Catalyst structure – performance trends for sibunit carbon based cathodes for PEMFC

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CATALYST STRUCTURE – PERFORMANCE TRENDS FOR SIBUNIT CARBON BASED CATHODES FOR PEMFC

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PEM Fuel Cell – challenges to commercialization

- Durability
- Cost
- Performance (efficiency)
PEM Fuel Cell – cost

Fuel Cell system costs decreased to $73/kW but need further reductions

80 kW, direct hydrogen, automotive fuel cell system cost breakdown*

* Based on DTI DFMA 2008 cost analysis projected to volume of 500,000 units per year, using Pt cost of $1100 per troy ounce

Nancy L.. Garland, DoE, '08 Electric Drive Transportation Association Conference & Exposition, 2-4 December 2008, Washington DC, USA
PEM Fuel Cell – how to reduce the catalyst cost?

- **Use less Pt and improve its utilization**
  
  catalyst - porous structure
  electrode - catalytic layer structure

- **Alloy Pt with transition metals: Pt M**

- **Non-Pt catalysts**

  Sluggish oxygen reduction reaction (ORR) causes major performance losses

  Focus on the **CATHODE**
Sibunit

- **Catalyst porous structure**
  - Sibunit carbon
  - Boreskov Institute of Catalysis (BIC) in Novosibirsk, Russia

EU FP6 project “IPHE-GENIE”
Carbons of Sibunit family

Sibunit BIC, Novosibirsk
IHP, Omsk

Synthesis and formation of Sibunit texture

A – condensation (deposition of pyrocarbon onto carbon black particles)

B, C, D, E – activation (oxidative gasification of the PC/CB composite)

Texture of the Sibunit support materials

Porous carbon of the Sibunit family used as the catalyst support: pore size distributions calculated from the desorption branch of the nitrogen adsorption isotherm in accordance with the *BJH* model.

- **BET surface area**: 450 - 550 m²/g
- **Total pore volume**: 0.6 – 1.4 cm³/g

Porous carbon of the Sibunit family used as the catalyst support: pore size distributions calculated from the desorption branch of the nitrogen adsorption isotherm in accordance with the *BJH* model.
40wt% Pt/Sibunit 1562P catalyst

TEM

$D_{SV}=2.86 \text{ nm}$

XRD

$D_v=3.3 \text{ nm}$

CO chemisorption

$D_S=3.37 \text{ nm}$
MEA preparation (typical)

INK

- Pt/Carbon
- 1,2-propanediol
- Stabiliser
- Nafion (N:C ratio varied)

ELECTRODE

- screen-printed on GDL
- thin layer of ionomer (Nafion)

MEA

- 5-layer structure
- membrane
- hot-pressed

Patented:
US2004086773
WO0171840
US7186665
EP1285475
**MEA testing protocol**

**Start-up**
- at 500 mA/cm$^2$ for 16-17 hours
- $T_{\text{cell}} = T_{\text{humidifier}} = 65 ^\circ \text{C}$, 1 bar(a), $\lambda_{\text{air}} = 2$, $\lambda_{\text{H}2} = 1.5$

**Polarization curves**
- in air and in oxygen
- OCV - 2.0 A/cm$^2$ (2.5 A/cm$^2$) - 0.5 A/cm$^2$ - OCV
- step time - 5 minutes
- $T_{\text{cell}} = T_{\text{humidifier}} = 65 ^\circ \text{C}$, 1 bar(a), $\lambda_{\text{air}} = 2$, $\lambda_{\text{H}2} = 1.5$

**Extra characterisation tools**
- Electrochemical Impedance Spectroscopy (EIS)
- electrical + proton resistance
- Cyclic voltammetry (CV)
- active surface area of Pt, Pt utilisation
- Hydrogen cross-over
Polarisation measurements

65°C, 100% RH, 1 bar(a)

$\lambda_{H2} = 1.5, \lambda_{air, O2} = 2.0$

step time 5 min

40wt% Pt/Sibunit 1562P
H2315 C2
FuMAPEM 950
Fumion ionomer

$m_{Pt \text{ cathode}} = 0.26 \text{ mg/cm}^2$

-air
-oxygen
Catalyst kinetic activity

Kinetic activity ORR @ 0.9 V

Mass activity:

- 40wt%Pt/Sibunit 1562P
  - 63 ± 5 A/g
- 40wt% Pt/Vulcan XC72R (Hispec 4000, JM)
  - 30 ± 8 A/g

Specific activity:

- 40wt%Pt/Sibunit 1562P
  - 104 ± 10 µA/cm²
- 40wt% Pt/Vulcan XC72R (Hispec 4000, JM)
  - 114 ± 10 µA/cm²

Pt utilisation:

- 40wt% Pt/Sibunit 1562P
  - 60-80%
- 40wt% Pt/Vulcan XC 72R (Hispec 4000, JM)
  - 60-80%

Pore structure effect – Pt utilisation

Pt utilisation = ECSA / SA

ECSA – from in situ CV measurements
SA – gas-phase CO chemisorption

Pores with \( d > 10 \text{ nm} \) are well accessible for the ionomer

Small mesopores \( 3-4 \text{ nm} \) → much higher Pt utilisation → Sib 619P > Sib 1562P > Sib 29PVR
**Pore structure effect – Pt utilisation**

**Ordered mesoporous carbon CMK-3**

Pore diameter 3.65 nm

Pt utilisation ≈ 80%


Small mesopores:

3-4 nm – unaccessible for the ionomer tend to flood

*water acts as a proton conductor*

Transport processes at the cathode

- **Transport of $H^+$, $O_2$, and $H_2O$:**
  - efficient ionomer pathways
  - thin electrode
  - thin ionomer layer
  - sufficiently large pores
  - hydrophobic / hydrophilic pathways

- **Electron transport:**
  - conducting carbon network
Pore structure effect – $H^+$ transport in cathode layer

<table>
<thead>
<tr>
<th>Composition</th>
<th>Resistance Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 wt% Pt/Sibunit 619P</td>
<td>0.100 - 0.170 Ohm cm$^2$</td>
</tr>
<tr>
<td>40 wt% Pt/Sibunit 1562P</td>
<td>0.100 - 0.140 Ohm cm$^2$</td>
</tr>
<tr>
<td>40 wt% Pt/Vulcan XC 72R (Hispec 4000, JM)</td>
<td>0.100 - 0.140 Ohm cm$^2$</td>
</tr>
<tr>
<td>40 wt% Pt/Sibunit 29PVR</td>
<td>0.090 - 0.130 Ohm cm$^2$</td>
</tr>
</tbody>
</table>

No pronounced effect of the support pore structure on $H^+$ transport in the catalytic layer
Pore structure effect – $O_2$ and water transport

Large pores with $d > 10$ nm are efficient in $O_2$ transport and water removal
Small mesopores – 3-4 nm – tend to flood, impeding $O_2$ transport

H2315 C2 GDL
Rp ~ 0.10-0.13 Ohm cm$^2$
Pore structure effect – \(O_2\) and water transport

- **Transport of \(O_2\) and \(H_2O\):**
  
  Knudsen diffusion in the pores with diameter < ca. 100 nm @ \(p = 1\) bar(a)
  
  \[D_k = 97 \cdot r \sqrt{T/M}\]

  Capillary condensation @ low \(P/P_0\) in small mesopores

\[O_2\] \[H_2O\]

*Pore structure of the catalytic layer - important!*
Corrosion stability of Sibunit carbons

Voltage hold at 1.2 V vs. RHE, 80°C in 1M H$_2$SO$_4$ for 24 hrs

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \]

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{surface groups} \]

Corrosion stability of Sibunit carbons

Sibunit carbons are more corrosion resistant due to a higher degree of graphitisation of the surface

Conclusions

• Pore structure of the carbon support was shown to significantly influence the performance of the Pt/C cathode catalysts:
  – **Pt utilisation** increases when small mesopores, 3-4 nm, are present in the catalyst. Pores with the diameter smaller than ca. 10 nm are not accessible for the ionomer. Water plays an important role as a proton conductor.
  – **Transport properties** – O$_2$ diffusion and H$_2$O removal – are improved for the catalysts having large mesopores, > 10 nm, and macropores. Flooding through capillary condensation is also diminished.

• Sibunit carbons exhibit higher corrosion resistance compared to the conventional carbon blacks due to a higher graphitisation degree of the surface.

• Sibunit carbons offer a unique possibility to tune porous structure without changing other textural parameters (for example, microstructure at the surface), therefore, enabling fundamental studies of the structure – performance relationship.
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