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

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Energy research Centre of the Netherlands

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

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PEM Fuel Cell – challenges to commercialization

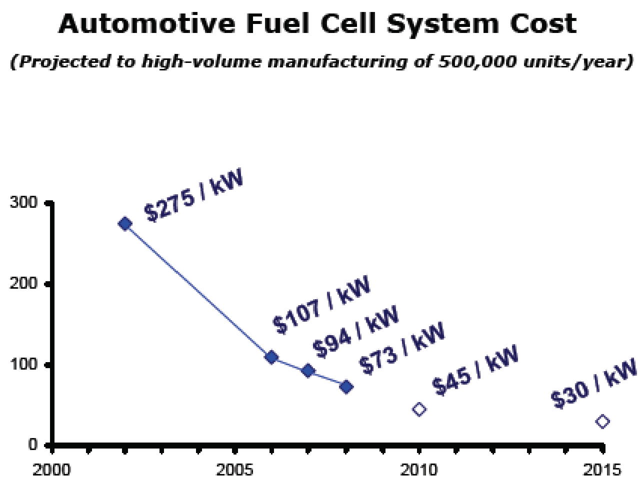
- Durability
- Cost
- Performance (efficiency)

Nancy L.. Garland, DoE, '08 Electric Drive Transportation Association Conference & Exposition, 2-4 December 2008, Washington DC, USA

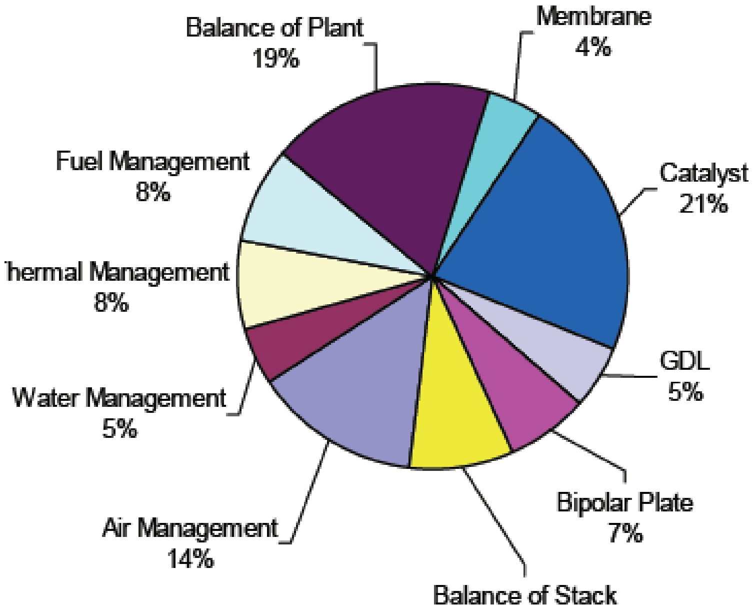
ECN

PEM Fuel Cell – cost

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



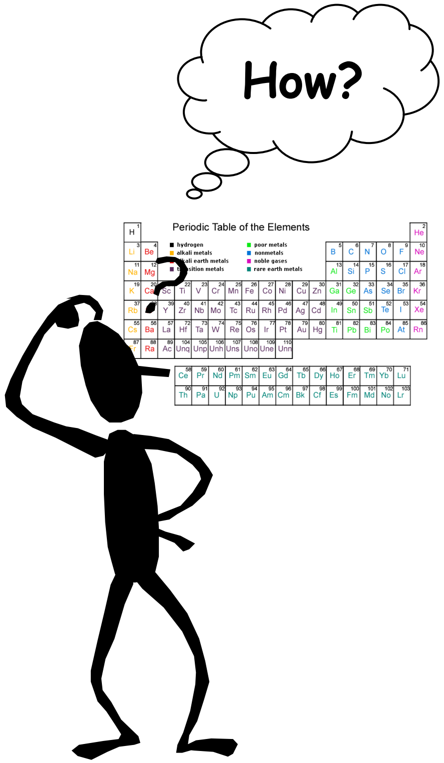
80 kW, direct hydrogen, automotive fuel cell system cost breakdown*



* *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

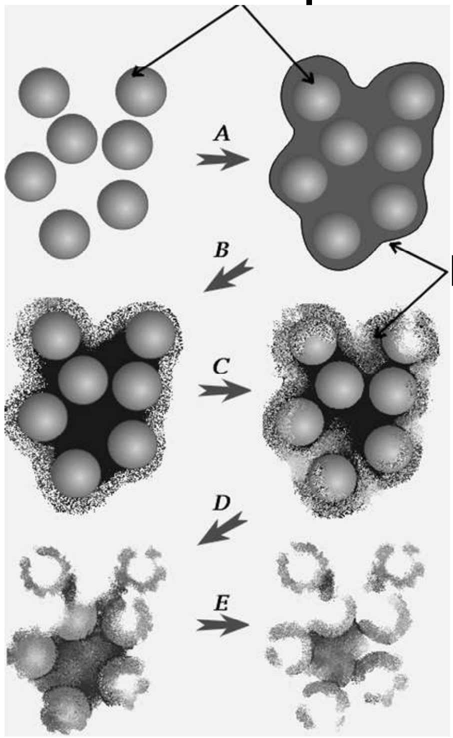
Sibunit BIC, Novosibirsk
IHP, Omsk

Synthesis and formation of Sibunit texture

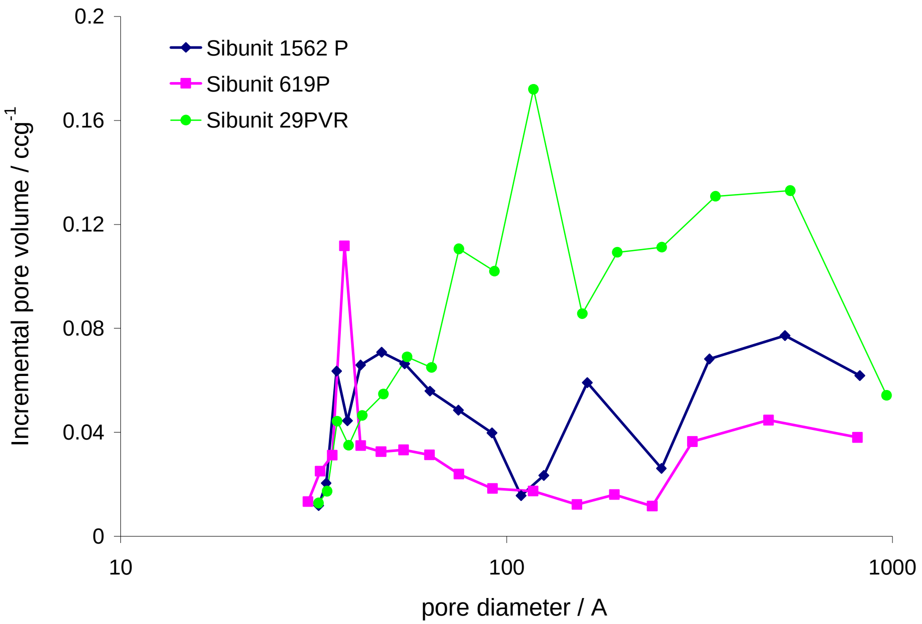
A – condensation (deposition of pyrocarbon onto carbon black particles)

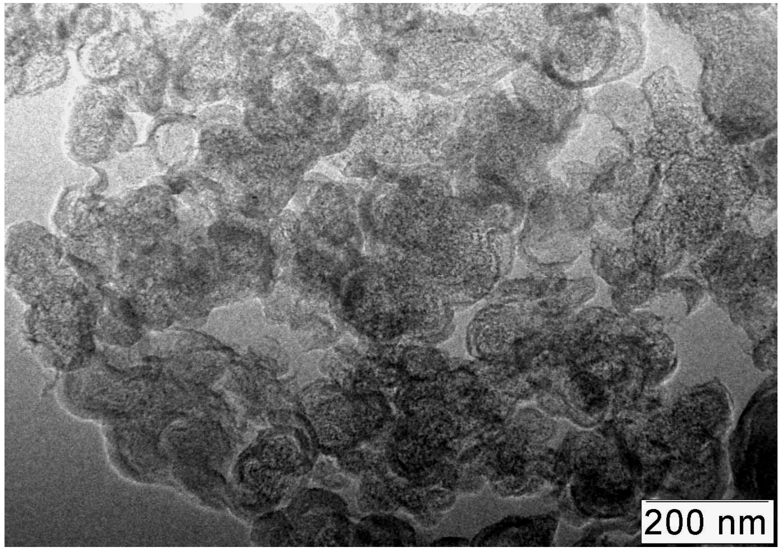
B,C,D,E – activation (oxidative gasification of the PC/CB composite)

Likholobov V.A., et.al.
React. Kinet. Catal. Lett. 54, 381 (1995)



Texture of the Sibunit support materials



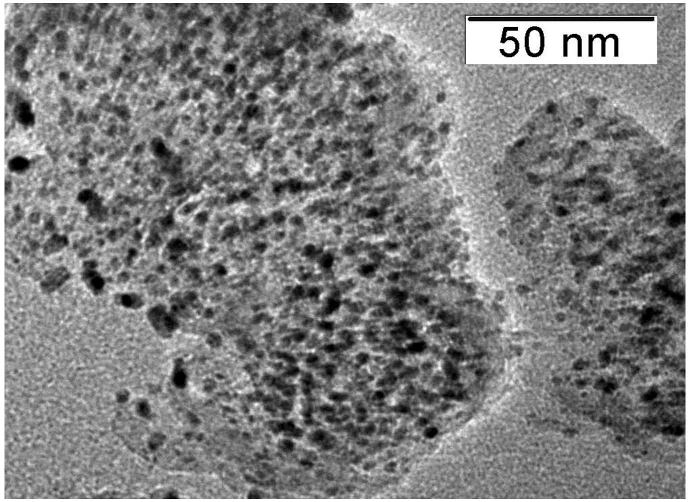


BET surface area - 450 -550 m^2/g, total pore volume - 0.6 – 1.4 cm^3/g

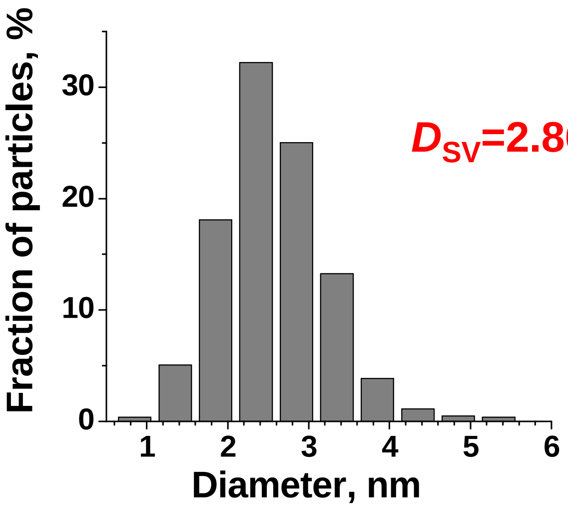
Porous carbon of the Sibunit family used as the catalyst support: pore size distributions calculated from the desorption branch of the nitrogen adsorption isotherm in accordance with the *BJH* model.

ИК СО РАН

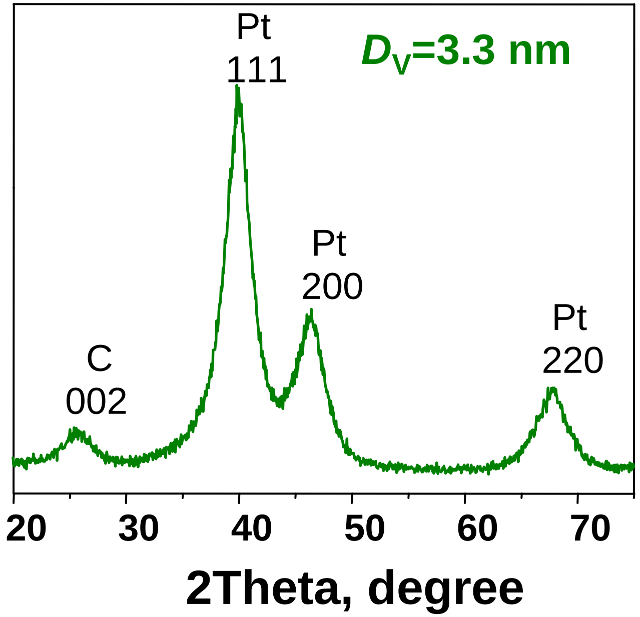
40wt% Pt/Sibunit 1562P catalyst



TEM



D_{SV}=2.86 nm



D_V=3.3 nm

XRD

CO chemisorption

D_S=3.37 nm

MEA preparation (typical)

Patented:
US2004086773
WO0171840
US7186665
EP1285475

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

MEA testing protocol

Start-up	at 500 mA/cm^2 for 16-17 hours
	$T_{cell} = T_{humidifier}$ = 65 ℃, 1 bar(a), $\lambda_{air} = 2$, $\lambda_{H2} = 1.5$
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
	$T_{cell} = T_{humidifier}$ = 65 ℃, 1 bar(a), $\lambda_{air} = 2$, $\lambda_{H2} = 1.5$
Extra characterisation tools	<u>Electrochemical Impedance Spectroscopy (EIS)</u>
	electrical + proton resistance
	<u>Cyclic voltammetry (CV)</u>
	active surface area of Pt, Pt utilisation
	<u>Hydrogen cross-over</u>

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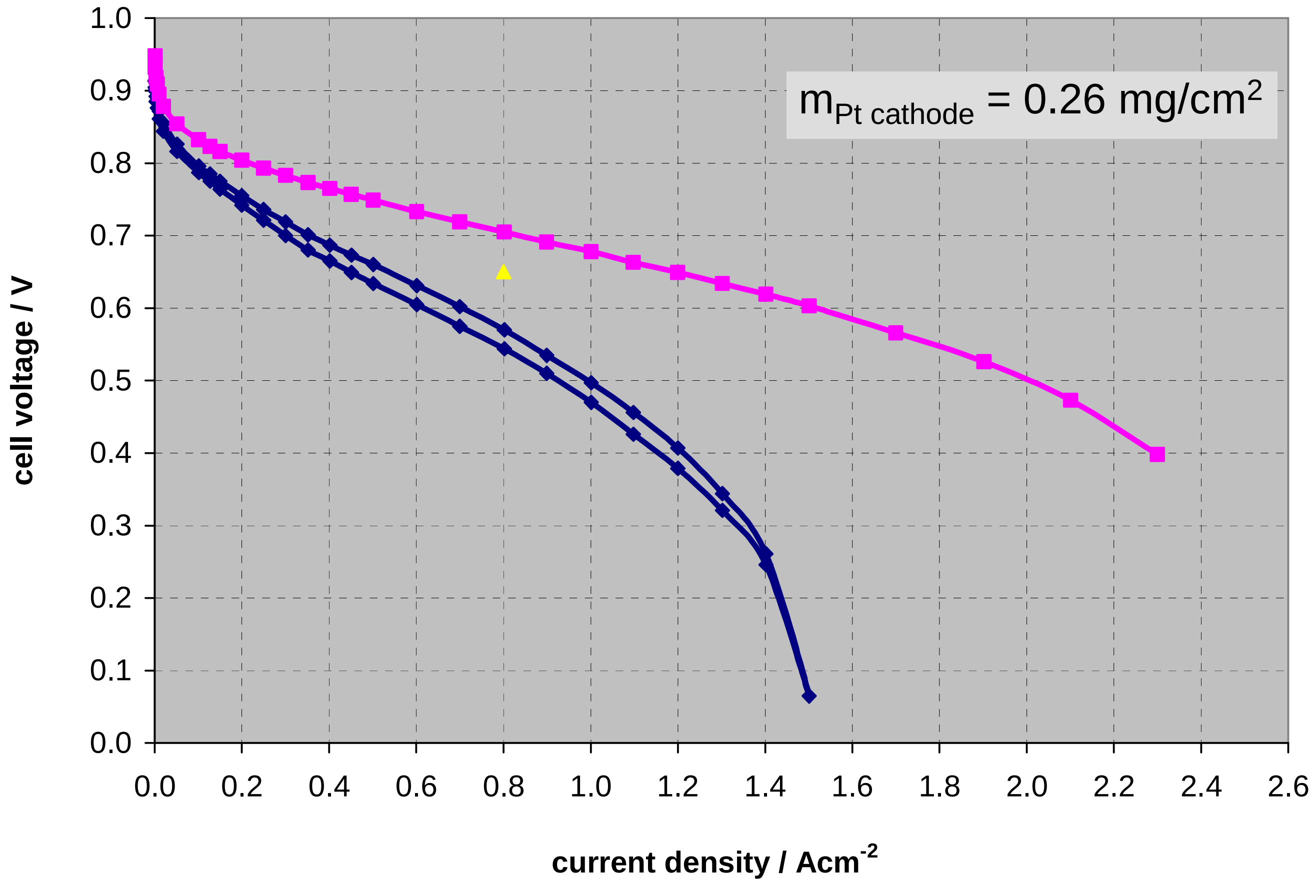
Polarisation measurements



65℃, 100% RH, 1 bar(a)
λ_{H2} = 1.5, $\lambda_{air,\ O2}$ = 2.0

step time 5 min

40wt% Pt/Sibunit 1562P

H2315 C2

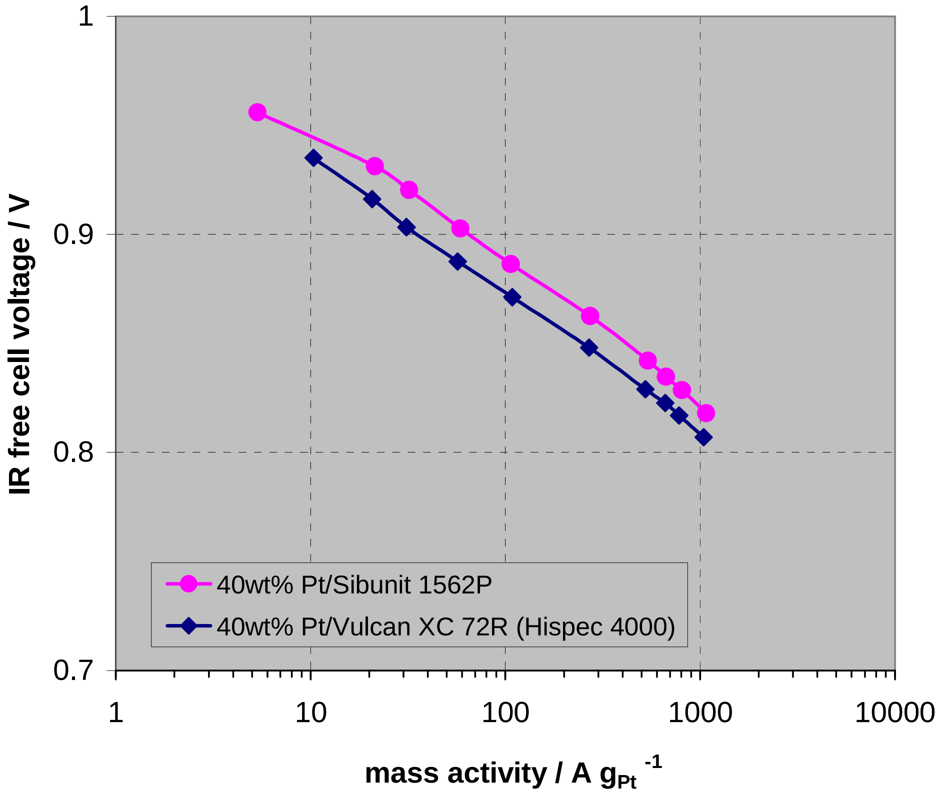
FuMAPEM 950

Fumion ionomer

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:

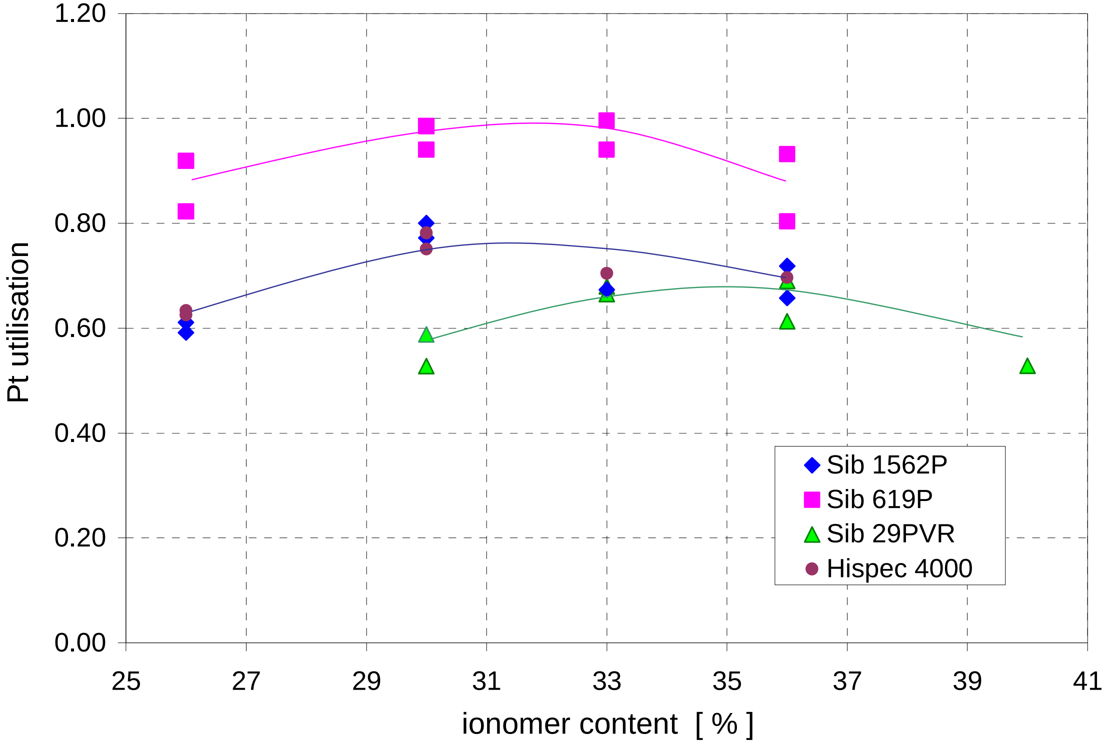
40wt%Pt/Sibunit 1562P	104 ± 10 μA/cm^2
40wt% Pt/Vulcan XC72R (Hispec 4000, JM)	114 ± 10 μA/cm^2

Pt utilisation:

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

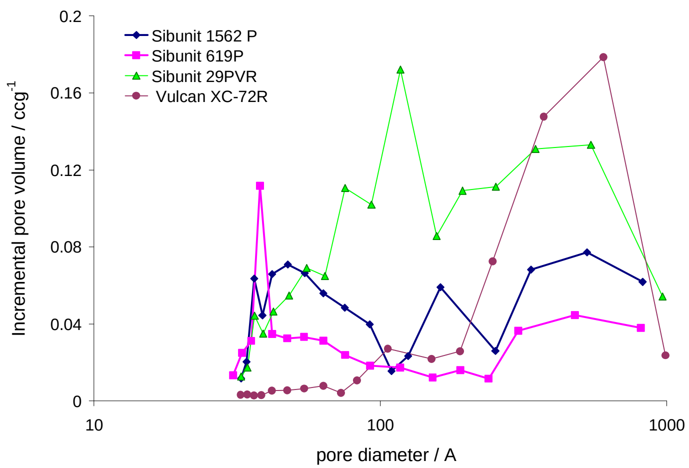
N.P. Lebedeva, A.S. Booij, I.N. Voropaev, P.A. Simonov, A.V. Romanenko, Fuel Cells, 9 (2009) 439-452

Pore structure effect – Pt utilisation



Pt utilization = ECSA / SA

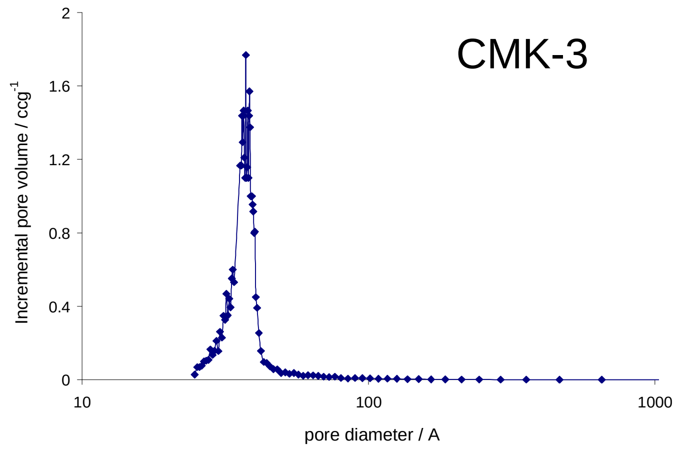
ECSA – from in situ CV measurements
SA – gas-phase CO chemisorption

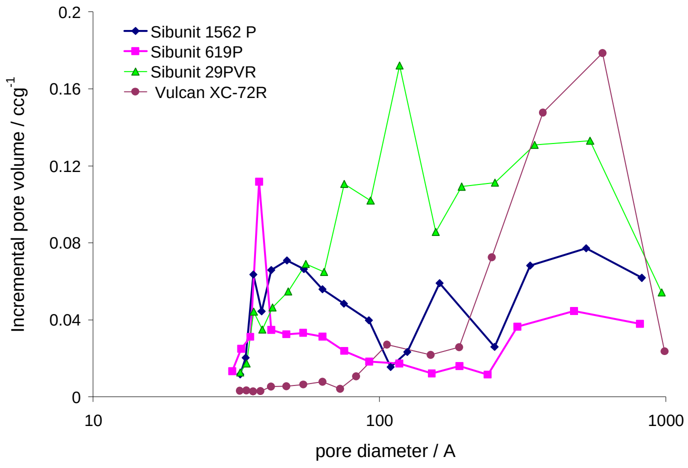


Pores with d > ca. 10 nm are well accessible for the ionomer

Small mesopores 3-4 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 %

N.P. Lebedeva, A.S. Booij, G.J.M. Janssen, ECS Transactions 16 (2008) 2083.

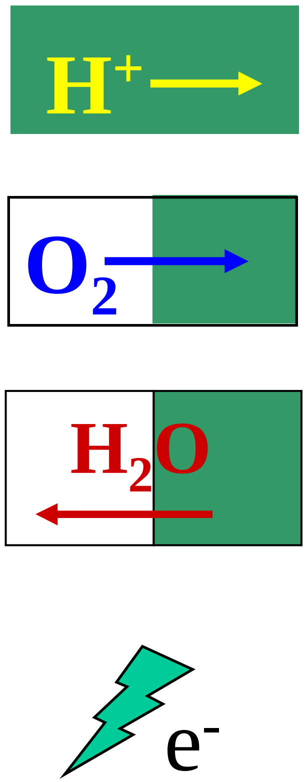
Small mesopores:

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

water acts as a proton conductor

J.McBreen, *J.Electrochem.Soc.* 1985, *132*, 1112
Q.Wang *et al*, *J.Electroanal.Chem*. 2004, *573*, 61
U.A. Paulus *et al*, *J.Electroanal.Chem*. 2003, *541*, 77

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

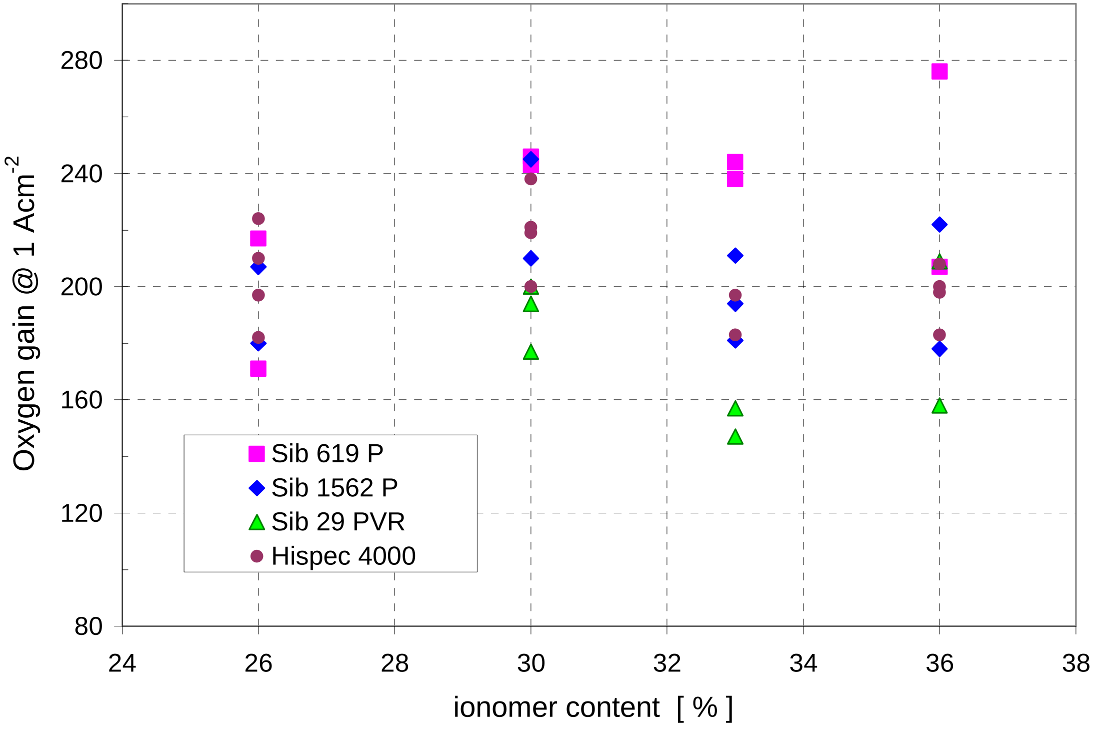
- ***Electron transport*:**
  - conducting carbon network

Pore structure effect – H^+ transport in cathode layer

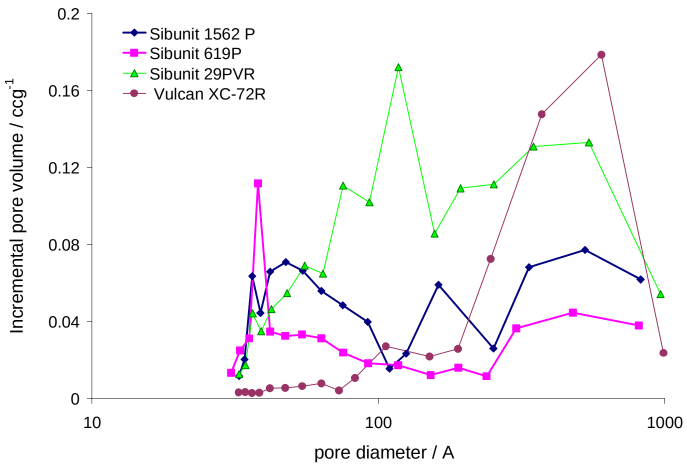
40 wt% Pt/Sibunit 619P	0.100 - 0.170 Ohm cm^2
40 wt% Pt/Sibunit 1562P	0.100 - 0.140 Ohm cm^2
40 wt% Pt/Vulcan XC 72R (Hispec 4000, JM)	0.100 - 0.140 Ohm cm^2
40 wt% Pt/Sibunit 29PVR	0.090 - 0.130 Ohm cm^2

No pronounced effect of the support pore structure on H^+ transport in the catalytic layer

Pore structure effect – O_2 and water transport



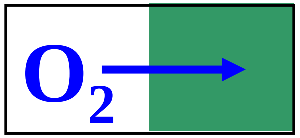
H2315 C2 GDL
Rp ~ 0.10-0.13 Ohm cm2



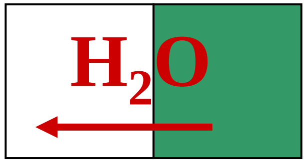
Large pores with d > 10 nm are efficient in O_2 transport and water removal
Small mesopores – 3-4 nm – tend to flood, impeding O_2 transport

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)
$Dk = 97 \cdot r\sqrt{T/M}$

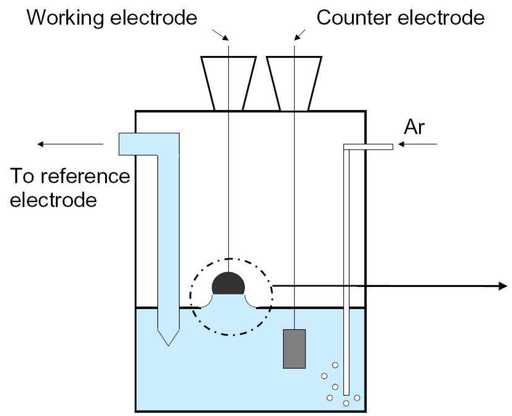


capillary condensation @ low P/P_0 in small mesopores

Pore structure of the catalytic layer - important !

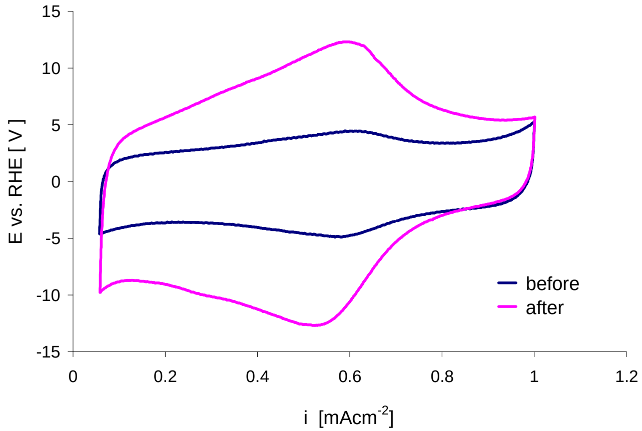
Corrosion stability of Sibunit carbons

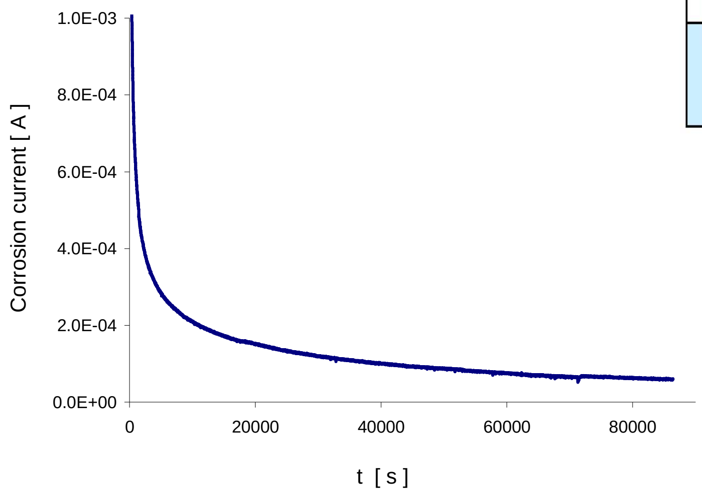
Voltage hold at 1.2 V vs. RHE, 80℃ in 1M H_2SO_4 for 24 hrs



$$C + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$$

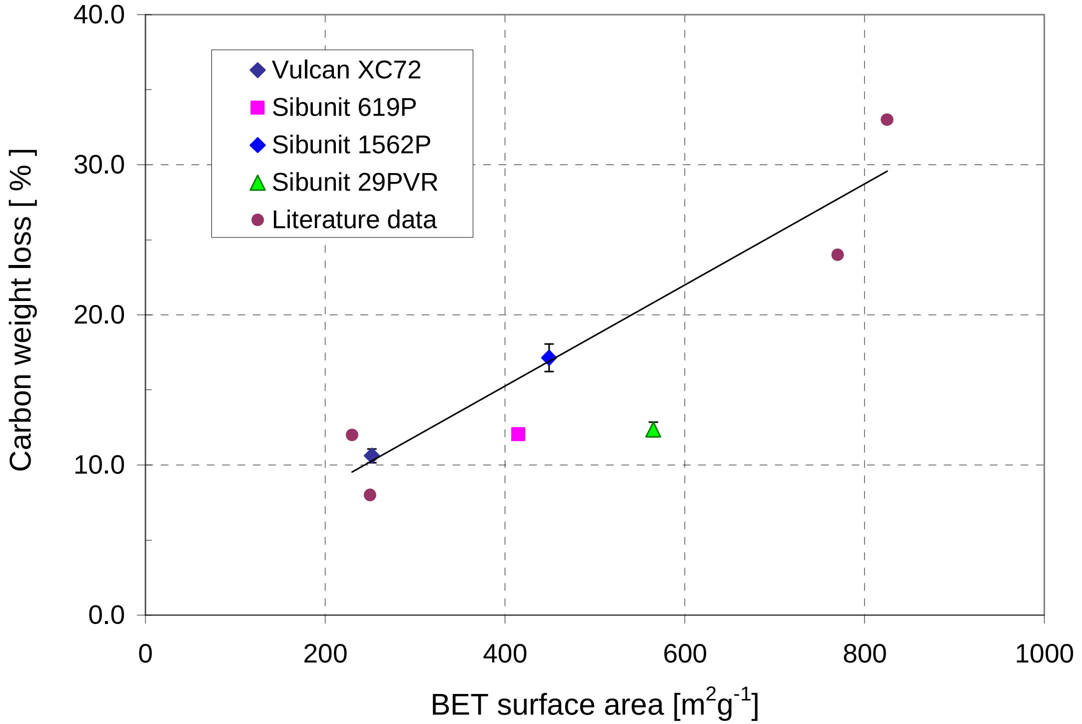
$$C + H_2O \rightarrow \text{surface groups}$$



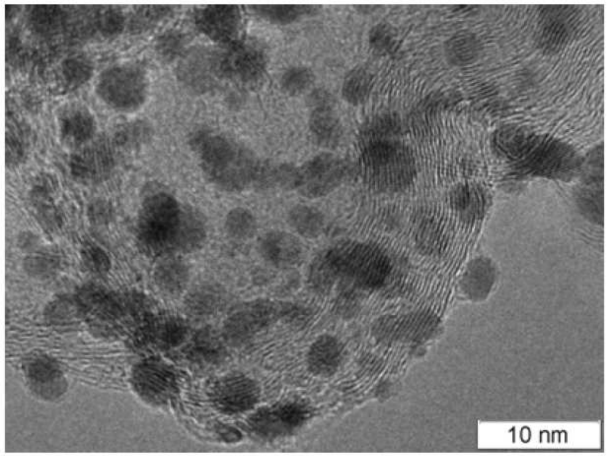


S.C. Ball, S.L. Hudson, D. Thompsett, B. Theobald, Journal of Power Sources 171 (2007) 18–25

Corrosion stability of Sibunit carbons



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



S.C. Ball, S.L. Hudson, D. Thompsett, B. Theobald, Journal of Power Sources 171 (2007) 18–25

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_2O 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

Acknowledgement

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Vera Smit-Groen (NRG, Petten) – XRD analysis

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