PLANOVOC
PLAsma technologies assisted by naNOporous substrates for VOCs breakdown

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UNIVERSITÀ DEGLI STUDI DI TORINO

TORINO

University of Torino was founded in
1404 by Ludovico
of Savoia

ILLUSTRIOUS ALUMNI AND TEACHERS

The first famous graduate: **Erasmus of Rotterdam**, **1506**

Famous scientists and leading personalities who were students or teachers here throughout the centuries:
L. Lagrange, A. Avogadro, A.L. Cauchy, S. Cannizzaro, A. Sobrero, G. Peano, A. Gramsci, P. Levi, C. Pavese, P. Gobetti, P. Togliatti, N. Bobbio

Nobel Prize laureates:
S. E. Luria, R. Dulbecco, R. Levi Montalcini

Heads of State: **L. Einaudi, G. Saragat**.

4

74000 Students
2000 Teach-Res
1800 Tech-Admin
750 M€ Budget
6 Schools
27 Departments
1 PhD School

International rankings (2018)

2nd in **Italy** and among the **top 300** Universities worldwide, for **ARWU Shangai**

6th in **Italy** and **171st worldwide** for **NTU Taiwan**

8th in **Italy** and **232nd** worldwide for **US News Best Global Universities**

2nd in **Italy** and **47th** worldwide for **Greenmetric** universities sustainability ranking

3rd in Italy with **10 departments selected** aby the Italian Ministry of Education, Universitiy and Research (MIUR) as "**Dipartimenti di Eccellenza**" (Departments of Excellence)

over **€ 11 million** earned through research and consultancy activities (2017)*

The Chemistry Department

Establishment

The new Department was established in **2012** as a result of the recent innovation of the Italian University system.
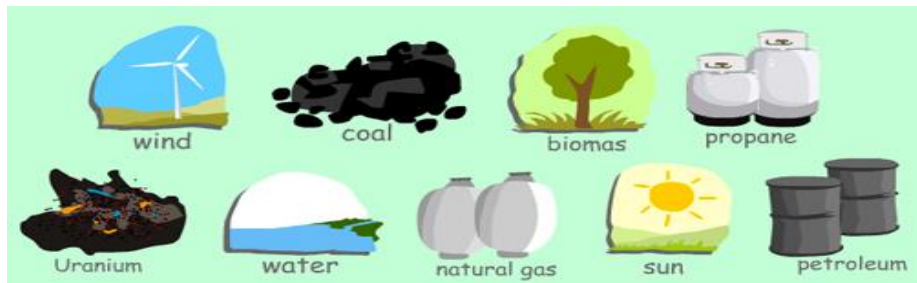
Staff

The Department's STAFF includes about **250** professors, researchers, technicians and administrative employees. The doctorate students and post-doc researchers are about one half of the staff.
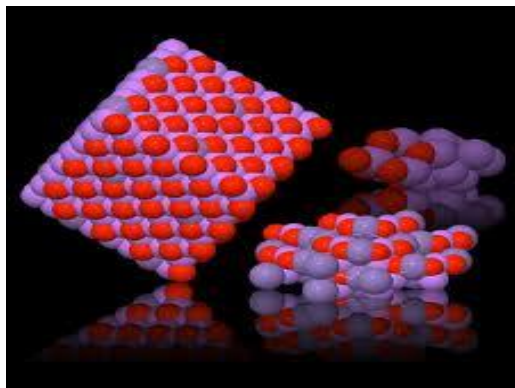
Students

Teaching activities at the Department of Chemistry involve about **2.000** students

Our vision

Better use of natural resources

Human Health

New materials

Cultural heritage protection

New clean-energy technologies

Industrial collaborations

The collaboration with industries reaches an overall budget of about **2 M€ per year**.

3 Spin-offs

26 patent applications between 2010-2015 (4 patents per year on average)
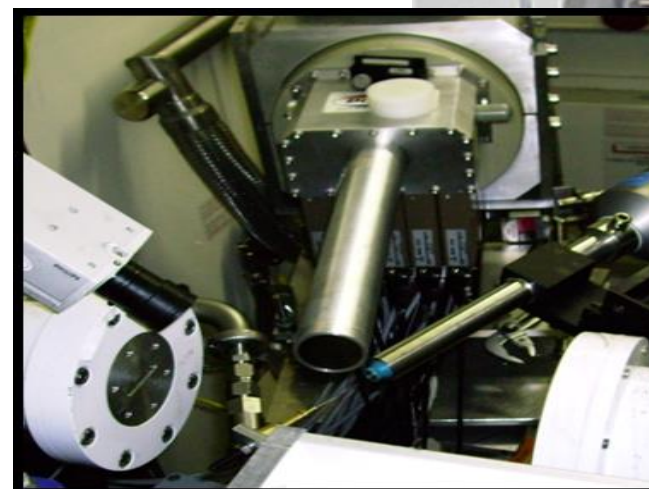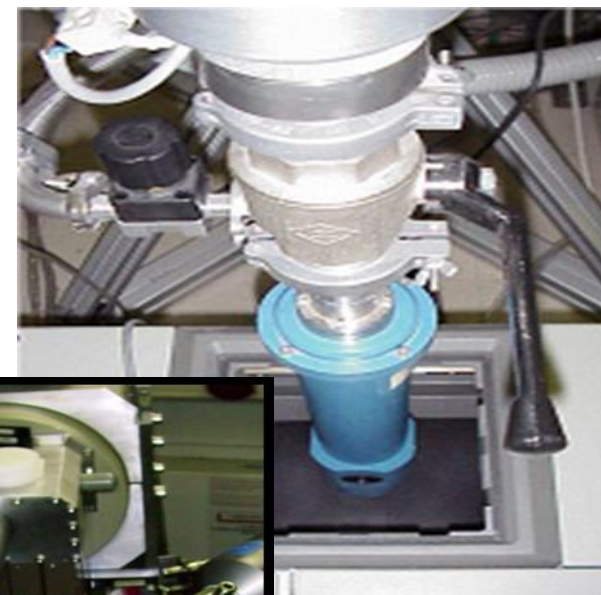
More than 50 ongoing contracts

Facilities and Equipment

The Department of Chemistry and individual research groups collectively maintain a **MULTI-MILLION EUROS INVENTORY OF STATE-OF-THE-ART INSTRUMENTATION**

➢ Synthesis Facilities

➢ Vibrational and Electronic Spectroscopies

➢ Magnetic Resonance Spectroscopies

➢ X-ray diffraction

➢ Chromatography

➢ Mass spectroscopy

➢ Computational Facilities

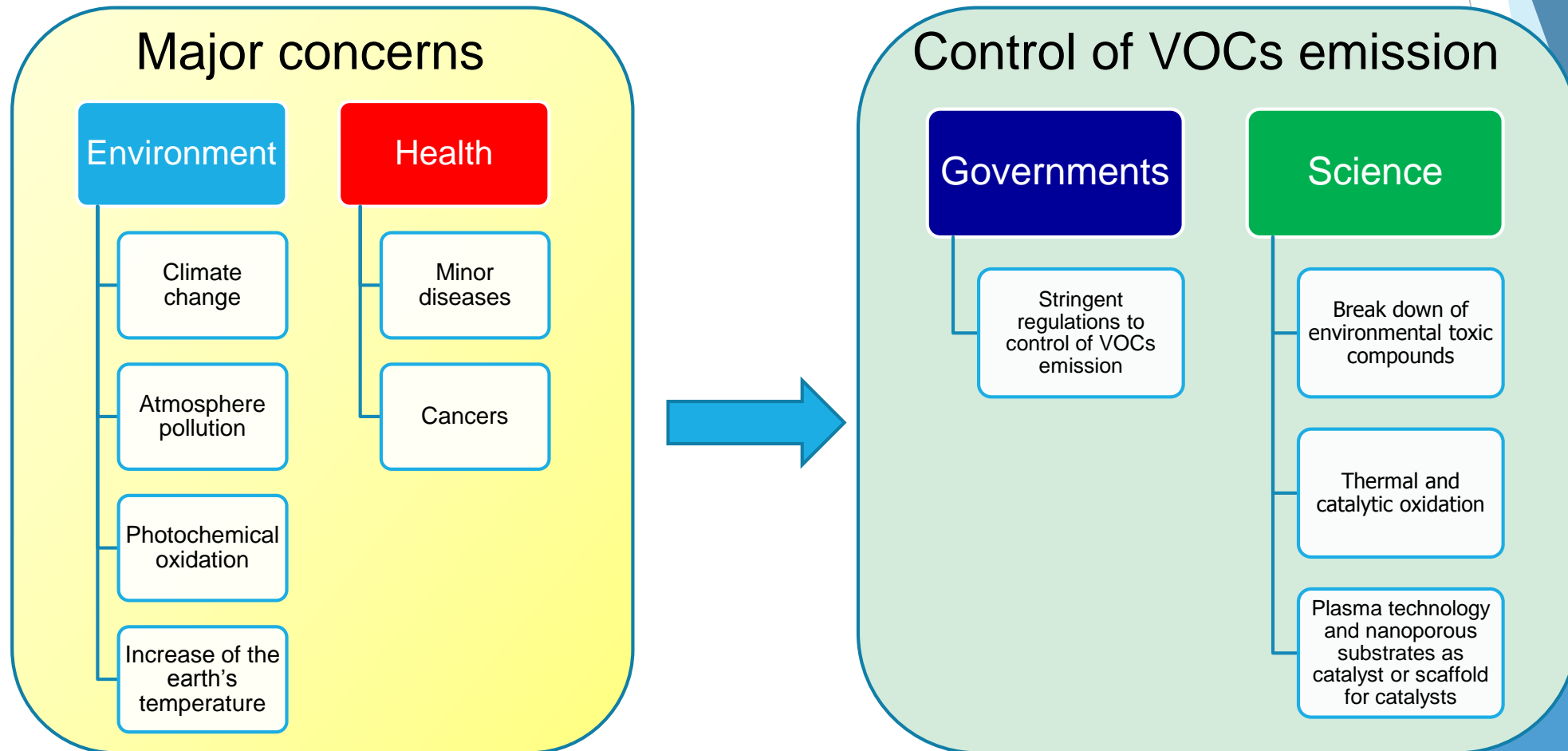➢ Teaching Laboratory Facilities

➢ 600 MHz NMR spectroscopes

www.unito.it/sites/default/files/elenco_infrastrutture_ricerca_maggio2019.pdf

- ❑ *Introduction*
  - ❑ *Motivation*
  - ❑ *Nanoporous Materials*
  - ❑ *De-alloying and porous metals*
  - ❑ *Nanoporous metals for plasma technology*
  - ❑ *Hints and cases from the literature*
- ❑ *Nanoporous substrates for plasma assisted VOC breakdown*

OUTLINE

Motivation

Volatile Organic Compounds (VOCs): most common air pollutants emitted from petrochemical and manufacturing industries (i.e. solvent thinners, degreasers, cleaners, lubricants, liquid fuels and molecules as methane, ethane, tetrachloroethane, methyl chloride, various chlorohydrocarbons, perfluorocarbons and dioxins).
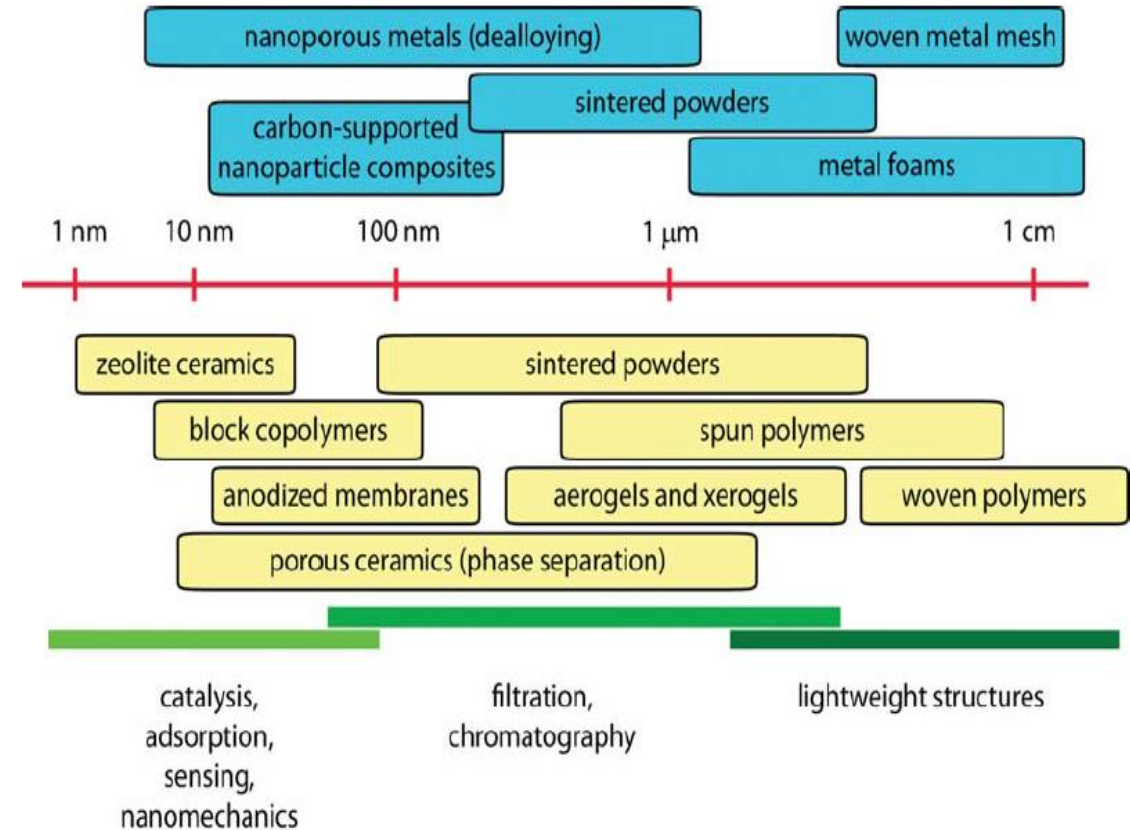
Nanoporous Materials

❑ Promising class of materials formed by a network of ligaments and pores.

Main features:

✓ drastically reduction of their mass (compared to the bulk one)

✓ relevant increase of their surface area.

✓ Interesting properties and applications vs size of pores and ligaments [1,2];

[1] Wilkinson, A. D. M. a. A., *Blackwell Scientific Publications, 2 edition* (1997)
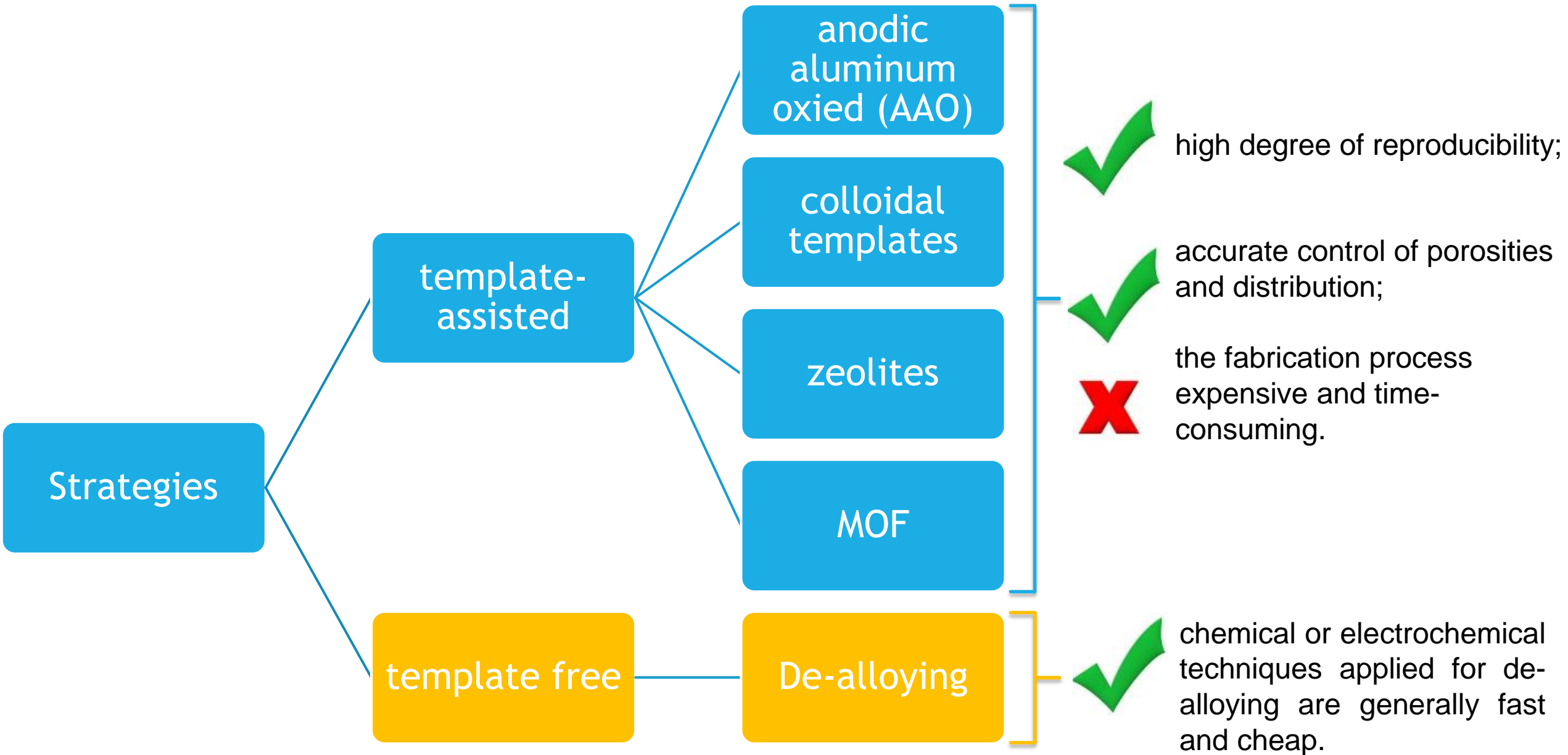[2] Erlebacher, J., and Seshadri, R., *MRS Bulletin* (2011) **34** (8), 561

A hierarchy of porous materials, with average pore size increasing from left to right. Conductors are shown in blue and insulators in yellow. Applications for porous materials with distribution of length scales are shown in green. Adapted from reference [2].
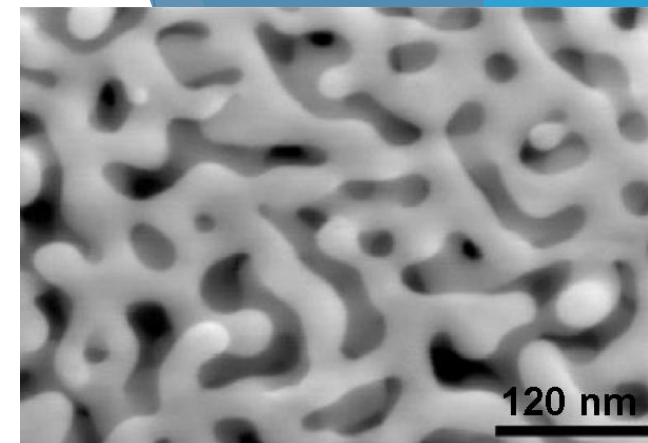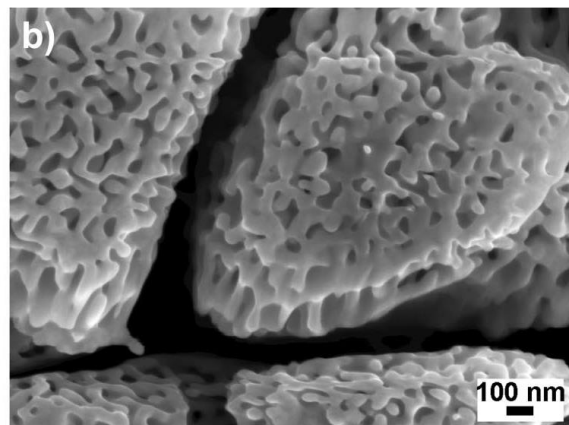
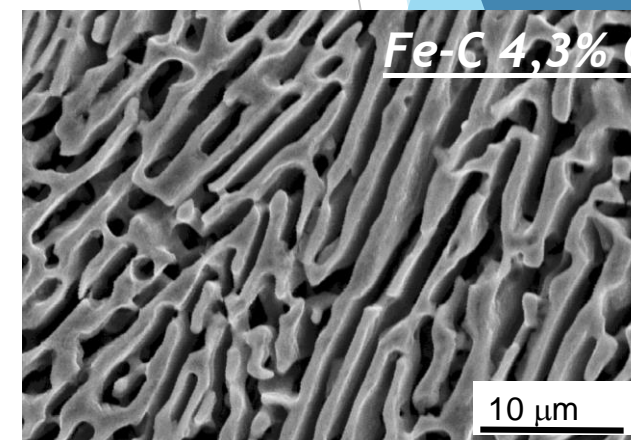# Strategies for Nanoporous materials

De-alloying and porous metals

De-alloying is defined as a selective removal of a phase or an element from a bulk alloy, either by chemical or electrochemical means with formation of a porous material made of the noble element.

❑ in the 60s of the XX century:
➢ studied as a corrosion problem on brasses;
❑ in solid solutions of binary systems,
➢ Au-Cu, Au-Ag[3], Au-Sn and Cu-Mn, Cu-Zr, Ti-Al;
❑ in binary systems removing a single   phase
➢ Au-Al[4] (bimodal distr. pores)
❑ in Fe-C eutectics or eutectoids[5], Ni-base superalloys

120 nm

[3] J. Erlebacher et al., Nature 2001

Fe-C 4,3% C

10 µm

[5] L.Battezzati, F.Scaglione, JALCOM (2011).

100 nm

[4] Z. Zhang et al., J. Phys Chem. 2009

Features of de-alloyed materials:

➢ nanoporous metals;
➢ interconnected pores and tunnels together with fine crystallites;
➢ spongy-like material made of an almost pure inert metal.

Applications
- ✓ catalysis
- ✓ sieves
- ✓ sensors

Key parameters for de-alloying
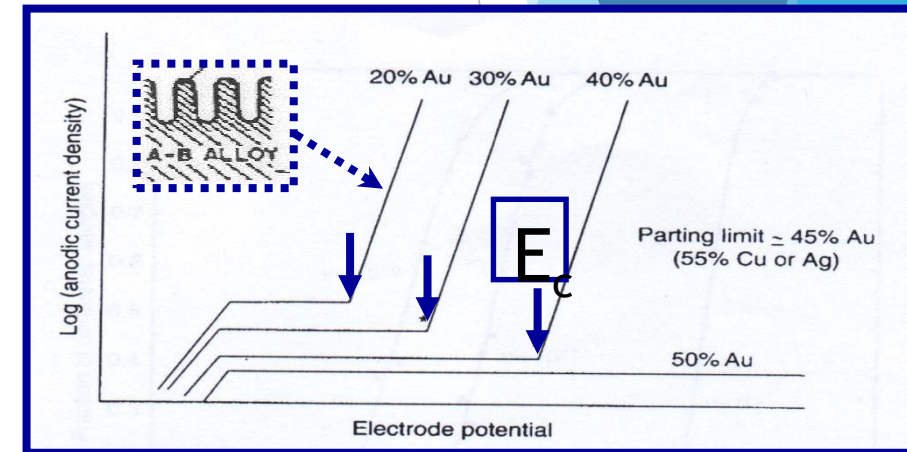
❑ Difference in electrochemical potential between alloy components (elements or phases).

❑ Critical potential E_c

    ❑ is a function of the most noble element amount [6];

    ❑ is also defined as the potential corresponding to a current density of 1 mA/cm^2.

[6]H.W. Pickering, Corros.Sci. 1983; 23(10): 1107-1120. H.W. Pickering, Y.S. Kim Corros Sci. 1982; 22 (10): 621.
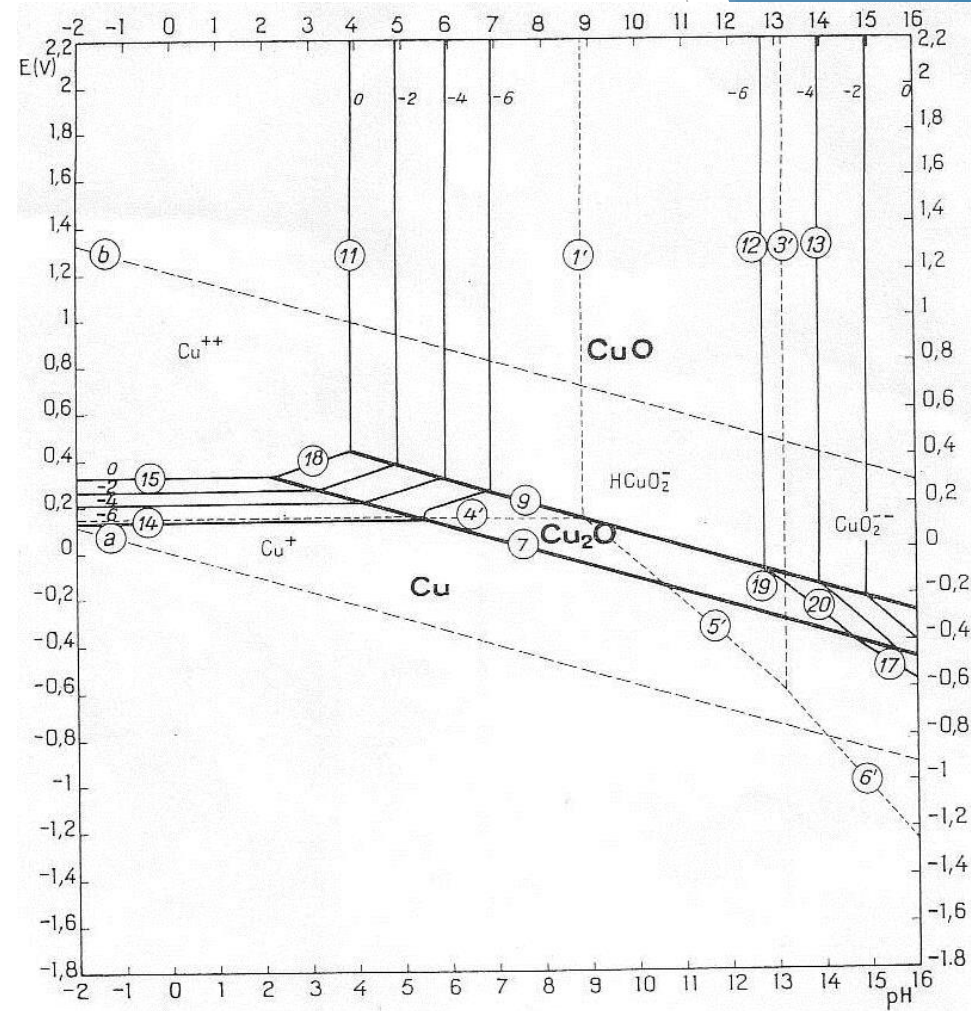
❑ Parting limit:

maximum content of the most noble element at which interconnected porosity is formed.

➢ For Au-Ag and Au-Cu alloys ~45 at. % Au
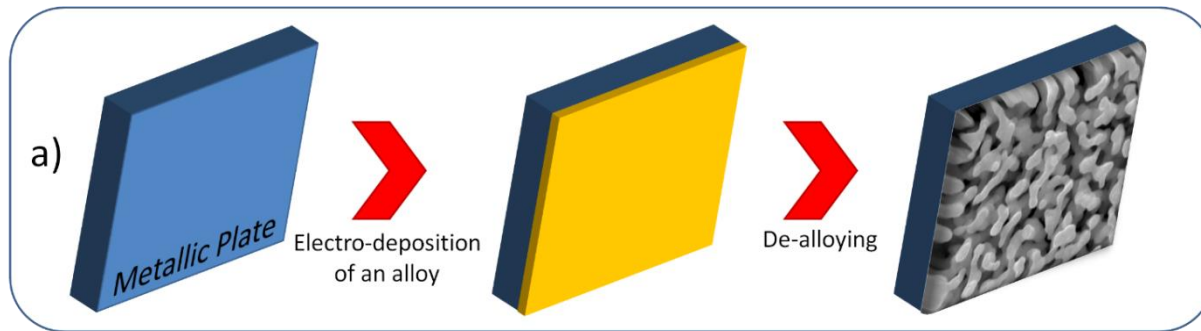
❑ Electrolyte composition:

➢ various acids or bases;

➢ pH from Pourbaix Diagrams.
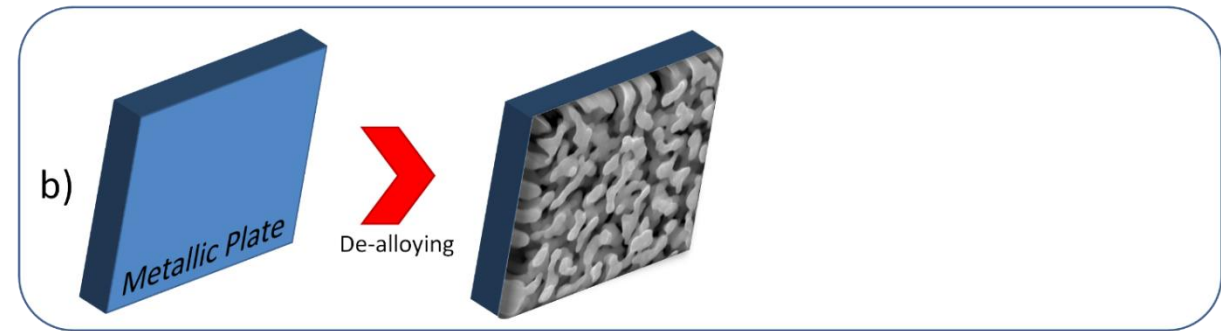
Nanoporous metals for plasma technology

The aim of the PLANOVOC project is to show that porous or nanoporous metals could be coupled with plasma technology to increase the breakdown of VOCs during the treatment of industrial wastes.

Thanks to their high surface area catalytic properties, these materials could be used into the reaction chamber on stainless steel plates, working as conductive electrodes.

STRATEGY a)

➤ Electro-deposition of a coherent and stable micrometric layer (with defined composition);

➤ De-alloying process to form a nanoporous network on the surface.

➤ The porous layer could be a catalyst itself or a scaffold where adhere catalysts in a second step or both solutions.

STRATEGY b)

➤ Careful selection of the alloys for the plate,

➤ De-alloyed to form a rough or nanoporous layer at the surface;

➤ This layer would act as a catalyst or scaffold for catalysts.

Hints and cases from the literature

❑ Electro-deposition of alloys on stainless or mild steel to form a corrosion protection or wear resistance to the alloy underneath.

➢ Zn-Ni coatings deposited from acid chloride bath on mild steels substrates as a cathode [7].

➢ Process parameters, i.e. temperature, pH and composition of the bath, applied current and time of deposition, can be properly set to change the composition of the coating or the thickness of the layer.

➢ Being Zn less noble than Ni, it can be selectively de-alloyed, leaving a Ni porous layer.

[7] Bhat, R.*, et al.*, *Anal. Bioanal. Electrochem.* (2018) **10** (12), 1562

❑ Two applied potential step electro-deposition to coat AISI304 stainless steel with a Ni-Co oxide coating.

➢ After annealing of the deposited layer, the growth of a spinel-type Ni-Co oxide nanostructures is observed.

➢ This layer is itself a catalyst for the Oxygen Evolution Reaction (OER) [8].

➢ A Ni coating can be electro-deposited by an alkaline $NH_4OH/$ NH_4Cl buffer solution, where finishing and roughness are a function of treatment parameters [9].

[8] Barauskienė, I., and Valatka, E., (2019), 1
[9] Skital, P. M., *et al.*, *Trans. Nonferrous Met. Soc. China* (2019) **29** (1), 222

❑ Aluminum electrodeposited from ionic liquids on high strength steel [10].

➤ A coherent alumina layer could be formed by thermal treating the deposited sample. Similarly, Cu-Ti/TiO_2 nanocomposites coatings can be electro-deposited on low carbon steels [11].

❑ De-alloying on

➤ Steels

➤ Iron based rapidly solidified Fe–C eutectics [12],

➤ Fe-Si systems by chemical or electrochemical de-alloying [13],

➤ Commercial Incoloy 825 nickel superalloy by liquid metal de-alloying forming a porous FeCr-based microstructure [14].

➤ However liquid metal de-alloying requires a pure Mg molten baths as electrolyte and proper equipments and safety devices for the operator.

[10] Böttcher, R.*, et al.*, *Transactions of the IMF* (2019) **97** (2), 82
[11] Khorashadizade, F.*, et al.*, *Journal of Alloys and Compounds* (2019) **770**, 98
[12] Battezzati, L., and Scaglione, F., *Journal of Alloys and Compounds* (2011) **509**, S8
[13] Wang, S.*, et al.*, *Materials* (2018) **11** (5)
[14] Mokhtari, M.*, et al.*, *Scripta Materialia* (2019) **163**, 5

Nanoporous substrates for plasma assisted VOC breakdown

According with the **STRATEGY a)**, a nanoporous layer is formed after electro- deposition of a proper alloy and its subsequent de-alloying. The nature of this nanoporous layer develops different scenarios.

➢ If the layer is nanoporous but not a catalyst itself for the VOCs breakdown reaction, a proper catalyst can be inserted inside pores by painting or wetting the layer with a proper catalyst solution. In this case, porosity can be tuned to place properly the catalyst and to guarantee an homogeneous distribution of it on the entire nanoporous volume.

➢ Know the nature and composition of the better catalyst for VOCs breakdown, it could be prepared directly inside pores during de-alloying and oxidation step. Selection of materials and electro-deposition techniques becomes important parameters for the process.

➢ In the simplest case, the nanoporous layer is a catalyst itself for the VOCs breakdown reaction and it can be used in the reaction chamber as it is produced.

Nanoporous substrates for plasma assisted VOC breakdown

The **STRATEGY b)** needs a careful selection of the plate's material. The literature shows that different types of steels can be coated with metals, alloys and or oxides. Stability of these layers is, in some cases, rather good, being laid to confer corrosion or wear resistance to the bulk materials. Assuming a proper deposited composition, a de-alloying step can then be performed to get a nanoporous layer. Even in this case, the nature of the nanoporous layer can be approached using the same approach considered in the previous case.