pre-ignition issues on hydrogen and methanol

Table 1 – Properties of typical gasoline, methanol, ethanol and hydrogen relevant to internal combustion engines [6,19,31].
* Includes atmospheric nitrogen. NA: not available. NTP: normal temperature (293 K) and pressure (101325 Pa).

Property	Gasoline	Methanol	Ethanol	Hydrogen
Chemical Formula	Various	CH ₃ OH	C ₂ H ₅ OH	H ₂
Oxygen Content by Mass [%]	0	50	34.8	0
Density at NTP [kg/l]	0.74	0.79	0.79	0.00008
Lower Heating Value [MJ/kg]	42.9	20.09	26.95	120
Volumetric Energy Content [MJ/l]	31.7	15.9	21.3	0.010
Stoichiometric Air to Fuel Ratio [kg/kg]	14.7	6.5	9	34.2
Energy per Unit mass of air [MJ/kg]	2.95	3.12	3.01	3.51
Research Octane Number (RON)	95	109	109	130 ($\lambda = 2.5$)
Motor Octane Number (MON)	85	88.6	89.7	NA
Sensitivity (RON-MON)	10	20.4	19.3	NA
Boiling point at 1 bar [°C]	25–215	65	79	–253
Heat of vaporisation [kJ/kg]	180–350	1100	838	461
Reid Vapour Pressure [psi]	7	4.6	2.3	NA
Mole ratio of products to reactants*	0.937	1.061	1.065	0.852
Flammability limits in Air [λ]	0.26–1.60	0.23–1.81	0.28–1.91	0.15–10.57
Laminar flame speed at NTP, $\lambda = 1$ [cm/s]	28	42	40	210
Adiabatic Flame Temperature [°C]	2002	1870	1920	2117
Specific CO ₂ Emissions [g/MJ]	73.95	68.44	70.99	0.00

So, many researchers and officials in China think that it should take an important role in automobile industry development and petroleum fuel substitute. This paper will carry out further study on the effects of methanol, and its fraction on engine power performance, economy, combustion, regulated and non-regulated emission and cold start.

EFFECT OF METHANOL ON ENGINE PERFORMANCE

This paper is intended to study engine performance, emissions when it utilizes low fraction of methanol gasoline fuel blends. In this study, a 3-cylinder with a bore of 68.5 mm, total displacement about 0.8-l PFI engine was adopted and fueled with the prepared fuel blends. Engine performance, emissions including regulated and non-regulated pollutants were studied.

Engine power and fuel economy

Several kinds of fuel blends were prepared for the different purpose of engine test, containing 10%, 15%, 20%, 25% and even 30% of methanol in volume (named M10, M15, M20, M25 and M30), respectively. The test engine remains its original set of parameters, especially the 7 degrees Centigrade.

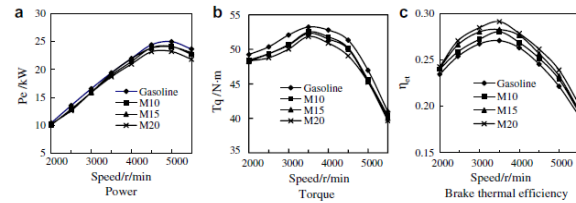


Fig. 1. Engine performance under WOT conditions at original ignition timing.

A spark ignition timing. When it ran on the above fuel blends and based gasoline as showed in Fig. 1, the WOT operation performance of engine power, torque and brake thermal efficiency are measured. With the increase fraction of methanol, engine power and torque decrease, while the brake thermal efficiency is improved. Considering that motors are seldom run on WOT conditions, even when fuel is changed to be M20, it has little effect on power performance. However, if the spark ignition time is advanced 2degrees Centigrade without any further optimizations, under WOT full load operation conditions, the engine power is almost no reduction, and brake specific fuel consumption (BSFC) can be decreased as well. This is showed in Fig. 2.

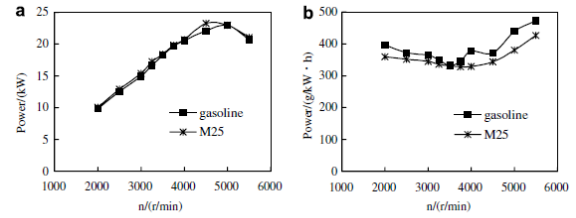


Fig. 2. Engine performance under WOT conditions with ignition timing advanced 2°.

Effects on engine combustion characteristics

Cylinder pressure diagram shows that, under the same engine speed and throttle opening, see 50% WOT operation in Fig. 3, when the engine fueled with M20, the maximum pressure is higher than that of pure gasoline operation. The indicated mean effective pressures (IMEP) are 0.91 MPa for M20 and 0.88 MPa for pure gasoline. Engine thermal efficiencies are 0.284 and 0.262, respectively. The start of combustion (defined as 5% accumulative heat release) and rapid burning phase (defined as heat release increasing from 5% to 90%) were got from the heat release calculation with the cylinder pressure. Fig. 4 indicates the changes of SOC and RBP under constant torque of 30 N m operating conditions. Though SOC is advanced due to the methanol addition in most cases and RBP becomes shorter at high speed operating conditions, the spark ignition timing still can be advanced 2 or 3degrees CA, because of higher octane number of blend fuels, then the engine combustion will be centralized near top dead center (TDC) and engine power and thermal efficiency will be improved.

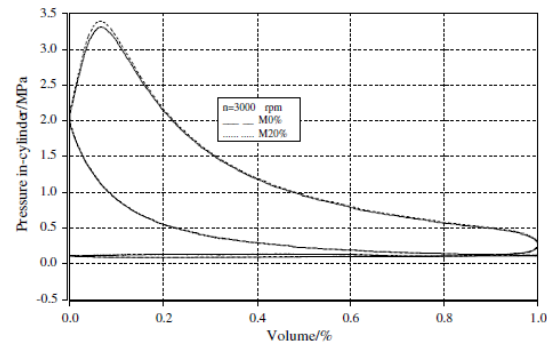


Fig. 3. Comparison of pressure-volume diagram between gasoline and blend fuel.

Effects on regulated emissions and conversion

The regulated gaseous emissions include CO, HC and NOx. When methanol is added into

gasoline, the fuel blend contains more oxygen, which reduces CO and HC emissions. Also, when the engine utilizes fuel blends, after TWC, CO and HC emissions are better than that of pure gasoline operation. The effect on NO_x emission is ignorable, neither prior to nor post the TWC. Therefore, methanol used in SI engine can reduce regulated emissions of HC and CO in this study.

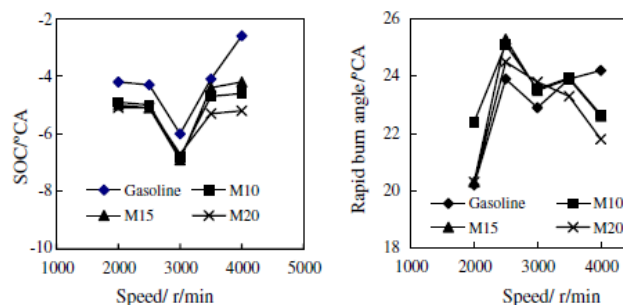


Fig. 4. Engine combustion phases analyses under 30 N m operating condition

Effects on non-regulated emissions and conversion

In this study, the unburned methanol and formaldehyde were measured and they are generally called to be non-regulated emissions. Both formaldehyde and methanol are measured by gas chromatography method. The column is polyethylene glycol (PEG) type with flame ionization detector (FID). Methanol emission increases with the increase of engine load under different speeds, however, methanol contents in fuel blends have no significant direct effects on its emission in the experimental range. Actually, because of cyclic combustion variation of SI engine combustion and the small sampling volume (500 l), the results are not so repeatable. Formaldehyde emission of M20 is about 10 times as high as gasoline; however, the total concentration is still within 200 ppm. With TWC, methanol and formaldehyde can be oxidized effectively. Within the calibration range, formaldehyde cannot be measured. It's safe to say that commercial TWC can convert formaldehyde sufficiently.

Effects on cold start and warming-up process

FTP tests show that about 80% HC and CO emissions are from cold start and warm-up periods [8–10], so cold start investigation becomes an important branch in control of engine emissions. And also, there is no report concerned on the combustion and emission characteristics of methanol/gasoline blend fueled engine. When engine fueled with M30, HC and CO are much better than that of gasoline operation. HC emission reduces more than 50% in the first few seconds (cold start period) and nearly 30% in the following period (warming-up). CO reduces nearly 25%. The engine speed is quite similar, while the exhaust temperature is higher, which is good to activate TWC earlier.

SUMMARY AND FUTURE PROSPECTS

In the last few years there has been a considerable improvement in the activity of methanol electro-oxidation catalysts, through improved operating conditions and better dispersion and control of the imposition of existing platinum-ruthenium materials. Electrode technology has also advanced with the introduction of solid polymer electrolytes, such as Nafion[®], which has extended the operational temperature and reduced the complexity of modern cells. The single cell data presented by various groups demonstrate the influence of parameters such as temperature, pressure, concentration of reactants and electrode structure. The present level of technology requires high temperatures (130°C) and pressures before practical cell power densities can be obtained. Most groups appear to use high noble metal loading of up to 4 mg/cm² on the anode to increase the methanol turnover to a useful rate. This level of catalyst loading is too high for transportation applications and clearly indicates that the anode catalyst activity has still to increase, perhaps by a factor of at least ten, to reduce the noble metal loadings to more acceptable levels of below 0.5 mg/cm². Optimisation of the electrode structure, leading to higher catalyst

utilisation, will also contribute to increased cell performance. Methanol cross-over from the anode to the cathode appears to be a major limitation at present. This is reflected in the high platinum catalyst loadings and the high gas pressure and flow rates which are necessary for reasonable cathode performance. The performance of the DMFC would be improved considerably if a methanol-impermeable electrolyte or a methanol-tolerant cathode existed. In order to minimise the effects of methanol cross-over, alternative membrane materials have been sought. Present electrolyte materials are restricted by poor water management and therefore can only operate at temperatures below 100°C at ambient pressures. If the operational temperature could be increased to 150°C at ambient pressures, this would considerably enhance the kinetics of the anode reaction. However, this requires new materials which do not require humidification to maintain high conductivity.

An alternative to new membrane technology is to employ methanol tolerant cathode catalysts. A possible class of materials are high surface chervil phase composites which consist of molybdenum, ruthenium and sculpture. Although these may not offer the same oxygen reduction performance as platinum-based materials, this may outweigh the performance loss attributable to methanol cross-over seen with platinum-based materials. The DMFC has always been considered as the ideal fuel cell. Its simplified system design and direct use of liquid fuel have in the past been outweighed by the very low power densities achievable. The poor performance of the cell was due to the poor kinetics of the anode reaction and fuel cross-over. Although performance levels are not yet sufficient for commercial application, if the progress made over the past two to three years is continued, then this fuel cell could emerge from the shadows of its hydrogen-fuelled counterparts.

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