Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

<u>Size</u>, microstructure and texture in heterogeneous electrocatalysis

E. R. Savinova

LMSPC-UMR 7515 du CNRS-UdS-ECPM, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France

Фрумкинские Чтения, Москва, МГУ, 15 октября 2010 г.

cnrs dépasser les frontières

UNIVERSITÉ DE STRASBOURG

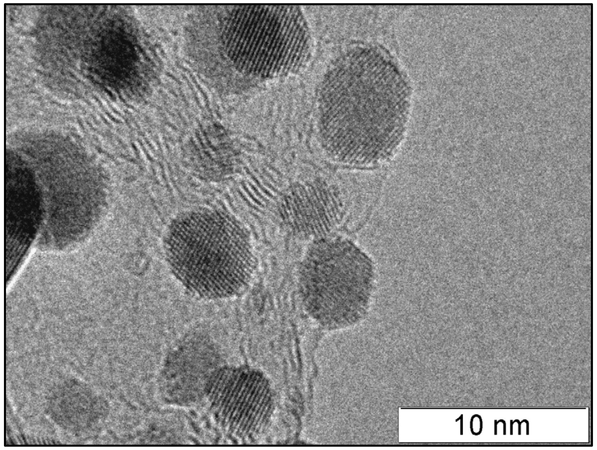
ecpm ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS STRASBOURG

FRC International Center for Frontier Research in Chemistry

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Introduction

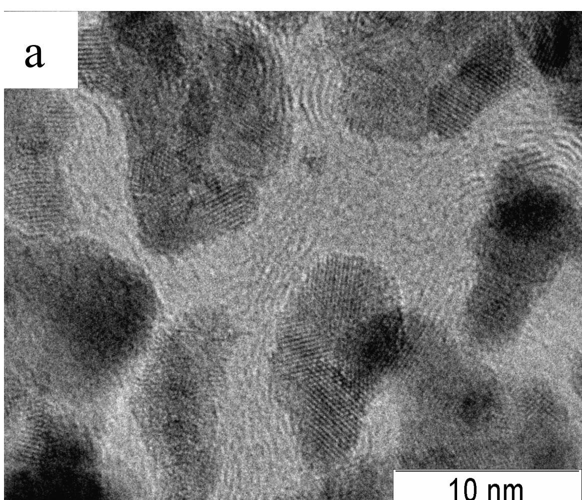
5%Pd/C



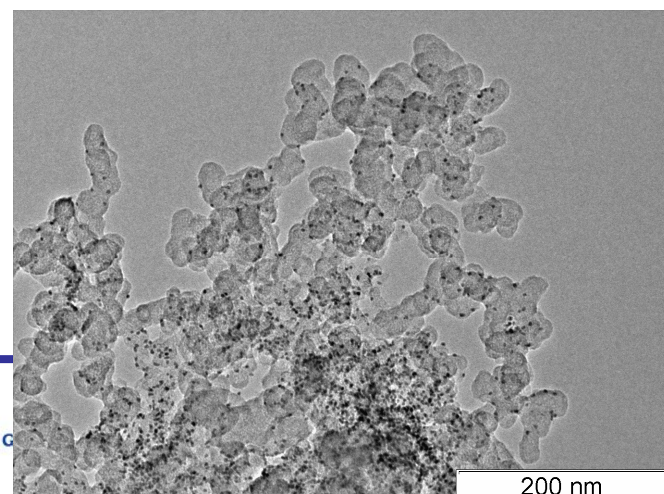
Heterogeneous electrocatalysis:

Size
Structure
Microstructure
Texture

50wt%PtRu/C



20wt%Pt/C



STRASBOURG

FRC
International Center for Frontier Research in Chemistry

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Outline

- Part 1: Design of nanosized and nanostructured materials
- Part 2: Particle size effects
- Part 3: Microstructure effects
- Part 4: Catalytic layer texture effects

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Part 1:
Design of nanosized and nanostructured materials

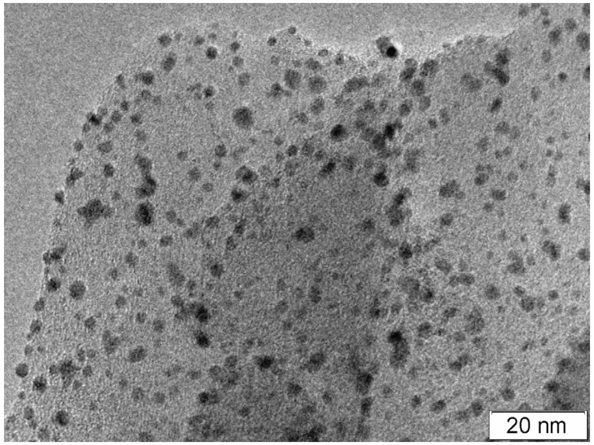
Control of the particle size and dispersion

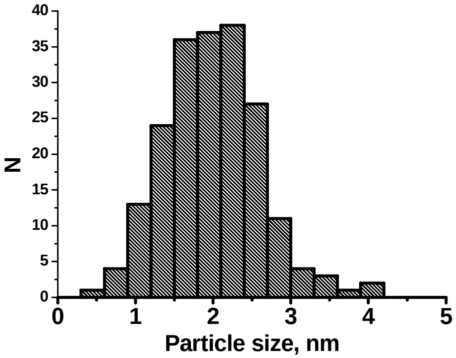
Pt supported on carbon

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Deposition-reduction method of Pt/C preparation (P.A. Simonov , BIC)

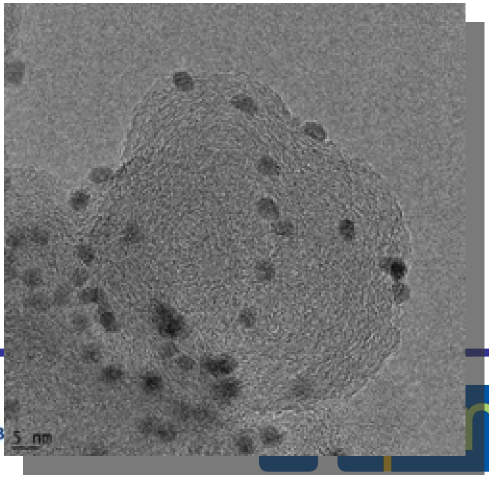
$$C + PtCl_4^{2-} \xrightarrow{H_2}$$

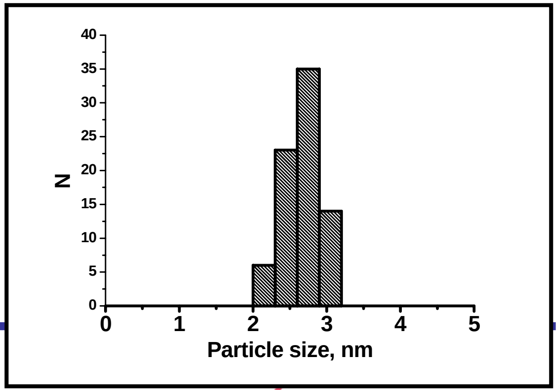




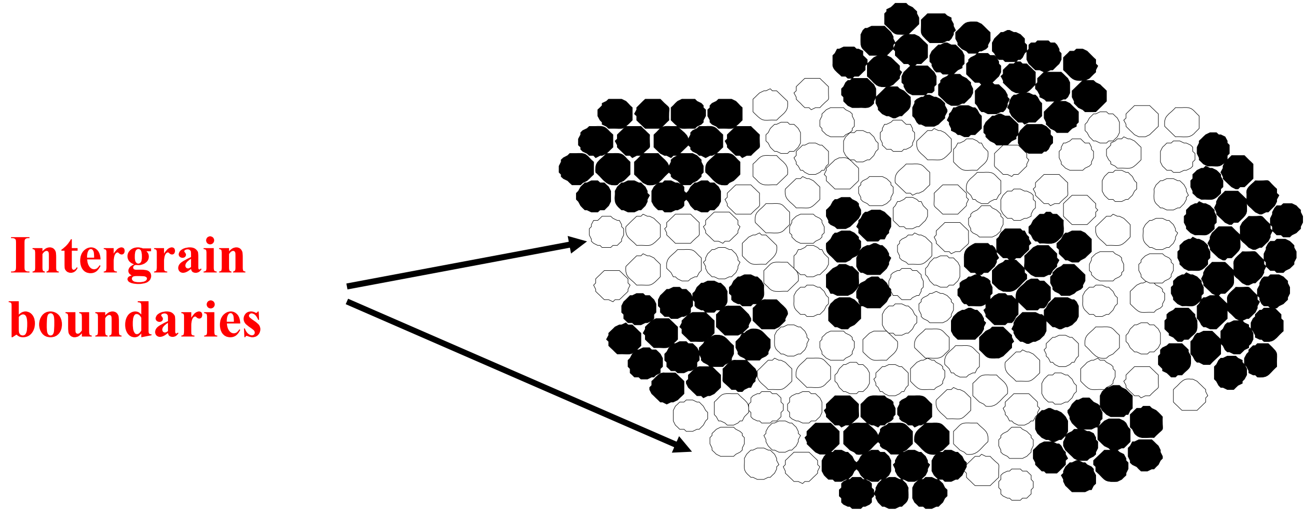
Phase transfer synthesis of alkylamine stabilized Pt nanoparticles (A. Kuznetsov, UdS)

Pt^{4+}	Organic phase
$NaBH_4$	Aqueous phase





Nanostructured materials



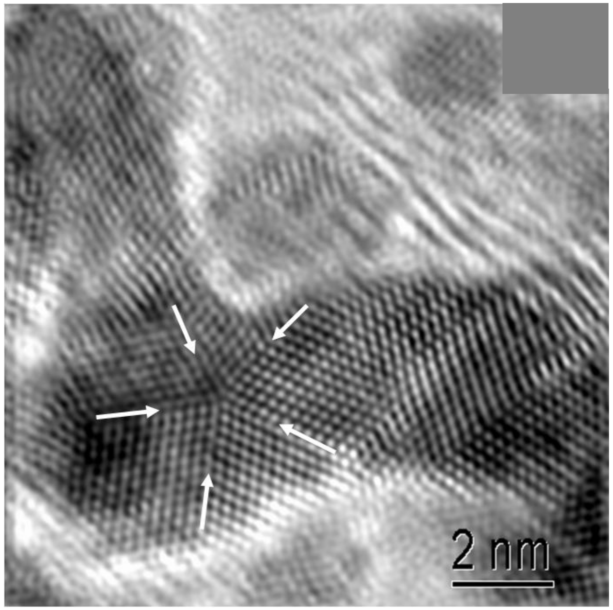
H. Gleiter, Nanostruct. Mater. 1 (1992) 1.

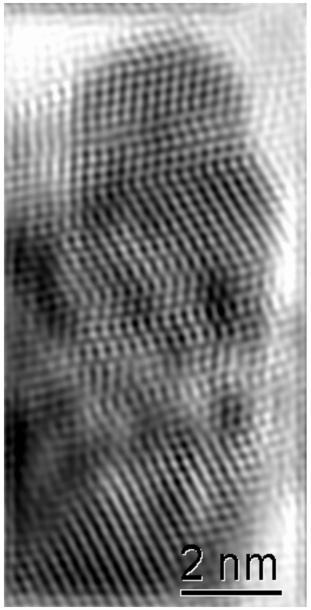
Wet chemical preparation of nanostructured materials

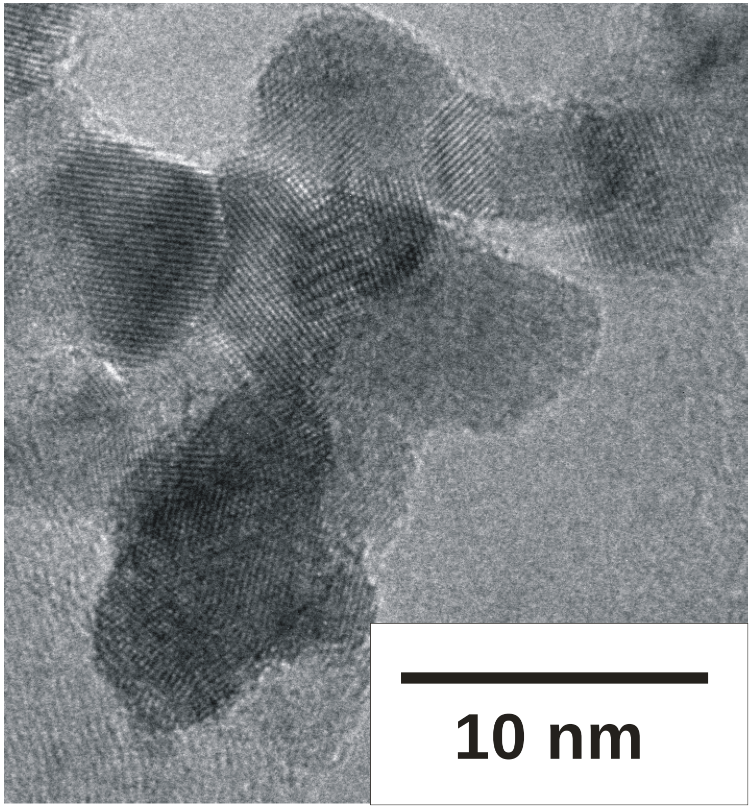
Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Ordered multiple-twinned particles (FT HRTEM)

Disordered intercrystalline grain boundaries (HRTEM)







Multiple-twinned particles with intersecting grain boundaries
Pentagonal bipyramids with 5-fold symmetry axis

Multiple-twinned particles with parallel GBs: Formation of dislocation planes

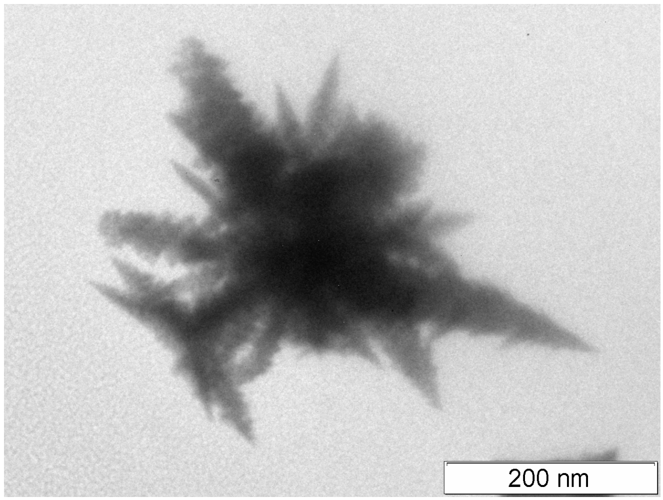
ECOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

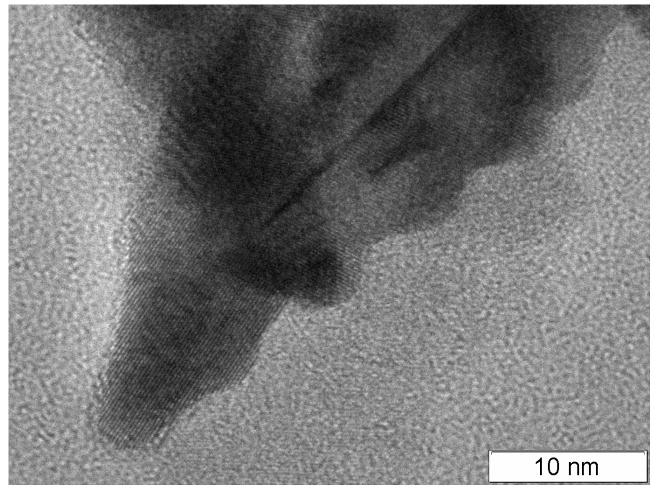
FRC
International Center for Frontier Research in Chemistry

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

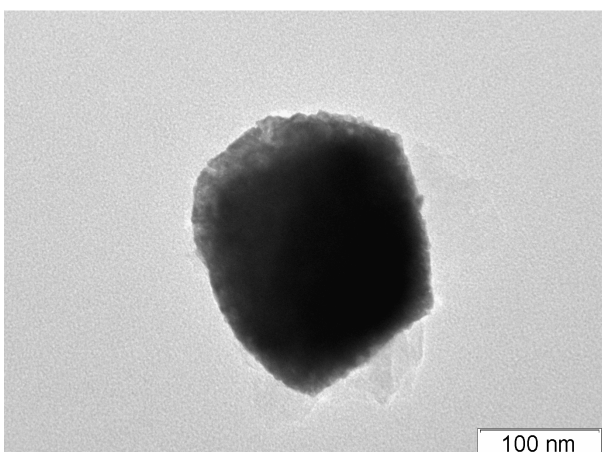
Electrochemical preparation of nanostructured materials

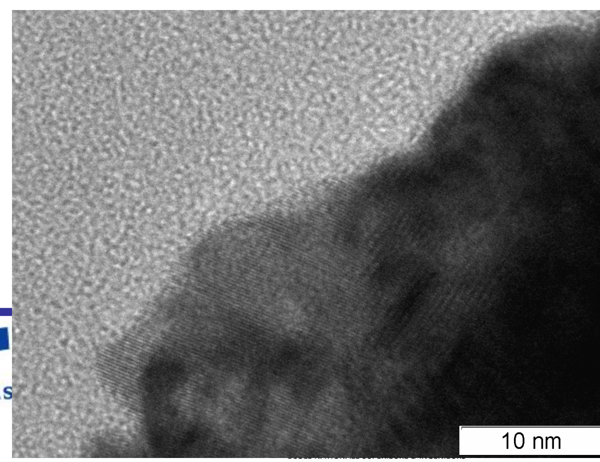
Pt/GC deposited at 115 mV vs. RHE





Pt/GC deposited at 185 mV vs. RHE

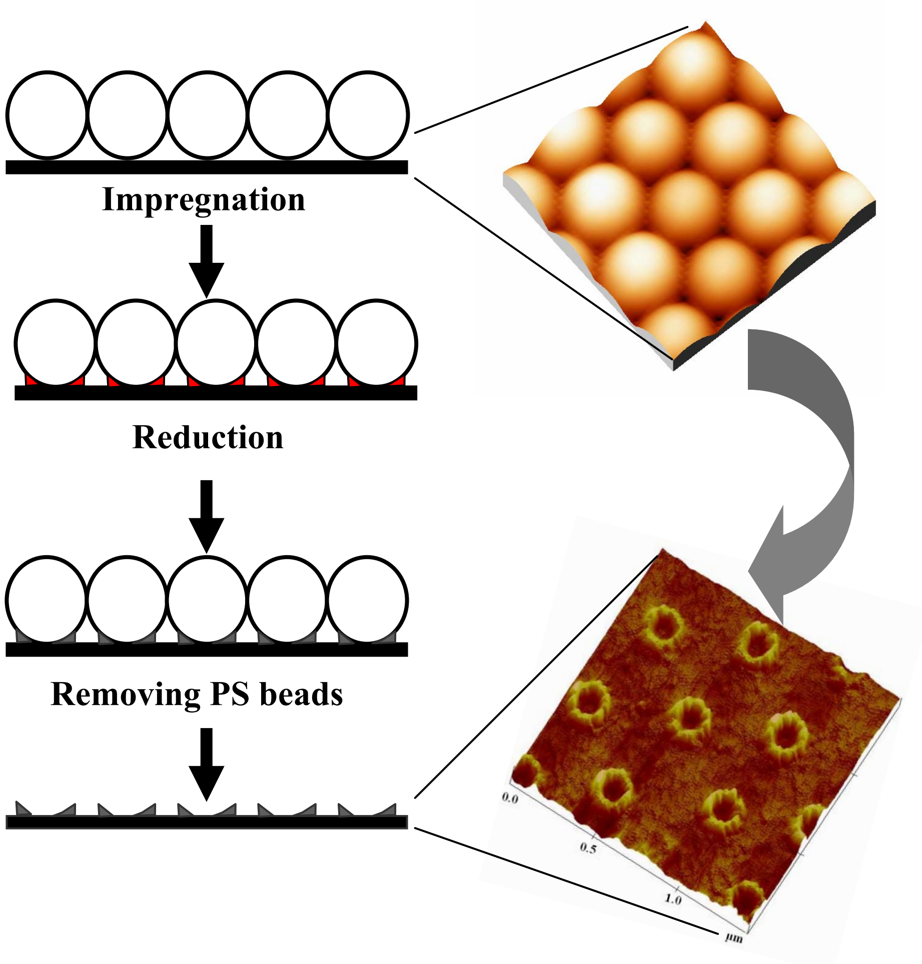




A.N. Simonov, O.V. Cherstiouk, S.Yu. Vassiliev, V.I. Zaikovskii, A. Yu. Filatov, N.A. Rudina, E.R. Savinova, G.A. Tsirlina, in preparation.

International Center for Frontier Research in Chemistry

2D nanoparticle arrays
PS nanosphere lithography



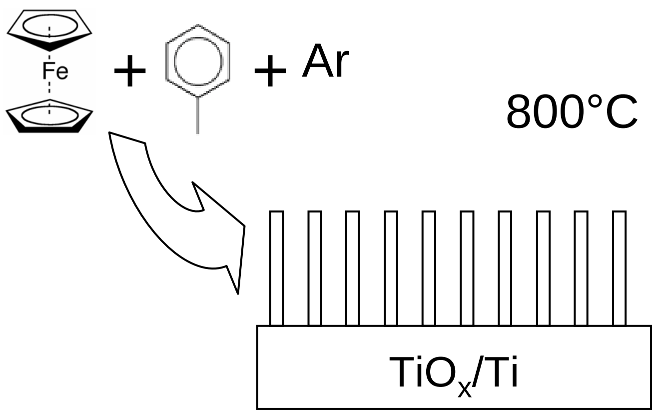
Maryam Bayati, Piotr Patoka, Michael Giersig, Elena R. Savinova, Langmuir 2010

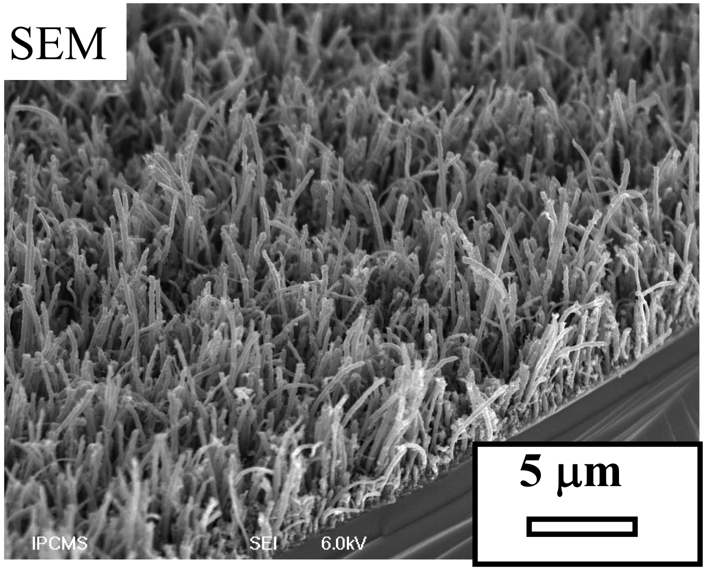
3D electrode arrays

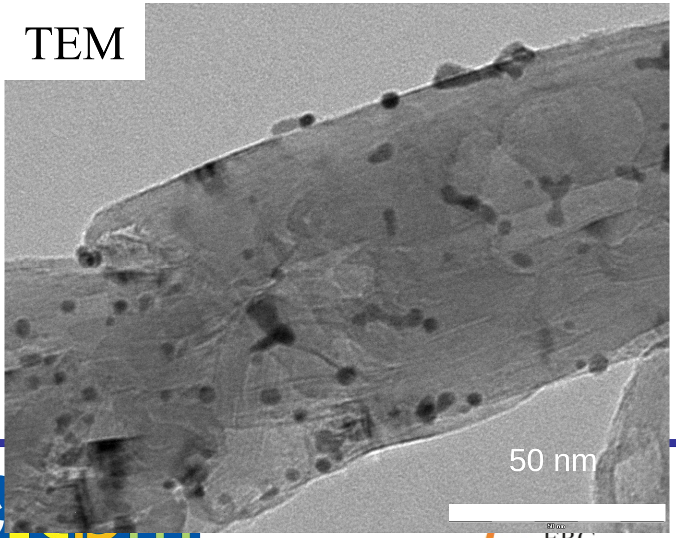
Pt supported on vertically aligned CNFs

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

catalytic chemical vapor deposition







*P. S. Ruvinskiy, A. Bonnefont, M. Houllé, C. Pham-Huu, and E.R. Savinova, Electrochim. Acta, 55 (**2010**) 3245-3256.*

UNIVERSITÉ DE STRASBOURG

ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

FRC
International Center for Frontier Research in Chemistry

Part 1: Conclusions

- Modern nanotechnology approaches allow preparation of nanosized and nanostructured materials with well defined particle size and microstructure

- Importance of post-mortem and in situ characterization

Laboratoire des Matériaux, Surfaces et Procédés pour la Ca[...]

Part 2:
Particle size effects

Influence of the particle size on H, O/OH and CO adsorption/reaction

UNIVERSITÉ DE STRASBOURG

ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

FRC
International Center for Frontier Research in Chemistry

Particle size effects in electrocatalysis

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Electrochimica Acta 48 (2003) 3851–3860

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Model approach to evaluate particle size effects in electrocatalysis: preparation and properties of Pt nanoparticles supported on GC and HOPG

O.V. Cherstiouk, P.A. Simonov, E.R. Savinova *

Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5, 630090 Novosibirsk, Russia

Received 7 November 2002; received in revised form 16 December 2002; accepted 21 December 2002

UNIVERSITÉ DE STRASBOURG

ECPM ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS STRASBOURG

FRC International Center for Frontier Research in Chemistry

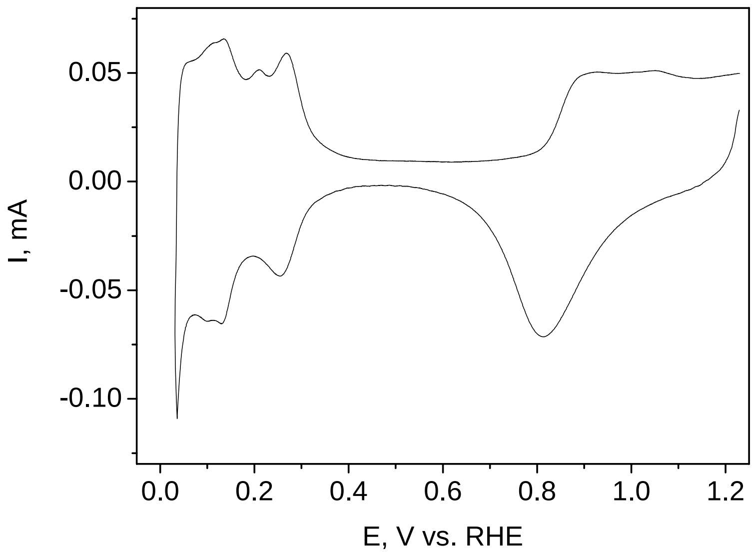
H_{UPD}: measurement of the Pt surface area

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

CV of Pt foil in 0.1 M H_2SO_4 at 20 mV/s

Extended electrode surfaces:

S. Trasatti and O. A. Petrii, *Journal of Electroanalytical Chemistry*, **327**, 353-376 (1992).



Nanomaterials:

- electrochemisorption: H_{UPD}, CO stripping, Cu_{UPD}, etc.
- physical characterization methods: TEM, XRD, STM, etc.
- gas phase chemisorption

UNIVERSITÉ DE STRASBOURG

ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

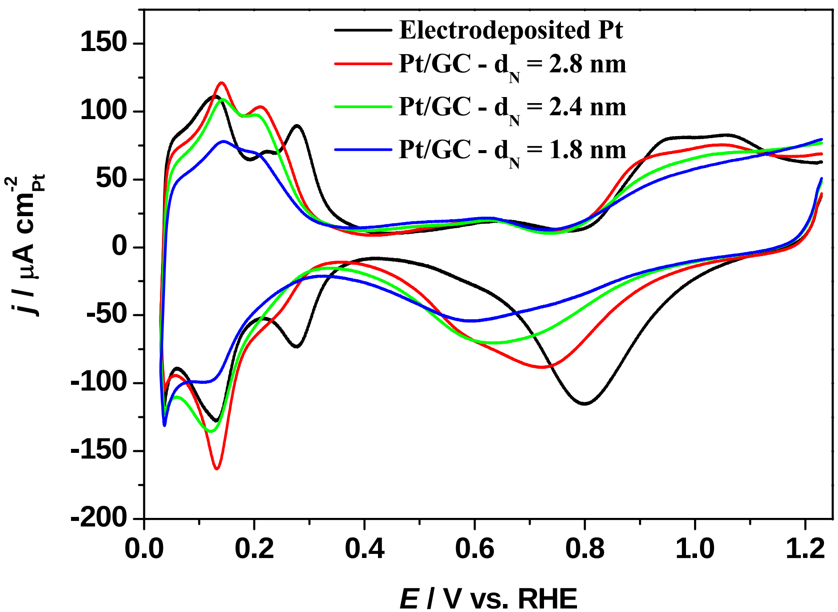
FRC
International Center for Frontier Research in Chemistry

Adsorption properties of Pt/C: influence of the particle size on H_{UPD}

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

CVs in supporting electrolyte: H_2SO_4 0.1 M

Pt/C



- Increased irrevesribility of the surface oxide reduction

- Decrease of the H_{UPD} coverage

Ensemble effect?
3-fold and 4-fold hollow sites:

Influence of the (surface) oxide?

Data replotted from:

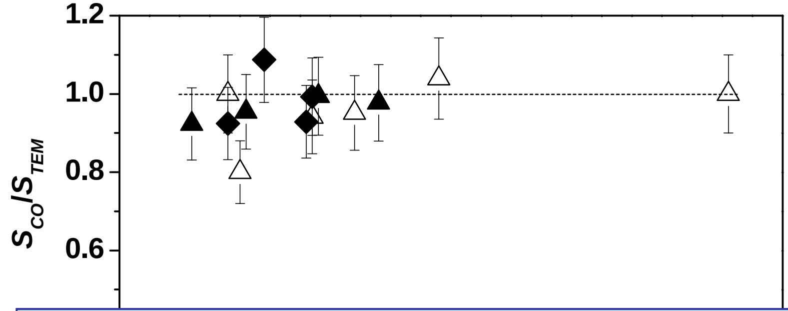
F. Maillard et al., *Faraday Discussions*, **125**, 357-377 (2004).

F. Maillard et al., *PCCP*, **7**, 385-393 (2005).

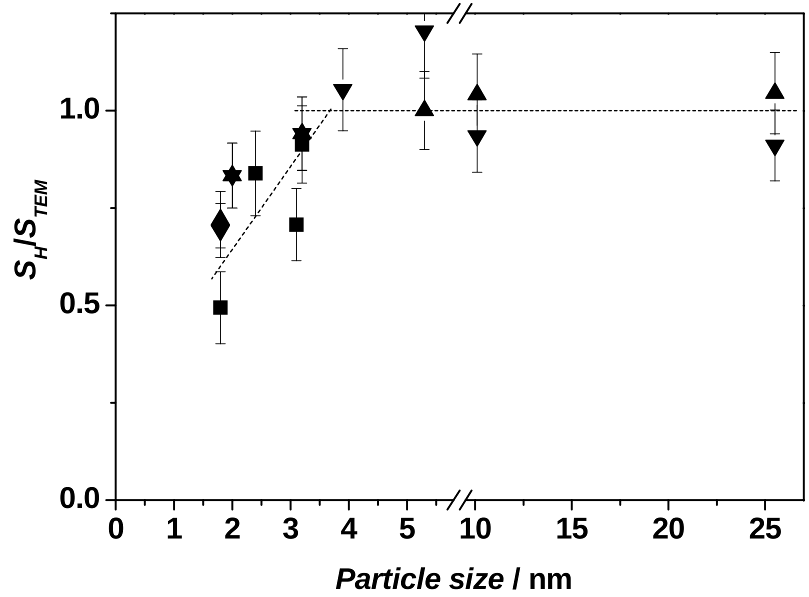
H_{UPD} versus CO stripping

Surface area determination: Pt supported on carbon

CO stripping



H_{UPD}



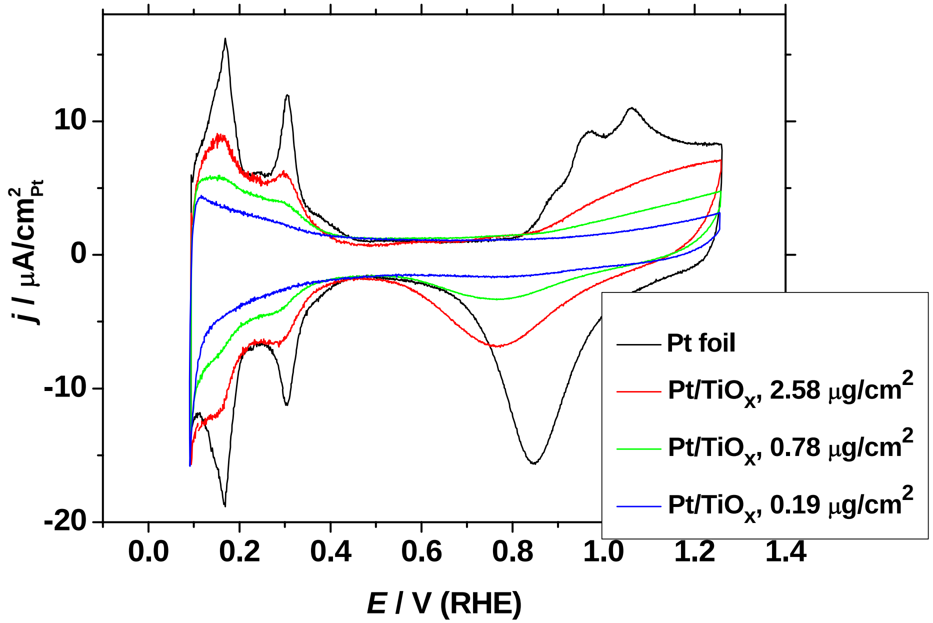
Conventional method of the surface evaluation based on H_{UPD} coulometry is inappropriate for particles with the size below 3.5 nm

F. Maillard, et al., *Faraday Discussions*, **125**, 357-377 (2004).
F. Maillard, et al.PCCP, **7**, 385-393 (2005).
L. Genies et al., *Electrochimica Acta*, **44**, 1317-1327 (1998).
H. Ye et al., *Langmuir*, **23**, 11901-11906 (2007).
A. Kabbabi, PhDThesis 1994.
B. Z. Jusys and R. J. Behm, *J.Phys.Chem. B*, **105**, 10874-10883 (2001).

Adsorption properties of Pt: Influence of the particle size on H and O/OH adsorption

Pt/TiO_x

CVs in supporting electrolyte: H_2SO_4 0.1 M, 0.01 V/s



Pronkin et al.

Part 2: Conclusions

• Particle size strongly affects adsorption and electrocatalytic properties of metals (oxides?)

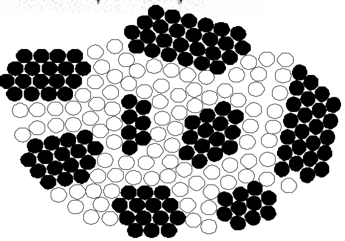
• Conventional approaches utilized for the measurement of the surface area may not be applicable to nanomaterials

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Part 3:
Microstructure effects

Microstructure effects in CO and MeOH oxidation on Pt and PtRu electrodes

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse



PAPER www.rsc.org/pccp | Physical Chemistry Chemical Physics

On the influence of the metal loading on the structure of carbon-supported PtRu catalysts and their electrocatalytic activities in CO and methanol electrooxidation

Alexei N. Gavrilov,[a] Elena R. Savinova,*[bc] Pavel A. Simonov,[b] Vladimir I. Zaikovskii,[b] Svetlana V. Cherepanova,[b] Galina A. Tsirlina[a] and Valentin N. Parmon[b]

Received 21st May 2007, Accepted 23rd July 2007
First published as an Advance Article on the web 16th August 2007
DOI: 10.1039/b707598g

Surface Science 603 (2009) 1892–1899

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

ELSEVIER

The assessment of nanocrystalline surface defects on real versus model catalysts probed via vibrational spectroscopy of adsorbed CO

Elena R. Savinova [a,*], Francoise Hahn [b], Nicolas Alonso-Vante [b]

[a] l'Ecole Européenne Chimie Polymères Matériaux, Université Louis Pasteur, UMR 7515 du CNRS-UdS-ECPM, 25 rue Becquerel, F 67087 Strasbourg, France
[b] Laboratory of Electrocatalysis, UMR-CNRS 6503, Université de Poitiers, F-86022 Poitiers, 40, avenue du recteur Pineau, France

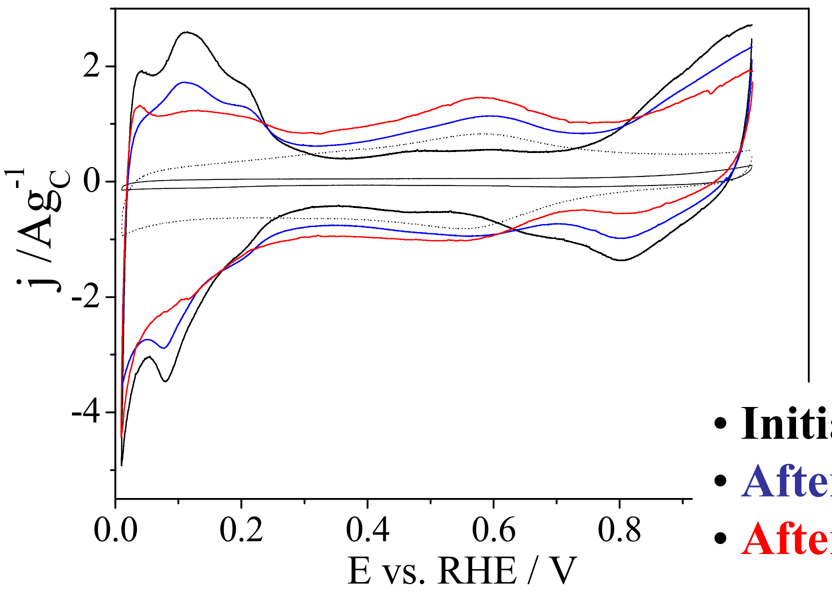
cnrs

Microstructure effects in Pt/C degradation

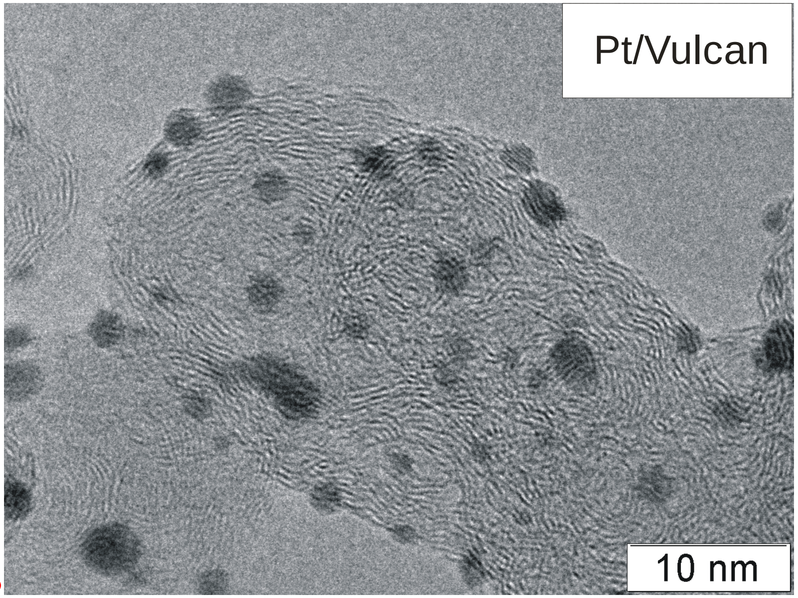
Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Cyclic voltammograms for Pt/C samples and corresponding carbon supports before and after corrosion

Vulcan XC-72



- **Initial**
- **After 8 hours**
- **After 82 hours**



Model accelerated corrosion studies were performed in 2 M H_2SO_4 at 80°C at 1.2 V

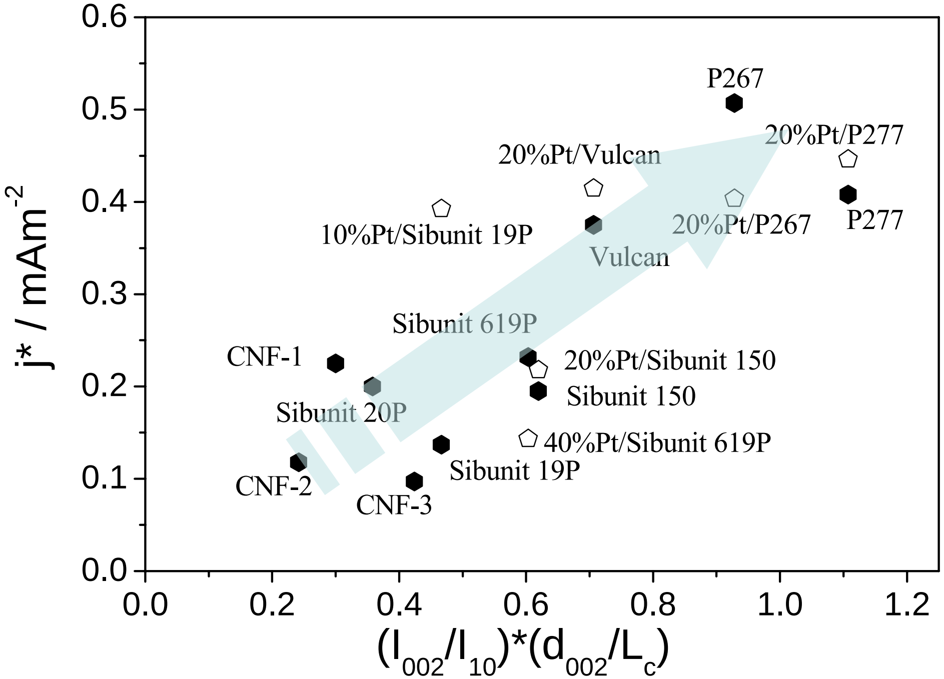
ECPM
École Européenne de Chimie, Polymères et Matériaux
École Nationale Supérieure d'Ingénieurs
Strasbourg

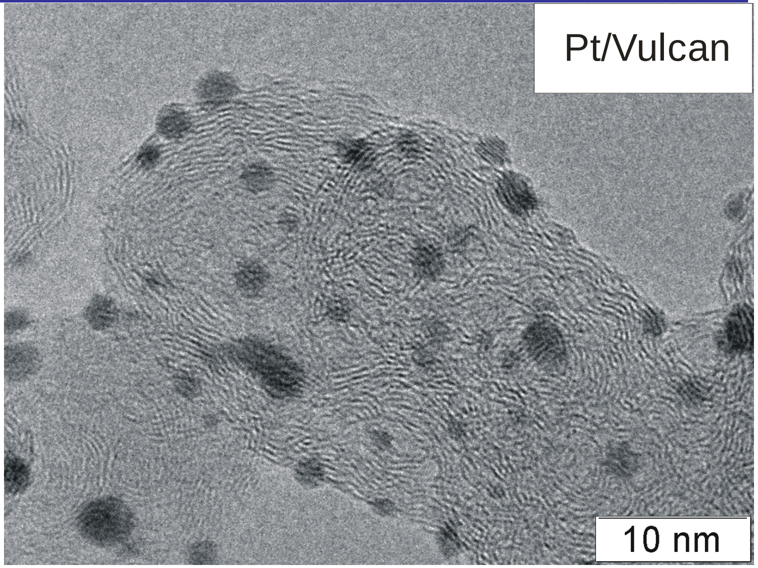
FRC
International Center for Frontier Research in Chemistry

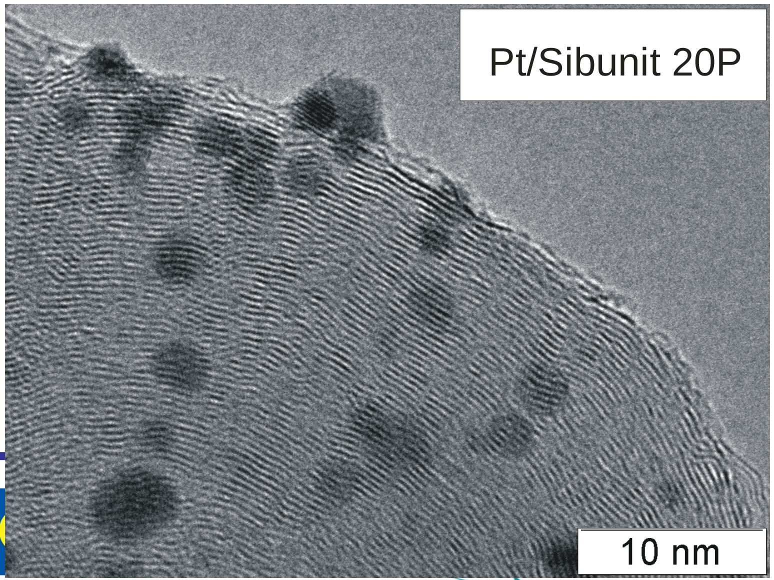
Carbon corrosion

Influence of Microstructure

Influence of structural parameter







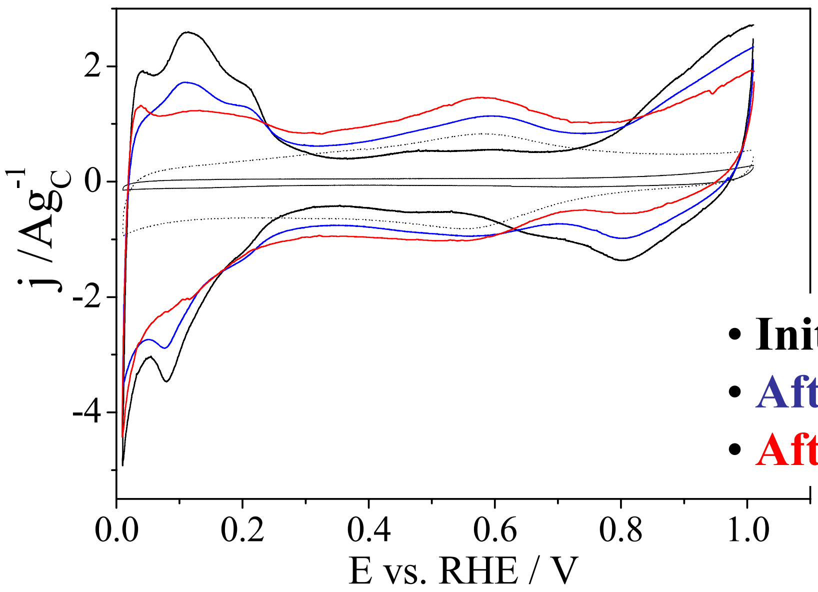
Model accelerated corrosion studies were performed in 2 M H_2SO_4 at 80°C at 1.2 V

Corrosion of carbon-supported Pt catalysts
Influence of Microstructure

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

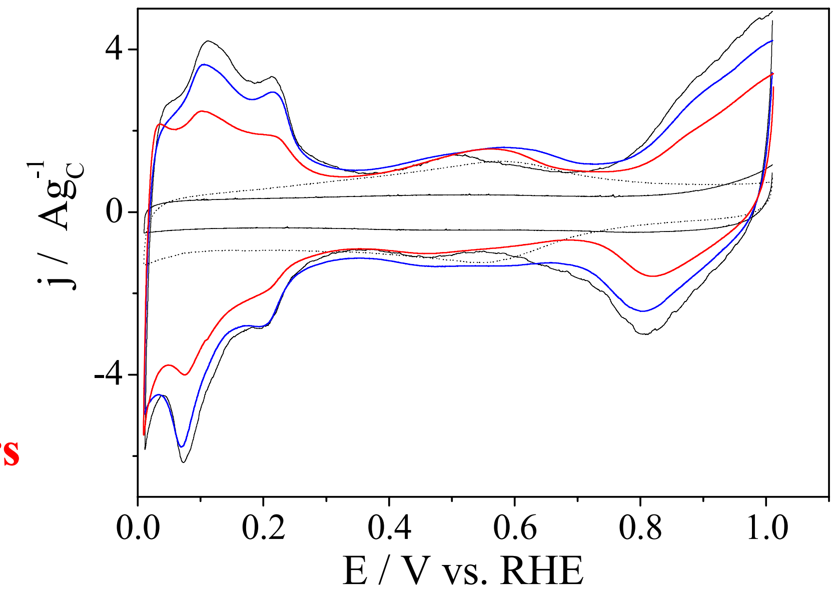
Cyclic voltammograms for Pt/C samples and corresponding carbon supports before and after corrosion

Vulcan XC-72



- **Initial**
- **After 8 hours**
- **After 82 hours**

Sibunit 619 P

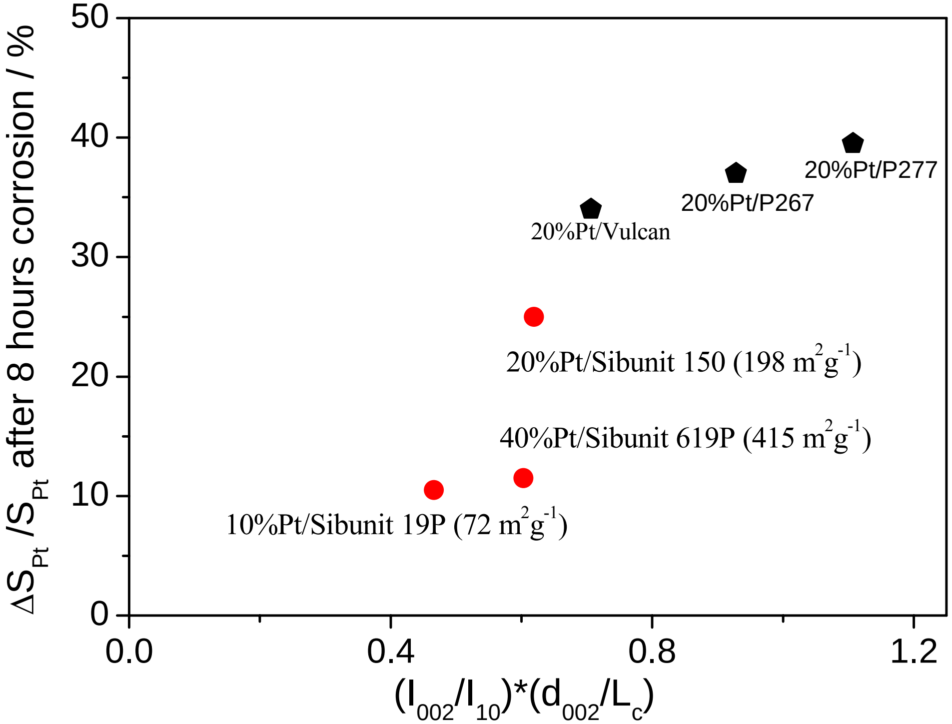


ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

Corrosion of carbon-supported Pt catalysts
Influence of Microstructure

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Relative decrease of the surface area of supported Pt catalysts after 8 hours of corrosion



The surface area of Pt is measured using the H_{UPD} charge

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Part 3: Conclusions

Presence of grain boundaries strongly affects electrocatalytic activity and stability of electrode materials

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Part 4:
Texture effects

ORR on 3D ordered catalytic layers

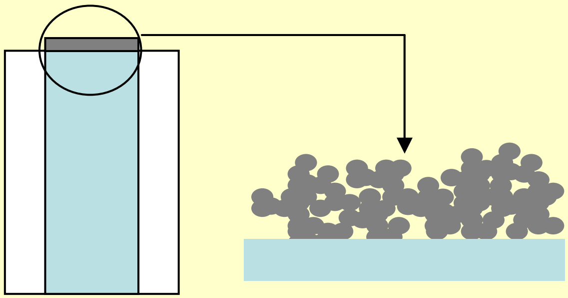
UNIVERSITÉ DE STRASBOURG

ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

FRC
International Center for Frontier Research in Chemistry

2D arrays and conventional thin layer approach

Thin-film RDE and RRDE method



T.J. Schmidt, et al. J. Electrochem. Soc. 145 (1998) 2354

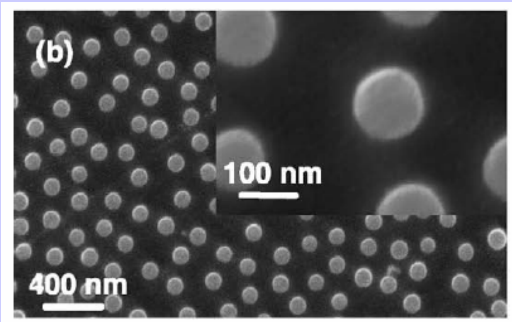
Advantages

• Allows studies of “real” catalysts

Limitations

• No control of the particle interparticle distance
• Ill defined structure
• Mathematical modeling rests on apparent parameters (average pore size, tortuosity factor, etc.)

2D microelectrode arrays



Y. E. Seidel, et al. Faraday Discuss., 2008, 140, 167

Advantages

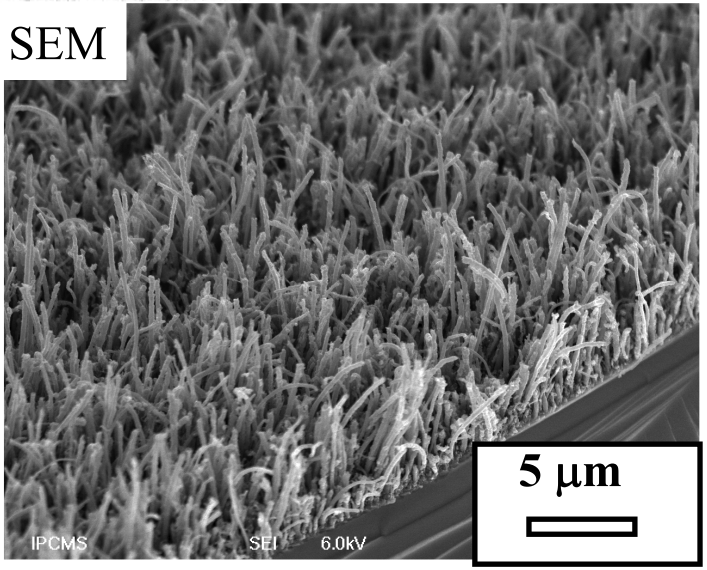
• Control of the separation distance → Well defined diffusion pattern
• Allow to disentangle reaction and diffusion

Limitations

• Smooth support → large particles
• “Material” gap between model and “real” electrodes
• Active surface area smaller than the geometric

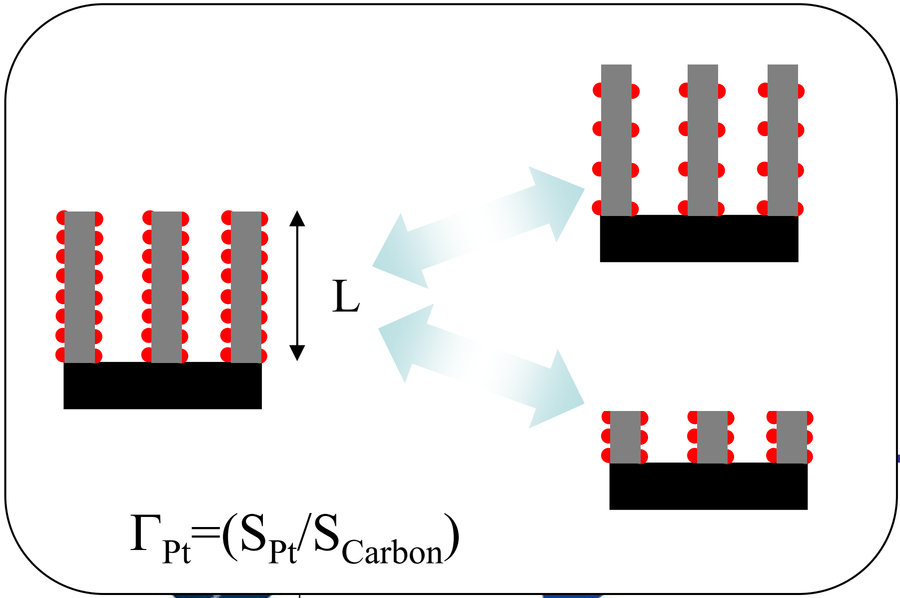
Concept of 3D nanoparticle arrays

Laboratoire des Matériaux, Surfaces

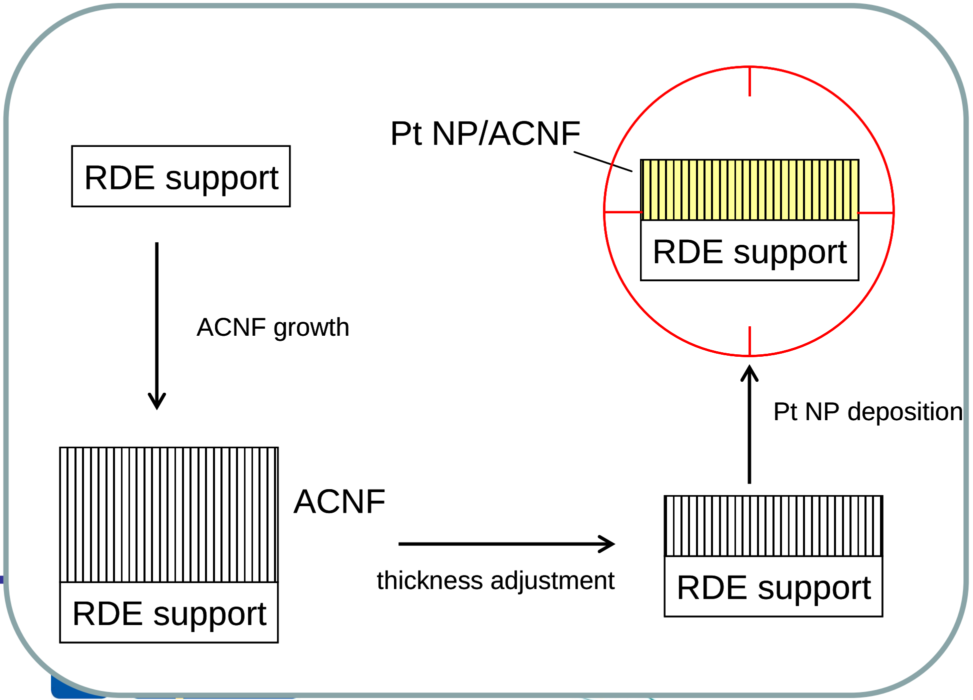


- 1 µm < L < 15 µm
- $0.01 < \Gamma_{Pt} < 0.30$
- $0.05 < m_{Pt} < 40\ \mu g/cm^2$
- $0.01 < S_{Pt} < 7\ cm^2$ (A_{geo}=0.2 cm²)

Compare to:
40 wt % Pt/Vulcan Γ_{Pt}~0.19



$\Gamma_{Pt}=(S_{Pt}/S_{Carbon})$



3D nanoparticle arrays: advantages

❖ **Supported nanoparticles** → model behavior of "real" catalysts

❖ Ordered structure → **control of the interfacial conditions** and **mass transport**

❖ Independent variation of key parameters: L, Γ_{Pt}, and nano-fiber density

❖ Wide variation of the active surface area

❖ Mathematical modeling based on actual rather than apparent parameters: pore diameter, length and tortuosity

❖ Of interst for fuel cell applications

*P. S. Ruvinskiy et al. Electrochim Acta 55 **(2010)** 3245-3256*
P.S. Ruvinskiy et al. PCCP 2010

What can one learn by applying 3D arrays in electrocatalysis?

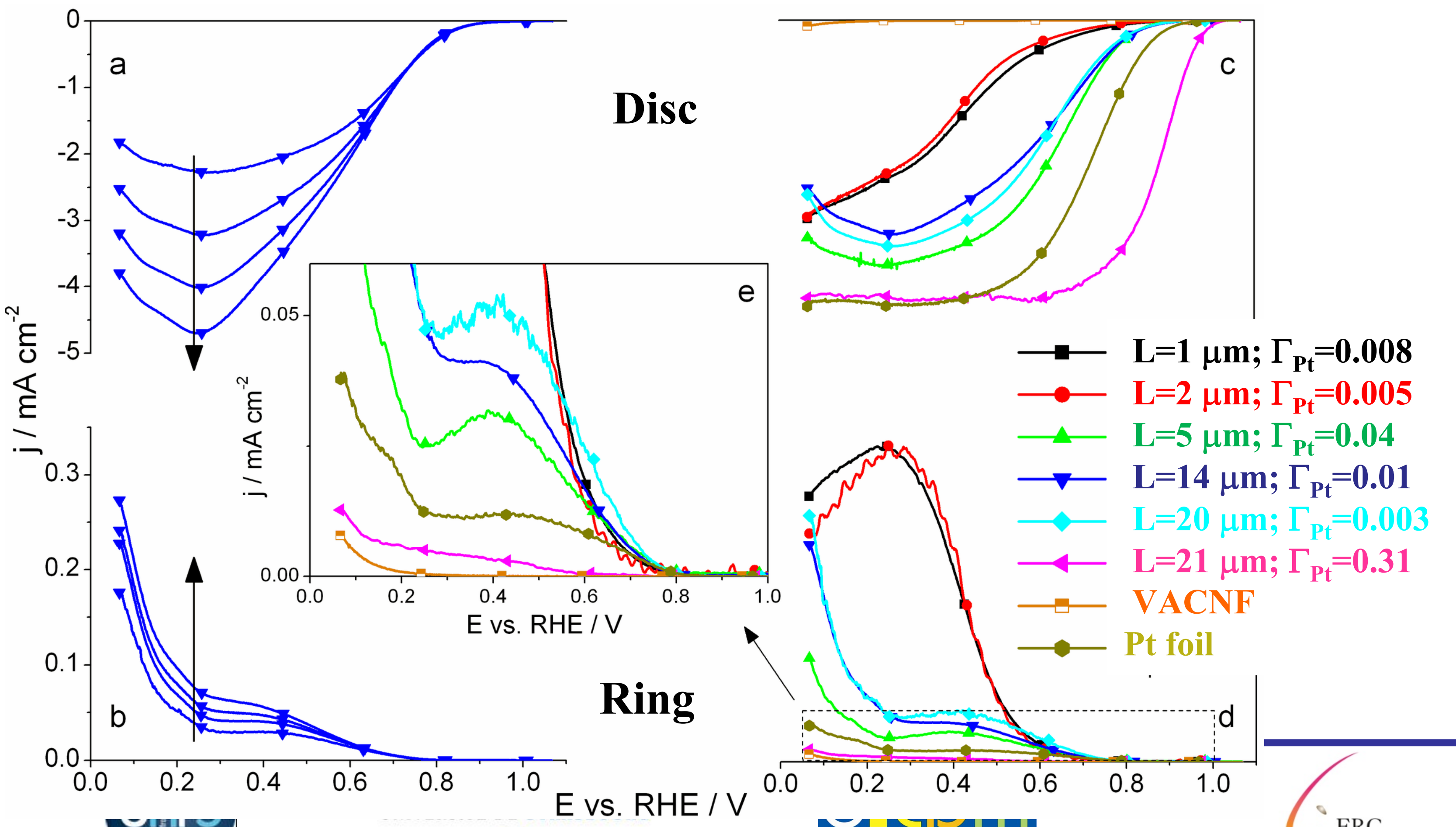
❖ Disentangle ***mass transport*** and ***kinetic effects***

❖ Study ***kinetics*** and ***mechanisms*** of electrochemical reactions on supported ***nanoparticles*** under ***well defined mass transport conditions***

❖Determine ***effectiveness factor*** of the catalytic particles

RRDE study of the ORR

Experimental RRDE curves for the ORR: O_2 saturated 0.1M H_2SO_4, 30°C

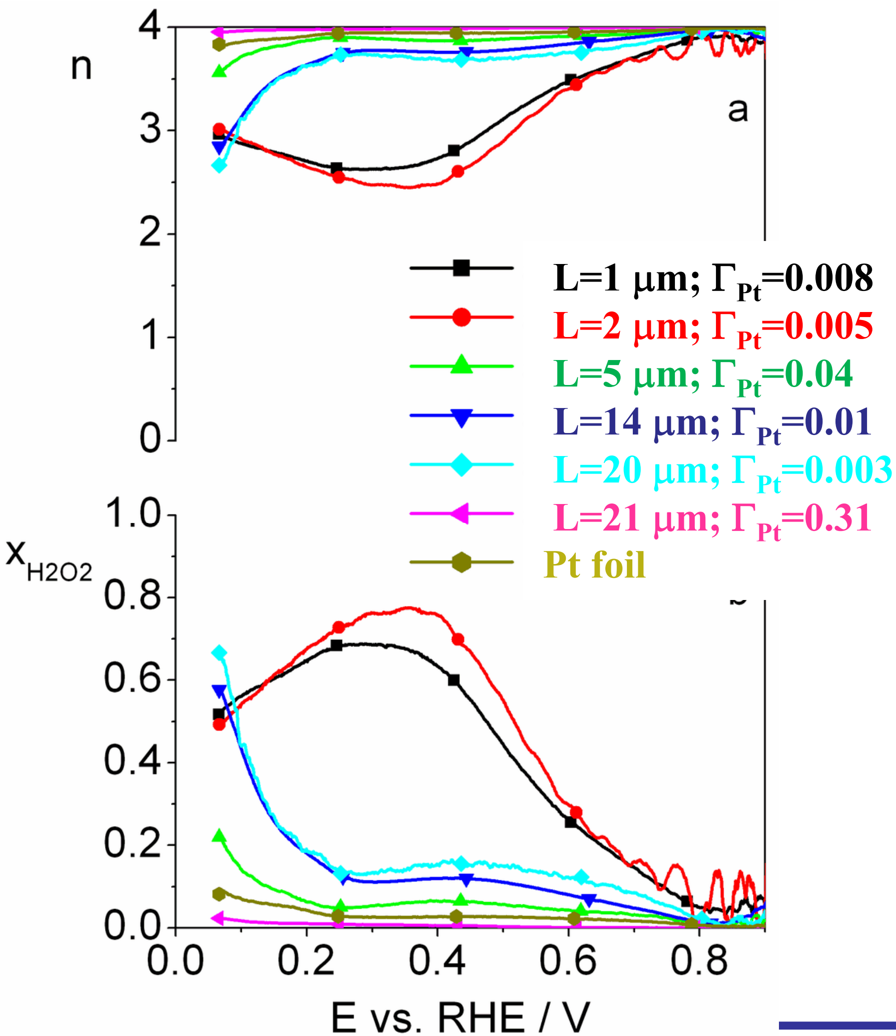


RRDE study of the ORR

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

$$n = \frac{4I_D}{\left[I_D + \left(I_R/N\right)\right]}$$

$$x_{H_2O_2} = \frac{2\left(I_R/N\right)}{\left[I_D + \left(I_R/N\right)\right]}$$

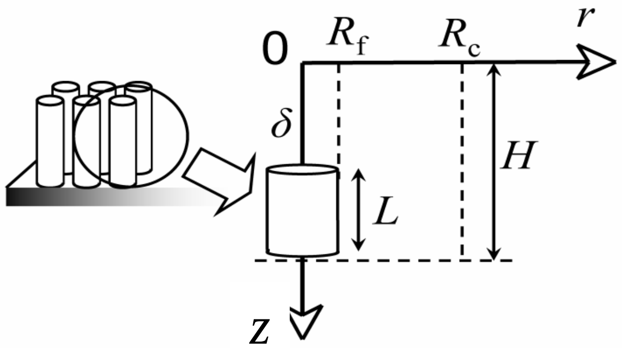


UNIVERSITÉ DE STRASBOURG

ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

FRC
International Center for Frontier Research in Chemistry

Model description



R_f 100 nm, R_c=300 nm

- Diffusion domain approximation: cylindrical unit cells which are diffusionally independent
- Liquid electrolyte (0.1 M H_2SO_4) → potential distribution in the channel is not considered
- Diffusion is treated under steady-state

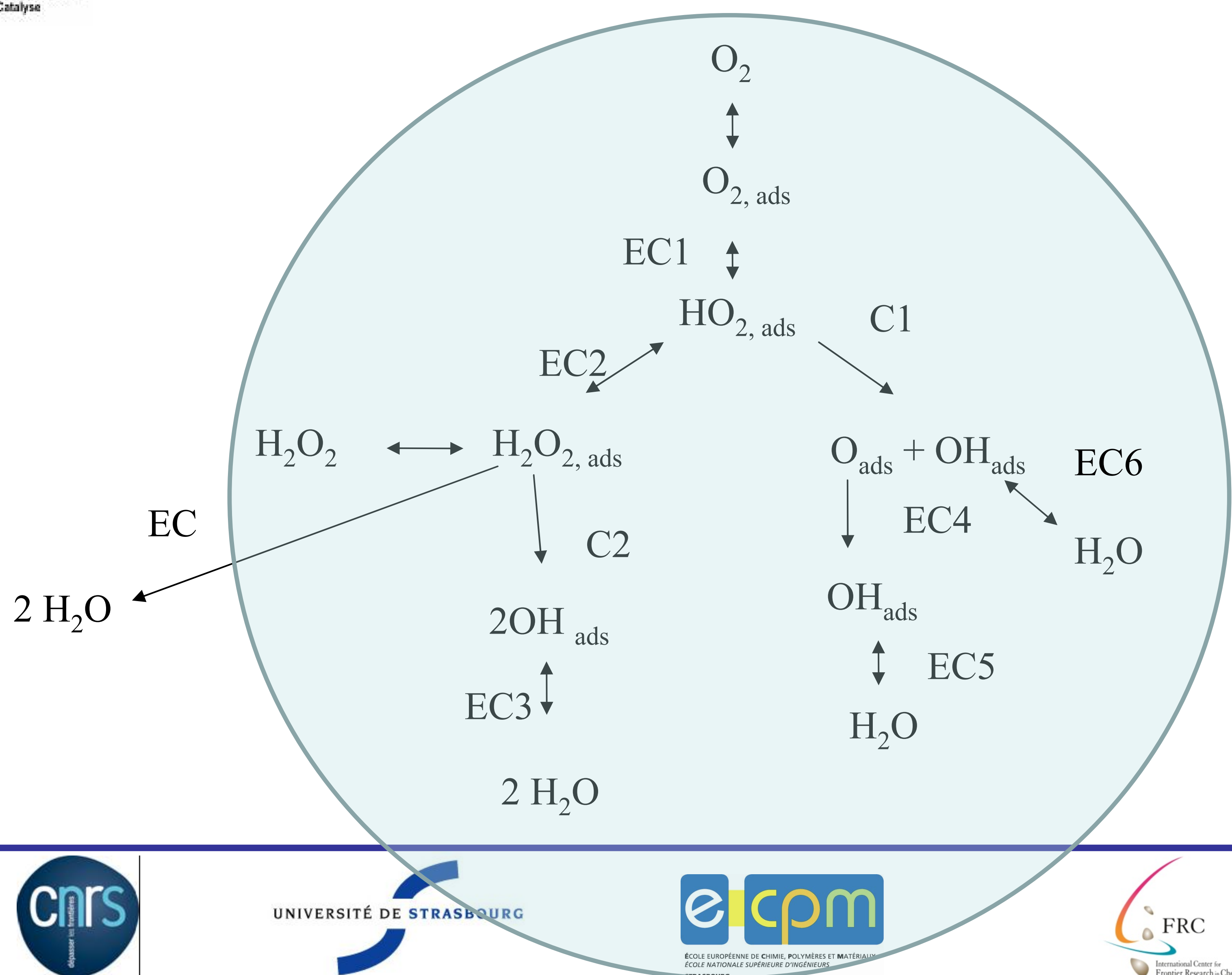
$$D_{A_i}\left(\frac{\partial^2[A_i]}{\partial r^2}+\frac{1}{r}\frac{\partial[A_i]}{\partial r}+\frac{\partial^2[A_i]}{\partial z^2}\right)=0$$

- Simulation performed using a free finite element software Freefem+
- Three mechanisms for the ORR

Modeling performed by A. Bonnefont

C. Amatore, J.-M. Saveant, D. Tessier, J. Electroanal. Chem. 147(1983) 39.
T.J. Davies, R.G. Compton, J. Electroanal. Chem. 585 (2005) 63.
T.J. Davies, S. Ward-Jones, C.E. Banks, J.d. Campo, R. Mas, F.X. Munoz, R.G. Compton, J. Electroanal. Chem. 585 (2005) 51.

Tentative mechanism of the ORR

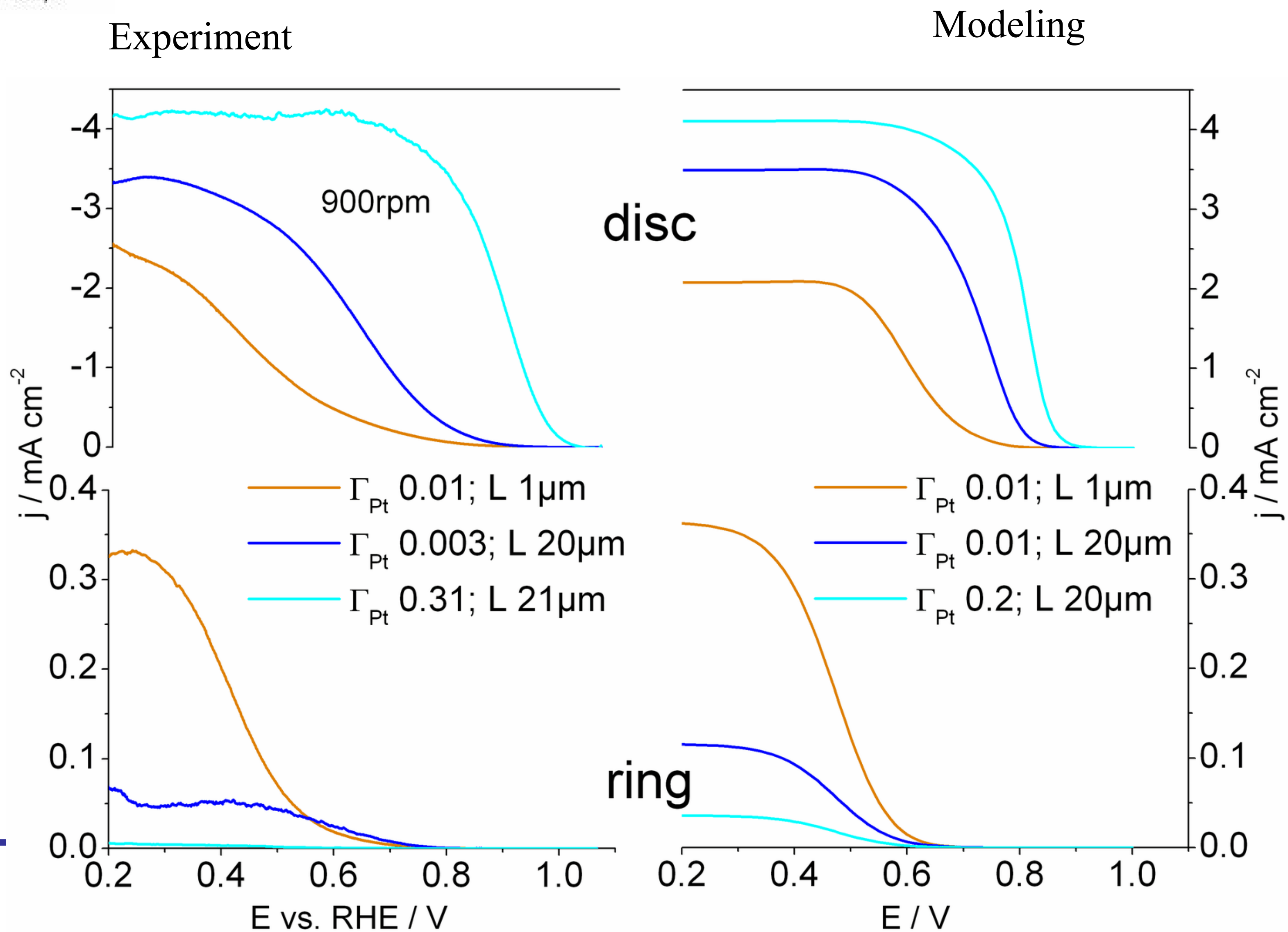


Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

UNIVERSITÉ DE STRASBOURG
ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
FRC International Center for Frontier Research in Chemistry

ORR: Experiment vs. Modeling

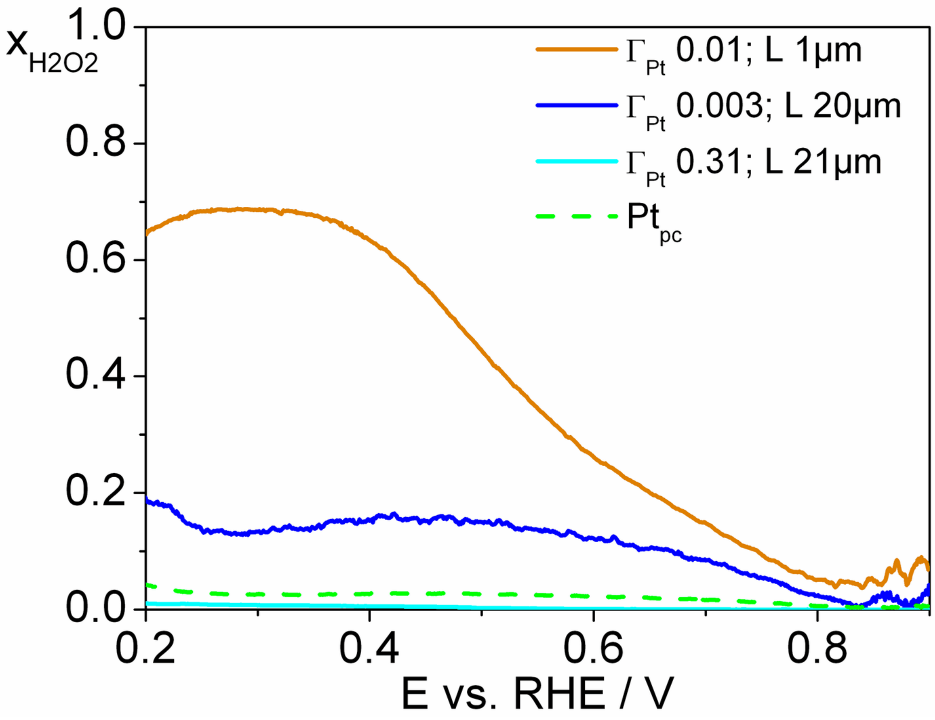
Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse



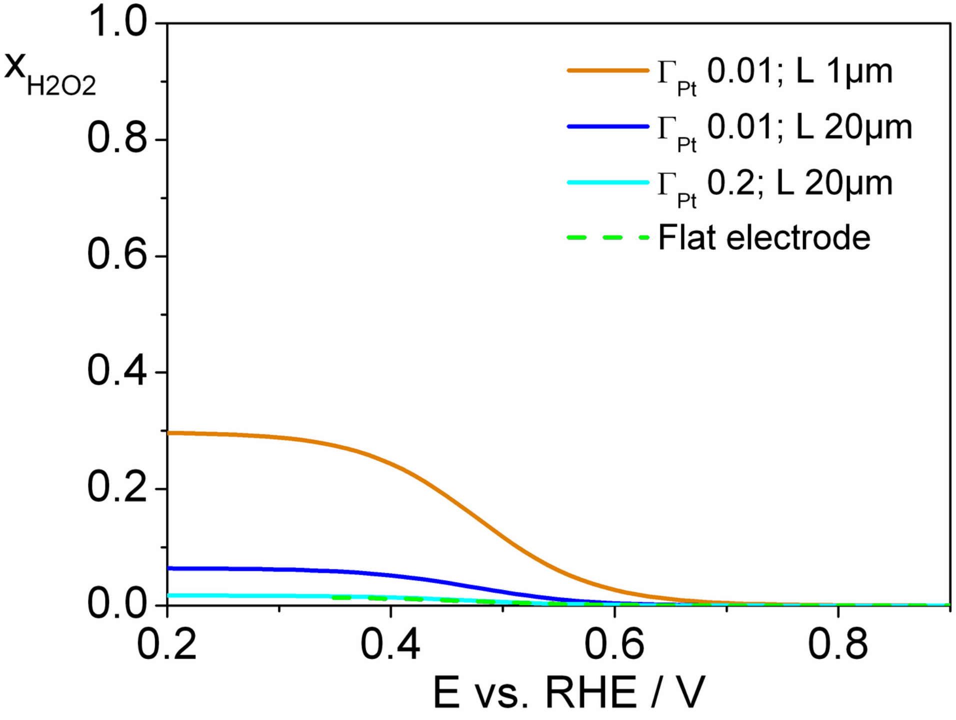
ORR: Experiment vs. Modeling

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Experiment



Modeling



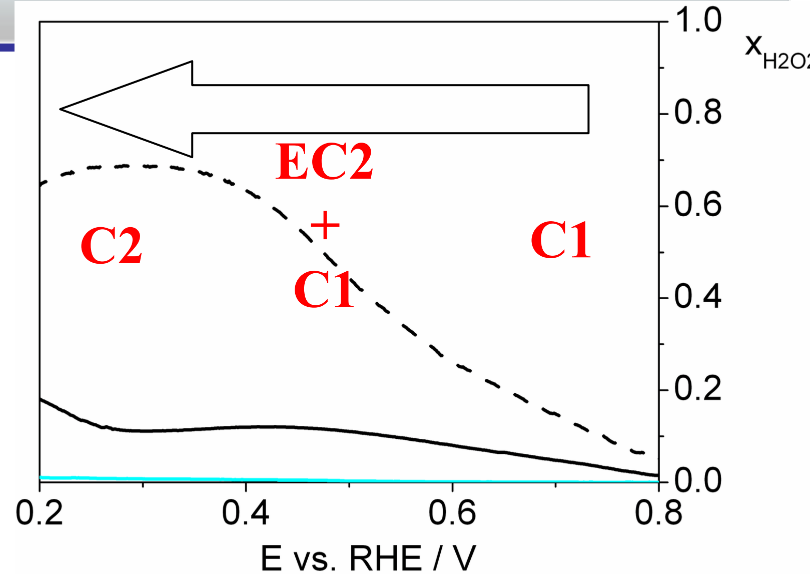
UNIVERSITÉ DE STRASBOURG

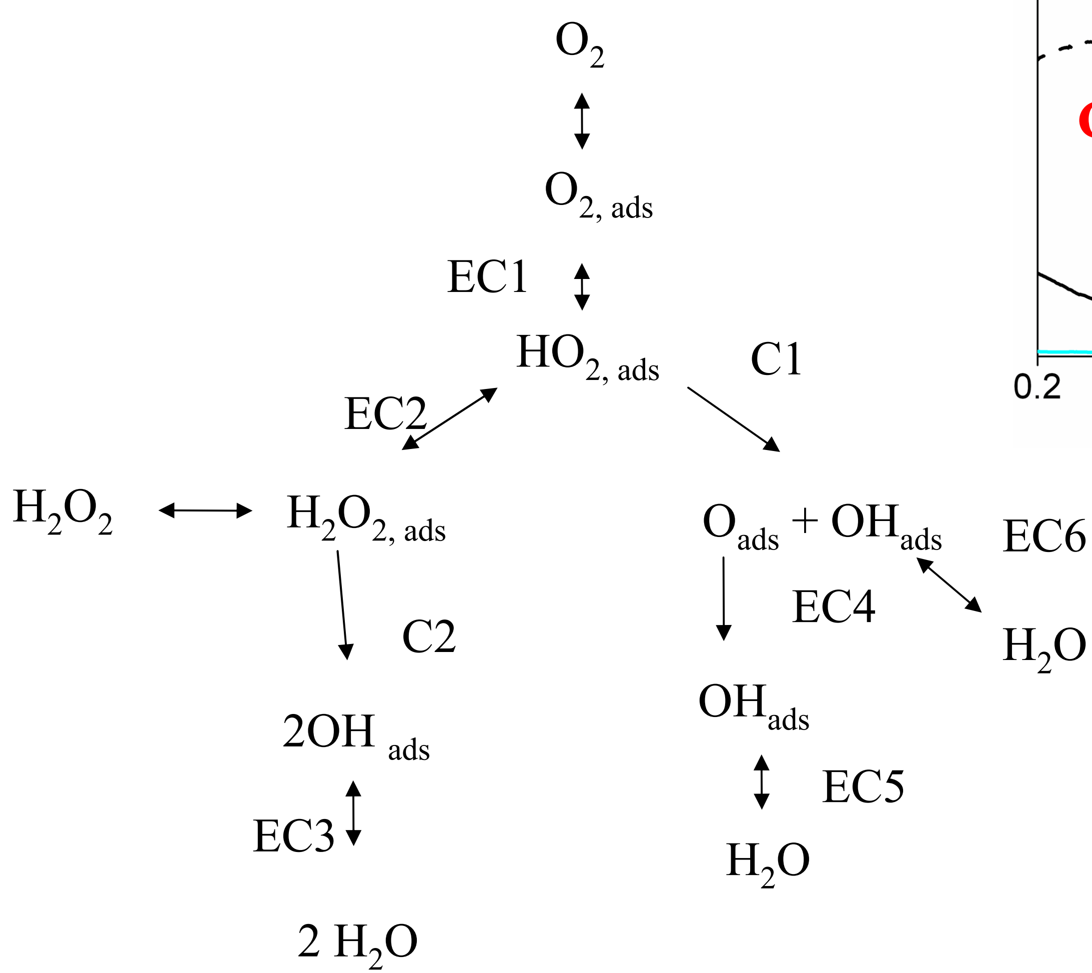
ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

FRC
International Center for Frontier Research in Chemistry

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

Tentative mechanism of the ORR





UNIVERSITÉ DE STRASBOURG

ÉCOLE EUROPÉENNE DE CHIMIE, POLYMÈRES ET MATÉRIAUX
ÉCOLE NATIONALE SUPÉRIEURE D'INGÉNIEURS
STRASBOURG

FRC
International Center for Frontier Research in Chemistry

Part 4: Conclusions

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

•3D architecture strongly influences product distribution and effectiveness of the catalytic layers

•Application of 3D ordered catalytic layers allowes to obtain novel information on the ORR

•Significant contribution of H_2O_2-involving stage in ORR on Pt was demonstrated

• Ultra-thin/low Pt-coverage layers lead to the escape of the H_2O_2 and a decrease of the specific catalytic activity

•Dual path ORR model is in agreement with experimental data

Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse

ACKNOWLEDGEMENTS

Financial support

ANR-06-CEXC-004 Chaires d'excellence - 2006

EU DEMMEA project

FRC (UdS)

CNRS

Colleagues and PhD students from MSU, BIC, UdG and UdS

PhD scholarship (P. S. Ruvinsky): "Ministère de l'Enseignement Supérieur et de la Recherche" (France)