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Direct dimethyl ether high temperature polymer electrolyte membrane fuel cells with improved performance

DTU

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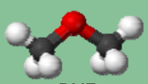
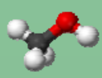
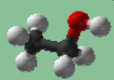
Outline

A high temperature polybenzimidazole (PBI) polymer fuel cell was fed with dimethyl ether (DME) and water vapour mixture on the anode at ambient pressure with air as oxidant. A peak power density of 79 mW/cm² was achieved at 200°C. A conventional polymer based direct DME fuel cell is liquid fed and suffers from low DME solubility in water. When the DME - water mixture is fed as vapour miscibility is no longer a problem. The increased temperature is more beneficial for the kinetics of the direct oxidation of DME than of methanol. The Open Circuit Voltage (OCV) with DME operation was 50 to 100 mV higher than that of methanol, indicating less fuel crossover.

Dimethyl ether


DME


Methanol


Ethanol

DME is:

- A clean colourless gas
- Liquid at 6 bar(a)
  - handled like LPG
- Little or not toxic
- Not a greenhouse gas
  - decomposes in atmosphere in tens of hours)

	Methane	Methanol	Dimethyl ether	Ethanol	Gasoline	Diesel
Formula	CH_4	CH_3OH	CH_3OCH_3	CH_3CH_2OH	C_7H_{16}	$C_{14}H_{30}$
LHV (kJ cm⁻³)	0.0346	15.82	18.92	21.09	32.05	35.66
LHV (kJ g⁻¹)	47.79	19.99	28.62	26.87	43.47	41.66
Boil.p (◦C)	−162	64	−24.9	78	38–204	125–400

As a fuel:

- Cetane rating 55 – 60 (45 for petroleum-derived diesel)
- Burns with no particulate matter (soot)
- Very low NO_x, no SO_x
- Excellent diesel engine fuel


DME powered diesel truck from Volvo

Manufacture:

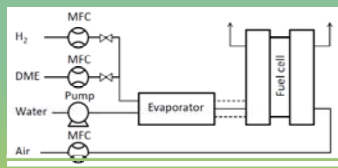
- From biomass
- From syngas

Other uses:

- Aerosol propellant
- Cooking gas
- Refrigerating agent

Experimental

The idea is to increase the working temperature above the boiling point of water and feed the DME-water mixture as vapour. Then miscibility is not a problem. A phosphoric acid doped PBI system has operation range of 120-200 °C (*11,12*) and is thus well-suited for the purpose.



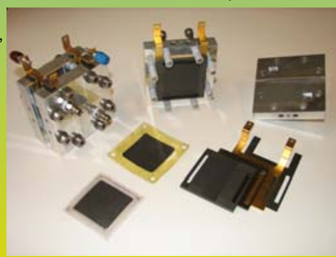
Schematic setup

MEAs hot-pressed

- Anode 40 wt% Pt, 20 wt% Ru, 40 wt% C, Johnson Matthey
- Cathode 60 wt% Pt, 40 wt% C, Johnson Matthey
- Electrolyte 40 µm H_3PO_4-doped PBI membrane, Danish Power Systems
- Protective polysulfone film

Operating conditions

- 150 or 200 °C
- 32 mL/min DME and 0.07 mL/min H_2O
- 0.23 mL/min 1:1 molar MeOH-water


Single cell, MEAs and cell housing.

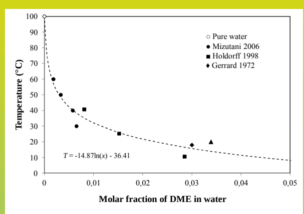
Direct conversion in a PEMFC

DME is normally fed as an aqueous solution in conventional PEM fuel cells.

Anode reaction:

$CH_3OCH_3 + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$

DME-water ratio required 1:3 ⇒ 46 wt% solution of DME in water, but DME solubility is only ca. 7.6 wt% at 20°C(*2*). At 80°C of a traditional polymer fuel cell operation temperature the solubility is even lower and a saturated DME-solution separates into two phases (*3*). This impedes the process.



Equilibrium molar fractions of DME in water at different temperatures.

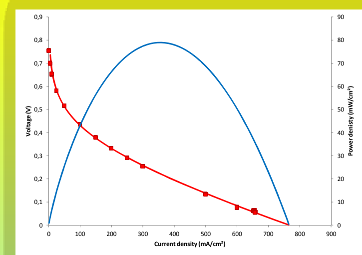
Peak power densities reported with conventional polymer fuel cells:

- Ambient pressure, air as oxidant: 20 to 40 mW/cm² (*3-5*).
- Ambient pressure, pure oxygen: 30 to 56 mW/cm² (*6-10*).

For most applications only air is available. The two-phase problem can be avoided by pressurizing the system, but this consumes energy and is not an attractive option for direct fuel cell systems which are meant to be simple.

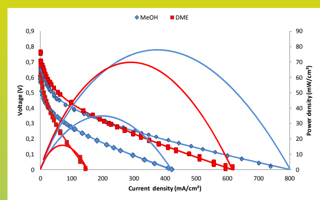
One of the major drawbacks of direct methanol fuel cells is the methanol crossover. DME crossover is less pronounced in hydrophilic environment due to the lower dipole moment.

Results

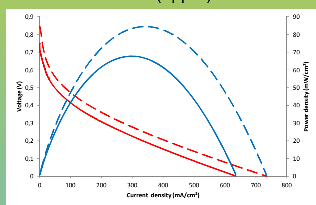


Performance curves of a direct DME fuel cell based on acid doped PBI at 200°C. Ambient pressure, air as oxidant.

Anode catalyst: PtRu/C (Johnson-Matthey, 1:1, 60 wt%, 4.0 mg metal pr cm²)
Cathode catalyst: Pt/C (Johnson-Matthey, 60 wt%, 0.7 mg Pt pr cm²)



Comparison of direct fuelling with DME and methanol at 150°C (lower) and 200°C (upper).



Effect of air (lower) vs. oxygen (upper) at ambient pressure as oxidants on direct DME performance.

References

Further on DME:

IDA International DME Association

http://www.aboutdme.org

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Publication

J. O. Jensen, A. Vassiliev, M. I. Olsen, Q. Li, C. Pan, L. N. Cleemann, T. Steenberg, H. A. Hjuler and N. J. Bjerrum, Direct Dimethyl Ether Fuelling of a High Temperature Polymer Fuel Cell, *J. Power Sources* **211** 173-176 (2012).