Direct Dimethyl Ether High Temperature PEM Fuel Cells

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

Publication date: 2014

Link back to DTU Orbit


General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Direct Dimethyl Ether
High Temperature
PEM Fuel Cells

Anton Vassiliev
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
  Dielsel – 45

**Current uses**

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

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

Comparison of LHV gravimetric and volumetric.
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

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
Electrode surface

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

**Hydrogen**

2 electron transfer

\[ \text{H}_2 + \text{Pt} \rightarrow \text{Pt-H} + \text{H}^+ + e^- \]

\[ \text{H}_2 + 2\text{Pt} \rightarrow 2\text{Pt-H} \]

\[ \text{Pt-H} \rightarrow \text{Pt} + \text{H}^+ + e^- \]

Overall reaction

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]

**Methanol**

6 electron transfer

\[ \text{CH}_3\text{OH} + \text{Pt} \rightarrow \text{Pt-COH} + 3\text{H}^+ + 3e^- \]

\[ \text{Pt-COH} \rightarrow \text{Pt-CO} + \text{H}^+ + e^- \]

\[ \text{H}_2\text{O} + \text{Pt} \rightarrow \text{Pt-OH} + \text{H}^+ + e^- \]

\[ \text{Pt-CO} + \text{Pt-OH} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + e^- \]

Overall reaction

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6e^- \]

**Dimethyl ether**

12 electron transfer

\[ (\text{CH}_3)_2\text{O} + \text{Pt} \rightarrow \text{Pt-COCH}_3 + 3\text{H}^+ + 3e^- \]

\[ \text{Pt-COCH}_3 + \text{H}_2\text{O} \rightarrow \text{Pt-COH} + \text{CH}_3\text{OH} \]

\[ \text{Pt-COH} \rightarrow \text{Pt-CO} + \text{H}^+ + e^- \]

\[ \text{CH}_3\text{OH} + \text{Pt} \rightarrow \text{Pt-CO} + 4\text{H}^+ + 4e^- \]

\[ 2\text{H}_2\text{O} + 2\text{Pt} \rightarrow 2\text{Pt-OH} + 2\text{H}^+ + 2e^- \]

\[ 2\text{Pt-CO} + 2\text{Pt-OH} \rightarrow 2\text{Pt} + 2\text{CO}_2 + 2\text{H}^+ + 2e^- \]

Overall reaction

\[ (\text{CH}_3)_2\text{O} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12e^- \]
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 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 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

57 kJ/mol

35 kJ/mol
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

Current Density / mA cm\(^{-2}\)

\[ R_{\text{An}}^{\text{ac}} = \frac{\Delta U \text{ (Anode)}}{\Delta i} \]

\[ R_{\text{Cath}}^{\text{ac}} = \frac{\Delta U \text{ (Cathode)}}{\Delta i} \]

\[ R_{\text{cell}}^{\text{dc}} = \frac{\Delta U}{\Delta i} \]

\(Z_{\text{im}} \ (\Omega \text{ cm}^2)\)

\(Z_{\text{re}} \ (\Omega \text{ cm}^2)\)

\(H_2/\text{Air}\)

\(\text{DME/Air}\)

\(\text{MeOH/Air}\)

10 mA/cm\(^2\)

40 mA/cm\(^2\)

70 mA/cm\(^2\)

100 mA/cm\(^2\)

200 mA/cm\(^2\)

DTU Energy Conversion, Technical University of Denmark
**Impedance – hydrogen/air, 200° C, fitting**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>R1 Ω/cm²</th>
<th>Q2-Yo Ssekⁿ/cm²</th>
<th>R2 Ω/cm²</th>
<th>Q3-Yo Ssekⁿ/cm²</th>
<th>R3 Ω/cm²</th>
<th>C2 F/cm²</th>
<th>C3 F/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>mA/cm²</td>
<td></td>
<td></td>
<td>0.7955</td>
<td>0.0092</td>
<td>0.1596</td>
<td>0.0165</td>
<td>16.8900</td>
<td>0.0040</td>
<td>0.0149</td>
</tr>
<tr>
<td>mA/cm²</td>
<td></td>
<td></td>
<td>0.6992</td>
<td>0.0124</td>
<td>0.1664</td>
<td>0.0149</td>
<td>4.6740</td>
<td>0.0049</td>
<td>0.0137</td>
</tr>
<tr>
<td>mA/cm²</td>
<td></td>
<td></td>
<td>0.6284</td>
<td>0.0144</td>
<td>0.1763</td>
<td>0.0141</td>
<td>2.8600</td>
<td>0.0058</td>
<td>0.0138</td>
</tr>
<tr>
<td>mA/cm²</td>
<td></td>
<td></td>
<td>0.5803</td>
<td>0.0141</td>
<td>0.1876</td>
<td>0.0143</td>
<td>2.1320</td>
<td>0.0056</td>
<td>0.0143</td>
</tr>
<tr>
<td>mA/cm²</td>
<td></td>
<td></td>
<td>0.5139</td>
<td>0.0262</td>
<td>0.1931</td>
<td>0.0185</td>
<td>1.2370</td>
<td>0.0069</td>
<td>0.0165</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
>1000%: 0 / 7
Impedance – hydrogen/air, 200° C, fitting

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

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

Theoretical:

\[ b = \frac{2.3RT}{\alpha F} \]

\[ b = 0.187 \]

Assuming \( \alpha = 0.5 \)

Practical:

\[ b = 0.164 \]

\[ \alpha = 0.57 \]

\[ y = 0.494 + 0.164x \]

DTU Energy Conversion, Technical University of Denmark
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>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Ωcm²</td>
<td>0,4587</td>
<td>0,4963</td>
<td>0,5047</td>
<td>0,4994</td>
</tr>
<tr>
<td>C2</td>
<td>F/cm²</td>
<td>0,0016</td>
<td>0,0020</td>
<td>0,0022</td>
<td>0,0023</td>
</tr>
<tr>
<td>R2</td>
<td>Ωcm²</td>
<td>0,0460</td>
<td>0,1093</td>
<td>0,1593</td>
<td>0,1672</td>
</tr>
<tr>
<td>G-Yo</td>
<td>Ssek^0,5/cm²</td>
<td>0,09172</td>
<td>0,118</td>
<td>0,1406</td>
<td>0,1529</td>
</tr>
<tr>
<td>G-Ka</td>
<td>sek^-1</td>
<td>13,28</td>
<td>28,25</td>
<td>38,57</td>
<td>43,03</td>
</tr>
<tr>
<td>C3</td>
<td>F/cm²</td>
<td>0,0254</td>
<td>0,0194</td>
<td>0,0177</td>
<td>0,0170</td>
</tr>
<tr>
<td>R3</td>
<td>Ωcm²</td>
<td>29,55</td>
<td>6,93</td>
<td>4,167</td>
<td>3,298</td>
</tr>
<tr>
<td>R31</td>
<td>Ωcm²</td>
<td>19,36</td>
<td>11,09</td>
<td>9,003</td>
<td>10,2</td>
</tr>
<tr>
<td>L31</td>
<td>Henri-cm²</td>
<td>19,85</td>
<td>4,73</td>
<td>1,751</td>
<td>0,9866</td>
</tr>
</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>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>Ω cm²</td>
<td>0.3777</td>
<td>0.4013</td>
<td>0.4033</td>
<td>0.3985</td>
</tr>
<tr>
<td>C2</td>
<td>F/cm²</td>
<td>0.007123</td>
<td>0.007093</td>
<td>0.0070</td>
<td>0.0067</td>
</tr>
<tr>
<td>R2</td>
<td>Ω cm²</td>
<td>5.544</td>
<td>3.604</td>
<td>2.343</td>
<td>1.2120</td>
</tr>
<tr>
<td>G-Yo</td>
<td>S sek^0.5/cm²</td>
<td>0.03427</td>
<td>0.05004</td>
<td>0.05778</td>
<td>0.05603</td>
</tr>
<tr>
<td>G-Ka</td>
<td>sek^-1</td>
<td>0.9812</td>
<td>5.774</td>
<td>9.946</td>
<td>13</td>
</tr>
<tr>
<td>C3</td>
<td>F/cm²</td>
<td>0.004042</td>
<td>0.004634</td>
<td>0.0047</td>
<td>0.0047</td>
</tr>
<tr>
<td>R3</td>
<td>Ω cm²</td>
<td>0.1926</td>
<td>0.1564</td>
<td>0.1492</td>
<td>0.1346</td>
</tr>
</tbody>
</table>

**Diagram:**

- **Model:** R(Q(RG))(QR)
- **Wgt:** Modulus
- **Z', ohm-sq. cm**
- **Iter #: 6**
- **Chsq:** 1.26E-03
- **# of pars with rel. std. errors >20%:** 5 / 9
- **>1000%:** 0 / 9

---

DTU Energy Conversion, Technical University of Denmark
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

Serienergy®

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**

*H₂ equivalent circuit*

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

*MeOH equivalent circuit*

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

*DME equivalent circuit*

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

Kramers-Kronig transformation

\[ \text{Chi Sq} = 4.7 \times 10^{-04} \]

\(0.0 \times 10^{+00} \quad 2.0 \times 10^{-02} \quad 4.0 \times 10^{-02} \quad 6.0 \times 10^{-02} \quad 8.0 \times 10^{-02} \quad 1.0 \times 10^{-01} \)

\[1.0 \times 10^{-01} \text{ Hz} \quad 6.3 \times 10^{+03} \text{ Hz} \]

H\textsubscript{2}/Air

DME/Air

MeOH/Air