Direct Dimethyl Ether High Temperature PEM Fuel Cells

Vassiliev, Anton; Jensen, Jens Oluf; Li, Qingfeng; Bjerrum, Niels J.

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Direct Dimethyl Ether
High Temperature
PEM Fuel Cells

Anton Vasiliev
Jens Oluf Jensen, Qingfeng Li,
Niels J. Bjerrum

Proton Conductors,
Department of Energy Conversion and Storage,
Technical University of Denmark,
Kemitorvet 207, DK-2800 Lyngby, Denmark
Outline

- DME – general facts
- DME via PBI based HT-PEM fuel cells
- Direct DME FC vs. DMFC
- Single cell diagnostics
Dimethyl ether, DME

- Clear and colorless gas
- Liquid at 5.1 bar or -25 °C
- Handled like LPG
- Low toxicity, non-carcinogenic
- Not a greenhouse gas
  (decomp. in the atmosphere < 100 h)
- Does not degrade the ozon layer
- Burns with a visible blue flame

DME as a fuel

- Excellent diesel fuel
- No particulate matter (soot)
- High cetane rating, 55-60
  Diesel – 45

Current uses

- Propellant
- Aerosol
- Agricultural chemicals
- Cosmetics
- Cooking gas

DME

Methanol

Ethanol
Fuels

LHV gravimetric (MJ/kg)

- Hydrogen
- Methane
- Methanol
- Ethanol
- DME
- Gasoline
- Diesel

LHV volumetric (MJ/L)

at 700 bar

Liquefied

Hydrogen
Methane
Methanol
Ethanol
DME
Gasoline
Diesel

LHV gravimetric
LHV volumetric

LHV gravimetric (MJ/kg)

LHV volumetric (MJ/L)
DME in fuel cells

- No C-C bonds promotes full conversion
- Less hydrophilic than methanol leads to lower cross-over

\[(CH_3)_2O + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-\]

Fuel fed as humidified gas at temperatures > 100 °C

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

Test setup for direct HT PEMFC
- Single cell test
Spraying the electrodes

- Sprayed by robot
  - Uniform catalyst layer
  - Precise control of catalyst loading
  - Reproducible electrodes

- Control of metal loading
  - Low Energy X-ray analysis
    - Excitation < 25kV
    - High level of gray scale contrast

\[
y = 207.16x + 74.566 \\
R^2 = 0.9922
\]
Electrode surface

Catalyst – 60 wt% PtRu on 40% carbon from Johnsson & Matthey
Direct DME PEMFC – oxidation mechanism

**Hydrogen**

- 2 electron transfer
  - $H_2 + Pt \rightarrow Pt-H + H^+ + e^-$
  - $H_2 + 2Pt \rightarrow 2Pt-H$
  - $Pt-H \rightarrow Pt + H^+ + e^-$

**Methanol**

- 6 electron transfer
  - $CH_3OH + Pt \rightarrow Pt-COH + 3H^+ + 3e^-$
  - $Pt-COH \rightarrow Pt-CO + H^+ + e^-$
  - $H_2O + Pt \rightarrow Pt-OH + H^+ + e^-$
  - $Pt-CO + Pt-OH \rightarrow 2Pt + CO_2 + H^+ + e^-$

**Overall reaction**

- $H_2 \rightarrow 2H^+ + 2e^-$
- $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

**Dimethyl ether**

- 12 electron transfer
  - $(CH_3)_2O + Pt \rightarrow Pt-COCH_3 + 3H^+ + 3e^-$
  - $Pt-COCH_3 + H_2O \rightarrow Pt-COH + CH_3OH$
  - $Pt-COH \rightarrow Pt-CO + H^+ + e^-$
  - $CH_3OH + Pt \rightarrow Pt-CO + 4H^+ + 4e^-$
  - $2H_2O + 2Pt \rightarrow 2Pt-OH + 2H^+ + 2e^-$
  - $2Pt-CO + 2Pt-OH \rightarrow 2Pt + 2CO_2 + 2H^+ + 2e^-$

**Overall reaction**

- $(CH_3)_2O + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^-$
DDMEFC performance

25 cm² cell area, 60 wt% 4.0 mg/cm² PtRu on 40 wt% C catalyst (JM), air at ambient pressure as oxidant.

50 μm H₃PO₄-doped PBI membrane, 0.7 mg/cm² Pt on 60% C (JM) cathode.

DME flow - 32 mL/min, H₂O flow – 0.07 mL/min, 200° C.
Effect of loading on DDMEFC performance

25 cm² cell area, 60 wt% PtRu on 40wt% C catalyst (JM), air at ambient pressure as oxidant.

50 μm $\text{H}_3\text{PO}_4$-doped PBI membrane, 0.7 mg/cm² Pt on 60% C (JM) cathode.

DME flow - 32 mL/min, $\text{H}_2\text{O}$ flow – 0.07 mL/min, 200° C.
Effect of loading on DMFC performance

25 cm² cell area, 60 wt% PtRu on 40 wt% C catalyst (JM), air at ambient pressure as oxidant.

50 μm H₃PO₄-doped PBI membrane, 0.7 mg/cm² Pt on 60% C (JM) cathode.

MeOH/H₂O flow – 0.23 mL/min, 200° C.
DME vs. MeOH

25 cm² cell area, 3.7 mg/cm² PtRu on 40% C catalyst (JM), air at ambient pressure as oxidant.

50 μm H₃PO₄-doped PBI membrane, 0.7 mg/cm² Pt on 60% C (JM) cathode.

DME flow - 32 mL/min, H₂O flow – 0.07 mL/min, MeOH/water flow – 0.23 mL/min
Test setup for direct HT PEMFC - Durability
DDMEFC durability

25 cm² cell area, 4 mg/cm² PtRu on 40% C catalyst (JM), air at ambient pressure as oxidant.

50 μm H₃PO₄-doped PBI membrane, 1.15 mg/cm² Pt on 60% C (JM) cathode.

DME flow - 32 mL/min, H₂O flow – 0.07 mL/min. 100 mA/cm²
DDMEFC durability

25 cm² cell area, 4 mg/cm² PtRu on 40% C catalyst (JM), air at ambient pressure as oxidant.

50 μm H₃PO₄-doped PBI membrane, 1.15 mg/cm² Pt on 60% C (JM) cathode.

DME flow - 32 mL/min, H₂O flow – 0.14 mL/min. 100 mA/cm²
DDMEFC durability

Pristine

~ 300 h
at 100 mA/cm²

200 °C  180 °C  160 °C
DDMEFC durability

Pristine

~ 300 h at 200 °C, 100 mA/cm²
Impedance - 200° C

Cell Voltage / mV

$R_{an} = \frac{\Delta U \text{ (Anode)}}{\Delta i}$

$R_{cath} = \frac{\Delta U \text{ (Cathode)}}{\Delta i}$

$R_{cell} = \frac{\Delta U}{\Delta i}$

Current Density / mA cm$^{-2}$

H$_2$/Air

DME/Air

MeOH/Air

10 mA/cm$^2$

40 mA/cm$^2$

70 mA/cm$^2$

100 mA/cm$^2$

200 mA/cm$^2$
## Impedance – hydrogen/air, 200° C, fitting

<table>
<thead>
<tr>
<th></th>
<th>10 mA/cm²</th>
<th>40 mA/cm²</th>
<th>70 mA/cm²</th>
<th>100 mA/cm²</th>
<th>200 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Ωcm²</td>
<td>0,7955</td>
<td>0,6992</td>
<td>0,6284</td>
<td>0,5803</td>
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<td>Q2-Yo</td>
<td>Ssek^n/cm²</td>
<td>0,0092</td>
<td>0,0124</td>
<td>0,0144</td>
<td>0,0141</td>
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<td>Q2-n</td>
<td>0&lt;n&lt;1</td>
<td>0,8871</td>
<td>0,8700</td>
<td>0,8684</td>
<td>0,8661</td>
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<tr>
<td>R2</td>
<td>Ωcm²</td>
<td>0,1596</td>
<td>0,1664</td>
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<td>0,1876</td>
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<tr>
<td>Q3-Yo</td>
<td>Ssek^n/cm²</td>
<td>0,0165</td>
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<td>Q3-n</td>
<td>0&lt;n&lt;1</td>
<td>0,9272</td>
<td>0,9698</td>
<td>0,9941</td>
<td>1,0000</td>
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<tr>
<td>R3</td>
<td>Ωcm²</td>
<td>16,8900</td>
<td>4,6740</td>
<td>2,8600</td>
<td>2,1320</td>
</tr>
</tbody>
</table>

### Membrane resistance

### Anode resistance

### Cathode resistance

---

**H₂/Air, 200°C, 70 mA/cm²**

- **Model**: R(QR)(QR)
- **Wgt**: Modulus

- **Iter #**: 5
- **Chsq**: 9.02E-04
- **# of pars with rel. std. errors >20%**: 2 / 7
- **# of pars with rel. std. errors >1000%**: 0 / 7

---

**DTU Energy Conversion, Techni**
Impedance – hydrogen/air, 200° C, fitting

\[ f = \frac{1}{2\pi RctCd} \]

\[ R_{ct} = \frac{d\eta_{ct}}{di} = \frac{d}{di} (a + \log(i)) = \frac{b}{i} \]

**Theoretical:**

\[ b = \frac{2,3RT}{\alpha F} \]

\[ b = 0,187 \]

Assuming \( \alpha = 0,5 \)

**Practical:**

\[ b = 0,164 \]

\[ \alpha = 0,57 \]

\[ y = 0,494 + 0,164x \]
Impedance – MeOH/air, 200° C, fitting

<table>
<thead>
<tr>
<th></th>
<th>MeOH10</th>
<th>MeOH40</th>
<th>MeOH70</th>
<th>MeOH100</th>
<th>MeOH200</th>
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<tbody>
<tr>
<td>R1</td>
<td>0,4587</td>
<td>0,4963</td>
<td>0,5047</td>
<td>0,4994</td>
<td>0,4562</td>
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<tr>
<td>C2</td>
<td>0,0016</td>
<td>0,0020</td>
<td>0,0022</td>
<td>0,0023</td>
<td>0,0029</td>
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<tr>
<td>R2</td>
<td>0,0460</td>
<td>0,1093</td>
<td>0,1593</td>
<td>0,1672</td>
<td>0,1739</td>
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<tr>
<td>G-Yo</td>
<td>0,09172</td>
<td>0,1182</td>
<td>0,1406</td>
<td>0,1529</td>
<td>0,2264</td>
</tr>
<tr>
<td>G-Ka</td>
<td>13,28</td>
<td>28,25</td>
<td>38,57</td>
<td>43,03</td>
<td>98,41</td>
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<tr>
<td>C3</td>
<td>0,0254</td>
<td>0,0194</td>
<td>0,0177</td>
<td>0,0170</td>
<td>0,0148</td>
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<td>R3</td>
<td>29,55</td>
<td>6,93</td>
<td>4,167</td>
<td>3,298</td>
<td>2,097</td>
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<td>R31</td>
<td>19,36</td>
<td>11,09</td>
<td>9,003</td>
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<td>L31</td>
<td>19,85</td>
<td>4,73</td>
<td>1,751</td>
<td>0,9866</td>
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</tbody>
</table>

Membrane resistance
Anode resistance
Cathode resistance
Inductance due to MeOH cross-over

MeOH/Air, 200°C, 200 mA/cm²
Model : R(C(RG))(CR(RL))  Wgt : Modulus

Iter #: 1
Chsq: 1,45E-03

# of pars with rel. std. errors
>20%: 2 / 9
>1000%: 0 / 9
Impedance – DME/air, 200° C, fitting

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>10 mA/cm²</th>
<th>40 mA/cm²</th>
<th>70 mA/cm²</th>
<th>100 mA/cm²</th>
<th>200 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Ωcm²</td>
<td>0,3777</td>
<td>0,4013</td>
<td>0,4033</td>
<td>0,3985</td>
<td>0,3961</td>
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<tr>
<td>C2</td>
<td>F/cm²</td>
<td>0,007123</td>
<td>0,007093</td>
<td>0,0070</td>
<td>0,0067</td>
<td>0,0070</td>
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<tr>
<td>R2</td>
<td>Ωcm²</td>
<td>5,544</td>
<td>3,604</td>
<td>2,3430</td>
<td>1,2120</td>
<td>0,6653</td>
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<tr>
<td>G-Yo</td>
<td>Ssek^0,5/cm²</td>
<td>0,03427</td>
<td>0,05004</td>
<td>0,05778</td>
<td>0,05603</td>
<td>0,08897</td>
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<td>G-Ka</td>
<td>sek^-1</td>
<td>0,9812</td>
<td>5,774</td>
<td>9,946</td>
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<td>10,58</td>
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<tr>
<td>C3</td>
<td>F/cm²</td>
<td>0,004042</td>
<td>0,004634</td>
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<td>0,0055</td>
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<tr>
<td>R3</td>
<td>Ωcm²</td>
<td>0,1926</td>
<td>0,1564</td>
<td>0,1492</td>
<td>0,1346</td>
<td>0,1199</td>
</tr>
</tbody>
</table>

DME/Air, 200°C, 200 mA/cm²
Model : R(Q(RG))(QR) Wgt : Modulus

Iter #: 6
Chsq: 1,26E-03
# of pars with rel. std. errors
>20%: 5 / 9
>1000%: 0 / 9
Summary

- DME – clean and benign fuel
- DME can be converted directly in a PBI-cell
- Performance close to that of methanol (not the case for LT)
- Higher OCV (~100 mV) indicates less crossover than for DMFC
- Total cell performance evaluated by i-E curves
- EIS is a powerful tool to deconvolute contributions from MEA components, but proceed with caution!
Acknowledgements

The Danish Agency for Science, Technology and Innovation (Vedvarende Energiteknologier)

Technical University of Denmark

Danish Power Systems

Sertenergy

Danish Technological Institute

Thank you for your attention
PBI membranes with phosphoric acid

PBI – Polybenzimidazole

Poly (2,2’-m-(phenylene)-5,5’-bibenzimidazole)

Well-known temperature resistant polymer

$T_g = \sim 430^\circ C$

When impregnated with phosphoric acid:
Proton conductor

Operation temperature

$120^\circ C < T < 200^\circ C$

Direct DME PEMFC performance

- Literature:

  J.-H. Yu et al.
  *Electrochemistry Communications* 7 (2005) 1385–1388

  J.-Y. Im et al.
  *Journal of Power Sources* 179 (2008) 301–304

Fig. 5. Effect of anode catalyst type on DDMEFC performance at 80 °C.

Fig. 1. Cell voltage and power density vs. current density curves for the direct fuel cells operated with moisturized DME gas and DME aqueous solution. The fuel cells were maintained at atmospheric pressure.
DME vs. MeOH

Fig. 7. Cell voltage $E$ and power density $P$ vs. current density $j$ curves in a single 5 cm$^2$ surface area FC with a Pt$_{0.8}$Ru$_{0.2}$/C at 110°C (Nafion® 117 membrane); (♦ and ◇) MeOH 2.0 M, $P_{O_2} = 3$ bar; $P_{MeOH} = 2$ bar; (▲ and △) DME 1.65 M, $P_{O_2} = 2$ bar; $P_{DME} = 3$ bar.

Electrochemical Impedance Spectroscopy

\[ Z_R(\omega) = \frac{V(t)}{I(t)} = R \]

\[ Z_C(\omega) = \frac{V(t)}{I(t)} = \frac{1}{i\omega C} \]

\[ Z_L(\omega) = \frac{V(t)}{I(t)} = i\omega L \]
Impedance – data validation

Kramers-Kronig transformation