Electro-catalytic properties of Pd-based nano-structured material for application in fuel cells

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Workshop – Bilateral project Italy-USA
"Hydrogen transport through nano-structured electrodes for energy application":
2nd year report

Columbia, 24th July, 2013

Bilateral project Italy-USA (2011-2013) "Hydrogen transport through nano-structured electrodes for energy application"

Project Outline:

- Platinum is commonly used as Fuel Cells Active material
- Platinum cost has an high impact on technology development
- Palladium has very interesting properties and lower cost
- Palladium can be used to replace Platinum

•Crucial point is to obtain control of material structure and morphology in electrodes preparation

Project Objectives:

✓ **1° year:**
- ✓ Study of the effect of nanostructure and impurities on catalytic activity and mass transfer of Pd foils

❑ **2° year:**
- ❑ Fabrication and characterization of nanostructured Pd-based electrocatalysts, by electrochemical and physical vapor deposition techniques.

2nd year activities

Objective:

Investigation of different deposition techniques for Pd catalysts with enhanced:

- Electrochemically Active Surface
- Stability
- Low Pd load (➔minimized cost)

Workplan:

Pd deposition on GDL substrates by Electrochemical Deposition (ED) and DC Sputtering (SP) techniques

SEM/EDX characterization➔ Pd deposits coverage and surface morphology

Catalytic activity for hydrogen (Cyclic Voltammetry in acidic solution)

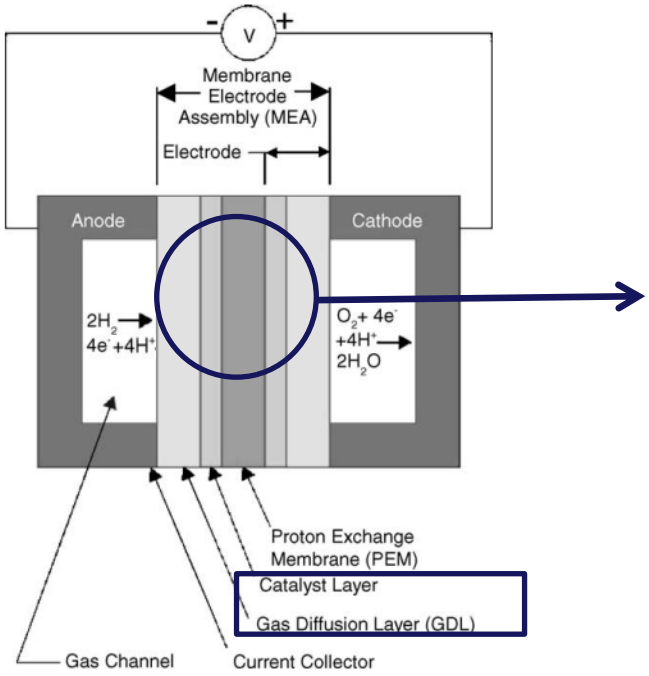
Electrochemical stability in acidic solution

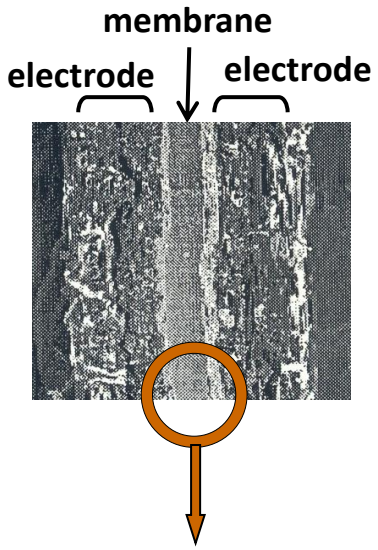
Catalytic activity for ethanol (Cyclic Voltammetry in alkaline solution)

Membrane Electrode Assembly (MEA)

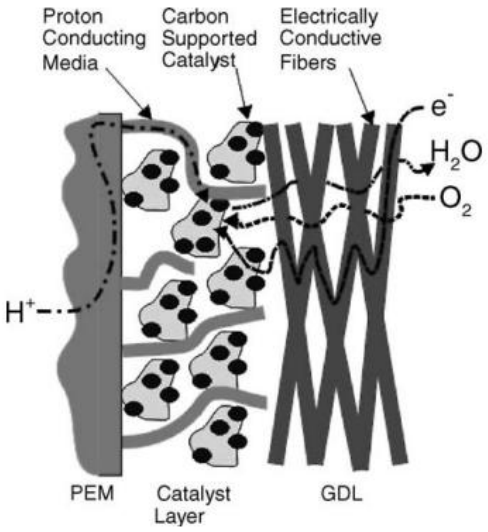
MEA components:

- Proton Exchange Mebrane
- Catalyst layer
- Gas Diffusion Layer (GDL)





The Gas Diffusion Electrode (GDE) includes the catalyst and the GDL



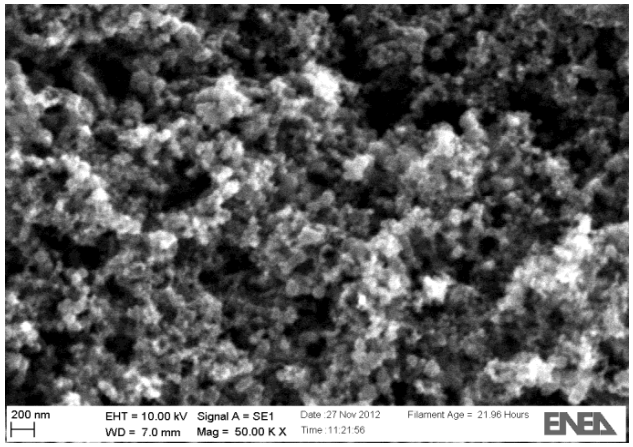
GDL is a porous and electrically conducting layer.

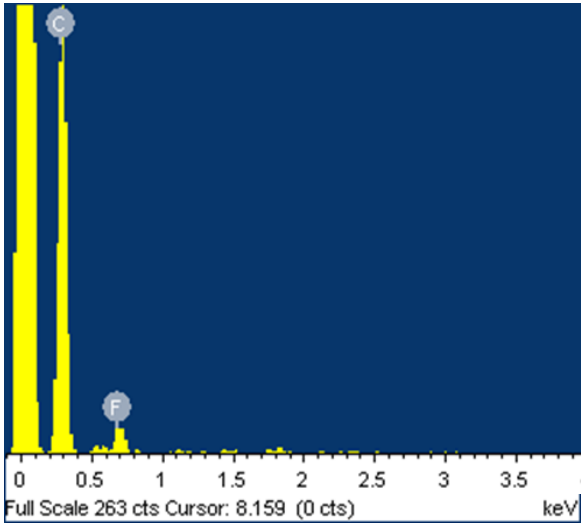
GDL must correctly ensure reactant gases diffusion to the catalyst, electron conduction and water management.

Typical GDL are constructed from porous carbon paper wet-proofed with a PTFE (Teflon) coating to ensure that pores are not congested with water

Gas Diffusion Layer (GDL) Substrate

Carbon Paper (Quintech, Toray Paper TP090) spray-coated by PTFE (20%w)/carbon layer

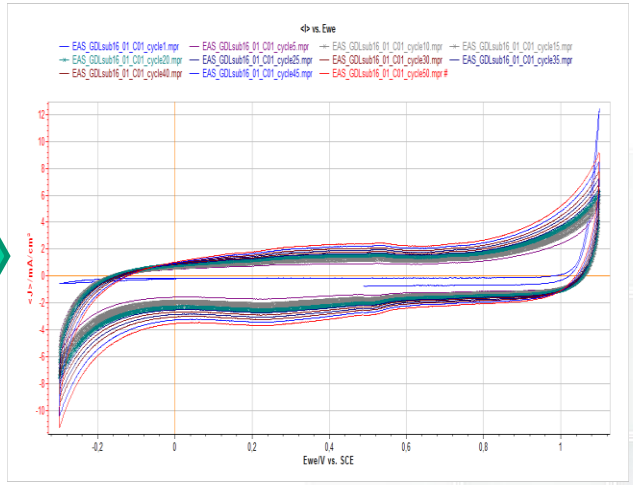




Pretreatment: Potentiodynamic Cycling

H_2SO_4 1M, 100mV/s, -0.3 ÷ 1.1 V (vs. SCE), 50 cycles

- As prepared: lens-shaped curve with no evident surface phenomena
- After 50 cycles: higher capacitance due to high material surface area and reversible redox peaks (+0.38 and +0.27 V vs. SCE) owing to functional groups containing oxygen on the carbon surface

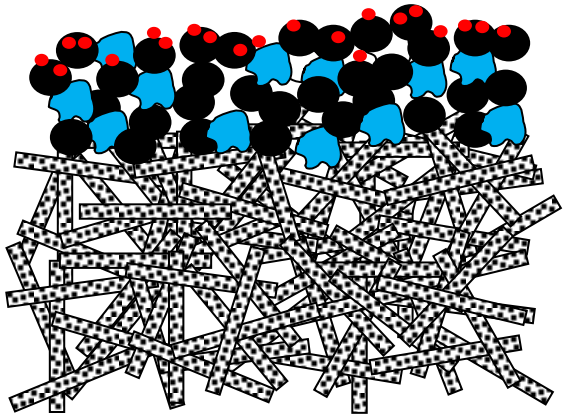


Pd catalyst deposition techniques

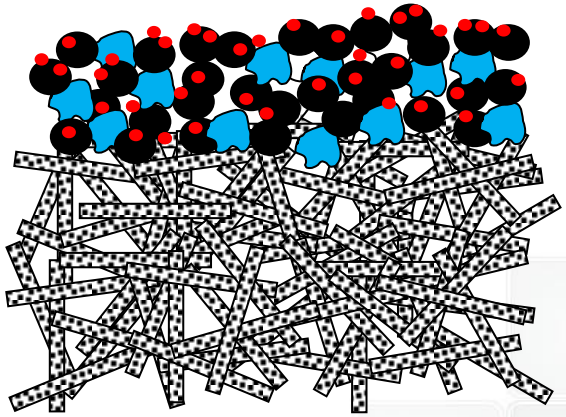
Localization of metallic catalysts on the surface of the GDL ensures catalyst will be located only in regions that have access to electrons and protons, and the catalyst loading will be highly reduced.

Electrodeposition (ED) and Sputtering (SP) techniques allow surface localization of the catalyst, despite traditional routes as impregnation followed by chemical reduction (CR)

Surface localization
(L_{Pt}<0.1 mg cm^{-2})

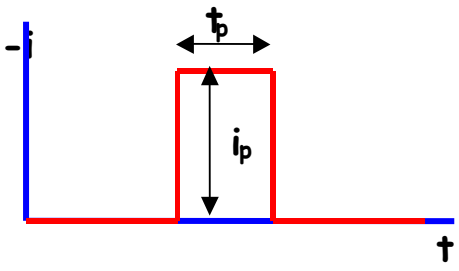


Bulk localization
(L_{Pt}=0.3-0.5 mg cm^{-2})

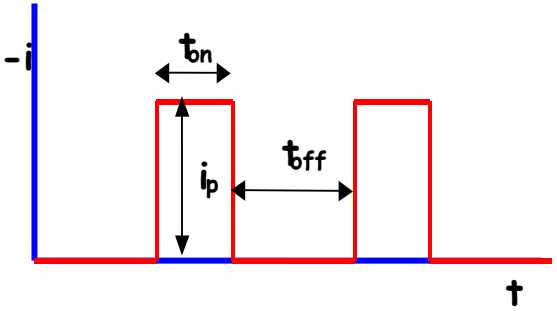


Electrochemical Deposition (ED)

Galvanostatic ED (GED)



Galvanostatic Pulsed ED (GPED)

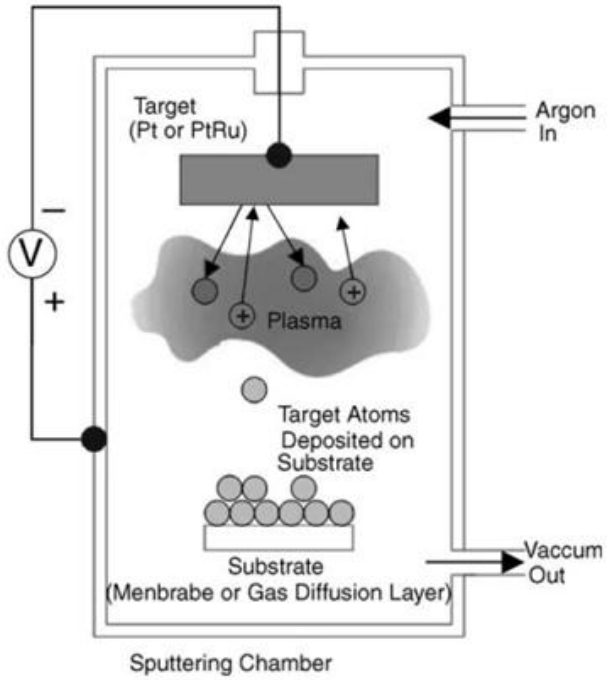


Pyrex electrochemical cell in a three electrode configuration:

- counter-electrode: Pt
- reference electrode: Saturated Calomel Electrode
  ($Hg\text{-}Hg_2Cl_2$ - KCl sat., +0.241 V vs. NHE)
- working electrode: GDE
- electrolyte: $PdCl_2$ 10 mM in HCl 1M
  $PdCl_2 + 2e^- \rightarrow Pd + 2Cl^-$

Galvanostat/Potentiostat: Biologic SP200

DC Magnetron Sputtering (SP)



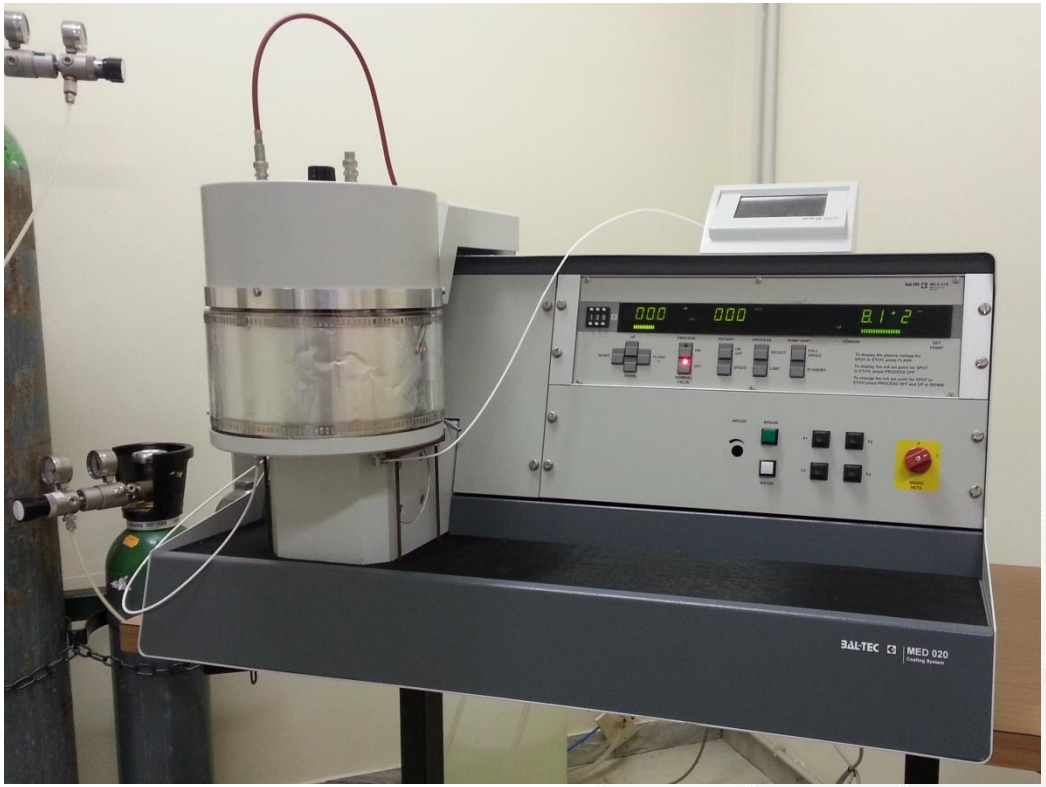
Baltec MED 20

Ar^+ ions V=370 V

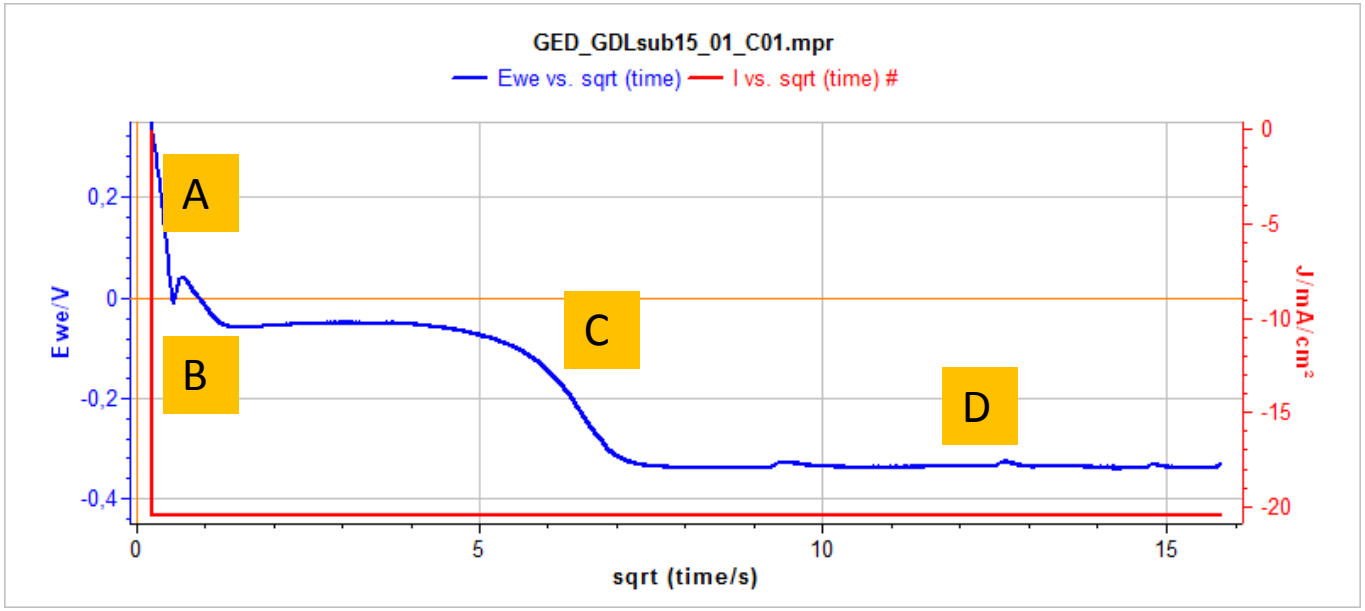
$P=1.2x10^{-2}$ mbar I=45 mA

Depositing atom energy ~10^1 eV

- The atoms are sputtered from the solid source material (target) by energetic ions bombardment
- A DC voltage is applied between target and substrate to produce the plasma



Galvanostatic ElectroDeposition (GED)



Pd Load

$L_{Pd} = Q_{GED}\ M/\ n\ F$

M = 106 a.u.
F = 96 487 C
n = 2

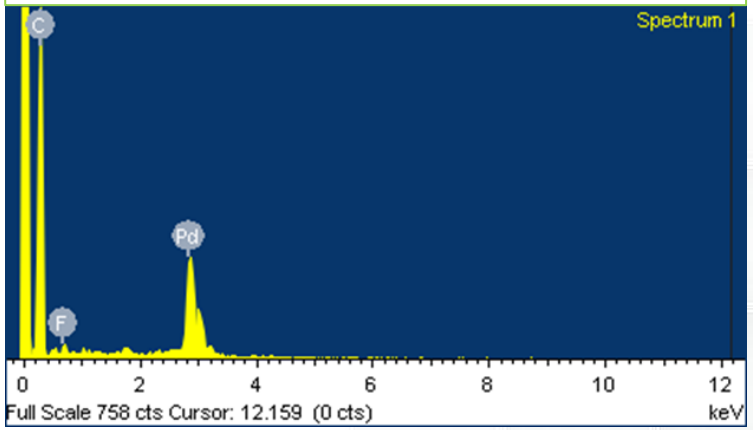
A. Adsorption of Pd^{2+} ions

B. Charge transfer ➔ Pd^{0} ad-atom formation

C. Nucleation and Nano-Cluster formation

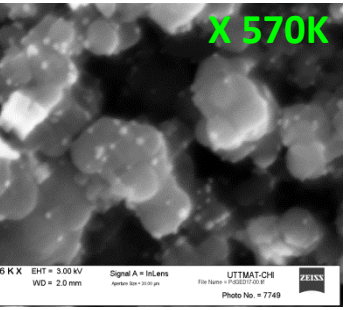
D. Cluster size increase and coalescence (continuous porous film)

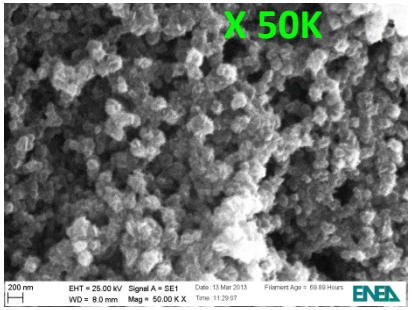
Energy Dispersive X-rays Spectroscopy (EDX)

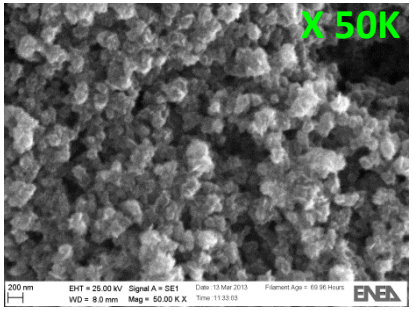


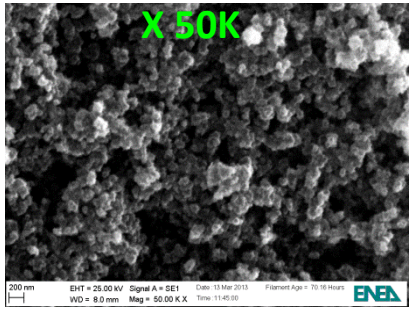
Morphology and coverage by GED

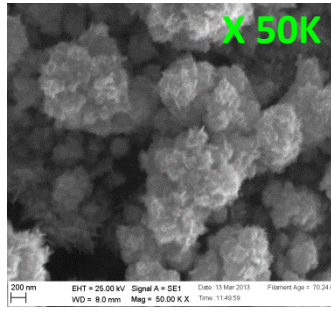
increasing QED

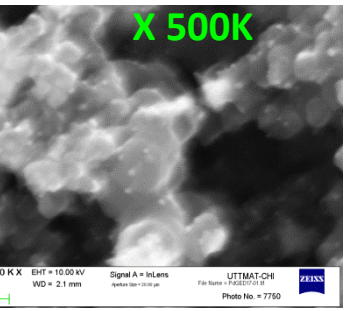


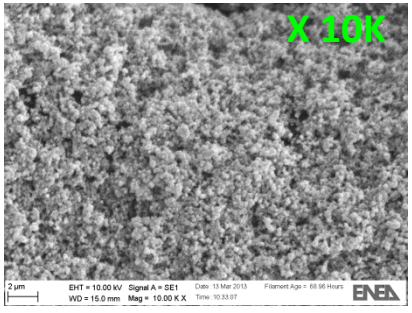


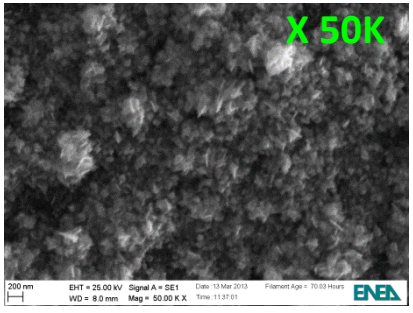


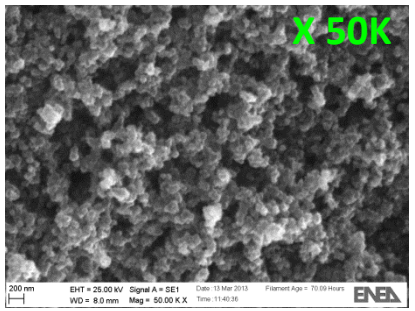


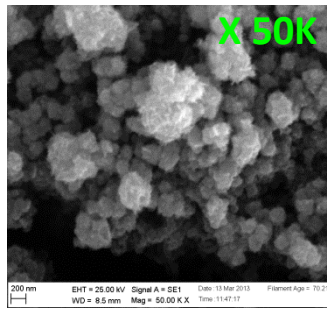


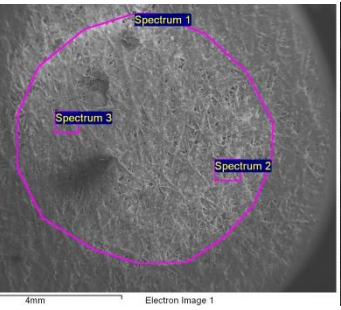


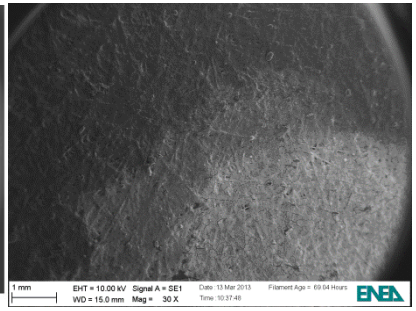


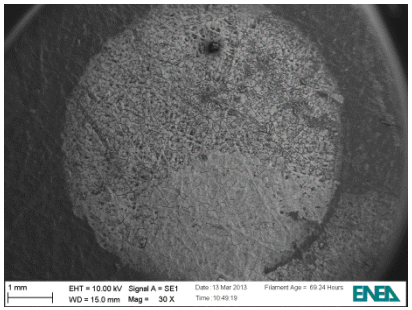


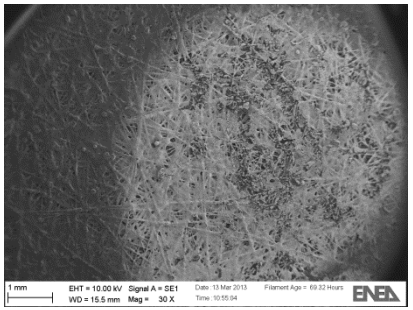


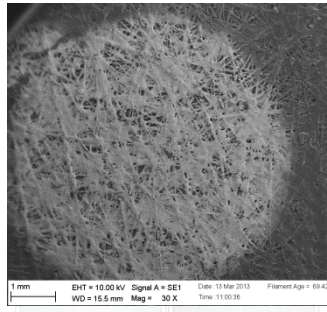












QED = 1276 mC/cm²

QED = 768 mC/cm²

QED = 1276 mC/cm²

QED = 2551 mC/cm²

QED = 5102 mC/cm²

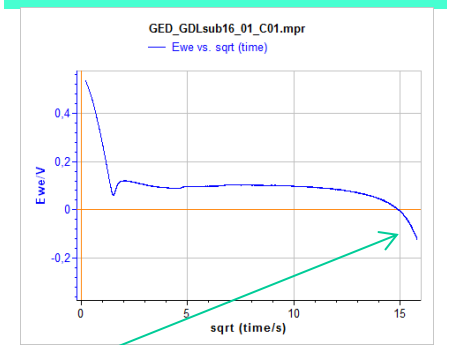
GED

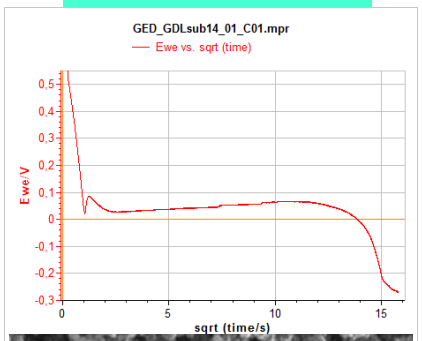
QED = 1276 mC/cm²
J = 5.1 mA/cm²

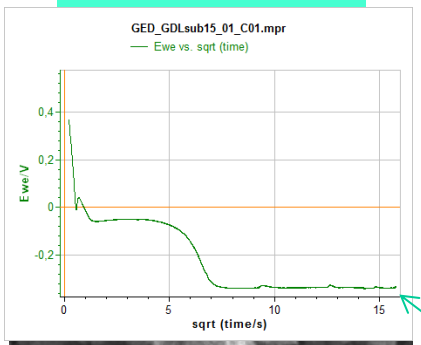
2551 mC/cm²
10.2 mA/cm²

5102 mC/cm²
20.4 mA/cm²

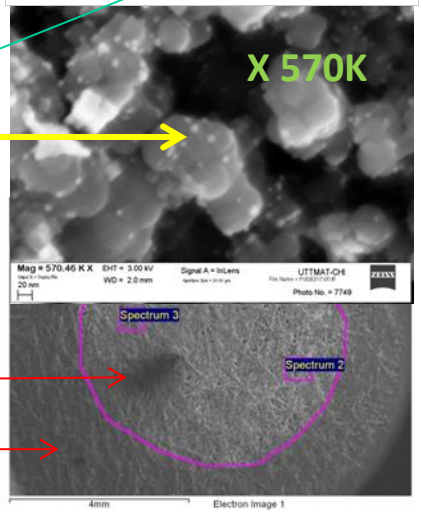
t= 250 s

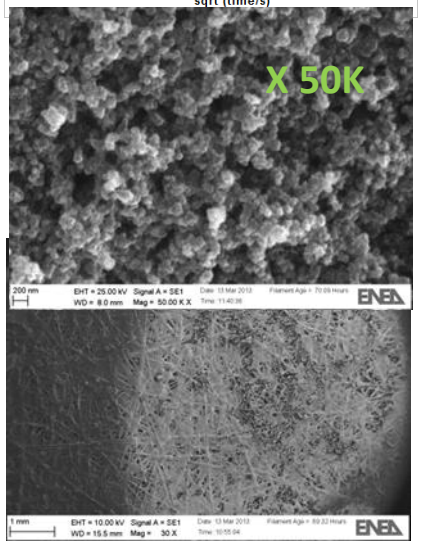


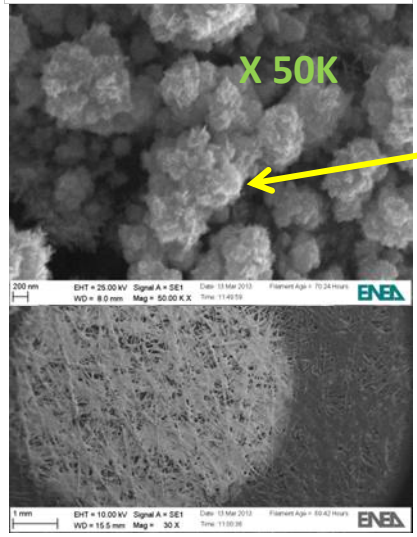




Nano-cluster 2-3 nm







Macro-clusters 0.5-1 μm

coated

un-coated

low coverage

medium coverage

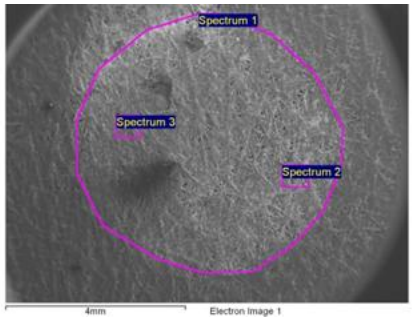
high coverage

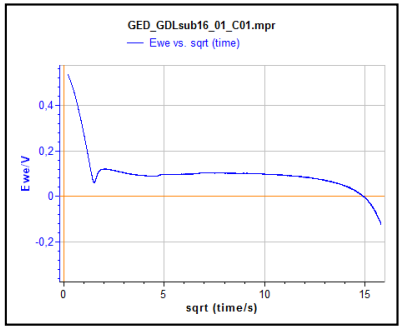
Pd coverage increases with deposition current density (J) and charge (Q_{ED})

GED Pd deposit coverage

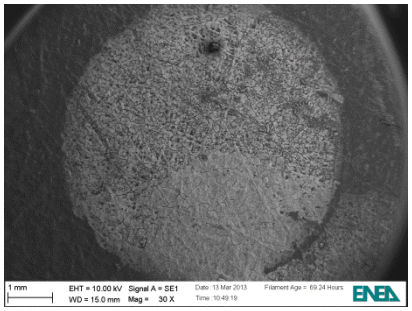
QED= 1276 mC/cm^2 J= 5.4 mA/cm^2 t_{ED}=250 s

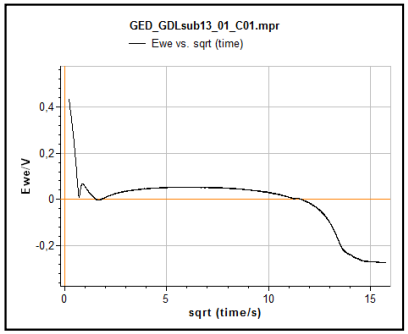
Pd (EDX) = 27 %w





Pd (EDX) = 88 %w





- ✓ For **low values of the nominal Pd load**, control of Pd coverage is scarce.
- ✓ Samples deposited at the same conditions (current density, deposition time and total charge) may result in different phases of the growth process (as indicated by the Ewe vs. time curve) and consequently different Pd coverage (as indicated by EDX analysis).
- ✓ Pd deposition efficiency is related to the charge flowing after the 2° potential plateau («coalescence» phase D).

Galvanodynamic Pulsed ED (GPED)

GPED deposition conditions

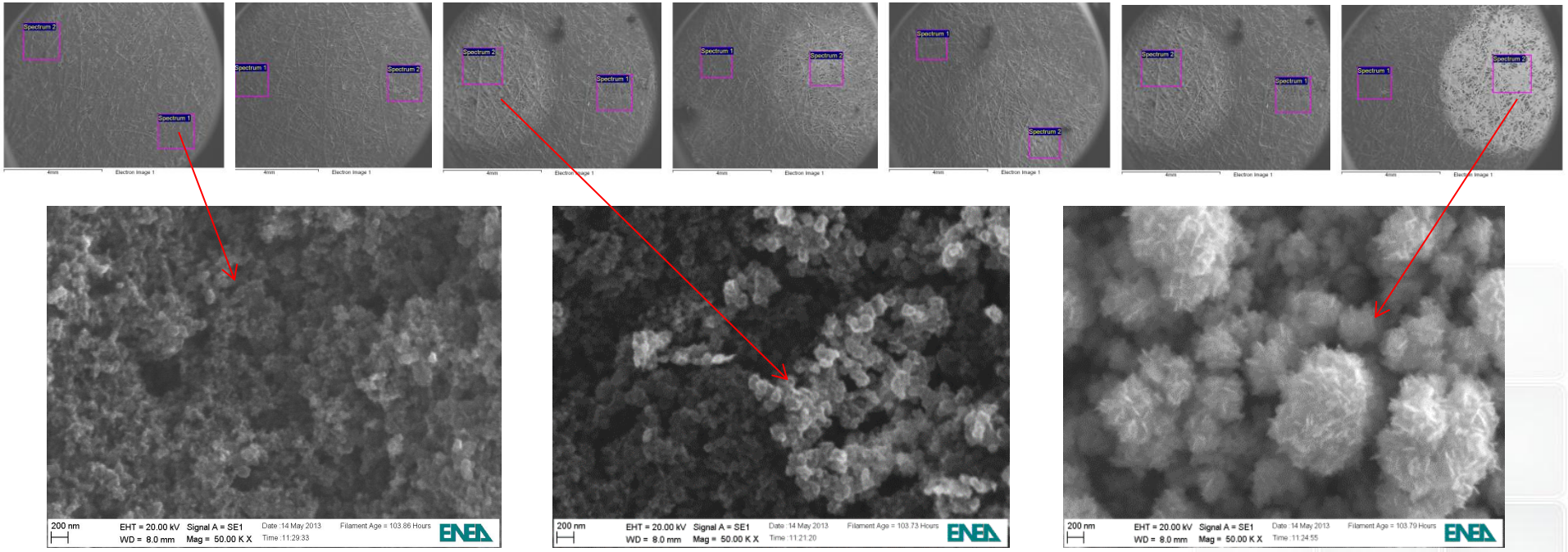
	I	A	I/A	dtON	dtOFF	nc	dtTOT	QGPED	LPd
	mA	cm2	mA/cm2	s	s		s	mC/cm2	μgr/cm2
Pd25GPED	-8.00	0.20	-40.82	0.10	0.70	17.00	1.70	69	38
Pd22GPED	-8.00	0.20	-40.82	0.10	0.70	34.00	3.40	139	77
Pd23GPED	-8.00	0.20	-40.82	0.10	0.70	103.00	10.30	420	232
Pd20GPED	-8.00	0.20	-40.82	0.10	0.70	212.00	21.20	865	477
Pd19GPED	-8.00	0.20	-40.82	0.10	0.70	313.00	31.30	1278	705
Pd21GPED	-8.00	0.20	-40.82	0.10	0.70	625.00	62.50	2551	1407
Pd24GPED	-8.00	0.20	-40.82	0.10	0.70	1250.00	125.00	5102	2814

Pd Load

$L_{Pd} = Q_{GPED}\ M/\ n\ F$

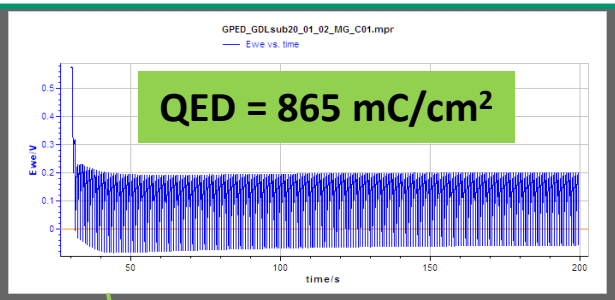
M = 106 a.u.
F = 96 487 C
n = 2

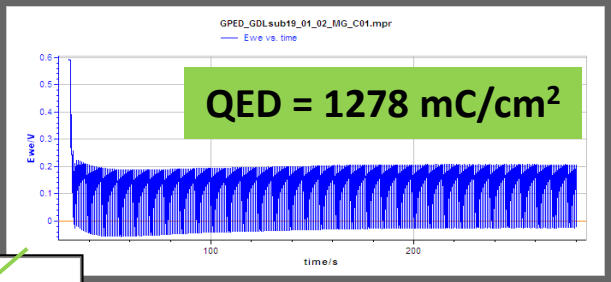
Q_{GPED} increasing

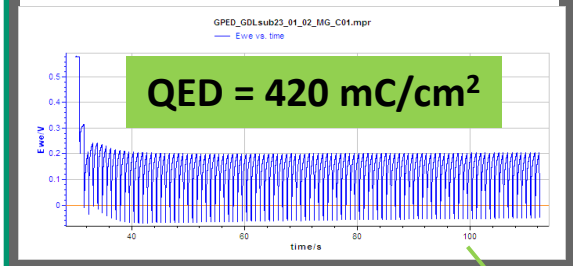


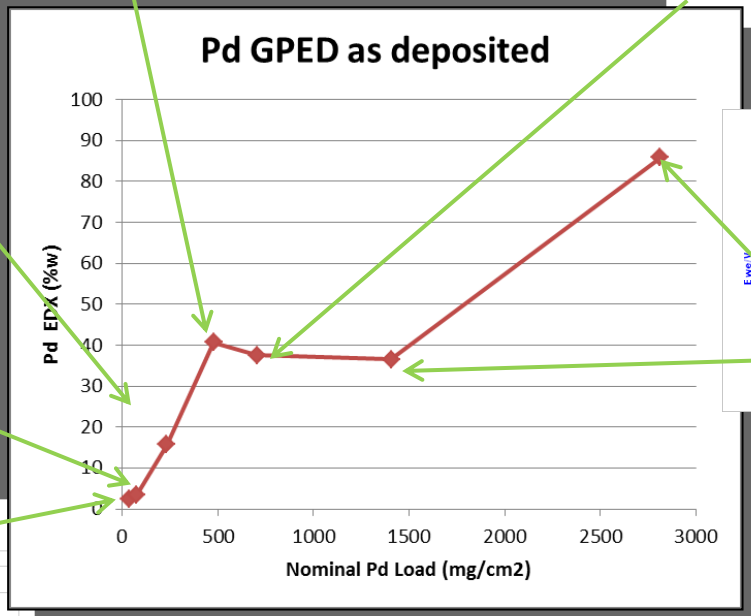
GPED Pd deposition microanalysis

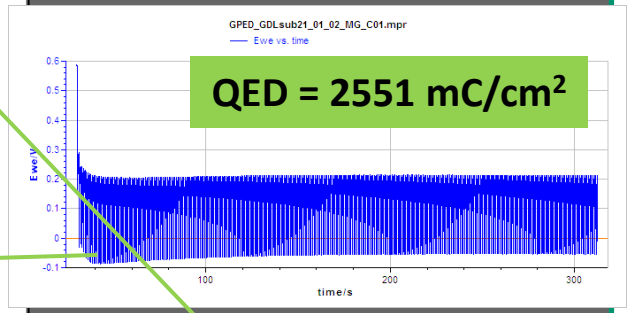
EDX results show high Pd content when the potential curve gets the 2° plateau

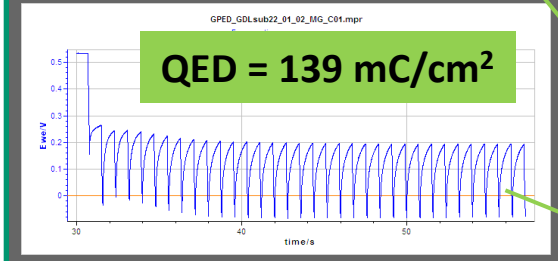


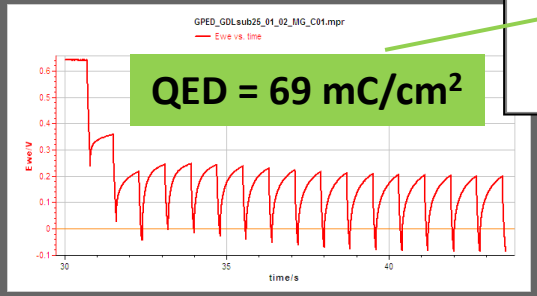


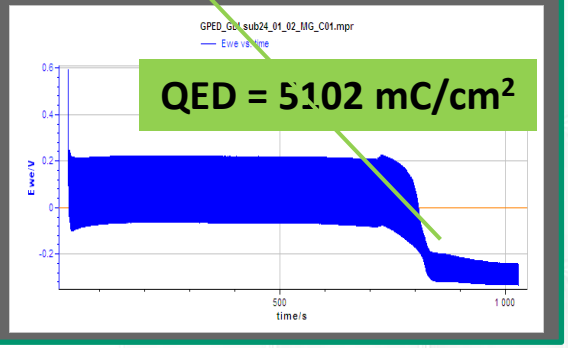












DC Sputtered films

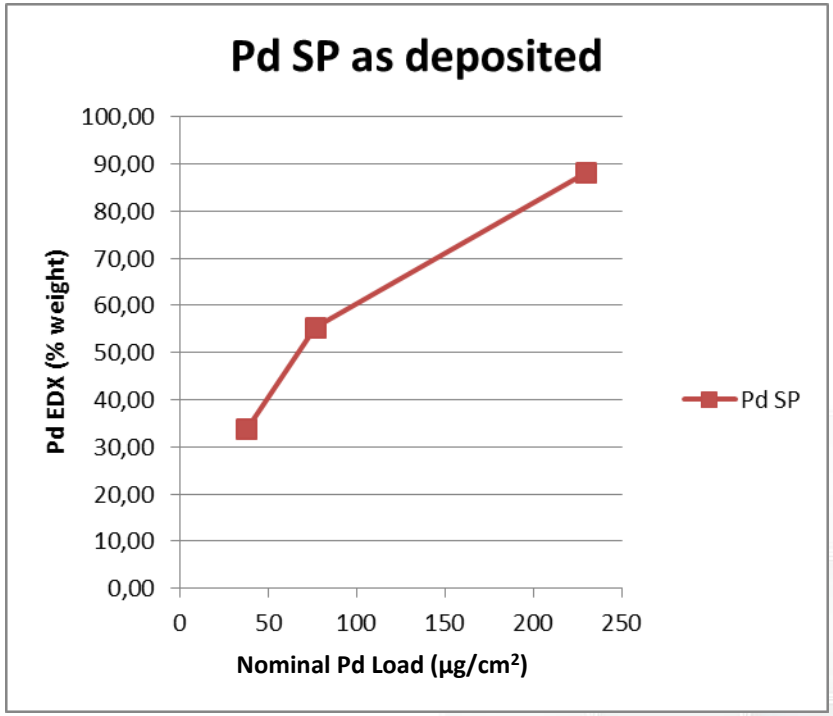
	t s	d nm	LPd microg/cm2
Pd12SP	600	240	230
Pd13SP	600	240	230
Pd14SP	200	80	77
Pd15SP	100	40	38
Pd16SP	200	80	77
Pd17SP	200	80	77
Pd18SP	100	40	38

Pd Load

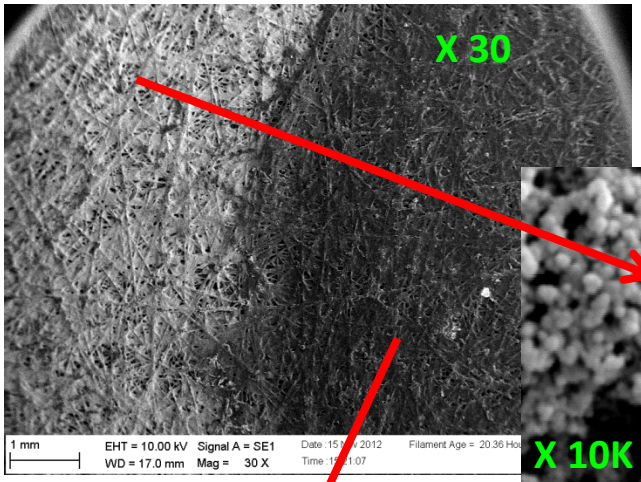
LPd = d ρ
d = film thickness
ρ = 12 g/cm^3

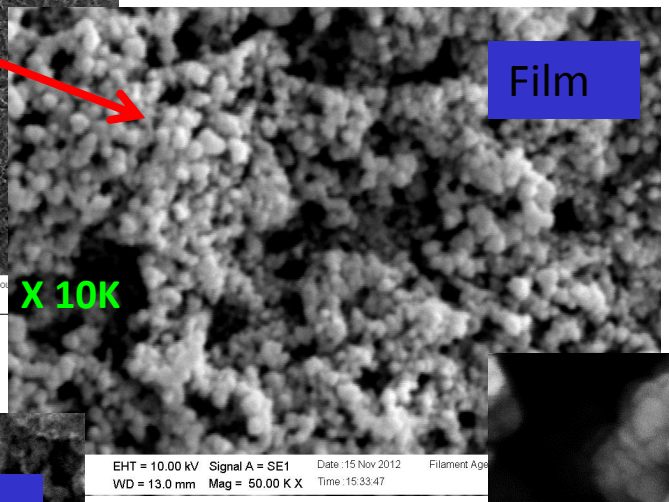
Pd film thickness is measured in-situ by quartz microbalance

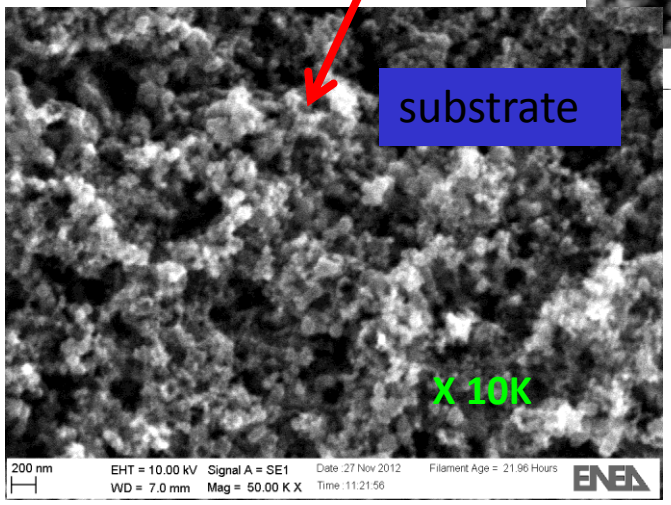
Thickness calibration is performed by profilometer measurements of films deposited on partially masked flat substrates

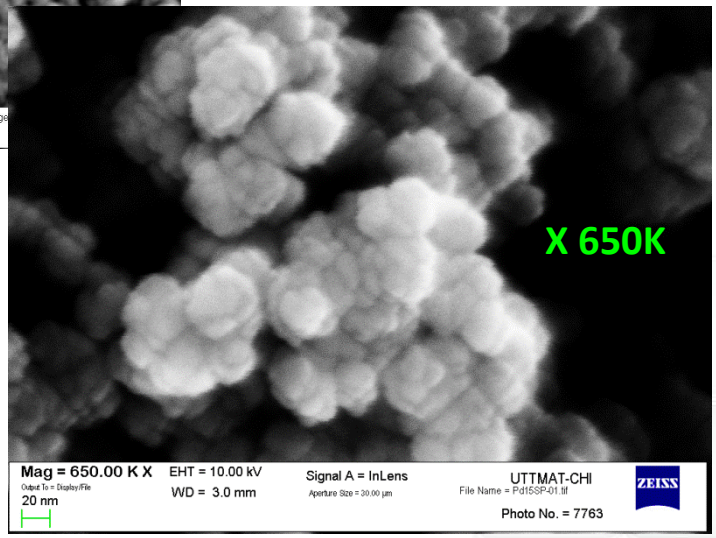


Morphology and coverage of SP films









Very thin films (40-240 nm)

Atoms are deposited on the very near surface

High coverage

Conformal coating of the porous substrate (2D growth)

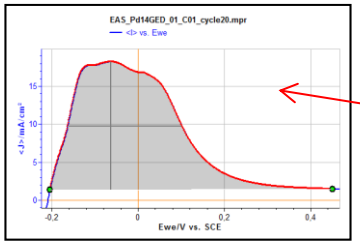
Electrochemical characterization

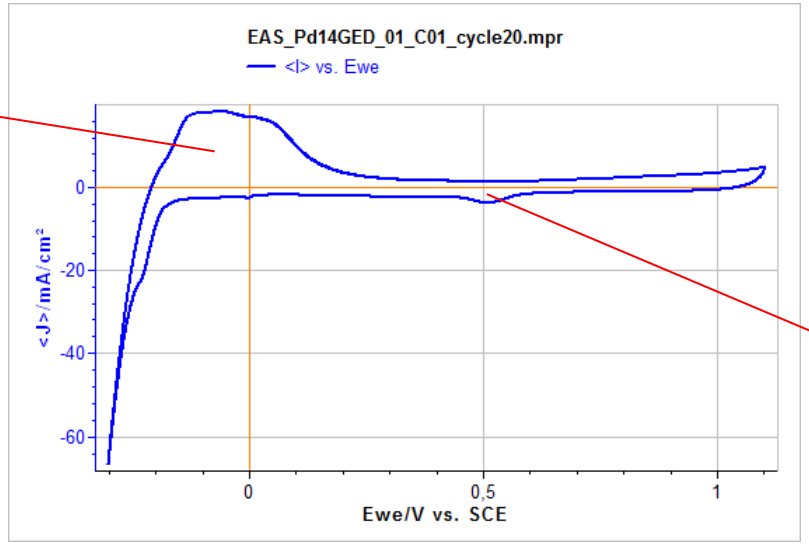
Cyclic Voltammetry in acidic solution

Pyrex electrochemical cell in a three electrode configuration:

- working electrode: GDE
- counter-electrode: Pt
- reference electrode: SCE (KCl sat) ($Hg\text{-}Hg_2Cl_2$) (+0.241 V vs. NHE)
- electrolyte: H_2SO_4 1 M
- Range: -0.3 V (vs. SCE) ÷ 1.1 V (vs. SCE)
- Scan rate: 10 mV/s , 15 mV/s, 20 mV/s

- **Electrochemical Real Surface (ERS)**





Hydrogen desorption charge (Q_H)

$Pd\text{-}H \Rightarrow Pd + H^+ + e^-$

$ERS_H = Q_H / Q_{Hrif}$

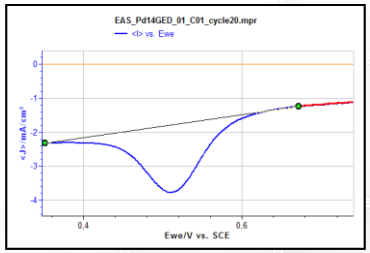
$Q_{H\ rif} = 210 \mu C/cm^2$

Pd oxide/idroxide reduction charge (Q_{Ox})

$PdO_y(OH)_x \Rightarrow Pd$

$ERS_{Ox} = Q_x / Q_{ox\ rif}$

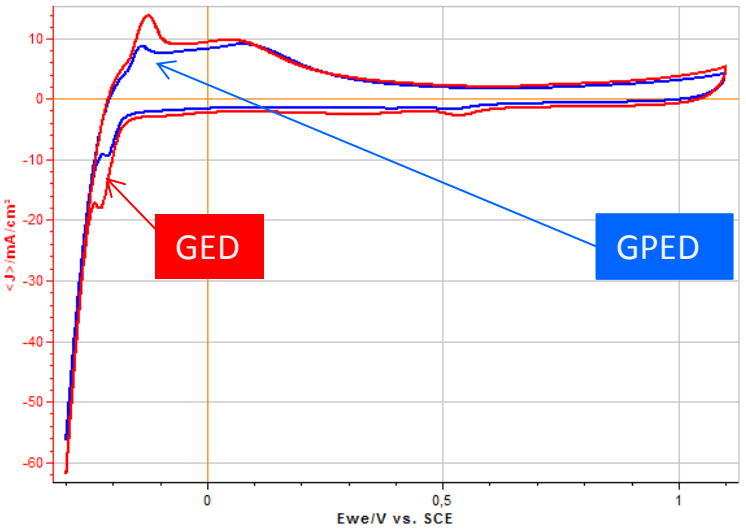
$Q_{Ox\ rif} = 424 \mu C/cm^2$



Comparison between GED and GPED catalysts active surface

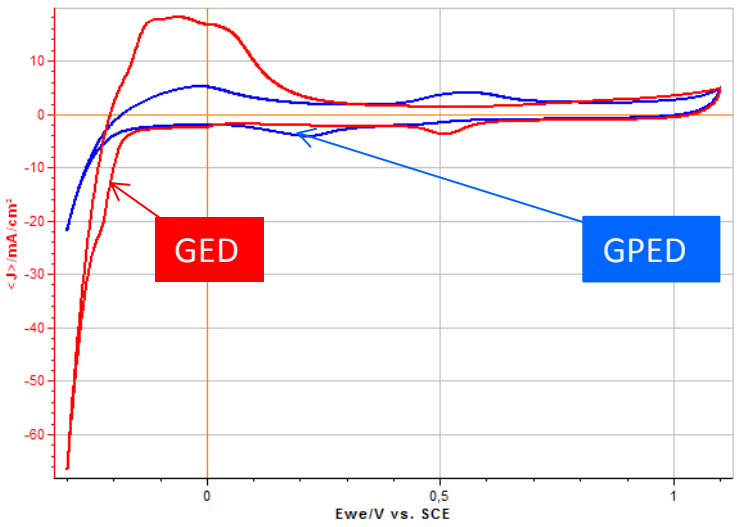
- Voltammetry spectra indicate that GED samples have higher active surface for hydrogen catalysis than GPED samples deposited by flowing the same tototal charge (Q_{ED}).
- The difference is more evident for higher Q_{ED} values.
- The peak related to Pd oxide/idroxide reduction is broadened and shifted to lower potentials in GPED samples.

Q_{ED} = 867 mC/cm²



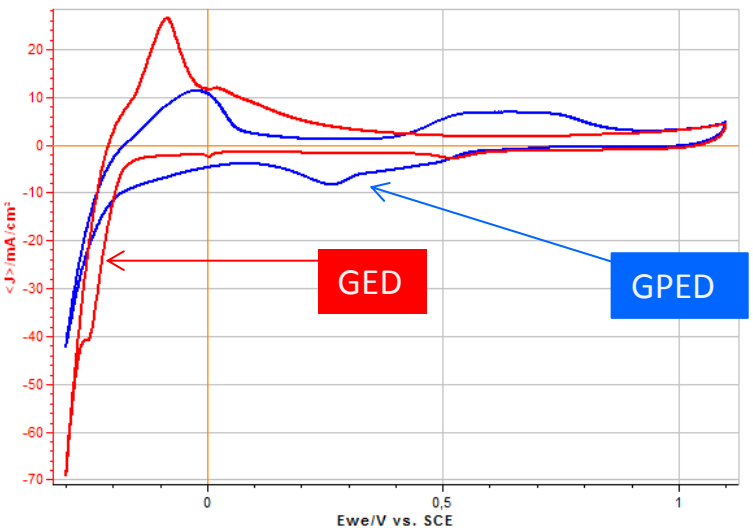
X 50K

Q_{ED}= 2551 mC/cm²



X 50K

Q_{ED}= 5102 mC/cm²



X 50K

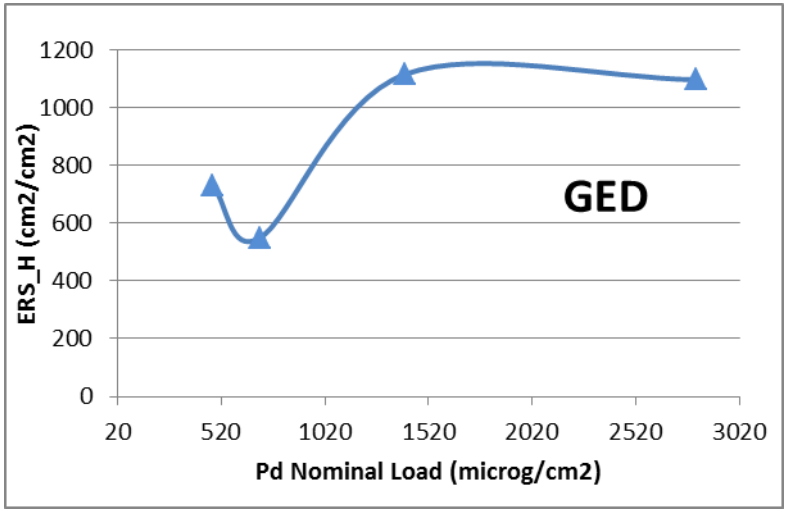
ERS for Hydrogen desorption in acidic solutions

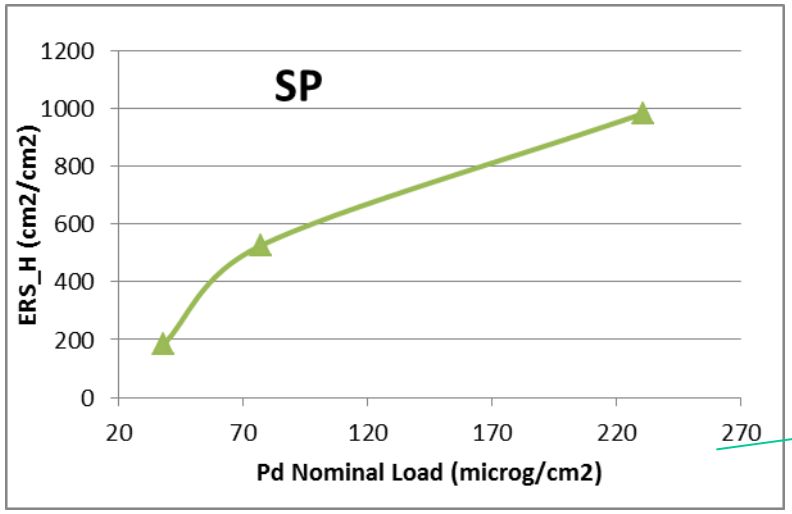
Maximum ERS values range between 800-1200 cm^2 for 1 cm^2 geometric area for the different techniques.

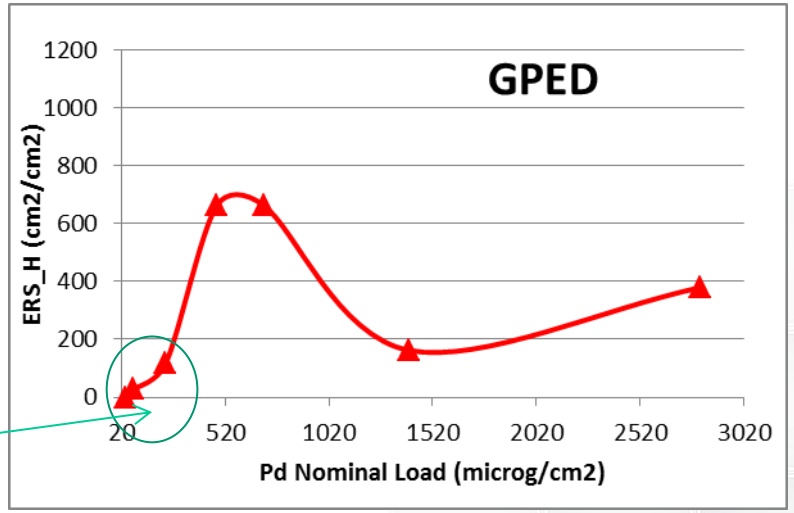
ERS values for Pd samples are comparable with that obtained for a sputtered Pt film of 230 $\mu g/cm^2$ (2280 cm2/cm2).

In the case of GPED samples ERS has a local maximum (around 500 $\mu g/cm^2$), below which it decreases monotonically for decreasing loads.

For very low Pd loads, ERS values increase with Pd load (SP and GPED samples).



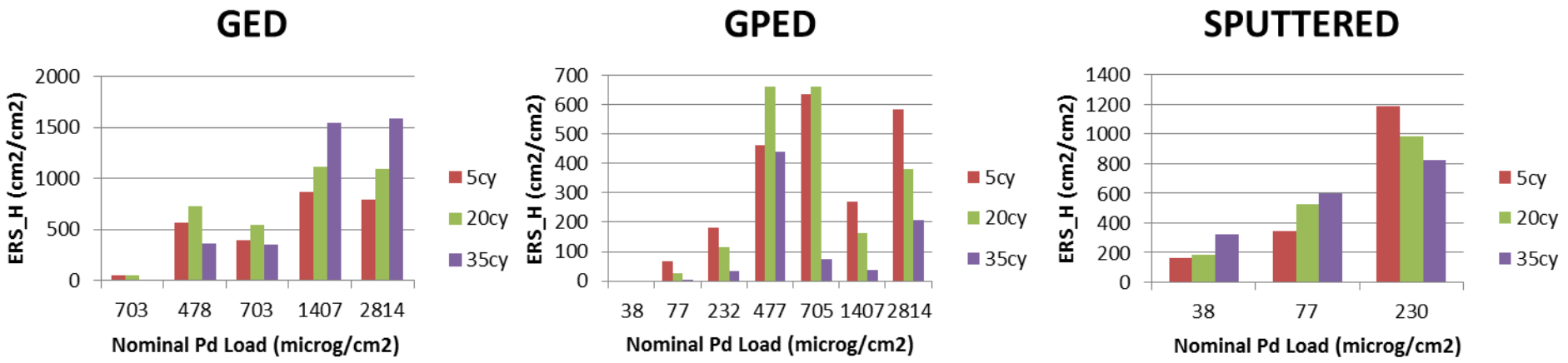




Pd catalysts stability in acidic solutions

- Catalysts stability is critical for Pd in acidic solutions due to the lower dissolution potential respect to Pt:

$$Pd \rightarrow Pd^{2+} + 2e^-, \quad E_0 = 0.99 + 0.029 \log[Pd^{2+}] \qquad Pt \rightarrow Pt^{2+} + 2e^-, \quad E_0 = 1.19 + 0.029 \log[Pt^{2+}]$$

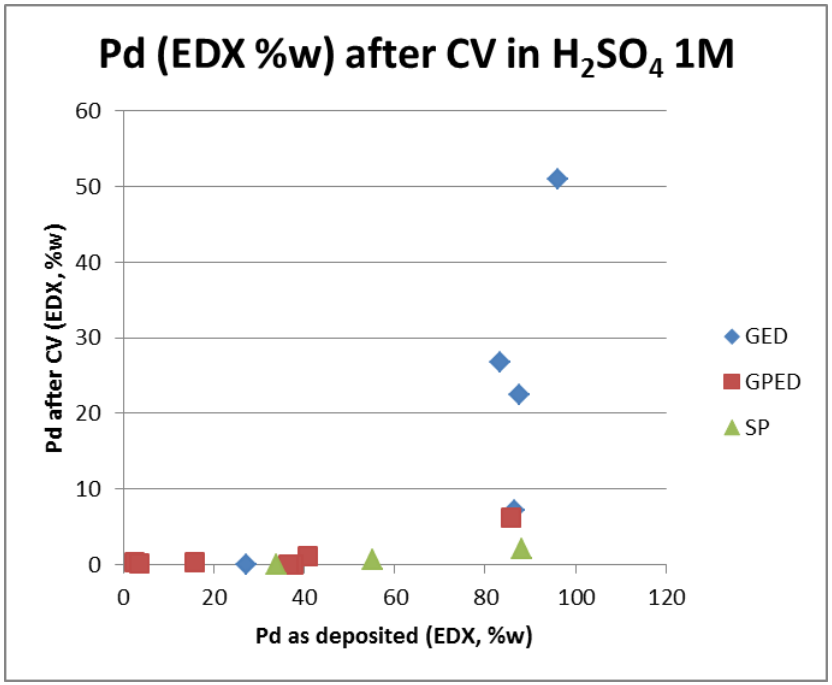


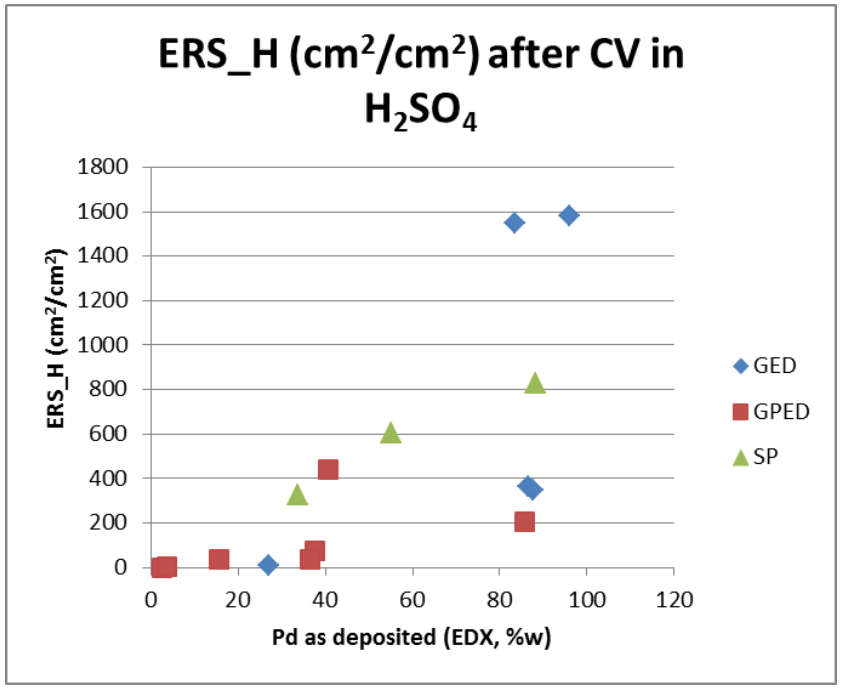
Cyclic voltammetry spectra in acidic solutions are recorded after different cycle numbers to evaluate catalysts stability.

ERS values change after cycling depending on the nominal Pd load and deposition technique.

GED samples deposited at higher loads seams to be more durable than GPED ones deposited by flowing the same total charge.

Pd content and ERS stability in acidic solutions





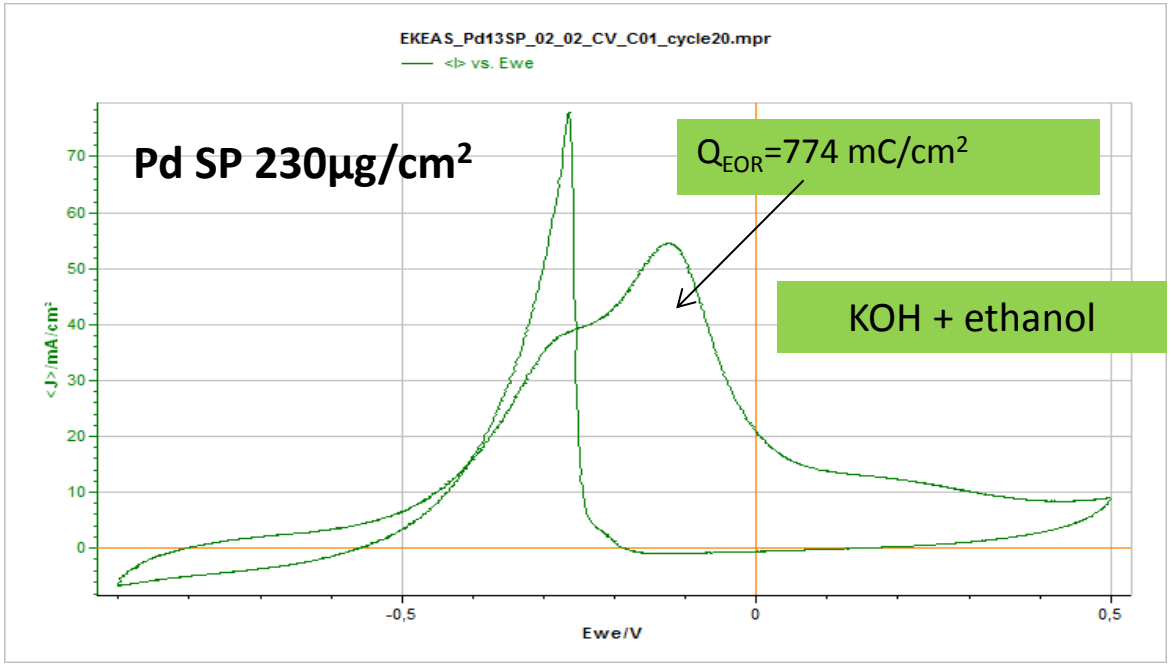
The residual Pd content after cycling in acidic solution shows a threshold behavior with the initial Pd load (≥80 % w, as measured by EDX).

For Pd initial loads higher than 40% ERS does not decrease consistently, despite the drastic decrease in the Pd content.

Electrochemical activity for ethanol oxidation

Cyclic Voltammetry

- working electrode: GDE
- counter-electrode: Pt
- REF: Hg/HgO/KOH 0,1M (-0.070 V vs. SCE)
- electrolyte: CH_3CH_2OH 1M in KOH 1 M
- Range: -0.9 V (vs. REF) ÷ 0,5 V (vs. REF)
- Scan rate: 20 mV/s

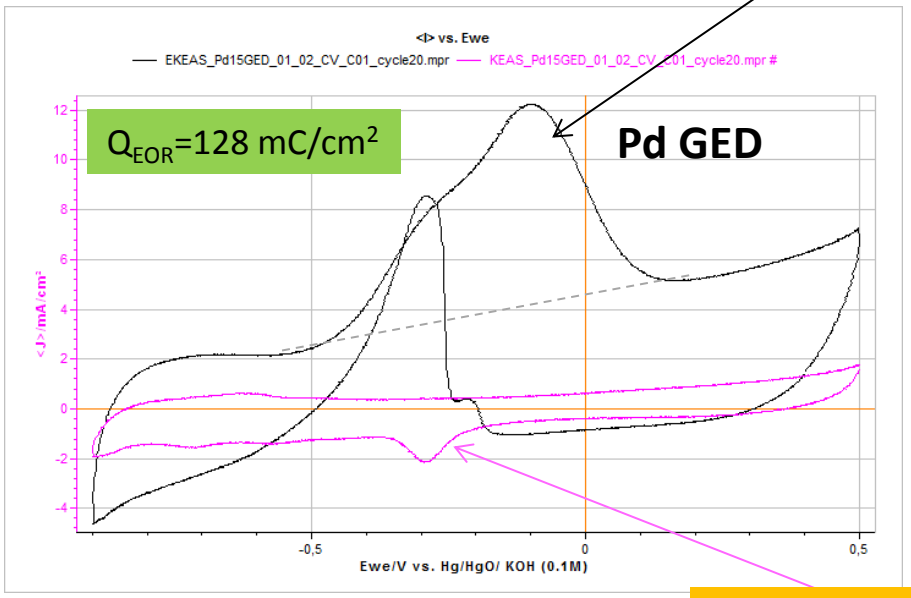


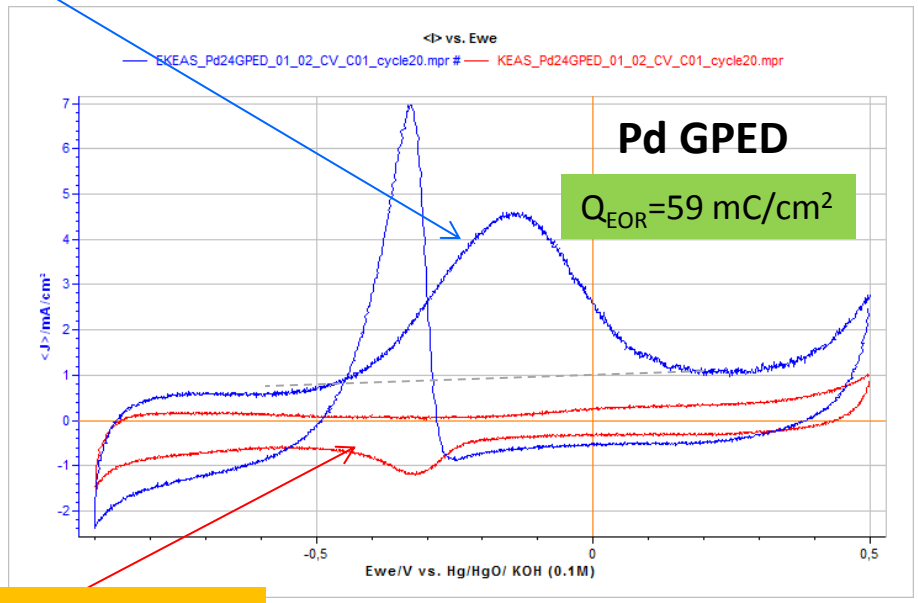
Results

- Electrochemical activity towards ethanol oxidation reaction (EOR) is revealed by the anodic peaks (-0,3 and -0,1 V vs. REF,) appearing in both the forward and reverse scan of CV spectra when ethanol is added to the alkaline solution.
- The charge corresponding to the forward scan anodic peak (Q_{EOR}) is related to the amount of oxidized ethanol.
- Q_{EOR} values are competitive with those found in literature for Pd catalyst with similar Pd load .

Electrochemical activity for ethanol oxidation

KOH + ethanol





KOH (without ethanol)

- GED and GPED Pd samples show appreciable Q_{EOR} even after the aggressive cycling in acidic solutions.

Conclusions

Pd catalysts have been deposited on nanostructured GDL electrodes by GED, GPED and sputtering, varying the total metal content.

Surface morphology and Pd coverage of the deposits have been related to the sequential phases of the growth process.

The electrochemical activity for hydrogen and ethanol oxidation has been characterized by cyclic voltammetry, respectively in acidic and alkaline solutions.

ERS values for Pd samples are comparable with that obtained for a Pt sample deposited in similar conditions, within a factor 2.

Q_{EOR} values are well competitive with those found in literature for Pd catalyst with similar Pd load.

Catalysts stability in acidic solutions has been tested showing that despite the drastic decrease of the Pd content after cycling in aggressive conditions ERS and Q_{EOR} values remain appreciable.

Perspectives

The potentiality of Pd to replace Pt in electrocatalysts for hydrogen fuel cells is promising as concerning the catalytic activity, but limited by poor stability in acidic solutions.

The potentiality of Pd electrocatalysts for ethanol oxidation in alkaline solutions is much higher than for use in acidic media.

The recent availability of anion exchange membranes (to be used in alkaline fuel cells) opens new perspectives and rises interest in Pd catalysts development for alcohol fuel cells.

Future work will be aimed to:

- Optimization of deposition techniques for enhanced catalyst activity toward ethanol oxidation and metal load minimization.
- Operating tests on prototype devices including the implemented catalysts and anion-exchange membranes.
- Optimization of deposition techniques to stabilize catalysts anchoring to support in acidic media.

Aknowledgments

The research activities on “Hydrogen transport through nano-structured electrodes for energy application) have been partially supported by the Italian Ministry of Foreign Affairs within the frame of Significant Bilateral Projects (Joint Declaration following the 10th Review Conference on Scientific and Technological Cooperation between Italy and the United States of America for the years 2011-2013).