



## Short communication

## Direct dimethyl ether fueling of a high temperature polymer fuel cell

J.O. Jensen<sup>a,\*</sup>, A. Vassiliev<sup>a</sup>, M.I. Olsen<sup>a</sup>, Q.F. Li<sup>a</sup>, C. Pan<sup>a</sup>, L.N. Cleemann<sup>a</sup>, T. Steenberg<sup>b</sup>, H.A. Hjuler<sup>b</sup>, N.J. Bjerrum<sup>a</sup><sup>a</sup> Energy and Materials Science Group, Department of Chemistry, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark<sup>b</sup> Danish Power Systems ApS, Rådhusvej 59, DK-2920 Charlottenlund, Denmark

## ARTICLE INFO

## Article history:

Received 14 November 2011

Received in revised form

24 February 2012

Accepted 15 March 2012

Available online 7 April 2012

## Keywords:

Dimethyl ether

Fuel cells

PBI

High temperature PEMFC

Direct DME

## ABSTRACT

Direct dimethyl ether (DME) fuel cells suffer from poor DME–water miscibility and so far peak powers of only 20–40 mW cm<sup>-2</sup> have been reported. Based on available literature on solubility of dimethyl ether (DME) in water at ambient pressure it was estimated that the maximum concentration of DME at 80 °C will be 300–600 times lower than the ratio 1 to 3 which is the stoichiometric ratio for full conversion to CO<sub>2</sub>. To overcome this dilution problem a high temperature polymer fuel cell was operated on DME–water vapor at ambient pressure and with air as oxidant. A peak power density of 67 mW cm<sup>-2</sup> was measured at 200 °C. A series of performance curves at temperatures ranging from 150 to 250 °C showed a pronounced temperature effect on the performance. Comparison was made between performances as direct DME and direct methanol cells and the difference was not as large as normally seen with conventional liquid fed cells below 100 °C.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Expectations are high to dimethyl ether (DME, CH<sub>3</sub>OCH<sub>3</sub>) as a synthetic fuel. George Olah et al. [1] decided to publish a second edition of the very useful monograph on the methanol economy after only three years. One major addition was a more detailed description of the possibilities with DME, which is even shown on the front page. DME is already used as a cooking gas in China and with a cetane number of 55–60 it can power a diesel engine more or less as we know it today (in contrast to the common alcohols). It hardly produces any soot on combustion apart from what may be caused by the engine lubrication. When using conventional diesel, soot is the most pronounced local pollution problem. Chemically, DME resembles methanol (CH<sub>3</sub>OH) with no carbon–carbon bonds and this is the reason for the clean combustion and the fact that it can be steam reformed at significantly lower temperature than ethanol even though it has the same overall formula. Like methanol it can be synthesized from biomass or from hydrogen in combination with a carbon source. It is gaseous at ambient conditions, but it is stored as a liquid at a pressure of about 6 bar absolute, similarly to liquefied petroleum gas (LPG). The energy content (28.62 kJ g<sup>-1</sup>, LHV) is higher than that of methanol (19,99 kJ g<sup>-1</sup>) and comparable

to that of ethanol (26.87 kJ g<sup>-1</sup>) [2]. Volvo is presently operating a test fleet of DME fueled diesel trucks and an international organization promoting DME as a near future fuel has been established [3]. With DME as an abundant fuel it would be highly desirable if it could also be converted directly in a polymer fuel cell similar to the conversion of methanol in a direct methanol fuel cell (DMFC) without any fuel processing (reforming). However, attempts to do so have not been as successful as direct methanol fuel cells yet.

Part of the reason for limited experience and low performance with direct DME cells is most likely to be the poor reaction kinetics with the present electrocatalysts, but low solubility of DME in water is a problem too. Like in direct methanol fuel cells DME is normally fed as an aqueous solution because oxygen atoms from the water are mandatory for CO<sub>2</sub> formation. The theoretical stoichiometric ratio of DME and water (1:3) predicts a 46 %wt solution of DME, but the DME solubility in water is claimed to be as low as 7.6 %wt at 20 °C [4]. At the working temperature of ca. 80 °C of a traditional polymer fuel cell the solubility of DME in water will be even lower, and consequently a DME solution initially saturated at room temperature then separates into two phases [5]. The low solubility impedes the electrode process since both DME and water must be present at the catalyst sites. When the fuel mixture is present as two immiscible phases, the concentration of either DME or water will be low at the catalytic sites.

Peak power densities reported with polymer fuel cells at ambient pressure and with air as oxidant are between 20 and

\* Corresponding author. Tel.: +45 45 25 23 14; fax: +45 45 88 31 36.  
E-mail address: [jojen@dtu.dk](mailto:jojen@dtu.dk) (J.O. Jensen).

40 mW cm<sup>-2</sup> [5–7]. With pure oxygen slightly higher power densities of 30–56 mW cm<sup>-2</sup> have been demonstrated [8–12], but for most applications only air is available. The phase splitting problem can be mitigated by pressurizing the fuel mixture. DME is likely already pressurized from the container, but for most polymer fuel cells this would require a balanced pressurization of the cathodic air and this consumes energy and is moreover not an attractive option for direct fuel cell systems which are meant to be simple.

In the present study the solubility of DME in water is treated based on the available literature to the extent relevant for liquid fed fuel cells. Subsequently, a vapor fed system is suggested. The idea is to increase the working temperature of the cell significantly above the boiling point of water and feed the fuel stream as vapor. This cannot be done with conventional polymer fuel cells which are limited to operation below 100 °C due to the need for high humidification. Instead a high temperature polymer fuel cell is used. A fuel cell system based on phosphoric acid doped polybenzimidazole (PBI) was first presented in 1995 [13] and has later been going through a significant development [14] and an early stage of commercialization by companies like BASF Fuel Cells and Danish Power Systems. The working temperature can be 120–200 °C because the membrane conductivity is not dependent on high humidification.

## 2. Experimental

The membrane electrode assembly (MEA) was prepared according to the following procedure. The electrodes were made from non-woven carbon cloth (Freudenberg) on which the catalyst layer was manually sprayed. The catalyst ink containing catalyst, phosphoric acid and additives was mixed in an ultrasonic bath for 1 h to obtain a uniform slurry. The anode catalyst (Johnson Matthey) was 40 wt% Pt and 20 wt% Ru on 40 wt% carbon black and the cathode catalyst (made in house) was 40 wt% Pt on carbon black. The resulting catalyst layers contained 3.7 mg metal per cm<sup>2</sup> on the anode side and 0.7 mg Pt per cm<sup>2</sup> on the cathode side. The electrode dimensions were 5 × 5 cm<sup>2</sup>.

A 50 μm PBI membrane (Danish Power Systems), was doped with phosphoric acid (85 wt%, room temperature, 2 weeks) and hot pressed between the electrodes at 100 kg cm<sup>-2</sup> for 7 min at 150 °C. Prior to hot pressing the membrane was fitted with a protective film covering the area outside the electrode.

The resulting MEA was sandwiched between two graphite flow field plates with PTFE gaskets and held together by two 20 mm aluminum end plates with heating elements. Operation of the fuel cell was performed in an in house built test station. See Fig. 1 for a schematic flow diagram. The evaporator was an electrically heated container filled with steel balls for heat distribution. DME and water were supplied via separate inlets by a mass flow controller and a calibrated peristaltic pump respectively. For

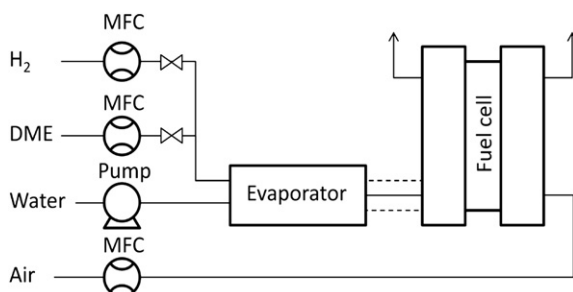


Fig. 1. The direct DME fuel cell setup schematically. MFC means mass flow controller.

experiments with methanol a stoichiometric methanol–water solution instead of pure water was fed through the water inlet in Fig. 1.

A start-up procedure was performed by heating the cell to 150 °C and supplying hydrogen (192 mL min<sup>-1</sup>) at the anode and air (905 mL min<sup>-1</sup>) at the cathode (reference for all gas flows: 0 °C, 1 atm). The cell was kept at 4 A (160 mA cm<sup>-2</sup>) for an hour. The cell was then heated to 200 °C and the fuel was changed to DME. A DME–water mixture with 32 mL min<sup>-1</sup> of gaseous DME and 0.07 mL min<sup>-1</sup> liquid water was introduced to the evaporator at 150 °C. The resulting vapor mixture was fed to the fuel cell via a heated insulated tube. No preheating was applied to the cathode air. The fuel cell outlet was through a short tube connected to the laboratory exhaust ventilation with no back pressure. The cell was operated at 2 A (80 mA cm<sup>-2</sup>) for 30 min to obtain stable measurements before the *i*–*V* curve was recorded.

## 3. Results and discussion

### 3.1. The miscibility problem

Before describing the results for the cells at elevated temperature, we shall try to quantify the problem of DME solubility as much as possible based on the available literature data. Reference tables for DME solubility in water as function of temperature at ambient pressure are not easily found in the open literature and most of the few values reported [4,10,15,16] are not easily traced to the original measurements. The data are plotted in Fig. 2 with a logarithmic trend line arbitrarily chosen. This is the closest we get to an ambient pressure boiling point curve of a water rich DME–water solution. It is uncertain how the curve further develops toward the boiling point of pure DME at –25 °C. Consequently, a DME solution with a molar fraction of 0.25 (according to the theoretical stoichiometry) seems impossible even at low temperature. Fig. 2 allows an estimate of the DME molar fraction at a typical PEMFC working temperature of 80 °C. Calculated from the trend line the molar fraction at 80 °C is 0.0004 or ca. 1/600 of the theoretical stoichiometry. Alternatively, a linear interpolation between the data point at 60 °C and 100 °C returns a molar fraction of 0.0009 or ca. 1/300 of the theoretical stoichiometry. These numbers are of course quite uncertain, but it is evident that the DME concentration will be orders of magnitude lower than desired.

Solubility data based on liquid–liquid equilibria are collected by Maczynski et al. [17] based on fundamental measurements

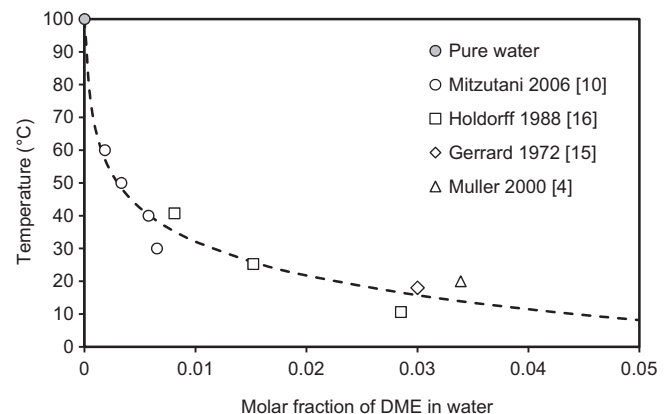


Fig. 2. Equilibrium molar fractions of DME in water at different temperatures and ambient pressure based on available literature data. The values of Holdorff were found by interpolation between pressures around 100 kPa. The trend line shown was arbitrarily chosen as  $T = -14.87 \ln(x) - 36.41$ .

[16,18,19]. In order to establish liquid–liquid equilibria the system must be kept at elevated pressure. Also in this case the data are not fully correlated, but it is indicated that the molar fraction of DME in water is ca. 0.18 at 25 °C and ca. 0.1 at 80 °C. The pressures applied during the measurements are close to the vapor pressure of pure DME at any of the given temperatures, i.e. 6 bar at 25 °C and 22 bar at 80 °C (there are many detailed vapor pressure measurements. See Wu and Jin [20] or Ihmels and Lemmon [21], who both combine their own measurements with a list of previous work). The lesson learned is that a molar fraction of 0.1 or 40% of the desired stoichiometry is stable at 80 °C, but that it requires pressurization to at least 22 bar. Higher concentrations of DME under this pressure will result in an additional DME rich phase.

DMFCs are operated at low methanol concentrations of typically ca. 1 M (3%wt) in order to reduce methanol crossover. Crossover is a major challenge for DMFCs. In a 1 M aqueous methanol solution the molar fraction is ca. 0.017 which is comparable to the room temperature value for DME in Fig. 2. One could then argue that even if a stable stoichiometric DME solution was possible, it would have to be diluted anyway to reduce crossover. The concentration change when shifting back to a real solution saturated at 80 °C would then not be much more than one order of magnitude. This argument will not likely hold. Methanol is miscible with water in any ratio and the high methanol permeability in common fuel cell membranes is related to the high solubility in the strongly hydrophilic environment. DME is much less hydrophilic as indicated by the low water solubility, and thus crossover is expected to be much less than that for methanol. Hence, dilution to limit crossover may not be necessary.

On this background, the concept of a vapor fed direct DME fuel cell is addressed in the following.

### 3.2. A vapor fed fuel cell

A number of single cells were made and tested at ambient pressure and with air as oxidant. The performance at 200 °C is shown in Fig. 3. It can be seen that the peak performance is  $67 \text{ mW cm}^{-2}$ , which is ca. 65% higher than previously reported for direct DME in a polymer fuel cell at ambient pressure [5–7]. The open circuit voltage is 0.77 V which still indicates some fuel crossover, although less than that for a typical good DMFC with diluted methanol. In this study the DME–water ratio was close to stoichiometric, i.e. a molar ratio of 1:3 and still the open voltage depression was less than for most direct methanol cells operated on

dilute methanol. This supports the assumption that the DME permeability is smaller than that of methanol. Good tight hydrogen powered PBI based fuel cells typically show open circuit voltages around 0.9 V.

Normally it makes little sense to operate a PBI based fuel cell at temperatures above 200 °C, because the degradation is very fast. However, in order to study the temperature effect on performance in a wider temperature window a cell from an early series of experiments was subjected to  $i$ – $V$  measurements at temperatures from 150 to 250 °C. The result is shown in Fig. 4. The low intercept with the voltage axis indicates that the full performance is not obtained either due to extremely high crossover rates or more likely some internal leaking. Anyway, apart from the intercept the voltage curve at 200 °C is comparable to that in Fig. 3. It is very clear that performance increases strongly with increasing temperature through the whole temperature range. In a DME air fuel cell significant kinetic overvoltages are expected on both anode and cathode, but with hydrogen–air powered PBI based cells the voltage increase from 175 to 200 °C is normally less significant than it appears in this case. A reasonable interpretation is therefore that it is mostly to be due to the DME kinetics that is improved at the high temperatures. The nearly linear shape of the curves, especially at 200–250 °C, and their similar slopes also indicate that the dominating reason for the performance increase is not related to the ohmic resistance of the cell but is merely a result of improved kinetics. This temperature dependence is a good reason to aim at a high temperature vapor fed system for direct DME. It is known that reforming of DME requires higher temperature than that for methanol [22] and despite the similarities between the two molecules, kinetics for breaking down DME is deemed to be slower.

When cells were operated on DME and methanol in sequence the performance was higher on methanol as expected, but not much higher. Fig. 5 shows corresponding performance curves for DME and methanol at 150 °C and 200 °C measured with the same cell. At 200 °C the peak power for DME is ca. 80% of that of methanol. It is very encouraging that the DME performance seems to follow the methanol performance. Other groups working with direct fueling of high temperature PEM fuel cells have demonstrated higher peak currents with methanol. Lobato et al. [23] reported  $138 \text{ mW cm}^{-2}$  for a vapor fed direct methanol PBI cell at 200 °C. The measurements were made with pure oxygen as oxidant instead of air and that always boosts the performance. One can easily gain a hundred mV or more at moderate to high current load

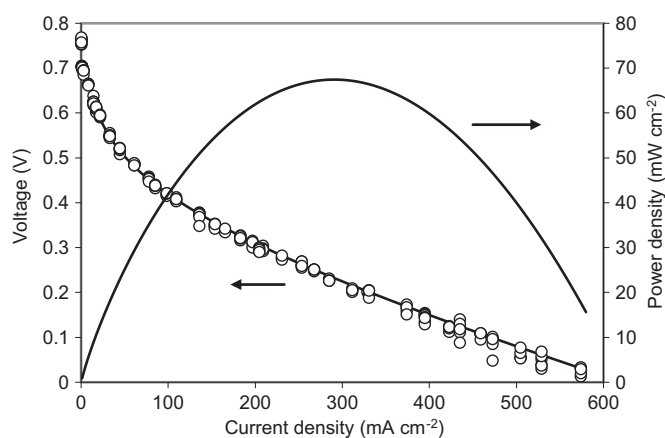


Fig. 3. Performance curve of the vapor fed direct DME fuel cell at 200 °C, ambient pressure and with air as oxidant. Markers indicate voltage measurements and the power curve with no markers was calculated from the voltage trend line.

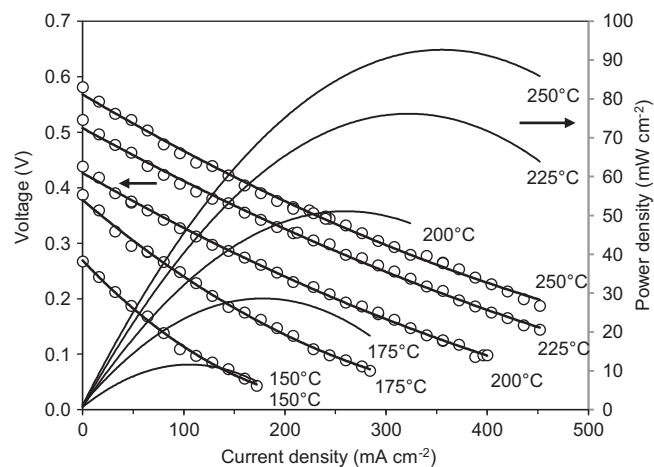


Fig. 4. Performance curves of a vapor fed direct DME fuel cell at temperatures ranging from 150 to 250 °C. All curves were measured at ambient pressure and with air as oxidant.

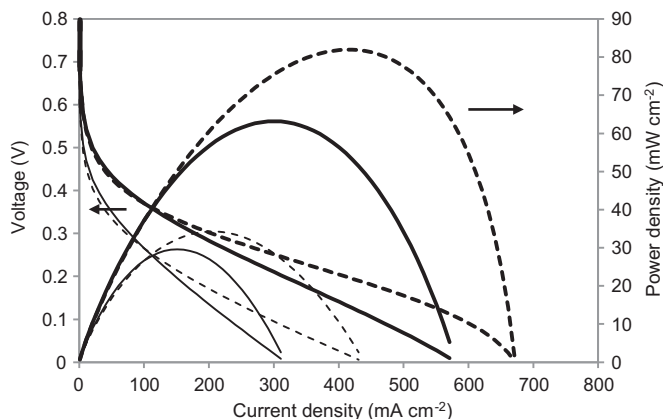


Fig. 5. Performance curves of a cell vapor fed with DME (full lines) or methanol (dotted lines) at 150 °C (fine) and 200 °C (bold).

by switching to pure oxygen. However, bearing that in mind, the results of Lobato still indicate that significantly higher performance with methanol is possible and if the performance with DME keeps up, correspondingly higher performance with DME should be possible too.

#### 4. Conclusions

The problem of low miscibility of DME and water was quantified to some extent based on available literature. It was estimated that the maximum concentration of DME in water at 80 °C is 300–600 times lower than the ratio 1 to 3 which is the stoichiometric ratio for full conversion to CO<sub>2</sub>. This is a fundamental problem for liquid fed direct DME fuel cells unless operated at high pressure.

A high temperature polymer fuel cell operating at 150–200 °C makes it possible to supply the DME–water mixture as vapor, and then there is no miscibility problem. A peak power density of 67 mW cm<sup>-2</sup> was demonstrated at 200 °C with air as oxidant. This is the highest value reported to date with a direct DME fed polymer fuel cell at ambient pressure. The open circuit voltage was as high as 0.77 V with DME supplied at 1:3 M ratio. This indicates that fuel crossover is less problematic in this case. This also corresponds well with the low solubility in water.

Finally, a comparison of direct DME and direct methanol was made with the same cell. The difference in performance was not as

large as normally seen with conventional liquid fed cells below 100 °C.

#### Acknowledgement

The authors wish to acknowledge The Danish Agency for Science, Technology and Innovation (Vedvarende Energiteknologier) and the ForskEL program (HotMEA) for financial support of the study.

#### References

- [1] G.A. Olah, A. Goepfert, G.K. Surya Prakash, *Beyond Oil and Gas: The Methanol Economy* Second updated and enlarged edition, Wiley-VCH, Weinheim, 2009.
- [2] T.A. Semelsberger, R.L. Borup, H.L. Greene, *Journal of Power Sources* 156 (2006) 497–511.
- [3] [www.aboutdme.org](http://www.aboutdme.org).
- [4] J.T. Muller, P.M. Urban, W.F. Holderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, *Journal of the Electrochemical Society* 147 (2000) 4058–4060.
- [5] R.H. Yu, H.G. Choi, S.M. Cho, *Electrochemistry Communications* 7 (2005) 1385–1388.
- [6] M.M. Mench, H.M. Chance, C.Y. Wang, *Journal of the Electrochemical Society* 151 (2004) A144–A150.
- [7] J.Y. Im, B.S. Kim, H.G. Choi, S.M. Cho, *Journal of Power Sources* 179 (2008) 301–304.
- [8] Y. Tsutsumi, Y. Nakano, S. Kajitani, S. Yamasita, *Electrochemistry* 70 (2002) 984–987.
- [9] K.D. Cai, G.P. Yin, L.L. Lu, Y.Z. Gao, *Electrochemical and Solid State Letters* 11 (2008) B205–B207.
- [10] I. Mizutani, Y. Liu, S. Mitsushima, K.I. Ota, N. Kamiya, *Journal of Power Sources* 156 (2006) 183–189.
- [11] S. Ueda, M. Eguchi, K. Uno, Y. Tsutsumi, N. Ogawa, *Solid State Ionics* 177 (2006) 2175–2178.
- [12] Y. Zhang, Y.J. Tong, L.L. Lu, M. Osawa, S. Ye, *Journal of the Electrochemical Society* 157 (2010) F10–F15.
- [13] J.S. Wainright, J.T. Wang, D. Weng, R.F. Savinell, M. Litt, *Journal of the Electrochemical Society* 142 (1995) L121–L123.
- [14] Q.F. Li, J.O. Jensen, R.F. Savinell, N.J. Bjerrum, *Progress in Polymer Science* 34 (2009) 449–477.
- [15] W. Gerrard, *Journal of Applied Chemistry and Biotechnology* 22 (1972) 623.
- [16] H. Holldorff, H. Knapp, *Fluid Phase Equilibria* 44 (1988) 195–209.
- [17] A. Maczynski, D.G. Shaw, M. Goral, B. Wisniewska-Gocłowska, *Journal of Physical and Chemical Reference Data* 37 (2008) 1119–1146.
- [18] T. Laursen, P. Rasmussen, S.I. Andersen, *Journal of Chemical & Engineering Data* 47 (2002) 198–202.
- [19] M.E. Pozo, W.B. Streett, *Journal of Chemical & Engineering Data* 29 (1984) 324–329.
- [20] J.T. Wu, J.G. Yin, *Journal of Chemical & Engineering Data* 53 (2008) 2247–2249.
- [21] E.C. Ihmels, E.W. Lemmon, *Fluid Phase Equilibria* 260 (2007) 36–48.
- [22] T.A. Semelsberger, R.L. Borup, *International Journal of Hydrogen Energy* 30 (2005) 425–435.
- [23] J. Lobato, P. Canizares, M.A. Rodrigo, J.J. Linares, R. Lopez-Vizcaino, *Energy & Fuels* 22 (2008) 3335–3345.