Direct Dimethyl Ether High Temperature PEM Fuel Cells

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Direct Dimethyl Ether High Temperature PEM Fuel Cells

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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

LHV gravimetric (MJ/kg)

LHV volumetric (MJ/L)

Liquefied

Hydrogen

Methane

Methanol

Ethanol

DME

Gasoline

Diesel

at 700 bar
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

<table>
<thead>
<tr>
<th>Hydrogen</th>
<th>Methanol</th>
<th>Dimethyl ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 electron transfer</td>
<td>6 electron transfer</td>
<td>12 electron transfer</td>
</tr>
<tr>
<td>$\text{H}_2 + \text{Pt} \rightarrow \text{Pt-H} + \text{H}^+ + e^-$</td>
<td>$\text{CH}_3\text{OH} + \text{Pt} \rightarrow \text{Pt-COH} + 3\text{H}^+ + 3e^-$</td>
<td>$(\text{CH}_3)_2\text{O} + \text{Pt} \rightarrow \text{Pt-COCH}_3 + 3\text{H}^+ + 3e^-$</td>
</tr>
<tr>
<td>$\text{H}_2 + 2\text{Pt} \rightarrow 2\text{Pt-H}$</td>
<td>$\text{Pt-COH} \rightarrow \text{Pt-CO} + \text{H}^+ + e^-$</td>
<td>$\text{Pt-COCH}_3 + \text{H}_2\text{O} \rightarrow \text{Pt-COH} + \text{CH}_3\text{OH}$</td>
</tr>
<tr>
<td>$\text{Pt-H} \rightarrow \text{Pt} + \text{H}^+ + e^-$</td>
<td>$\text{H}_2\text{O} + \text{Pt} \rightarrow \text{Pt-OH} + \text{H}^+ + e^-$</td>
<td>$\text{Pt-COH} \rightarrow \text{Pt-CO} + \text{H}^+ + e^-$</td>
</tr>
<tr>
<td></td>
<td>$\text{Pt-CO} + \text{Pt-OH} \rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + e^-$</td>
<td>$\text{CH}_3\text{OH} + \text{Pt} \rightarrow \text{Pt-CO} + 4\text{H}^+ + 4e^-$</td>
</tr>
<tr>
<td>Overall reaction</td>
<td>Overall reaction</td>
<td>Overall reaction</td>
</tr>
<tr>
<td>$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^-$</td>
<td>$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6e^-$</td>
<td>$(\text{CH}_3)_2\text{O} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12e^-$</td>
</tr>
</tbody>
</table>
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 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

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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

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

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

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

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

- MeOH/Air
- DME/Air
- H\(_2\)/Air
- MeOH/Air

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

\[ Z_{\text{re}} \text{ (}\Omega\text{cm}^2\) ]
### Impedance – hydrogen/air, 200° C, fitting

<table>
<thead>
<tr>
<th></th>
<th>R1</th>
<th>Q2-Yo</th>
<th>Q2-n</th>
<th>R2</th>
<th>Q3-Yo</th>
<th>Q3-n</th>
<th>R3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ωcm²</td>
<td>Ssek^n/cm²</td>
<td>0&lt;n&lt;1</td>
<td>Ωcm²</td>
<td>Ssek^n/cm²</td>
<td>0&lt;n&lt;1</td>
<td>Ωcm²</td>
</tr>
<tr>
<td>Membrane resistance</td>
<td>Anode resistance</td>
<td>Cathode resistance</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 mA/cm²</td>
<td>0,7955</td>
<td>0,0092</td>
<td>0,8871</td>
<td>0,1596</td>
<td>0,0165</td>
<td>0,9272</td>
<td>16,8900</td>
</tr>
<tr>
<td>40 mA/cm²</td>
<td>0,6992</td>
<td>0,0124</td>
<td>0,8700</td>
<td>0,1664</td>
<td>0,0149</td>
<td>0,9698</td>
<td>4,6740</td>
</tr>
<tr>
<td>70 mA/cm²</td>
<td>0,6284</td>
<td>0,0144</td>
<td>0,8684</td>
<td>0,1763</td>
<td>0,0141</td>
<td>0,9941</td>
<td>2,8600</td>
</tr>
<tr>
<td>100 mA/cm²</td>
<td>0,5803</td>
<td>0,0141</td>
<td>0,8661</td>
<td>0,1876</td>
<td>0,0143</td>
<td>1,0000</td>
<td>2,1320</td>
</tr>
<tr>
<td>200 mA/cm²</td>
<td>0,5139</td>
<td>0,0262</td>
<td>0,7978</td>
<td>0,1931</td>
<td>0,0185</td>
<td>0,9701</td>
<td>1,2370</td>
</tr>
</tbody>
</table>

### 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

**Graph**

- **Z, Msd.**
- **Z, Calc.**
- **Membrane resistance**
- **Anode resistance**
- **Cathode resistance**
Impedance – hydrogen/air, 200° C, fitting

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

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

Theoretical:

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

- \[ b = 0,187 \]
- Assuming \( \alpha = 0,5 \)

Practical:

- \[ b = 0,164 \]
- \[ \alpha = 0,57 \]
## 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>Ω cm²</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>Ω cm²</td>
<td>0.0460</td>
<td>0.1093</td>
<td>0.1593</td>
<td>0.1672</td>
</tr>
<tr>
<td>G-Yo</td>
<td>S scek⁰²⁰⁰⁰/霞²⁰⁰⁰⁰ 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>scek⁻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>Ω cm²</td>
<td>29.55</td>
<td>6.93</td>
<td>4.167</td>
<td>3.298</td>
</tr>
<tr>
<td>R31</td>
<td>Ω cm²</td>
<td>19.36</td>
<td>11.09</td>
<td>9.003</td>
<td>10.28</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**

### Diagram

![Impedance Diagram](image)

**Model:** $R(C(RG))(CR(RL))$

**Wgt:** Modulus

**Z', ohm-sq. cm**

**Z, Med.**

**Z, Calc.**

- **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>2.3430</td>
<td>1.1210</td>
</tr>
<tr>
<td>G-Yo</td>
<td>S s/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>s/cm²</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>

Model: \( R(Q(RG))(QR) \)

Wgt: Modulus

**Z', ohm-sq. cm**

- 251m
- 398m
- 501m
- 631m
- 794m
- 100m
- 126m
- 158m
- 251m

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

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