MEA & DM Characterization/Optimization for Low Pt Loadings and High Current Densities


Chair of Technical Electrochemistry
Technical University of Munich, Germany

- PEM fuel cell materials / structures
- Pt reduction strategies:
  - Pt needs for the HOR
  - ORR catalyst status / limitations
  - mass-tx loss phenomena
  - MPL/DM design for high-i
  - effect of catalyst morphology

Summary
Fuel Cell Electric Vehicle Challenges

since ≈2008: >300 mi. range 70 MPa H₂ (4-6 kg₃H₂ at 5%wt) with refuelling <5 mins.

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H₂ generation & distribution infrastructure...

- catalyst cost & supply (100kW car):
  current:  ≈0.3-0.5 gₚt/kW  ≔  30-50gₚt/car
  →  ≈5-10x vs. automotive emission catalysts

long-term:  <0.1gₚt/kW  ≔  <10gₚt/car
  →  large-scale commercial viability

- approaches to get to <0.1 gₚt/kW ?
H₂/Air Fuel Cell Components


C-fiber paper (7 μm fibres)

→ high electronic $R_{contact}$
PEFC Electrode Composition / Structure

- dominated by carbon-black structure

\[ \text{membrane} \]

\[ H^+ \rightarrow 46\% \text{Pt/carbon} \]

\[ \approx 40 \text{ nm} \]

Pt/C & ionomer at \( \approx 1 \text{ g}_{\text{ionomer}}/\text{g}_{\text{carbon}} \)


\[ \text{membrane} \]

\[ \text{Diffusion Medium} \]

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]

\[ \rightarrow 60\% \text{ void volume (}d_{\text{pore}} \approx 50-100 \text{ nm)} \]

\[ \rightarrow H^+-\text{tx resistance (}R_{H^+-\text{tx}}\text{) in electrodes}\]

\[ \rightarrow \text{assumes homogenous ionomer distr.} \]

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HOR/HER Kinetics via PEM H₂-Pump

- **H₂-pump**: minimized ohmic/transport losses & maximized kinetic resistance

  → high transport-limited current → ≈80 A/cm² at 100 kPa_{abs} H₂

  - thin membrane (≈20μm) and electrode (≈2μm)
    → minimize ohmic losses
  - ultra-low Pt loading on working electrode
    → increase kinetic resistance

  counter & reference electrode 0.4 mg_{Pt}/cm²
  working electrode 2 μg_{metal}/cm²

  determination of transport-resistance-free HOR/HER kinetics
HOR Kinetics on Pt/C

- HOR kinetics on Pt/C (100 kPa\textsubscript{a} H\textsubscript{2}, 100\%RH)

  → for $\eta$>100 mV: Tafel-reaction limited
  \[ (i_{\text{tx-limit}} > 50 \text{ A/cm}^2_{\text{geo}}) \]
  → gas-phase H\textsubscript{2} dissociation rate const.\textsuperscript{1)}:
  \[ k_{\text{H}_2/D_2} = 2.4 \text{ cm/s at 295 K} \]
  ≡ ”Tafel” reaction: $\text{H}_2 \leftrightarrow 2 \text{ H}_{\text{ad}}$
  with $i_{\text{Tafel}} \approx 0.5 \text{ A/cm}^2_{\text{Pt}}$


  → for $\eta$<50 mV: Tafel/Volmer(rds)
  \[ \text{H}_{\text{ad}} \to \text{H}^+ + \text{e}^- \]
  fit to: $i = i_0 \cdot \text{rf} \cdot \left( \text{e}^{\frac{\alpha_a \cdot F \cdot \eta}{R \cdot T}} - \text{e}^{\frac{\alpha_c \cdot F \cdot \eta}{R \cdot T}} \right)$

  → on Pt/C at 353 K\textsuperscript{2)}: $i_0 \approx 0.3 \text{ A/cm}^2_{\text{Pt}}$

  - $\alpha_a = \alpha_c = 0.5 \equiv 140 \text{ mV/dec.}$

predicted $\eta_{\text{HOR/HER}}$ at $i_{\text{geo}} = 3 \text{ A/cm}^2_{\text{geo}}$ & $0.05 \text{ mgPt/cm}^2$ (80°C and 100 kPa$_{\text{abs H}_2}$)

for typical Pt/C catalyst:

$A_{\text{Pt}} = 80 \text{ m}^2_{\text{Pt}}/g_{\text{Pt}} = 800 \text{ cm}^2_{\text{Pt}}/mg_{\text{Pt}}$

$\rightarrow rf = 40 \text{ cm}^2_{\text{Pt}}/\text{cm}^2_{\text{geo}}$

$\rightarrow$ required kinetic current:

$i_{k} = i_{\text{geo}} / rf = 0.75 \times 10^{-2} \text{ A/cm}^2_{\text{Pt}}$

$\eta_{\text{HOR}} < 10 \text{ mV}$ at $0.05 \text{ mgPt/cm}^2$ even at very low Pt anode loadings
H₂ Oxidation Reaction (HOR) Kinetics on Pt/C

- H₂ → 2 H⁺ + 2 e⁻ kinetics via rotating disk electrode (RDE) in liquid electrolytes
  → but, slow H₂-transport

very fast transport in PEM setup:
H₂-pump measurements¹,²)

fast transport in liquid electrolytes:
  - Floating VCF Pt/C Electrode³)
  - Scanning Electrochemical Microscopy (SECM) on Pt⁴)ₚₐₑ
  - Ultra Micro Electrode (UME)⁵)

ʪ: i₀ (RDE) ≈10²-fold too low
  → fast HOR/HER kinetics ✓

5) V. Bagotzky, N. Osetrova, J. Electroanal. Chem. 43 (1973) 233
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H$_2$/Air PEMFC Performance Model

$E_{cell}$

$\eta_{HFR}=90$ mV ($\eta_{mem}=30$ mV)

$\eta_{ORR}=410$ mV ($\eta_{HOR} < 5$ mV$^*$)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$\eta_{tx,H^+}=18$ mV

$\eta_{tx,O_2(dry)}=26$ mV

$\eta_{tx,O_2(wet)}=18$ mV

$\approx 25\mu m$ membrane and $\approx 0.05/0.40$ mg$_{Pt}$/cm$^2$$_{MEA}$


$\eta_{HOR} < 5$ mV$^*$

$\eta_{ORR}$

$\approx 0.5$ g$_{Pt}$/kW

need 10x better ORR catalysts to reach 0.05/0.04 mg$_{Pt}$/cm$^2$$_{MEA} \rightarrow \approx 0.1$ g$_{Pt}$/kW

at 1.5 A/cm$^2$:
Fuel Cell Cathode Catalyst Options

Options envisaged in 2009: ultra-high activity Pt-based or Pt-free

From: H.A. Gasteiger & N.M. Marković; Science 324 (2009) 48
**O₂ Reduction Reaction (ORR) Catalysts**

- **de-alloyed Pt-alloys**\(^1\): leaching of Ni-rich Pt-Ni alloys
  
  → proven in fuel cell stacks: \(\approx 0.4\) - \(0.6\) A/mg\(_{\text{Pt}}\)

- **shape-controlled Pt-alloys**\(^2\):
  
  \(\text{Pt}_3\text{Ni}\) octahedra → \(\text{Pt}_3\text{Ni}\) nanoframes
  
  → highest activity for C-supported catalysts so far

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likely ORR catalyst candidates for applications (green) & new concepts (white)

≈3-4x catalysts (0.4-0.6 A/mg\textsubscript{Pt}) feasible for next gen. FCEVs 
→ sufficient for reaching <0.1 g\textsubscript{Pt}/kW target?
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Best-Case High-i Performance Limit

- $i_m = 0.4 \text{ A/mg}_{\text{Pt}}$ (Pt-alloy)
- $L_{\text{an/ca}} = 0.05/0.05 \text{ mg}_{\text{Pt/cm}^2}$
- $t_{\text{membrane}} = 10 \mu\text{m} (0.1 \text{ S/cm})$
- $R_{\text{contact}} = 15 \text{ m}\Omega\text{cm}^2$
- $\rho_{\text{H+,cath.}} = 50 \text{ }\Omega\text{cm} (10 \mu\text{m thick})$
- $R_{O2-\text{tx}} = 0.5 \text{ s/cm} \text{ (for DM only)}$
- $\eta_{\text{HOR}}$ negligible (<10mV)

$\approx 0.06 \text{ g}_{\text{Pt}}/\text{kW at 0.60 V}$

→ would meet DOE target, if low-Pt cathodes can be made
→ low $R_{\text{contact}}$ & low $R_{O2-\text{tx}}$ req.
Low-Pt Cathode – Surface Film Resistance

- additional O₂ transport resistance found for low-loaded Pt cathodes

Figure 5. (a) Schematic of membrane, cathode, diffusion medium (DM), and bipolar plate (BP) and the transport therein. (b) Close-up view of the local O₂ transport to a Pt nanoparticle through the ionomer film. (c) Simulated mass-transport voltage losses at 1.75 A/cm² for a cathode with 0.10 mg_Pt/cm² Pt loading with operating conditions the same as those in Figure 4.


→ ηtx-film for >0.02 A/cm² Pt at 150 kPa_a H₂/air
→ ascribed to interfacial resistance

Low-Pt Cathode – Pt/Support Morphology

- effect of catalyst morphology on Pt mass activity and H\textsubscript{2}/air performance

→ poor high-i performance of buried Pt

→ lower ORR poisoning by buried Pt

controlled by carbon morphology

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Micro-Porous-Layer (MPL) Design

Denka carbon black

<table>
<thead>
<tr>
<th></th>
<th>Li100</th>
<th>Li400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary particle size (spec.) [nm]</td>
<td>35</td>
<td>48</td>
</tr>
<tr>
<td>BET – surface powder [m²/g]</td>
<td>64</td>
<td>37</td>
</tr>
<tr>
<td>DBP absorption [ml/100g]</td>
<td>175</td>
<td>140</td>
</tr>
</tbody>
</table>

- MPLs with 20 wt.% PTFE & different carbon blacks
- coated on commercial Freudenberg GDL substrate

perforation of MPLs via a thermally decomposable pore forming polymer:

\[ d_{\text{mean}} = 30 \, \mu m \text{ (order of } d_{\text{MPL}}) \]

\[ q_{\text{vol.}} [%] \quad d_{\text{particle}} [\mu m] \]

10 20 30 40 50 60 70 80
0 5 10 15 20 25 30

\[ \varepsilon = 79\% \quad d_{\text{pore}} = 64 \, \text{nm} \]
\[ \varepsilon = 68\% \quad d_{\text{pore}} = 67 \, \text{nm} \]
\[ \varepsilon = 68\% \quad d_{\text{pore}} = 328 \, \text{nm} \]
MPL Morphology

- change MPL structure (t≈30µm) by:
  - carbon black (Li100 & Li400) → smooth layers
  - perforation → large pores/cracks

**Effect on oxygen and water transport?**

**H₂/Air Performance – MPL Structure Effect**

- differential-flow H₂/air performance with 0.1/0.4 mg Pt/cm² (an/ca) Gore MEA (18 μm)

![Graphs showing performance at different conditions](image)

- **at 50°C / 300 kPa** (wet cond.):
  - Li400 w. larger 2ndary pores better than Li100 (Hg poros.)
  - MPLs with cracks superior

- **at 80°C / 170 kPa** (std. cond.):
  - minor differences

- suggests tx of H₂O liquid via cracks and O₂ via fine pores
  - MPL design relevant at potential FC operating conditions?

H₂/Air Performance at High Pressure

- differential-flow H₂/air performance with 0.1/0.4mgPt/cm² (an/ca) Gore MEA (18μm)

\[ E_{\text{cell}} \] vs. \[ i_{(\text{lim})} \] for GDL substrate with commercial MPL, Li400 MPL, and Li400 perforated MPL. Red dashed lines indicate optimized MPL showing improved performance by \( \approx 1.5 \)-fold (from 1.3 to 1.9 W/cm²).

- Differential pressure: \( P = 300 \text{kPa}_a \)
- Temperature: \( 80^\circ\text{C} / 100\%\text{RH} \)

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**effect of catalyst morphology on Pt mass activity and H2/air performance**

- carbon-support vs. Pt deposition method?

slides removed (unpublished data)
Summary

- MPL/GDL-substrate design critical for high-i performance
  → $\eta_{\text{unaccounted}}$ affected by $H_2O_{\text{liquid}}$ saturation

- $< 0.1 \ g_{Pt}/kW$ target can be met by improved catalysts & design for high-i
  → catalyst morphology is critical