

IEI Conferenza d'Istituto

29 febbraio – 1 marzo 2016

Composizione del Gruppo

Marco Musiani, Dirigente di ricerca

Sandro Cattarin, Primo ricercatore

Nicola Comisso, Ricercatore

Lourdes Vazquez-Gomez, Ricercatore

Enrico Verlato, CTER

Luca Mattarozzi, CTER TD

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Generalità sull'Attività di Ricerca

- Vari metodi chimici ed elettrochimici vengono impiegati nella preparazione e caratterizzazione di materiali per applicazioni in energetica, sensoristica e protezione anti-corrosione.
- L'attività combina aspetti di elettrodeposizione (o deposizione spontanea) ed elettrocatalisi (per elettrolizzatori o elettroanalisi).
- Le tecniche elettrochimiche impiegate comprendono voltammetria, cronoamperometria, cronopotenziometria, impedenza.
- Grazie all'apporto di colleghi IENI, si utilizzano più o meno regolarmente SEM, EDS, XRD, MS ...

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Comunicazioni

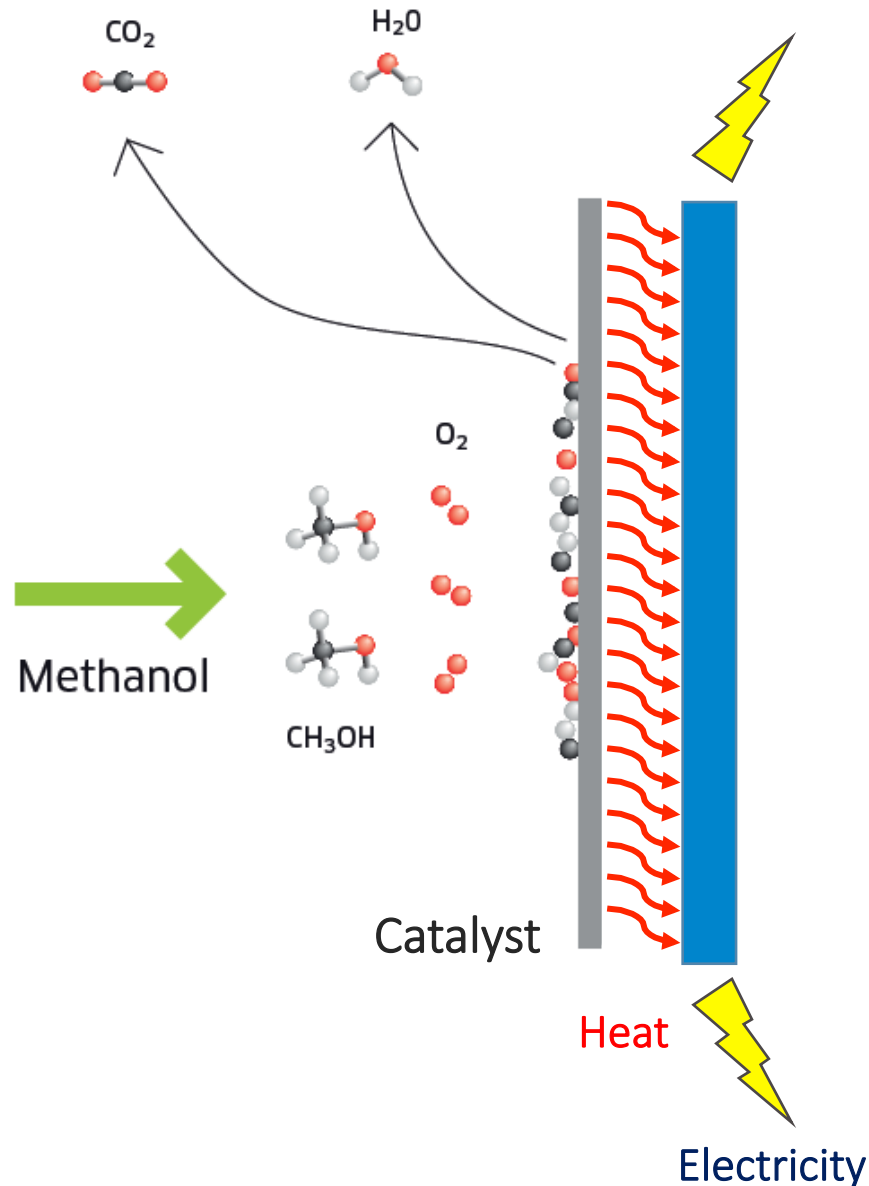
- **Marco Musiani** - Preparazione di catalizzatori per combustione catalitica mediante modifica elettrochimica di schiume metalliche
- **Luca Mattarozzi** - Elettrodeposizione di metalli porosi e leghe metalliche porose: loro applicazioni
- **Nicola Comisso** - Elettrodeposizione di ossidi metallici porosi

Preparazione di catalizzatori per combustione catalitica mediante modifica elettrochimica di schiume metalliche

Progetto finanziato da MSE – Ricerca di sistema

Collaborazione con Istituto Ricerche sulla Combustione IRC – CNR Napoli

Catalytic Combustion vs. Flame Combustion



- Ultra low emissions NO_x , CO, VOC
- Stable in wide operating range: outside “normal” flammability
- Suitable for micro burners
- Well suited for **process intensification** via integration with heat-exchanger

- Heat produced directly on a solid surface (catalyst) rather than in gas phase
- Efficiently transferred to drive:
 - Thermo Electric Generators
 - Photo Voltaics Cells
 - Fuel Reformers/ Fuel Cells
- Decentralized Combined Heat and Power generation, Portable devices



Structured Catalysts / Catalytic Burners



Metallic Open Cell Foams

- Large geometric contact area
- Enhanced mass/heat transfer
- Light-weight / Low thermal inertia
- High mechanic and thermal resistance
- Extremely low pressure drops
- Shaped in almost any geometry
- Tailored properties: Porosity, Density, Thermal conductivity, ...

Active phase:

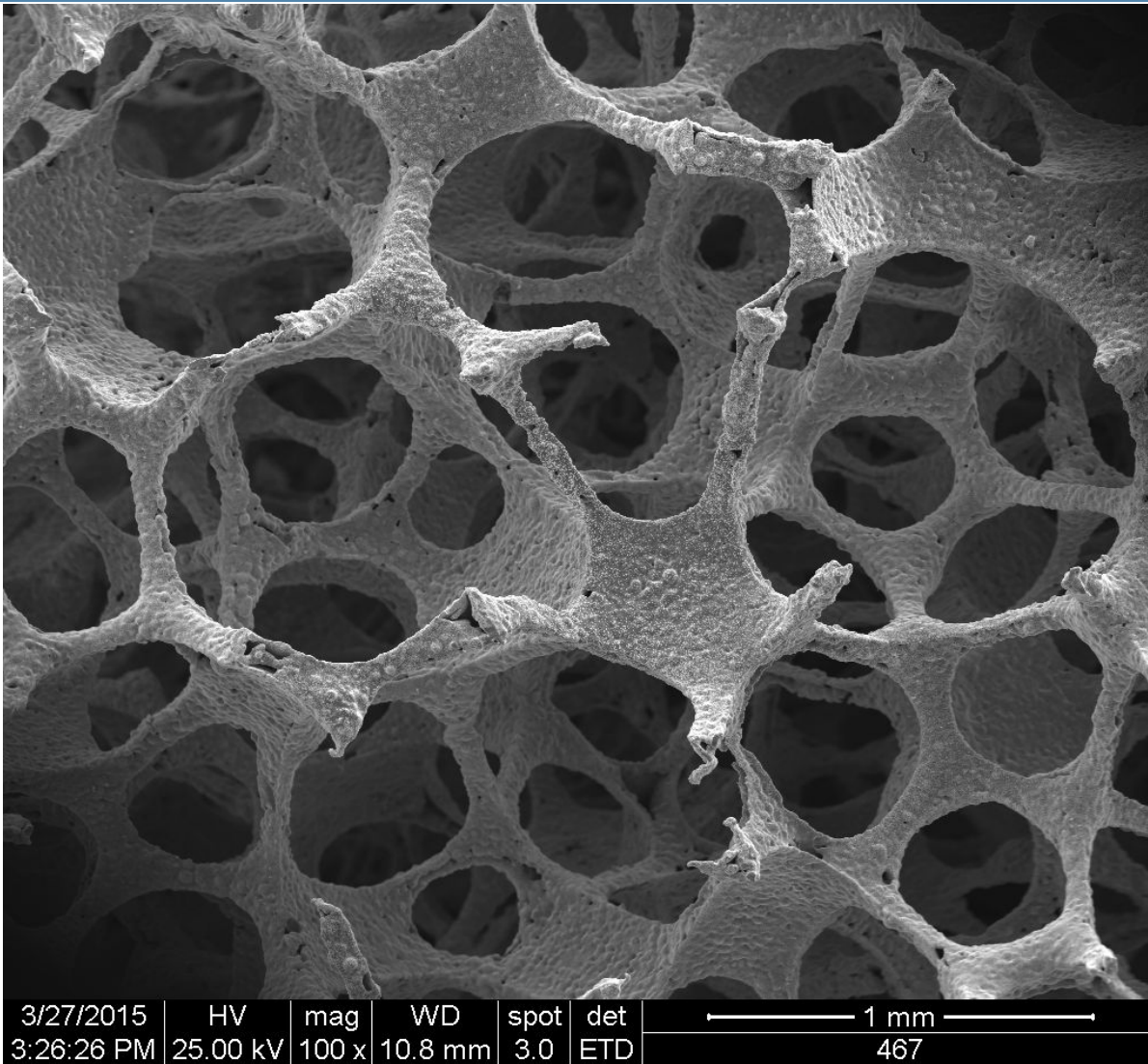
- ✓ Supported Noble Metals Pt, Rh, Pd dispersed on intermediate washcoat layer
- ✗ Cumbersome preparation methods / inhomogeneous coating / pore blocking

State-of-the-Art Preparation of LTC or CPO Catalysts

The procedure for the preparation of supported catalyst is quite complex. An example:

- (i) growth of an Al_2O_3 layer on the FeCrAlloy support (5 min at 1200°C , in O_2 0.5 vol% in N_2);
- (ii) γ -alumina powder is prepared by reacting aluminum nitrate with urea at 600°C (with different amounts of La as stabilizer);
- (iii) impregnation of alumina with $\text{Pd}(\text{NO}_3)_2$ aqueous solution, drying at 120° overnight, calcination at 500°C in air for 2 h to obtain PdO, or hydrogen reduction at 400°C to obtain metallic Pd;
- (iv) preparation of a slurry of the Pd-alumina catalyst and methyl cellulose in diluted nitric acid solution;
- (v) repetitive dipping and drying of the FeCrAlloy support in the slurry;
- (vi) final calcination at 1000°C for 12 h.

Fecralloy Foam



Fecralloy	Fe	Cr	Al
20 ppi	72.1	19.6	8.2
30 ppi	69.5	20.3	10.2
50 ppi	70.1	20.8	9.1
60 ppi	71.0	20.1	8.9
80 ppi	68.2	23.6	8.2

50 ppi foam

0.34 g cm⁻³ apparent density

95% void volume

Excellent mechanical stability

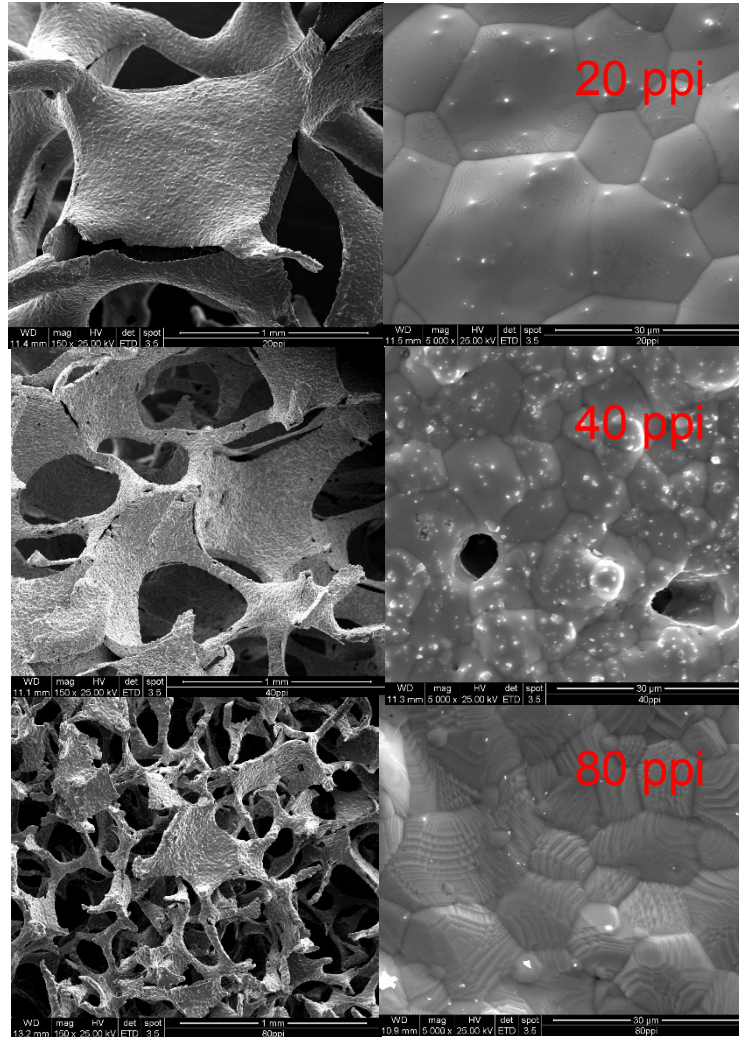
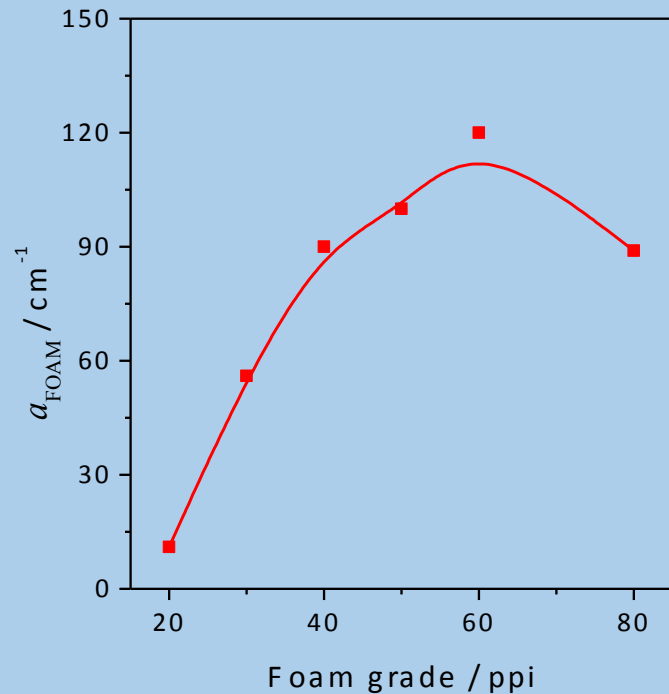
Outstanding resistance high temperatures

Easy mass/heat transport

Very good electrical conductivity

Fecralloy: not only advantages

The specific surface area, estimated by EIS, does not always increase with the grade



Foams with different grade have different micro-roughness

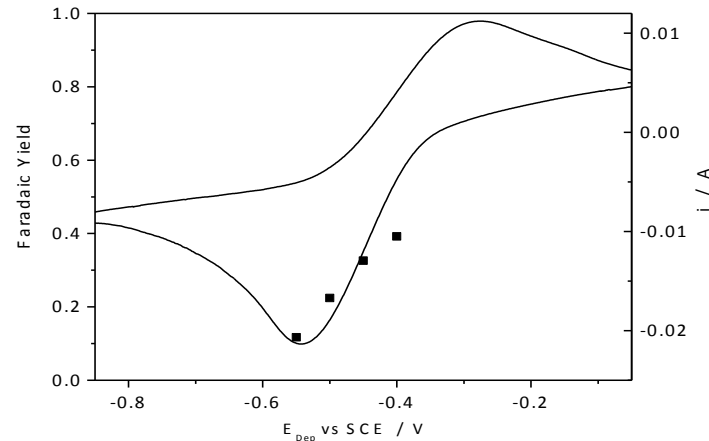
Unreliable manufacturing

Different batches of 50 ppi Fecralloy foams have specific surface area between 35 and 100 cm^{-1}

Pt Electrodeposition onto FeCrAlloy Foam electrodes

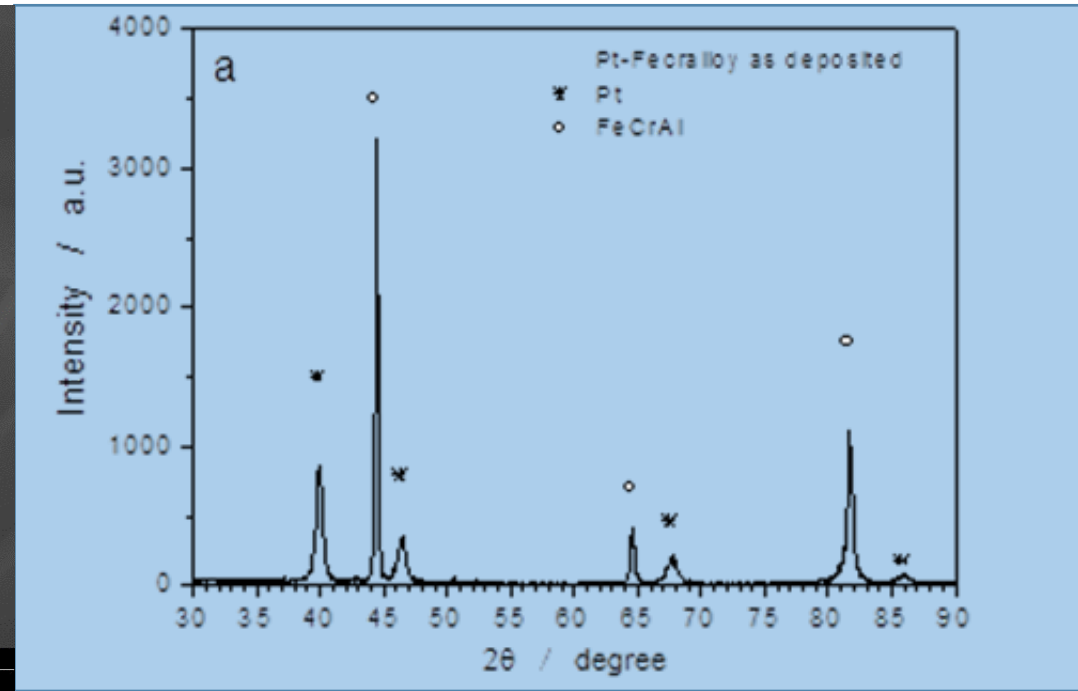
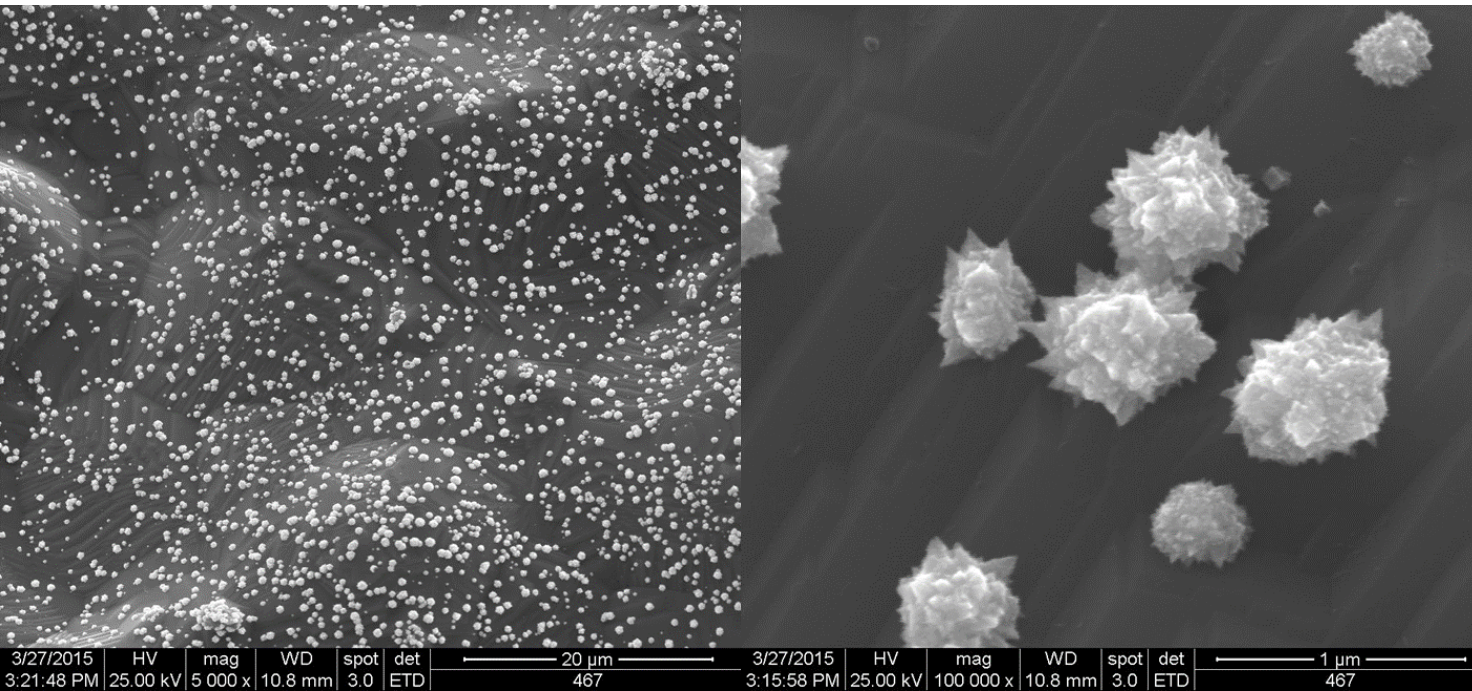
Experimental conditions

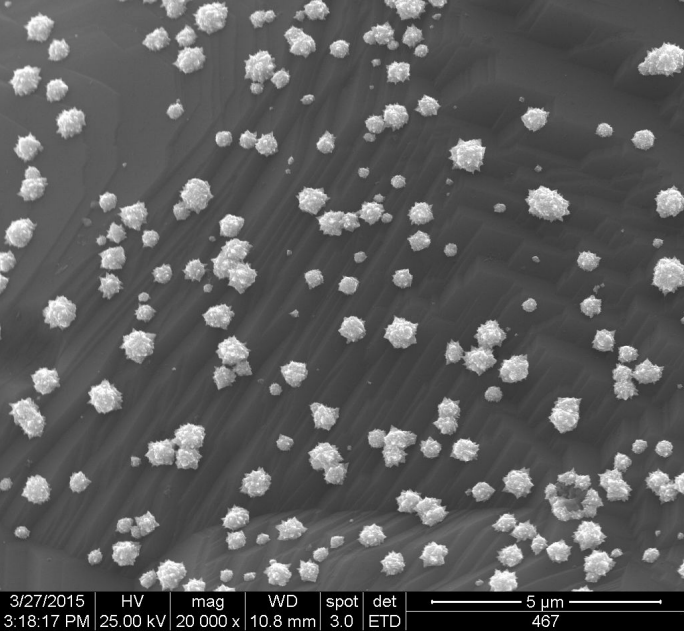
- FeCrAlloy foam samples were washed with dichloromethane, acetone and water
- Deposition at -0.4 V vs. SCE in 1×10^{-3} M or 2×10^{-3} M H_2PtCl_6 , at pH 2.0
- Current efficiency 35-40%.



Pt Loading 0.1 to 15 mg cm⁻³

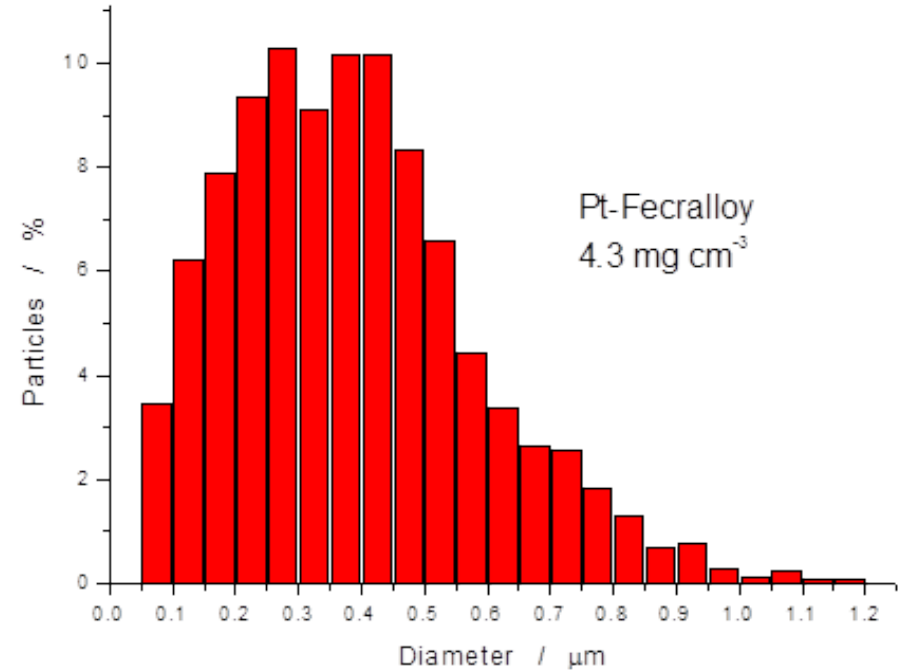
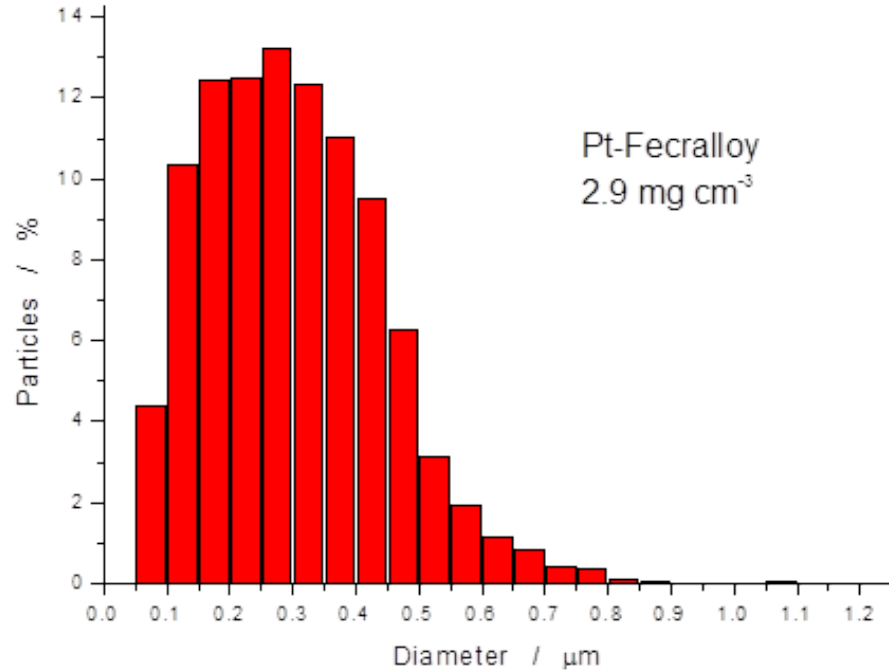
controlled through deposition charge and checked with UV-Vis spectroscopy.





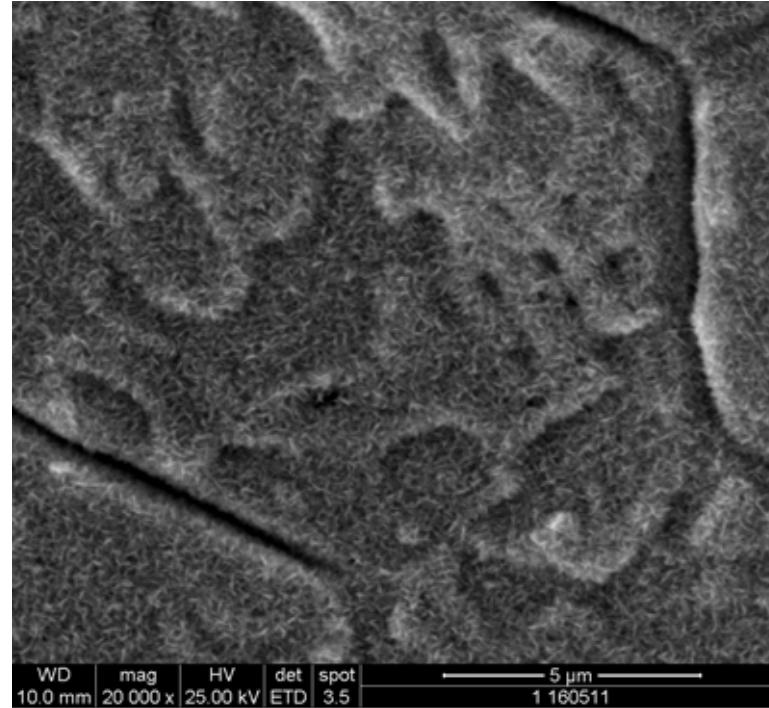
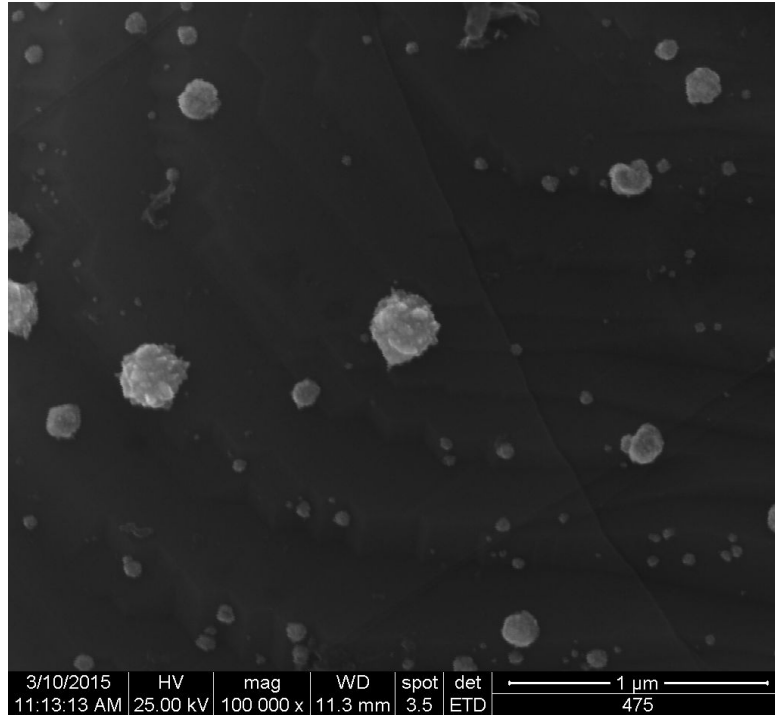
Pt Loading	Number of particles	Pt covered area
2.9 mg cm ⁻³	8.6 x 10 ⁷ cm ⁻²	9.9 %
4.3 mg cm ⁻³	8.65 x 10 ⁷ cm ⁻²	16.4 %

Pt particles are nucleated simultaneously at the most reactive sites. Then they grow in size, not in number

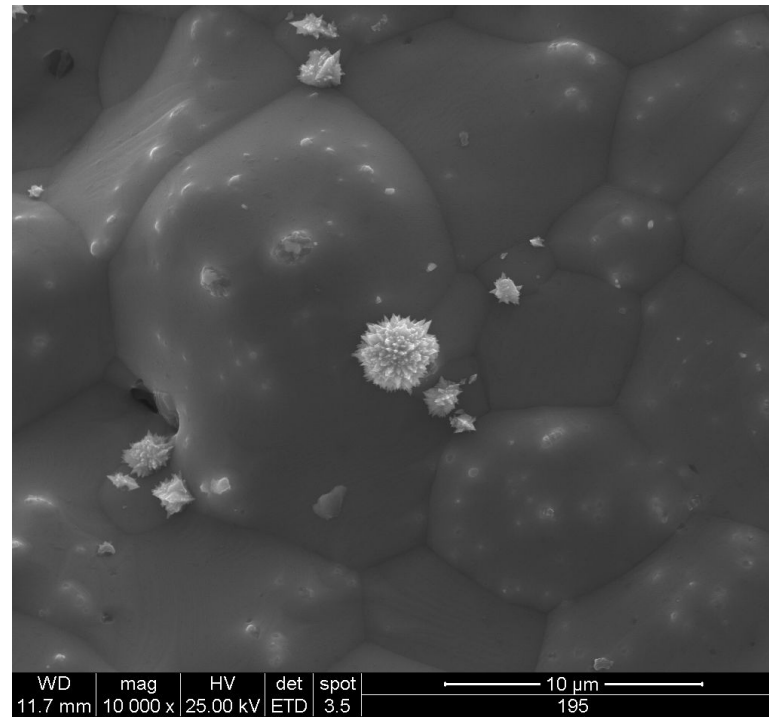


The chemical nature and surface state of the foam influenced the morphology of the deposits more than the nature of the noble metal or the deposition mode.

Pt-Fecralloy
Electrodeposition



Pt-Ni Foam
Galvanic displacement

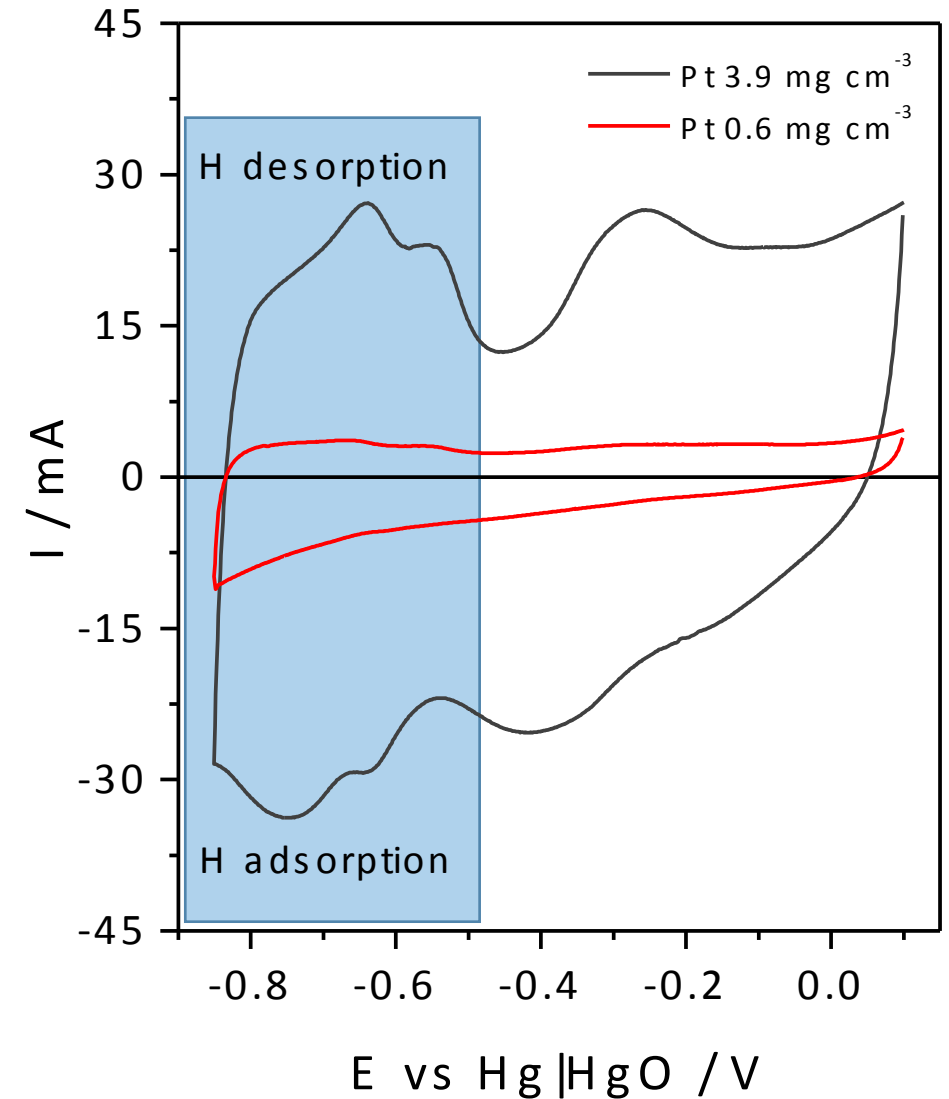


Pd-Fecralloy
Galvanic displacement

Pt electrochemically active surface area

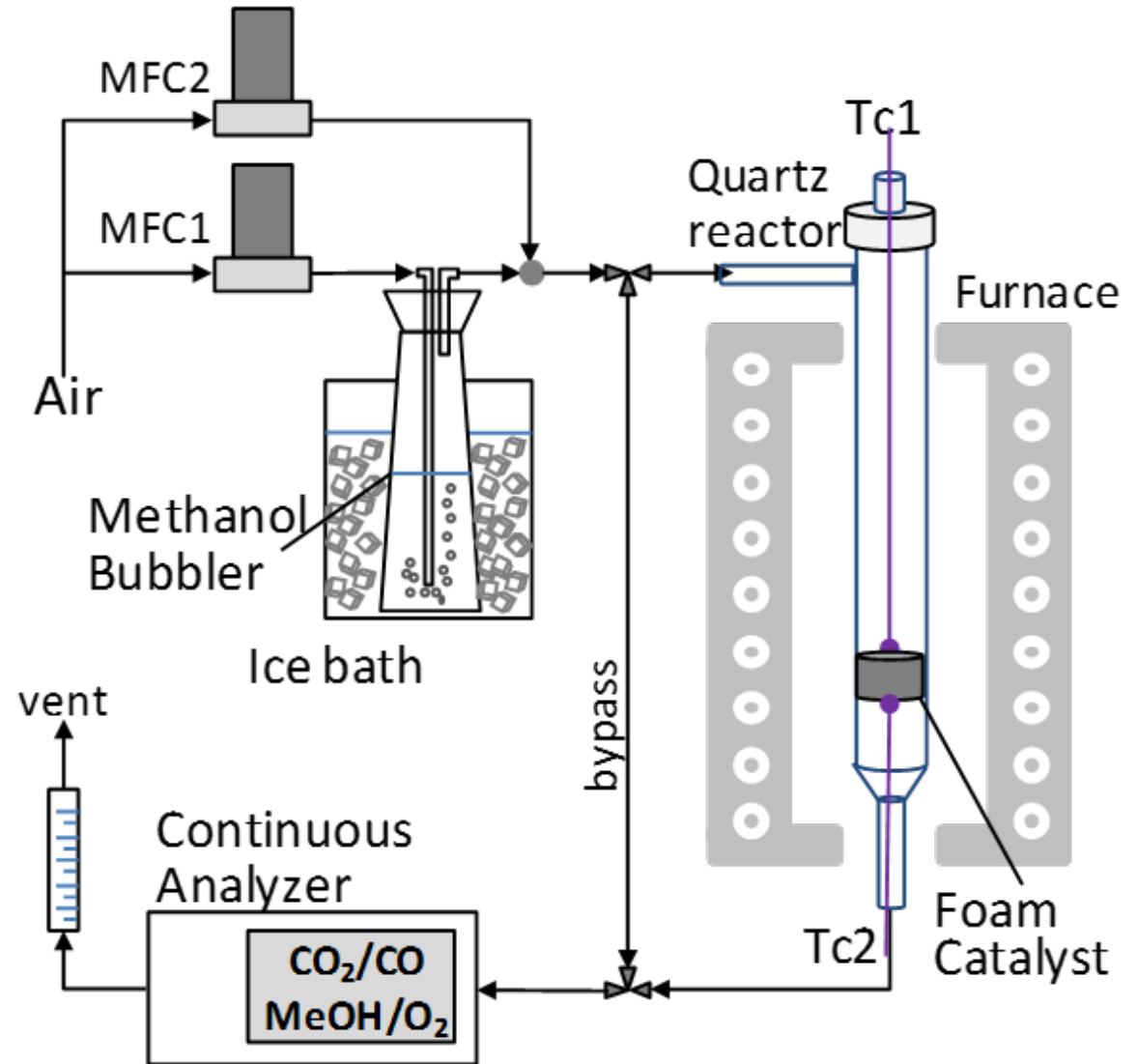
It may be estimated from the hydrogen adsorption/desorption charge (in 1M KOH).

$[\text{H}_2\text{PtCl}_6] \times 10^3$ M	Pt Loading mg cm^{-3}	Pt surface area $\text{m}^2 \text{g}^{-1}$
1	0.14	6.1
1	0.47	5.4
1	0.62	5.6
1	1.38	5.6
1	1.62	7.7
1	1.93	7.4
2	1.73	22.2
2	2.95	15.7
2	4.29	14.0
2	10.8	12.3



Low-temperature Catalytic Combustion of CH₃OH

- Pt-Fecralloy catalysts were tested under lean dry conditions.
- The reactor was operated at nearly atmospheric pressure, under pseudo-isothermal conditions.
- Temperature was ramped from **50°C to 600°C (3°C/min)**.
- A lean methanol in air feed (**0.5 – 2.0 % vol.**) was prepared by mixing two air streams, one of which was passed through a methanol saturator. Total flow-rate to the reactor was normally set at 40 Sdm³ h⁻¹.



Low-temperature Catalytic Combustion of CH₃OH

- The effluent gas was continuously analyzed for CO, CO₂, CH₄, NO and O₂. The CH₄ detector gave a linear response to methanol, thus it was used to measure its concentration in the feed stream after a specific calibration.
- The removal of water formed in the products before the analysis precluded a correct measurement of the outlet methanol concentration.
- The methanol yield to CO₂ (y_{CO_2}) was defined as the molar ratio of CO₂ formed (outlet) per methanol in the feed.
- The CO₂ production rate was normalized vs. foam volume, Pt mass and Pt surface area.

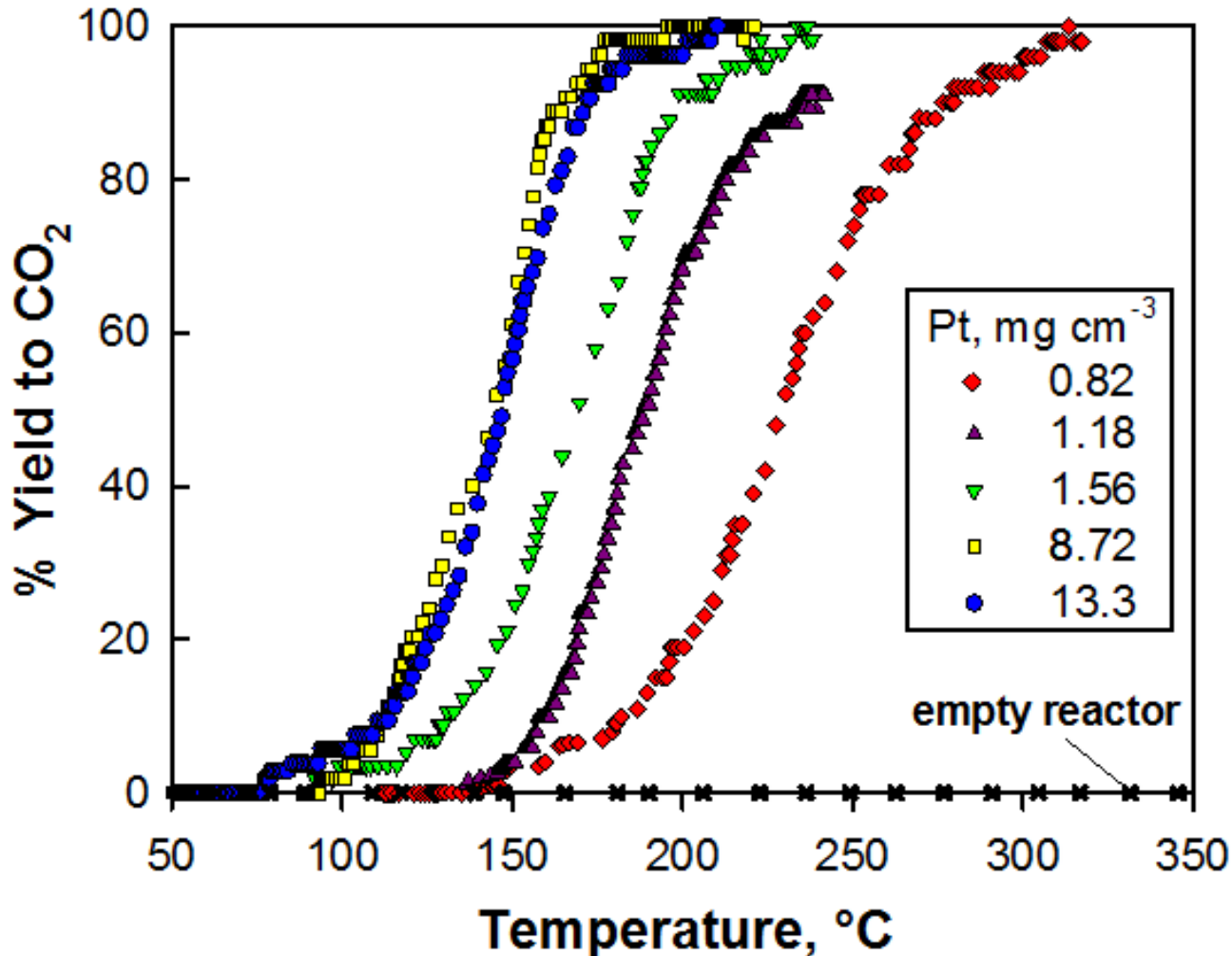
$$R_v CO_2 \cong \frac{F \cdot y_{CO_2}}{V_{Foam}}$$

$$R_w CO_2 \cong \frac{F \cdot y_{CO_2}}{W_{Pt}}$$

$$R_s CO_2 \cong \frac{F \cdot y_{CO_2}}{A_{Pt}}$$

The apparent activation energy of the catalytic deep oxidation was estimated by Arrhenius plots of $R_w CO_2$

Low-temperature Catalytic Combustion of CH₃OH



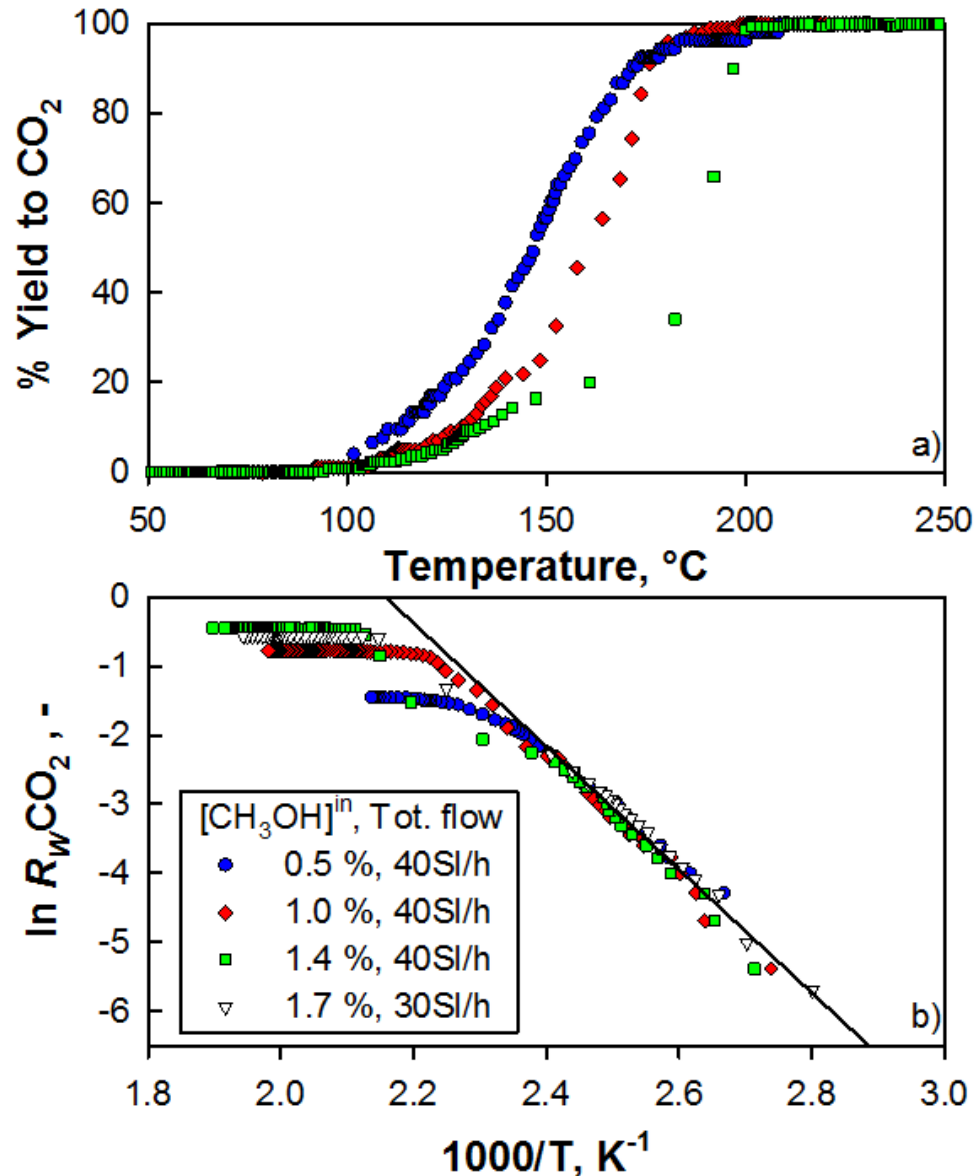
Homogeneous oxidation of CH₃OH (empty reactor): 550-750° (much CO at low T).

Oxidation of CH₃OH on blank Fecralloy foam: 375-700°C (comparable CO and CO₂).

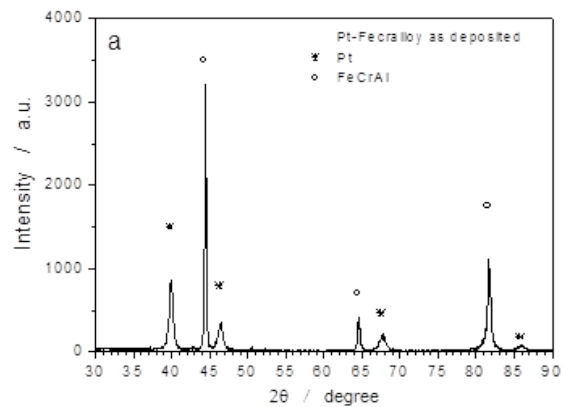
Oxidation of CH₃OH on Pt-Fecralloy:

- 80-300°C
- Negligible CO production
- O₂ consumption 1.5 times CO₂ production:
$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$$
- Higher Pt loading causes higher activity (a 16 times increase in Pt mass causes a 70°C decrease of temperature at 10% conversion).

Low-temperature Catalytic Combustion of CH₃OH



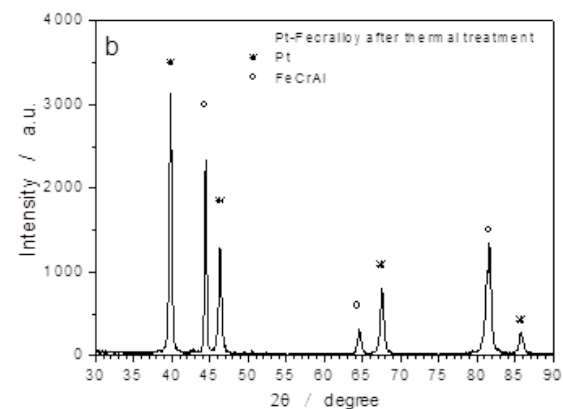
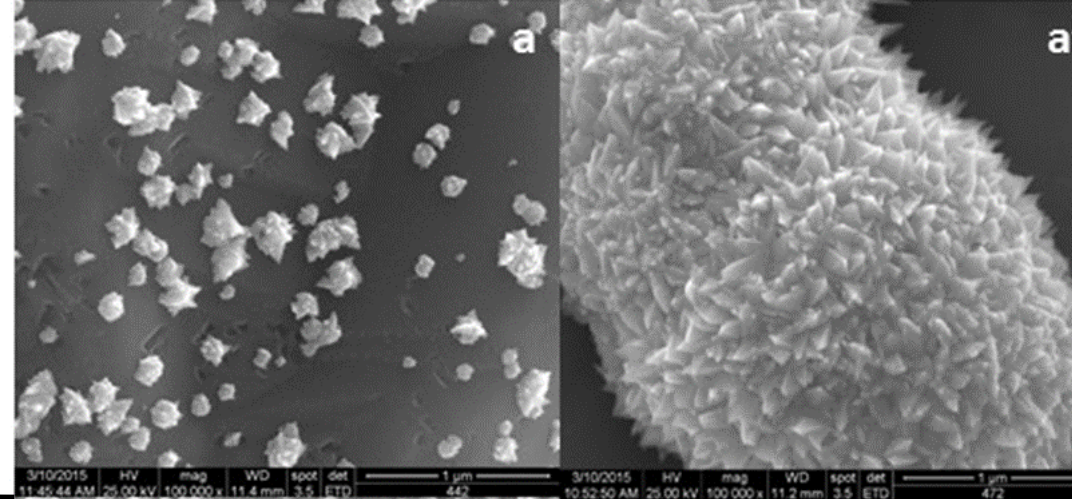
- No diffusion limitations.
- CO₂ formation rate independent of the concentration of methanol (0.2 – 2.0% vol.): quasi 0th order.
- Apparent activation energy of CH₃OH combustion: 68-70 kJ mol⁻¹, in agreement with literature
- The CO₂ formation rate per unit Pt mass has a sharp maximum around 1.5 mg cm⁻².
- Oxidation rates do not correlate with Pt surface area.
- A synergistic role of Pt and oxides on the Fecralloy substrate (e.g. FeOx) is suggested.



Pt-Fecralloy

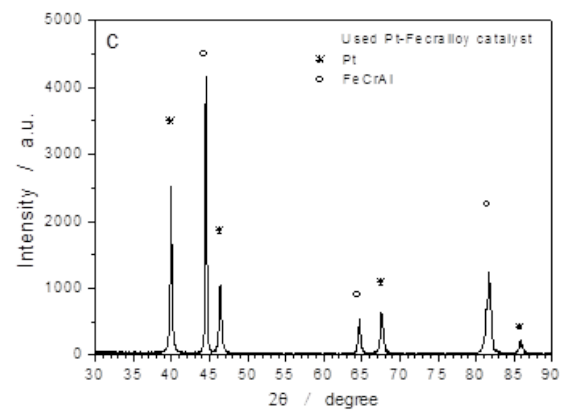
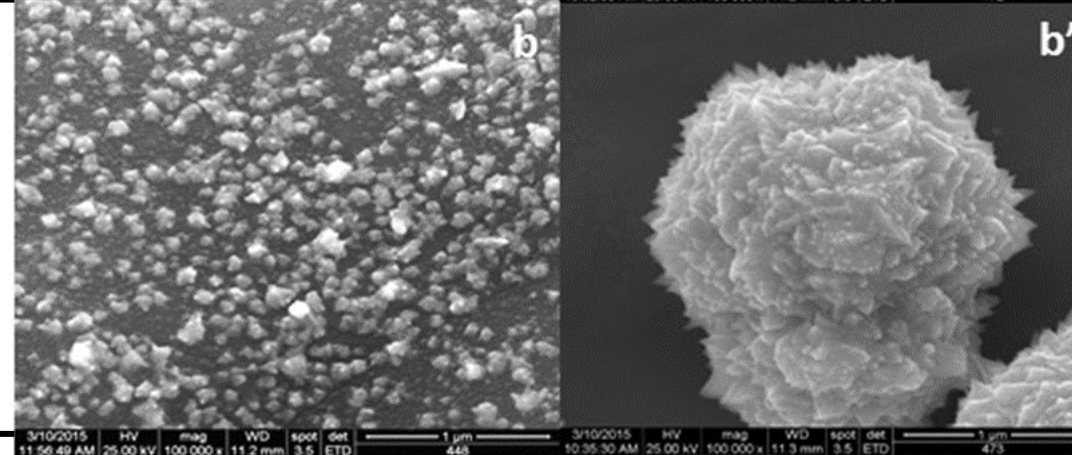
As-prepared

Estimated Pt crystallite size: 40 nm



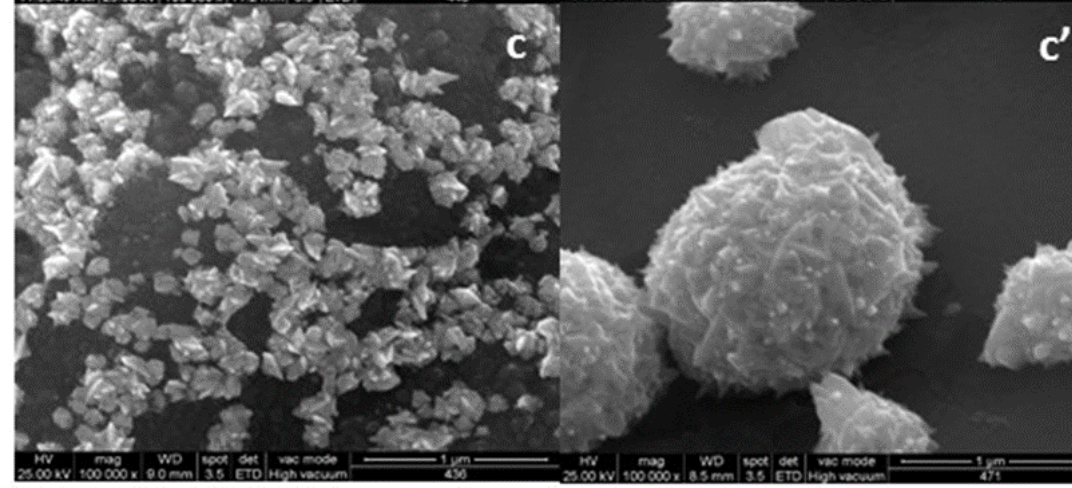
Treated in air at 600°C for 2 hours

Estimated Pt crystallite size: 65 nm

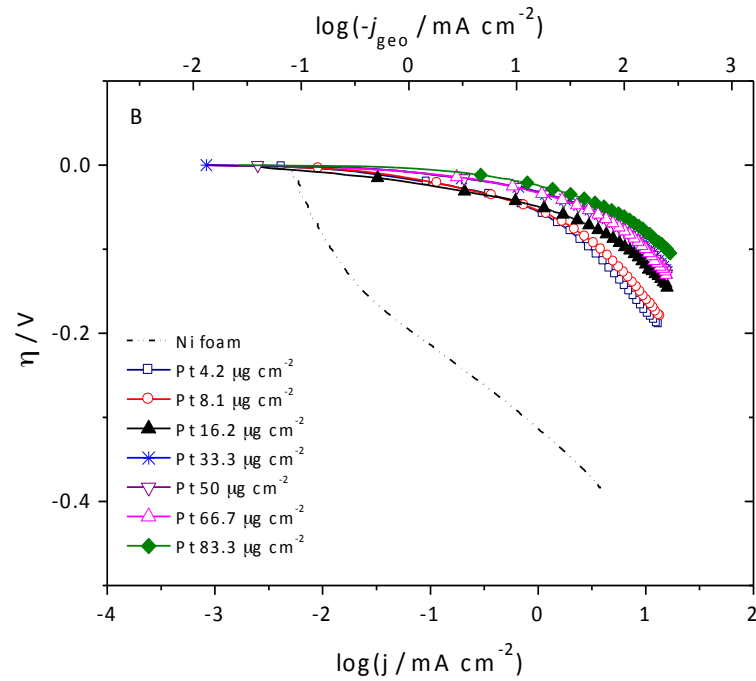


Used in the catalytic combustion of
 CH_3OH

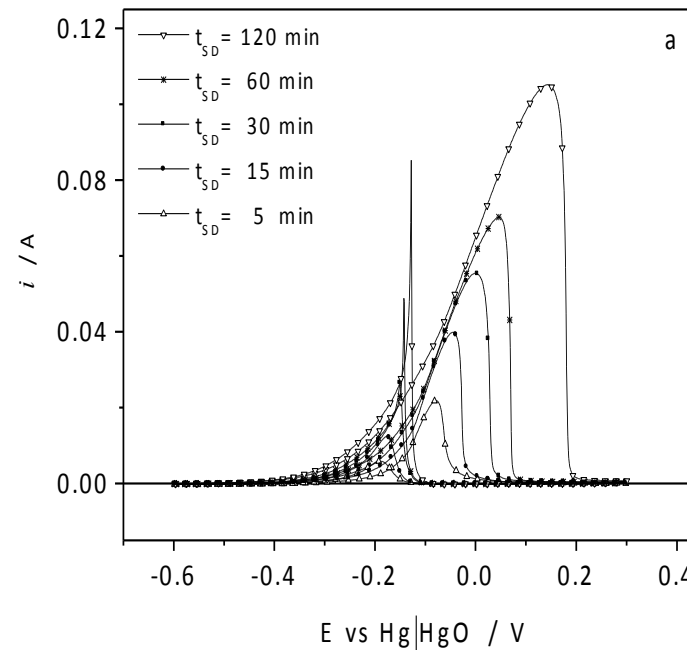
Estimated Pt crystallite size: 55 nm



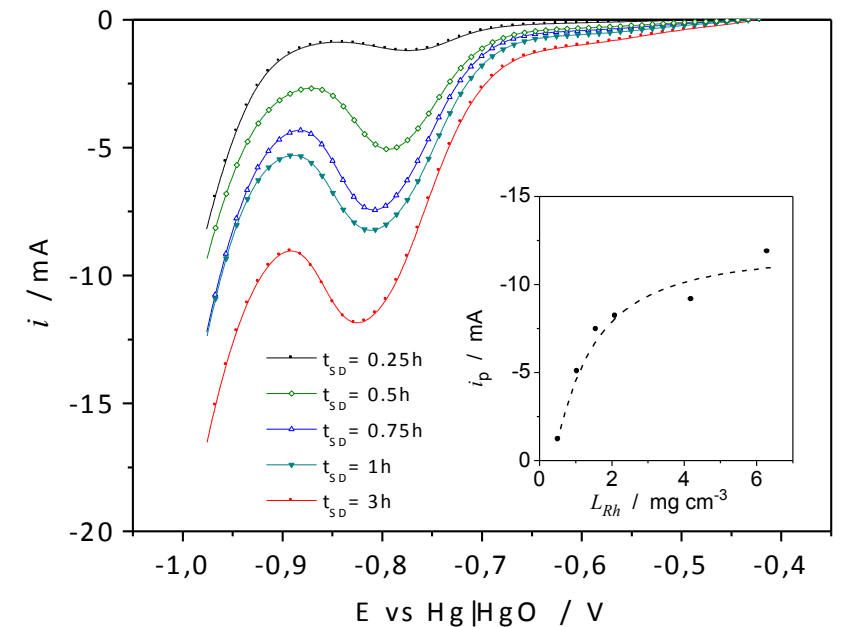
Noble metal modified Ni foam 3D Electrodes



Pt-Ni for HER



Pd-Ni for methanol oxidation



Rh-Ni for nitrate reduction